

Effect of Grape Maturity and Juice Treatments on Terpene Concentrations and Wine Quality of *Vitis vinifera* L. cv. Weisser Riesling and Bukettraube¹

J. Marais^a and C.J. van Wyk^b

a) Viticultural and Oenological Research Institute, Private Bag X5026, 7600 STELLENBOSCH, Republic of South Africa.

b) Department of Oenology, University of Stellenbosch, 7600 STELLENBOSCH, Republic of South Africa.

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The effect of grape maturity and different juice treatments, namely free-run, skin-contact, pressing and heat treatment on individual terpene concentrations in Weisser Riesling and Bukettraube juices and wines, as well as on different wine quality parameters, was investigated. Linalool, hotrienol, alpha-terpineol, nerol, geraniol, citronellol, 3,7-dimethylocta-1,5-dien-3,7-diol and the furan and pyran linalool oxides were analysed gas chromatographically. Wine quality parameters, such as terpene-like character, cultivar authenticity and overall wine quality of these wines were sensorially evaluated. Increases in grape maturity and the application of juice treatments, like skin-contact and heat treatment, caused significant increases in the concentrations of the majority of terpenes analysed. These changes were, to a limited extent, reflected in the intensities and qualities of some wine characteristics. Heat treatment emerged as the single factor, causing the most prominent increases in terpene concentrations and improvement in overall wine quality.

Various studies have been undertaken to investigate changes in concentration of terpene compounds during maturation of grapes of muscat and non-muscat cultivars (Bayonove & Cordonnier, 1970a, 1970b; Hardy, 1970; Bayonove & Cordonnier, 1971; Terrier, Boidron & Ribéreau-Gayon, 1972; Cordonnier, 1974; Rapp *et al.*, 1978; Versini, Inama & Sartori, 1981). Generally, increases in terpene concentrations were observed from the unripe stage to the attainment of grape maturity.

Decreases in terpene concentrations were normally found during the last stages of ripening and with over-ripeness. Preliminary studies in South Africa indicated decreases in the concentrations of certain terpenes of some cultivars with an increase in grape maturity (A. Rapp, 1980; personal communication). From the above-mentioned studies it is clear that the maximum aroma, in terms of terpenes, may be attained in grapes before the attainment of maximum sugar concentration.

It is well-known that certain terpenes e.g. linalool, geraniol and nerol predominate in the grape skin of some cultivars (Bayonove, Cordonnier & Ratier, 1974; Cordonnier & Bayonove, 1978; Cordonnier & Bayonove, 1981; Versini *et al.*, 1981). As a result, prolonged contact between juice and skins and pressing resulted in higher concentrations of some terpenes in the juices and corresponding wines (Kinzer & Schreier, 1980; Versini *et al.*, 1981). Heat treatment of model terpene solutions and muscat grape juices also resulted in higher terpene concentrations (Usseglio-Tomasset & Di Stefano, 1979; Usseglio-Tomasset & Di Stefano, 1980; Di Stefano, 1981; Usseglio-Tomasset, 1981). These increases could have been caused by transformations of free terpenes (Usseglio-Tomasset & Di Stefano, 1980; Di Stefano, 1981), the formation of terpenes from their non-volatile polyols (Williams, Strauss & Wilson,

1980a, 1980b) and/or the liberation of terpenes from their non-volatile bound glucosidic forms (Cordonnier & Bayonove, 1974; Di Stefano, 1981; Williams, Strauss & Wilson, 1981; Bayonove, Günata & Cordonnier, 1983; Günata, 1984). These bound terpenes were proved to be monoterpenes bound to complex disaccharides (Williams *et al.*, 1982a, 1982b, 1982c).

South African white wines made from cultivars such as Weisser Riesling, Gewürztraminer and Bukettraube sometimes tend to be relatively neutral with respect to aroma. This study was undertaken to investigate the effect of grape maturity and certain juice treatments on terpene concentrations and wine quality of the cultivars Weisser Riesling and Bukettraube.

MATERIALS AND METHODS

Harvesting of grapes:

Grapes of the cultivars Weisser Riesling and Bukettraube (1983 vintage), from the Stellenbosch region, were harvested at four and three ripening stages respectively. Approximately 400 kg of each cultivar was collected at each ripening stage. Grapes were harvested between 06h00 and 08h00 to prevent the possible detrimental effects of high temperatures.

Attempts were made to harvest each cultivar at two degrees Balling (°B) intervals between approximately 16°B and 22°B. In order to obtain a homogeneous harvest, the grapes were collected on a representative basis over the vine blocks; e.g. should four harvests be taken, then every fifth vine in the vineyard would be harvested at each harvesting.

Juice treatments and fermentation:

Each grape sample was crushed and destemmed and the juice immediately separated from the skins. The skin plus pulp fraction was weighed and the juice vol-

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ume and temperature measured. Each of the juice and skin fractions was divided into four equal lots and then subjected to the following treatments.

- 1) Lot one was free-run juice and was used as control.
- 2) Lot two was one part juice plus one part skin plus pulp and was subjected to four hours skin-contact at 15°C.
- 3) Lot three was made up of one part juice plus press juice from one part skin plus pulp, obtained by subjecting the latter to a pressure of 150 kg/cm² for 15 minutes.
- 4) Lot four was also free-run juice but was subjected to heat treatment at 70°C for 15 minutes by circulating steam through a stainless steel spiral immersed in the juice. To prevent local over-heating, the juice was stirred continually.

Bentonite (25 g/hl) was added to each juice and after mixing, the juice was settled overnight at 0°C. From the clear juices, samples were drawn for gas chromatographic analyses. Each clear juice was then divided into two equal parts and each part placed in a 20 litre CO₂ filled canister for duplicate fermentation.

In the case of Weisser Riesling, the °B and total titratable acidity (TTA) concentrations of the settled juices were adjusted by addition of cane-sugar and calcium carbonate respectively to obtain 21°B and a TTA concentration of ca. 8 g/l. In cases where the TTA values were lower than 8 g/l, the acid level was adjusted by addition of tartaric acid, so that a °B/TTA ratio of approximately 2.6 could be obtained.

Clear juices were stored at 20°C for eight hours before addition of 0.8 g/l of a 50% di-ammonium phosphate solution. Dry yeast (10 g/100 ml distilled water) of *Saccharomyces cerevisiae* strain 452 was rehydrated at between 40°C and 43°C for 20 minutes. The rehydrated yeast (3 ml/l juice) was then added to each juice and fermentation conducted at 13°C. After fermentation, the wines were removed from the lees, filtered and stabilized at 0°C for one week. The wines were then filtered and bottled at room temperature. Free SO₂ concentrations were adjusted to approximately 25 mg/l before fermentation, after the first racking and at bottling. After bottling the wines were stored at 0°C until gas chromatographic analysis and sensory evaluation.

Aroma component extraction and gas chromatography:

Samples (250 ml) of each Weisser Riesling and Bukettraube clear juice and wine were subjected to liquid-liquid extraction by Freon 11, these extracts thereafter concentrated and terpenes determined in relative concentrations by capillary gas chromatography (Marais, 1986).

Mass spectrometry:

Identities of terpenes were confirmed by comparing their mass spectra and retention times with those of authentic standards analysed under similar conditions. All analyses were performed on a Finnigan 4021 instrument (Marais, 1986). Terpenes analysed were trans- and cis-furan linalool oxide, linalool, hotrienol, alpha-terpineol, trans- and cis-pyran linalool oxide, citronellol, nerol, geraniol and 3,7-dimethylocta-1,5-dien-3,7-diol (terpene diol-1).

