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Relation between potassium and the malate and tartrate contents of grape berries

by

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Beziehungen zwischen der Kaliumversorgung und dem Malat- und Tartratgehalt von Traubenbeeren

Zusammenfassung. — Die Beziehungen zwischen Kalium und Malat bzw. Tartrat in Traubenbeeren wurden bei Shiraz-Trauben aus dem Gewächshaus und Sultana-Trauben aus dem Freiland untersucht. Bei den Shiraz-Beeren wurde der Kaliumgehalt über die Düngung, bei den Sultana-Beeren durch Verwendung unterschiedlicher Unterlagen variiert.

Zur Zeit der Säureakkumulation wurde in den Beeren keine Beziehung zwischen Kalium und Malat oder Tartrat gefunden. Während der Reife zeichnete sich jedoch eine unmittelbare Beziehung zwischen Kalium und Malat ab. Zwischen Kalium und Tartrat wurde in den reifen Beeren keine Beziehung festgestellt. Eine denkbare ursächliche Beziehung zwischen dem Kalium- und Malatgehalt der reifen Trauben wird diskutiert.

Reife Sultana-Trauben hatten auf den *Vitis-champini*-Unterlagen Dog Ridge und Salt Creek einen höheren Kalium- und Malatgehalt, mehr titrierbare Säure und höheren pH als Trauben von wurzelechten Reben. Auf den Unterlagen 101—14 und Teleki C gezogene Trauben zeigten mittlere Werte. Die önologische Bedeutung dieser Ergebnisse wird diskutiert.

Introduction

The acid characteristics of ripe grapes are important criteria of grape quality. The usual measures of acidity are titratable acidity and pH. They are largely determined by the relative concentrations and amounts of tartaric and malic acids and their salts, particularly those of potassium, which is the major mineral cation in grapes (PEYNAUD and RIBÉREAU-GAYON 1971, WINKLER *et al.* 1974).

Mineral nutrients influence the titratable acidity of ripe grapes (KOBAYASHI *et al.* 1961 a, 1961 b, MATTICK *et al.* 1972) but there are no data on their effect on the malate or tartrate contents of grapes.

Because potassium constitutes about 70% of the mineral cations in ripe grapes, its effect on the acid characteristics of grapes was investigated. Differences in the potassium content of grapes were obtained by varying the potassium supply to the roots or by the use of rootstocks (OUGH *et al.* 1968).

The potassium content of grapes increases throughout berry development (PEYNAUD and RIBÉREAU-GAYON 1971) whereas the concentrations of malate and tartrate reach a maximum before ripening starts and during ripening their concentrations fall as a consequence of berry growth and, in the case of malate, of malate degradation.

Methods

Experiment 1

V. vinifera cv. Shiraz cuttings were grown in "Perlite" in 4.5 l pots. The plants were maintained with Hoagland's solution until berry set when the potassium was withheld from half the plants. These will be referred to as "low-K" and those receiving potassium as "high-K" plants. Flowering was erratic and set was poor. In the following spring the vines were pruned back to a shoot carrying two inflorescences. The low-K plants were maintained with Hoagland's solution 2 containing ¼ of the normal potassium content and the high-K plants on complete Hoagland's solution. After set, potassium was withheld from the low-K plants.

10 plants were selected for uniformity of flowering from each set of vines. A sample of 5 berries was taken from each vine at 3, 5, 7 and 13 weeks after anthesis. The berries were freeze-dried and the dry weight of the pericarp determined.

The water-soluble constituents were extracted from the ground pericarp tissue by refluxing in water at 100 °C for 15 minutes.

Experiment 2

Two groups of 3 Shiraz vines growing in "Perlite" were supplied with different amounts of potassium to produce fruit with different potassium contents. The plants were maintained with Hoagland's solution 2 containing ¼ of, or the normal potassium content. A sample of 20 berries was taken from each vine when the fruit was 'ripe'. One half of each sample was analysed for potassium, malate and tartrate immediately after collection, the other half was analysed after holding it for 7 days at 30 °C in a humid atmosphere.

Experiment 3

Preliminary analyses of Sultana grapes growing on different rootstocks showed that no differences in potassium contents of grapes occurred during the acid accumulating stage but that during ripening large differences developed. These vines were then used to examine the relationship between potassium and malate during ripening.

The experimental design was a 5 × 5 Latin square with single vine plots (Sauer 1972). The scion variety, *V. vinifera* cv. Sultana (syn. Sultanina) clone H5 (C4H of Woodham and Alexander (1966)), was grafted to Dog Ridge and Salt Creek (*V. champini*), 101-14 (*V. riparia* × *V. rupestris*) and Teleki C (*V. berlandieri* × *V. riparia*) and was also growing on its own roots.

Samples of 100 berries were taken from each vine at intervals during the 1973—74 and 1974—75 seasons, the first before the onset of ripening and the last at commercial harvest. The berries were weighed, washed and frozen. The water soluble constituents were extracted by covering the frozen berries with water and autoclaving for 15 minutes. After cooling the berries were homogenised with a Waring blender and made upto volume.

The skin and pulp were separated in the second season by allowing the berries to thaw slightly and then pressing out the pulp. The skin and pulp fractions were then treated as described above.

Analyses

Potassium was determined by flame photometer, malate and tartrate by gas liquid chromatography (Buttrose *et al.* 1971) in experiments 1 and 2 and by ion exclusion chromatography (Monk and Forrest, personal communication) in experiment 3 and titratable acidity by titration to the phenolphthalein end point.

Table 1

Potassium, malate and tartrate contents of the pericarp tissue of grapes from low- and high-K Shiraz vines at different stages of berry development

Kalium-, Malat- und Tartratgehalt bei niedriger und hoher Kaliumversorgung der Reben in verschiedenen Stadien der Beerenentwicklung

Stage of development Weeks after flowering	Potassium status	K	% D.W. Malate	Tartrate
3	low	0.86	14.50	22.20
	high	1.25	15.60	23.60
5	low	1.70	21.60	16.80
	high	2.50	22.30	16.90
7 (lag)	low	1.60	25.30	