Sensory evaluation:

Wines were sensorially evaluated by a panel of 15

judges. Intensities of terpene-like character and cultivar authenticity, as well as the quality of cultivar authenticity and overall wine quality were evaluated on a 9-point scale.

Statistical analyses:

The statistical significance of the effects of grape maturity and juice treatments on terpene concentrations in Weisser Riesling and Bukettraube clear juices and wines was determined by means of a standard factorial analysis method. A multiple comparison of means was executed by means of the method of Scott & Knott (1974).

In the case of sensory evaluations, the statistical significance of the effects of grape maturity and juice treatments on each individual quality parameter of Weisser Riesling and Bukettraube wines was determined by means of the BMDP35 program, which entails a Friedman non-parametric two-way variance analysis.

RESULTS AND DISCUSSION

The main effects of grape maturity and juice treatments on average terpene concentrations in Weisser Riesling and Bukettraube juices and wines are given in Tables 1 to 4. The combined effect of grape maturity and juice treatments on individual terpene concentrations is also illustrated in Figures 1 to 6.

TABLE 1

The effect of grape maturity and juice treatments on terpene concentrations (µg/l) in Weisser Riesling juice extracts.

Terpene	Ripening stage				Juice treatment			
	1	2	3	4	FR	SC	P	H
trans-Furan linalool oxide	1,38a	1,73a	1,43a	1,68a	1,01b	1,04b	0,99b	3,19a
cis-Furan linalool oxide	0,72b	0,69b	0,81b	1,45a	0,66b	0,77b	0,44b	1,81a
Linalool	0,49b	4,26a	5,35a	0,35b	0,44a	1,77a	2,11a	6,13a
Hotrienol	8,92a	16,54a	17,46a	10,98a	10,02b	4,11b	6,34b	33,43a
alpha-Terpeneol	1,97b	5,24a	5,00a	0,53b	0,82b	1,77b	1,55b	8,61a
trans-Pyran linalool oxide	12,46a	3,72b	3,09b	2,19c	4,07a	7,19a	4,78a	5,42a
cis-Pyran linalool oxide	2,85a	1,63b	1,25b	2,20a	1,66b	2,58a	1,65b	2,04b
Nerol	0,12b	0,57b	1,00b	2,10a	0,64a	1,04a	1,09a	1,01a
Geraniol	2,47a	2,38a	1,37a	0,50a	0,52a	4,03a	0,59a	1,57a
Terpene diol-1	2,60b	13,87a	17,77a	4,21b	5,63a	7,62a	17,83a	7,38a

Ripening stage 1 = 16,1°B

Ripening stage 2 = 18,8°B

Ripening stage 3 = 18,7°B

Ripening stage 4 = 19,7°B

FR = Free-run

SC = Skin-contact

P = Press treatment

H = Heat treatment

Treatments designated by the same symbol do not differ significantly (P ≤ 0.05). Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1.

Although the furan and pyran linalool oxides and terpene diol-1 occurred in relatively high concentrations in some juices and wines of this study, their aroma threshold values are also high (Ribéreau-Gayon, Boidron & Terrier, 1975; Versini *et al.*, 1981). It can therefore be

assumed that these terpenes are of less importance with respect to their contribution to the aroma of juice and wine. On the other hand, linalool, hotrienol, alpha-terpineol, nerol and geraniol have relatively low aroma threshold values (Ribéreau-Gayon *et al.*, 1975; Ohloff, 1978). These last-mentioned terpenes were therefore considered to be of greater importance for the purpose of this study.

TABLE 2

The effect of grape maturity and juice treatments on terpene concentrations ($\mu\text{g/l}$) in Weisser Riesling wine extracts.

Terpene	Ripening stage				Juice treatment			
	1	2	3	4	FR	SC	P	H
trans-Furan linalool oxide	17.22a	14.86a	13.71a	13.01a	14.09a	14.12a	16.84a	13.75a
cis-Furan linalool oxide	2.05a	1.88a	1.53a	1.62a	1.65a	1.92a	1.60a	1.92a
Linalool	23.11d	40.38c	47.35b	60.11a	35.49b	46.36a	42.18a	46.92a
Hotrienol	23.32a	23.95a	16.80a	22.42a	27.30a	23.68a	14.58a	20.94a
alpha-Terpineol	9.86c	16.42b	18.53b	25.23a	14.36c	17.86b	16.83b	20.99a
cis-Pyran linalool oxide	6.52a	6.37a	5.10a	5.96a	5.81a	5.90a	5.45a	6.80a
Citronellol	2.76b	4.64a	3.68b	5.90a	3.82a	5.95a	4.24a	2.97a
Terpene diol-1	17.47a	25.43a	30.42a	28.79a	17.98a	31.04a	32.23a	20.86a

Ripening stage 1 = 16.1°B

Ripening stage 2 = 18.8°B

Ripening stage 3 = 18.7°B

Ripening stage 4 = 19.7°B

FR = Free-run

SC = Skin-contact

P = Press treatment

H = Heat treatment

Treatments designated by the same symbol do not differ significantly ($P \leq 0.05$). Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1.

TABLE 3

The effect of grape maturity and juice treatments on terpene concentrations ($\mu\text{g/l}$) in Bukettraube juice extracts.

Terpene	Ripening stage			Juice treatment			
	1	2	3	FR	SC	P	H
trans-Furan linalool oxide	1.12c	1.56b	2.00a	1.00b	1.09b	1.06b	3.09a
cis-Furan linalool oxide	0.35c	0.68b	1.01a	0.38b	0.31b	0.38b	1.65a
Linalool	13.37b	12.45b	24.62a	8.50b	15.67b	7.72b	35.36a
Hotrienol	6.61a	9.22a	15.82a	6.77a	3.18a	6.60a	25.66a
alpha-Terpineol	5.73a	4.46a	6.61a	1.62b	1.32b	1.31b	18.15a
trans-Pyran linalool oxide	6.69b	6.15b	7.50a	7.10a	6.66a	6.60a	6.75a
cis-Pyran linalool oxide	1.53c	2.01b	2.84a	2.27a	2.00a	2.04a	2.19a
Nerol	1.14a	0.57a	0.91a	0.43b	1.04a	0.18b	1.85a
Geraniol	2.59a	1.35a	2.71a	0.49c	2.61b	0.18c	5.59a
Terpene diol-1	9.21a	5.65a	3.22b	6.61a	9.22a	4.01a	4.27a

Ripening stage 1 = 18.1°B

Ripening stage 2 = 20.4°B

Ripening stage 3 = 20.0°B

FR = Free-run

SC = Skin-contact

P = Press treatment

H = Heat treatment

Treatments designated by the same symbol do not differ significantly ($P \leq 0.05$). Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1.

TABLE 4

The effect of grape maturity and juice treatments on terpene concentrations ($\mu\text{g/l}$) in Bukettraube wine extracts.

Terpene	Ripening stage			Juice treatment			
	1	2	3	FR	SC	P	H
trans-Furan linalool oxide	15.42b	14.14b	17.77a	15.60a	14.92a	16.65a	15.93a
cis-Furan linalool oxide	1.54b	1.62b	2.28a	1.33a	2.14a	2.05a	1.74a
Linalool	26.72c	38.81b	61.94a	36.78b	36.55b	37.91b	58.71a
Hotrienol	8.06a	10.24a	8.64a	8.03a	10.67a	8.20a	9.02a
alpha-Terpineol	9.96c	13.39b	18.42a	10.95b	10.14c	11.34b	23.25a
cis-Pyran linalool oxide	2.10b	3.26a	3.47a	2.44b	2.39b	2.63b	4.31a
Citronellol	2.57a	3.27a	3.23a	2.91a	3.50a	3.35a	2.34a
Terpene diol-1	7.42b	11.42a	14.63a	10.93a	9.21a	10.14a	14.35a

Ripening stage 1 = 18.1°B

Ripening stage 2 = 20.4°B

Ripening stage 3 = 20.0°B

FR = Free-run

SC = Skin-contact

P = Press treatment

H = Heat treatment

Treatments designated by the same symbol do not differ significantly ($P \leq 0.05$). Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1.

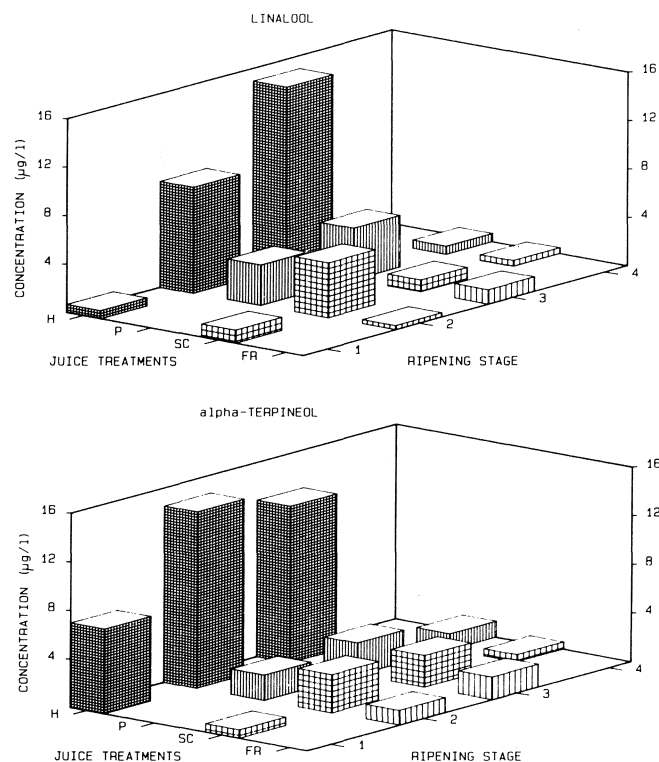


FIG. 1

The effect of grape maturity and juice treatments on the concentrations of linalool and alpha-terpineol in Weisser Riesling juices (Ripening stage 1 = 16.1°B, 2 = 18.8°B, 3 = 18.7°B and 4 = 19.7°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

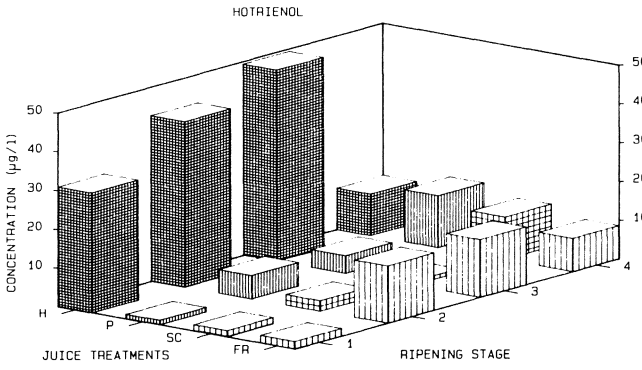
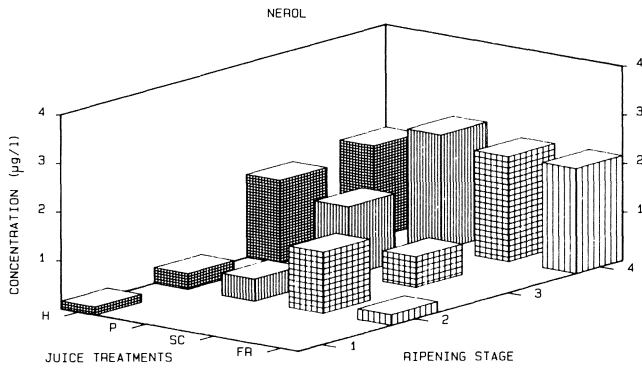


FIG. 2

The effect of grape maturity and juice treatments on the concentrations of nerol and hotrienol in Weisser Riesling juices (Ripening stage 1 = 16,1°B, 2 = 18,8°B, 3 = 18,7°B and 4 = 19,7°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

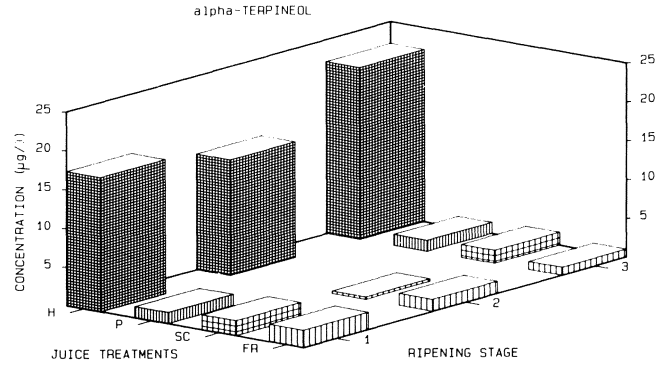
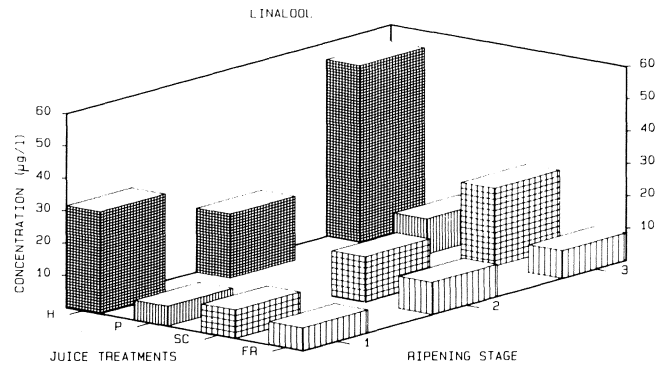


FIG. 4

The effect of grape maturity and juice treatments on the concentrations of linalool and alpha-terpineol in Bukettraube juices (Ripening stage 1 = 18,1°B, 2 = 20,4°B and 3 = 20,0°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

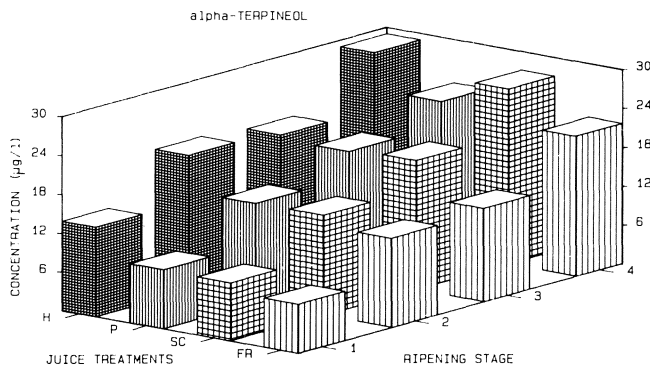
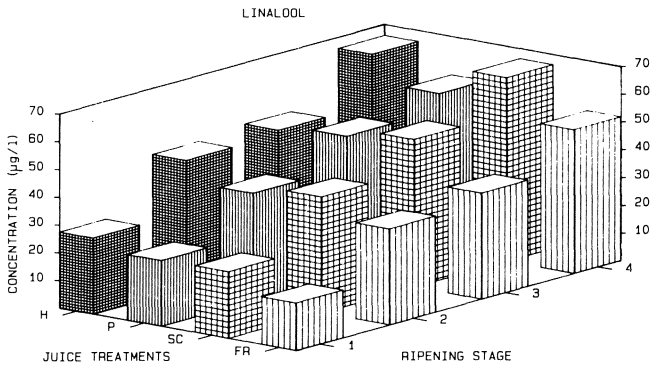


FIG. 3

The effect of grape maturity and juice treatments on the concentrations of linalool and alpha-terpineol in Weisser Riesling wines (Ripening stage 1 = 16,1°B, 2 = 18,8°B, 3 = 18,7°B and 4 = 19,7°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

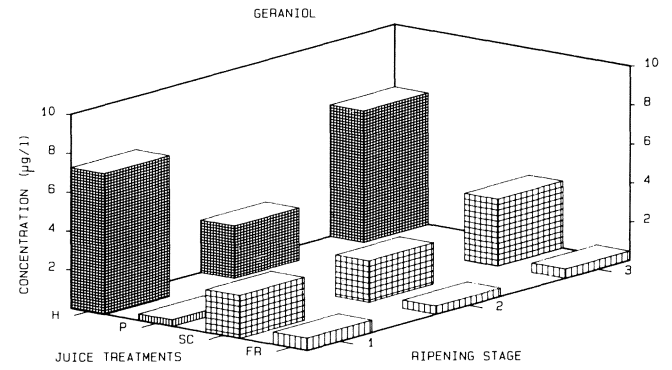
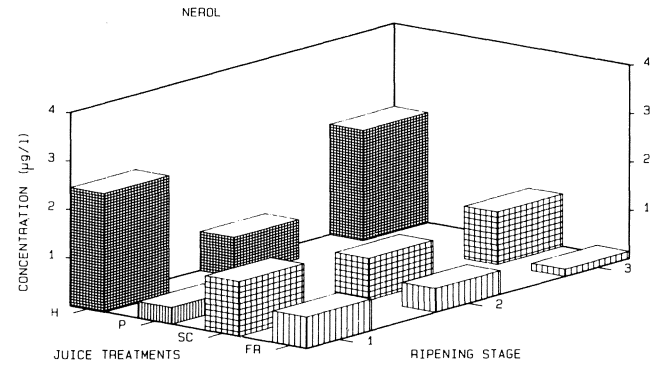


FIG. 5

The effect of grape maturity and juice treatments on the concentrations of nerol and geraniol in Bukettraube juices (Ripening stage 1 = 18,1°B, 2 = 20,4°B and 3 = 20,0°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

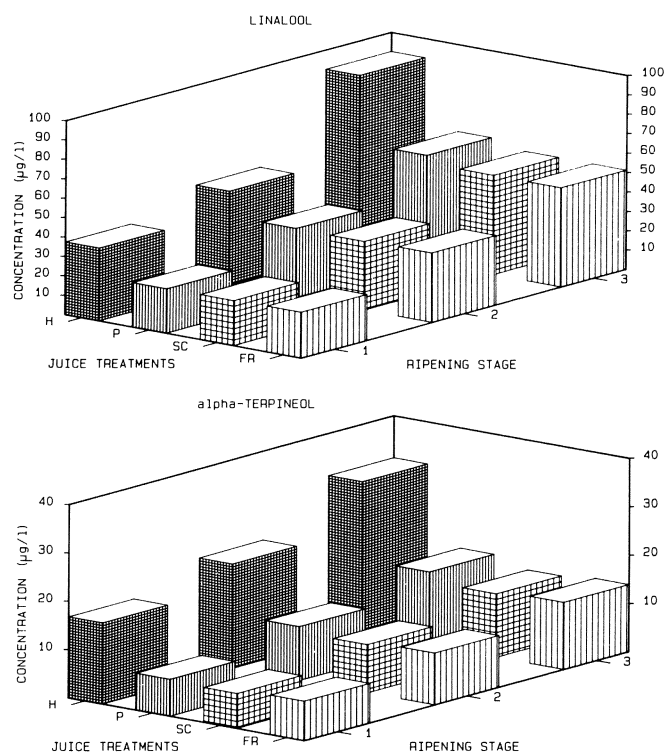


FIG. 6

The effect of grape maturity and juice treatments on the concentrations of linalool and alpha-terpineol in Bukettraube wines (Ripening stage 1 = 18,1°B, 2 = 20,4°B and 3 = 20,0°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

Effect of grape maturity on terpene concentrations in Weisser Riesling and Bukettraube juices and wines:

Relatively few significant changes occurred in terpene concentrations with an increase in grape maturity. The reasons for this tendency may be ascribed to various factors. The grapes of both cultivars were harvested over relatively limited °B intervals. Furthermore, limited quantities of grapes prevented replication of grape sampling at the different harvesting stages. Consequently, interactions could be responsible for the statistical insignificance in cases where tendencies in terpene concentrations were visually observed between main effects, e.g. hotrienol (Tables 1, 2 and 3). Nevertheless, significant changes in certain terpene concentrations in the juices and corresponding wines were observed in this study.

An increase in grape maturity resulted in increases in terpene concentrations in the majority of cases. Examples of significant increases in terpene concentrations are cis-furan linalool oxide and nerol (Table 1), linalool and alpha-terpineol (Table 2), the linalool oxides and linalool (Table 3) and the linalool oxides, linalool, alpha-terpineol and terpene diol-1 (Table 4). Although weather conditions caused sugar concentrations to stabilise between ripening stages 2 and 3 in the case of both Weisser Riesling and Bukettraube, some of the above-mentioned significant increases were nevertheless evident over these periods (Tables 2, 3 and 4). Figures 1, 2 and 3 also show increases in the individual concentrations of the relatively low threshold

terpenes, such as linalool, nerol, hotrienol and alpha-terpineol in Weisser Riesling juices and wines respectively. Increases in the individual concentrations of linalool and alpha-terpineol in Bukettraube wines were also evident (Fig. 6).

The above-mentioned results, namely increases in terpene concentrations with an increase in grape maturity, correspond with findings of Bayonove & Cordonnier (1970a, 1970b) and Bayonove & Cordonnier (1971). These authors reported increases in terpene concentrations from the unripe to ripe stage in grapes of various muscat cultivars. In preliminary studies on Morio Muscat grapes, grown in South Africa, increases in the concentrations of trans-pyran linalool oxide, nerol, geraniol and trans-geranic acid with an increase in grape maturity were also observed (A. Rapp, 1980; personal communication). This work, however, also indicated decreases in the concentrations of linalool, trans-pyran linalool oxide, nerol, geraniol, terpene diol-1 and trans-geranic acid in Weisser Riesling, Kerner and Gewürztraminer grapes from the unripe to the ripe stage. The reasons for these decreases in the case of certain cultivars are not known, but may possibly be ascribed to the relatively warm South African climatic conditions.

An increase in grape maturity also caused increases followed by decreases in concentration of certain terpenes. Linalool, alpha-terpineol and terpene diol-1 concentrations in Weisser Riesling juices significantly increased up to the third ripening stage, followed by a decrease in concentration at the fourth stage (Table 1). This tendency was also evident in certain terpene concentrations, especially where heat treatment was applied (Figs. 1 and 2). Bayonove & Cordonnier (1970a, 1970b) and Versini *et al.* (1981) found similar tendencies, specifically in the case of linalool in the grapes of different muscat cultivars. It appears as if decreases in these terpene concentrations are generated when a certain low level of total acidity concentration is reached.

The above-mentioned tendency, namely decreases in terpene concentrations in Weisser Riesling juices at the fourth stage, differed from the corresponding wines, where the concentrations of linalool and alpha-terpineol continued to increase at this ripening stage (compare Figs. 1 and 3). It appears as if additional quantities of these terpenes were formed or liberated from precursors during fermentation. The reasons for this phenomenon are not known, but could possibly be ascribed to the following factors. Linalool may be formed from nerol and/or geraniol, while alpha-terpineol may be generated by linalool, citronellol, nerol and/or geraniol (Usseglio-Tomasset & Di Stefano, 1980; Di Stefano, 1981). Linalool and alpha-terpineol may also be formed by acid-catalysed hydrolysis of 3,7-dimethyloct-1-en-3,7-diol (Williams *et al.*, 1980a, 1980b). Another possibility is the liberation of terpenes from their non-volatile bound glucosidic forms by either acid hydrolysis (Williams *et al.*, 1981; Williams *et al.*, 1982a, 1982b, 1982c) or by enzymatic actions (Cordonnier & Bayonove, 1974; Bayonove *et al.*, 1983; Günata, 1984). The formation of the relevant terpenes during fermentation by *Saccharomyces cerevisiae*, has not been reported.

An increase in grape maturity also caused decreases in concentration of certain terpenes, but this was the exception (e.g. trans-pyran linalool oxide and geraniol,

Table 1; terpene diol-1, Table 3). The concentration of cis-pyran linalool oxide decreased significantly, followed by a significant increase (Table 1). Surprisingly lower concentrations of linalool, nerol and geraniol were observed at the second ripening stage of Bukettraube juice, in comparison with the first and third stages, when heat treatment was applied (Figs. 4 and 5 respectively). Versini *et al.* (1981) also investigated the effect of grape maturity on terpene concentrations in Weisser Riesling grapes during the final ripening period of about one month. They reported increases in the concentrations of linalool, alpha-terpineol and the furan linalool oxides, decreases in the concentrations of trans-pyran linalool oxide, citronellol, geraniol and nerol oxide, as well as fluctuations in the concentrations of nerol, cis-pyran linalool oxide and hotrienol. It appears as if decreases or fluctuations in terpene concentrations in grapes usually occur in the final ripening stages.

Changes in the concentrations of nerol, geraniol and trans-pyran linalool oxide in wines specifically, could not be investigated properly under the conditions of this experiment, since their peaks often overlapped with other peaks during gas chromatographic analyses. Furthermore, the gas chromatographic data of terpene diol-1 should be interpreted with care, since this compound is relatively unstable and may easily rearrange in an acid medium to, amongst others, hotrienol and nerol oxide (Usseglio-Tomasset & Di Stefano, 1980; Di Stefano, 1981).

Changes in terpene concentrations with an increase in grape maturity may cause a desired aroma quality for the production of high quality wines at a specific maturation stage. Therefore, determination of volatile components, such as terpenes, together with °B, TTA and/or pH as a criterion for the correct time of harvesting, should be investigated. Various researchers have stressed the importance of harvesting grapes at the correct maturity (Wagner *et al.*, 1977; Cordonnier & Bayonove, 1978). It has to be kept in mind that investigations into the effect of grape maturity on terpene concentrations in the past were mainly carried out on free terpenes. Liberation of terpenes from their bound forms may occur continually during grape maturation and will have an effect on the changes in terpene concentrations (Williams *et al.*, 1983).

Effect of juice treatments on terpene concentrations in Weisser Riesling and Bukettraube juices and wines:

The free-run treatment was considered as the control in this experiment. Skin-contact caused significant increases in terpene concentrations in a limited number of cases, namely cis-pyran linalool oxide in Weisser Riesling juices (Table 1), linalool and alpha-terpineol in Weisser Riesling wines (Table 2) and nerol and geraniol in Bukettraube juices (Table 3, Fig. 5). Although not significant, skin-contact also had a prominent effect on the concentrations of trans-pyran linalool oxide and geraniol in Weisser Riesling juices (Table 1), terpene diol-1 in Weisser Riesling wines (Table 2) and linalool and terpene diol-1 in Bukettraube juices (Table 3, Fig. 4).

The above-mentioned results correspond with the findings of Bayonove *et al.* (1974), Cordonnier & Bayonove (1978), Cordonnier & Bayonove (1981) and Ver-

sini *et al.* (1981). These authors found that linalool, nerol and geraniol mainly occur in the berry skin of muscat and aroma-related cultivars. Skin-contact would therefore cause additional quantities of these terpenes to be taken up in the juice.

Press treatment of grapes has the same effect as skin-contact, namely the extraction of terpenes from the berry skins (Kinzer & Schreier, 1980; Cordonnier & Bayonove, 1981; Versini *et al.*, 1981). These authors reported marked increases in the concentrations of terpene alcohols and linalool oxides with an increase in pressure. Increases in terpene concentrations as a result of pressing, occurred in this study, namely in the cases of linalool, alpha-terpineol, nerol and terpene diol-1 in Weisser Riesling juices and wines (Tables 1 and 2 respectively).

It is evident that skin-contact and pressing did not have the expected prominent effect on terpene concentrations in this study. This can probably be ascribed to the fact that, in order to limit the uptake of phenolic compounds in the juices during these treatments, the application periods were not long enough.

Heat treatment resulted in significant increases in the concentrations of some terpenes and had, in comparison with skin-contact and pressing, a much more prominent effect. This effect was especially noticeable in the case of some of the more flavourful terpenes, such as linalool and alpha-terpineol in Weisser Riesling and Bukettraube juices and wines (Figs. 1, 3, 4 and 6 respectively). Interactions between grape maturity and juice treatments probably resulted in the lack of significance in the increases of linalool concentrations (Table 1). Heat treatment of juices also caused prominent increases in the concentrations of hotrienol and the furan linalool oxides in Weisser Riesling juices (Fig. 2, Table 1), the furan linalool oxides, hotrienol, nerol and geraniol in Bukettraube juices (Fig. 5, Table 3), as well as cis-pyran linalool oxide in Bukettraube wines (Table 4).

The above-mentioned results correspond with the findings of Usseglio-Tomasset & Di Stefano (1980), Usseglio-Tomasset (1981), Versini *et al.* (1981), Williams *et al.* (1980b) and Williams *et al.* (1981). These authors demonstrated marked increases in monoterpene concentrations in model terpene solutions, as well as in muscat grape juices when heat treatment was applied.

The effect of heat treatment can be explained by the studies of Williams *et al.* (1980a, 1980b), Williams *et al.* (1981), Williams *et al.* (1982a, 1982b, 1982c) and Williams *et al.* (1983) in which the existence of non-volatile bound glucosidic terpenes was demonstrated. During heat treatment, chemical bonds between monoterpenes and the relevant disaccharides may be cleaved with resultant liberation of bound aroma in the form of free volatile terpenes. This may lead to the intensifying of terpene or terpene-like characters in the juices and the wines produced from them.

Increases in the concentrations of terpenes, such as linalool, alpha-terpineol, nerol and geraniol may also be ascribed to other causes. According to Williams *et al.* (1980b) and Williams *et al.* (1983), terpenes may also be formed from the odourless polyhydroxylated linalool derivatives. Furthermore, the above-mentioned terpenes may also be formed during heat treatment in

an acid medium, as a result of transformations of monoterpenes normally present in the juice (Usseglio-Tomasset & Di Stefano, 1980; Di Stefano, 1981).

The prominent effect of heat treatment on terpene concentrations in juices, in comparison with the other juice treatments, almost disappeared or was less prominent in the corresponding wines (e.g. trans-, cis-furan linalool oxide and hotrienol, Tables 1 to 4; linalool and alpha-terpineol, Figs. 1, 3, 4 and 6). The reasons for this equalizing effect on terpene concentrations during fermentation have still to be elucidated.

Comparison between individual terpene concentrations in juices and their corresponding wines was not attempted, because of differences in the degree of terpene extractability. This problem may be solved when calibration of each terpene is performed in both juice and wine media. Unfortunately quantification of ter-

penes is a practical problem, since some terpenes are not commercially available in sufficient quantities.

Sensory evaluation:

Although the wines of both Weisser Riesling and Bukettraube showed small differences with respect to the relevant quality parameters, these were shown to be statistically significant. Sensory evaluation results for the effects of grape maturity and juice treatments are given in Tables 5 to 8.

The effect of grape maturity:

Weisser Riesling wines were produced with a significantly higher terpene-like character (intensity) and cultivar authenticity (intensity and quality) at the second ripening stage than those produced at the third stage

TABLE 5

The effect of grape maturity on quality parameters of Weisser Riesling wines.

Quality parameter	Ripening stage ^a				Level of significance
	1	2	3	4	
Terpene-like character (Intensity)	40,5	42,5	26,0	41,0	0,0676*
Cultivar authenticity (Intensity)	35,0	45,5	26,5	43,0	LSD = 16,20 0,0312**
Cultivar authenticity (Quality)	37,5	48,0	30,0	34,5	LSD = 18,17 0,0713*
Overall wine quality	38,0	44,5	32,5	35,0	LSD = 16,20 0,3589 Ns

a = The values for each ripening stage are the rank sums for all four juice treatments

Ripening stage 1 = 16,1°B

Ripening stage 2 = 18,8°B

Ripening stage 3 = 18,7°B

Ripening stage 4 = 19,7°B

Ns = Not significant

* = Significant at $P \leq 0,10$

** = Significant at $P \leq 0,05$

TABLE 6

The effect of grape maturity on quality parameters of Bukettraube wines.

Quality parameter	Ripening stage ^a			Level of significance
	1	2	3	
Terpene-like character (Intensity)	22,0	32,5	23,5	0,0837*
Cultivar authenticity (Intensity)	21,5	30,5	26,0	LSD = 10,45 0,2106 Ns
Cultivar authenticity (Quality)	23,0	30,5	24,5	0,2977 Ns
Overall wine quality	18,5	32,0	27,5	0,0264** LSD = 11,93

a = The values for each ripening stage are the rank sums for all four juice treatments

Ripening stage 1 = 18,1°B

Ripening stage 2 = 20,4°B

Ripening stage 3 = 20,0°B

Ns = Not significant

* = Significant at $P \leq 0,10$

** = Significant at $P \leq 0,05$

TABLE 7

The effect of juice treatments on quality parameters of Weisser Riesling wines.

Quality parameter	Juice treatments ^a				Level of significance
	FR	SC	P	H	
Terpene-like character (Intensity)	34,5	41,5	30,0	44,0	0,1762 Ns
Cultivar authenticity (Intensity)	35,0	41,5	26,5	47,0	0,0251** LSD = 18,17
Cultivar authenticity (Quality)	34,0	43,0	28,0	45,0	0,0560* LSD = 16,20
Overall wine quality	37,5	41,0	24,0	47,5	0,0082*** LSD = 22,01

a = The values for each juice treatment are the rank sums for all four ripening stages

FR = Free-run

SC = Skin-contact

P = Press treatment

H = Heat treatment

Ns = Not significant

* = Significant at $P \leq 0,10$

** = Significant at $P \leq 0,05$

*** = Highly significant at $P \leq 0,01$

TABLE 8

The effect of juice treatments on quality parameters of Bukettraube wines.

Quality parameter	Juice treatments ^a				Level of significance
	FR	SC	P	H	
Terpene-like character (Intensity)	35,5	22,5	30,0	42,0	0,0235** LSD = 16,91
Cultivar authenticity (Intensity)	36,0	20,0	26,5	47,5	0,0002*** LSD = 20,47
Cultivar authenticity (Quality)	34,5	19,5	28,5	47,5	0,0003*** LSD = 20,47
Overall wine quality	35,0	19,5	32,5	43,0	0,0043*** LSD = 20,47

a = The values for each juice treatment are the rank sums for all three ripening stages

FR = Free-run

SC = Skin-contact

P = Press treatment

H = Heat treatment

** = Significant at $P \leq 0,05$

*** = Highly significant at $P \leq 0,01$

(Table 5). Although not significant, overall wine quality also showed the highest value at the second ripening stage of 18,8°B. It has to be kept in mind that the °B and TTA concentrations of these wines were adjusted before fermentation.

In the case of Bukettraube, the wines produced at the second ripening stage had a significantly higher intensity of terpene-like character and overall wine quality than those produced at the first stage (Table 6). With respect to these two parameters it seems as if the highest quality Bukettraube wines were obtained at the second ripening stage of 20,4°B.

The effect of juice treatments:

With respect to Weisser Riesling, heat treatment resulted in wines with a significantly higher cultivar authenticity (intensity and quality) and overall wine quality than the press treatment (Table 7). Although not significant, the highest value for terpene-like character intensity was also obtained for heat treatment. Therefore, with respect to most relevant quality parameters, heat treatment produced the highest quality wines for Weisser Riesling.

In the case of Bukettraube, the wines produced by heat treatment had a significantly higher intensity of terpene-like character, cultivar authenticity (intensity and quality) and overall wine quality than those produced by skin-contact (Table 8). The reason for these low skin-contact values is not clear, but could be ascribed to other quality parameters, such as coarseness of aroma and taste. As in the case of Weisser Riesling, the prominent effect of heat treatment on the relevant quality parameters was also evident in Bukettraube wines.

Relationship between terpene concentrations and sensory evaluation results:

In order to be able to compare gas chromatographic data with sensory evaluation results, the rank sum values of the effects of grape maturity and juice treatments were applied in a combined form. As a result of the parametric and non-parametric nature of the gas chromatographic and sensory evaluation results respectively, as well as lack of replicates of grape samples, statistical correlations were not calculated. Therefore, visual comparisons were made between terpene concentrations and sensory evaluation values. Typical examples are the concentrations of linalool, alpha-terpineol and cis-pyran linalool oxide compared to the rank sum values of terpene-like character and overall quality of Weisser Riesling and Bukettraube wines (Figs. 7, 8 and 9). Relatively close relationships between terpene concentrations and the relevant parameter values, especially with respect to the effect of heat treatment, are evident. Although the actual concentrations of linalool and alpha-terpineol were not known in this study, it appears that increases in concentration, as a result of heat treatment, contributed to the intensifying of the terpene-like character and the enhancement of overall wine quality of the relevant wines (Figs. 7 and 8). Usseglio-Tomasset (1981) and Williams *et al.* (1983) also reported increases in wine aroma intensity, changes in nuances of wine aromas and an improvement in overall wine quality when heat treatment was applied to muscat grape juice. Although cis-pyran linalool oxide would be expected to be of less importance to overall wine quality, due to its high aroma

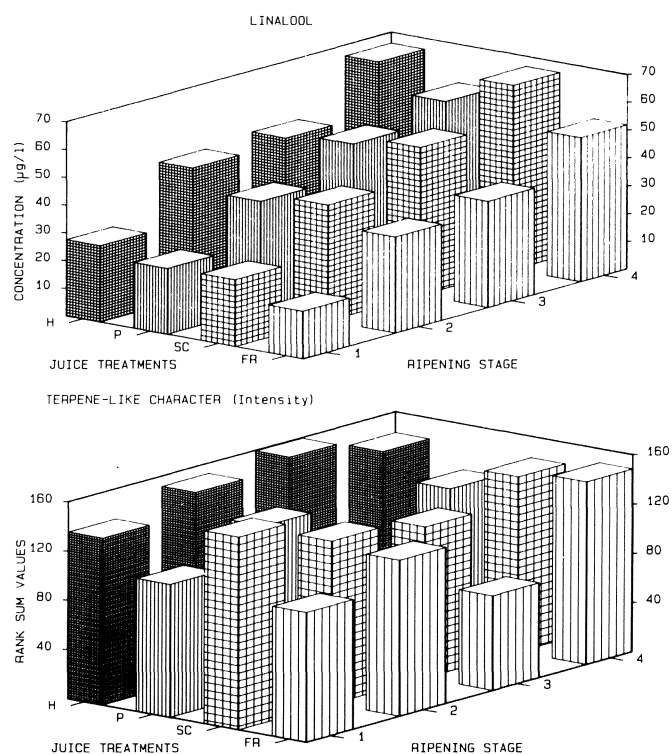


FIG. 7

A comparison of the concentration of linalool with the intensity of terpene-like character of Weisser Riesling wines (Ripening stage 1 = 16,1°B, 2 = 18,8°B, 3 = 18,7°B and 4 = 19,7°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

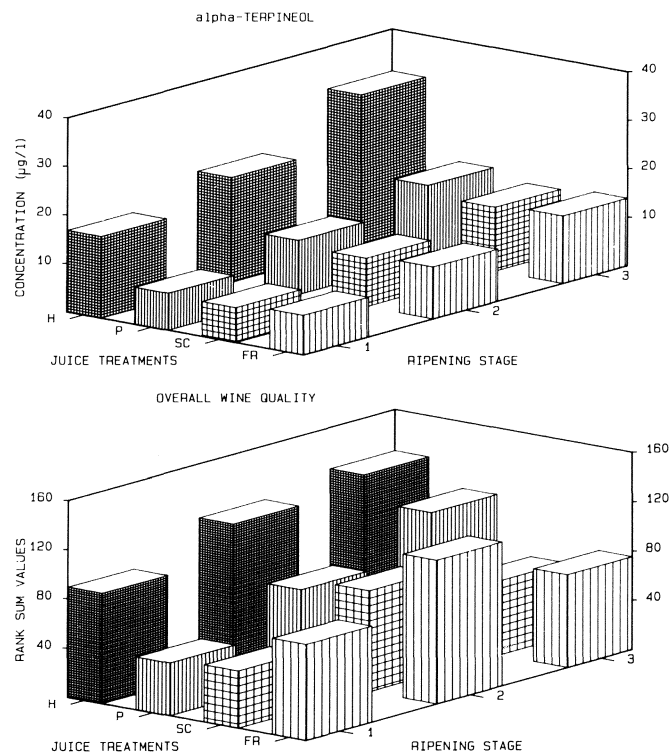


FIG. 8

A comparison of the concentration of alpha-terpineol with the overall wine quality of Bukettraube wines (Ripening stage 1 = 18,1°B, 2 = 20,4°B and 3 = 20,0°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

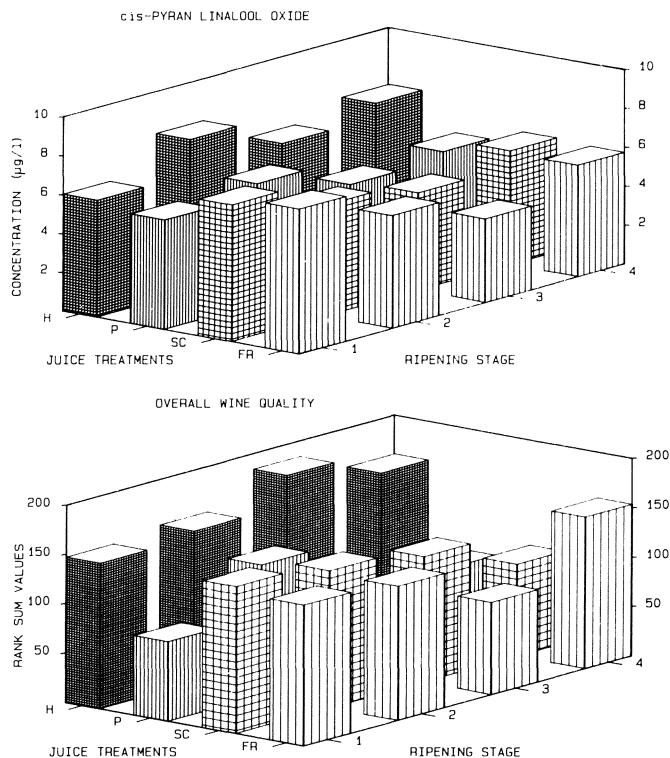


FIG. 9

A comparison of the concentration of cis-pyran linalool oxide with the overall wine quality of Weisser Riesling wines (Ripening stage 1 = 16,1°B, 2 = 18,8°B, 3 = 18,7°B and 4 = 19,7°B. FR = Free-run, SC = Skin-contact, P = Press treatment and H = Heat treatment. Terpene concentrations are expressed as relative concentrations, using a calibration factor of 1).

threshold value, it nevertheless appears to be an indicator of wine quality (Fig. 9). In cases where differences in tendencies between terpene concentrations and sensory results occurred, it may probably be ascribed to factors such as coarseness of aroma and taste of the wines. This latter wine parameter could have affected the sensory evaluation scores without being reflected in the concentrations of the relevant terpenes in the corresponding wines.

SUMMARY AND CONCLUSIONS

An increase in grape maturity mainly caused increases in concentrations of the terpenes analysed. Although the grapes of Weisser Riesling and Buketraube were harvested over relatively limited °B intervals, some changes in terpene concentrations were nevertheless significant. According to the sensory evaluations of terpene-like character, cultivar authenticity and overall wine quality, the second ripening stage produced the highest quality wines in both cases of Weisser Riesling and Buketraube. This tendency, however, was not reflected in the individual terpene concentrations. Nevertheless, the results of this study suggest the possible occurrence of a desired aroma quality for the production of high quality wines at a specific maturation stage. Studies in this respect will be repeated and expanded on different cultivars from different regions.

With respect to juice treatments, skin-contact and the press treatment had limited effects on terpene concentrations under the conditions of this investigation.

Heat treatment, on the other hand, resulted in significant increases in most of the terpene concentrations. This tendency was in some cases more prominent in juices, than in the corresponding wines and the effect of fermentation on this phenomenon will be investigated in future research. Heat treatment also resulted in increases in the intensities and qualities of the relevant quality parameters of Weisser Riesling and Buketraube wines. Close relationships, with regard to this aspect were found between terpene concentrations and sensory evaluation results. The enrichment in terpenes by juice treatments, such as heat treatment, may be the result of the liberation thereof from bound forms and may result in the production of aroma-rich white table wines. Skin-contact and heat treatment at different temperatures for different periods will be investigated in future studies, in order to utilize the full grape aroma potential.

LITERATURE CITED

- BAYONOVE, C. & CORDONNIER, R., 1970a. Recherches sur l'arôme du muscat. I. Evolution des constituants volatils au cours de la maturation du Muscat d'Alexandrie. *Ann. Technol. Agric.* **19**, 79-93.
- BAYONOVE, C. & CORDONNIER, R., 1970b. Recherches sur l'arôme du muscat. II. Profils aromatiques de cépages muscat et non muscat. Importance du linalol chez les muscats. *Ann. Technol. Agric.* **19**, 95-105.
- BAYONOVE, C. & CORDONNIER, R., 1971. Recherches sur l'arôme du muscat. III. Étude de la fraction terpénique. *Ann. Technol. Agric.* **20**, 347-355.
- BAYONOVE, C. & CORDONNIER, R. & RATIER, R., 1974. Localisation de l'arôme dans la baie de raisin: variétés Muscat d'Alexandrie et Cabernet Sauvignon. *C.R. Séances Acad. Agric. Fr.* **60**, 1321-1328.
- BAYONOVE, C., GÜNATA, Y.Z. & CORDONNIER, R., 1983. Mise en évidence de l'intervention des enzymes dans le développement de l'arôme du jus de Muscat avant fermentation: La production de terpenols. *XVIII Congrès International de la vigne et du vin de l'O.I.V.*, Le Cap Afrique du Sud; 24-28 Octobre, 93-111.
- CORDONNIER, R., 1974. L'arôme des vins. *Progr. agric. vitic.* **91**, 320-329.
- CORDONNIER, R. & BAYONOVE, C., 1974. Mise en évidence dans la baie de raisin, variété Muscat d'Alexandrie, de mono-terpènes liés révélables par une ou plusieurs enzymes du fruit. *C.R. Acad. Sc. Paris, Sér. D.* **278**, 3387-3390.
- CORDONNIER, R. & BAYONOVE, C., 1978. Les composantes variétales et fermentaires de l'arôme des vins. *Extrait de Parfum Cosmétiques arômes* **24**, 67-77.
- CORDONNIER, R. & BAYONOVE, C., 1981. Étude de la phase fermentaire de la vinification: Extraction et formation de certains composés de l'arôme; cas des terpenols, des aldéhydes et des alcools en C₆. *Connaiss. Vigne Vin.* **15**, 269-286.
- DI STEFANO, R., 1981. Terpene compounds of white Muscat from Piemonte. *Vini Ital.* **23**, 29-43.
- GÜNATA, Y.Z., 1984. Recherches sur la fraction liée de nature glycosidique de l'arôme du raisin: Importance des terpenyl glycosides, action des glycosidases. Thesis, Ph. D. University of Science and Methods of Languedoc, Inst. Prod. Vigne, Lab Arômes et Sub. Nat., INRA, Montpellier II, France.
- HARDY, P.J., 1970. Changes in volatiles of muscat grapes during ripening. *Phytochemistry* **9**, 709-715.
- KINZER, G. & SCHREIER, P., 1980. Influence of different pressing systems on the composition of volatile constituents in unfermented grape musts and wines. *Am. J. Enol. Vitic.* **31**, 7-13.
- 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.
- OHLOFF, G., 1978. Recent developments in the field of naturally-occurring aroma components. *Fortschritte der chemie organischer naturstoffe* **35**, 431-527.

- RAPP, A., HASTRICH, H., ENGEL, L. & KNIPSER, W., 1978. "Flavor of foods and beverages". Possibilities of characterizing wine quality and vine varieties by means of capillary chromatography. Academic Press, N.Y., S.F. Lond. 391-417.
- RIBÉREAU-GAYON, P., BOIDRON, J.N. & TERRIER, A., 1975. Aroma of Muscat grape varieties. *J. Agric. Food Chem.* **23**, 1042-1047.
- SCOTT, A.J. & KNOTT, M., 1974. A cluster analysis method for grouping means in the analysis of variance. *Biometrics* **30**, 507-512.
- TERRIER, A., BOIDRON, J.N. & RIBÉREAU-GAYON, P., 1972. Teneurs en composés terpéniques des raisins de *Vitis vinifera*. *C.R. Acad. Sc. Paris, Sér. D.* **275**, 941-944.
- USSEGLIO-TOMASSET, L., 1981. Les substances aromatiques du vin et la possibilité de les augmenter par de traitements thermiques. *Int. Oenol. Symp., (Pap.), 6th.* 353-361.
- USSEGLIO-TOMASSET, L. & DI STEFANO, R., 1979. Osservazioni sui costituenti terpenici delle uve e dei vini aromatici. *Vignevini* **6**, X, 33-38.
- USSEGLIO-TOMASSET, L. & DI STEFANO, R., 1980. Profilo aromatico del Moscato bianco del Piemonte. *Riv. Vitic. Enol.* **33**, 58-68.
- VERSINI, G., INAMA, S. & SARTORI, G., 1981. A capillary column gaschromatographic research into the terpene constituents of "Riesling Renano" (Rhine Riesling) wine from Trentino Alto Adige: Their distribution within berries, their passage into must and their presence in the wine according to different wine-making procedures. Organoleptic considerations. *Vini Ital.* **23**, 189-211.
- WAGNER, R., DIRNINGER, N., FUCHS, V. & BRONNER, A., 1977. Study of the intervarietal differences in the concentration of volatile constituents (linalool and geraniol) in the aroma of the grape. Interest of such analyses for the appreciation of the quality of the harvest. *Int. Symp. Qual. Vintage. Cape Town*, 137-142.
- WILLIAMS, P.J., STRAUSS, C.R. & WILSON, B., 1980a. New linalool derivatives in Muscat of Alexandria grapes and wines. *Phytochemistry* **19**, 1137-1139.
- WILLIAMS, P.J., STRAUSS, C.R. & WILSON, B., 1980b. 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., 1981. Classification of the monoterpenoid composition of muscat grapes. *Am. J. Enol. Vitic.* **32**, 230-235.
- WILLIAMS, P.J., STRAUSS, C.R. & WILSON, B., 1983. Recent developments in grape flavour research. *Aust. Grapegrower and Winemaker* **232**, 20-24.
- WILLIAMS, P.J., STRAUSS, C.R., WILSON, B. & MASSY-WESTROPP, R.A., 1982a. Use of C₁₈ reversed-phase liquid chromatography for the isolation of monoterpene glycosides and nor-isoprenoid precursors from grape juice and wines. *J. Chrom.* **235**, 471-480.
- WILLIAMS, P.J., STRAUSS, C.R., WILSON, B. & MASSY-WESTROPP, R.A., 1982b. 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., 1982c. 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.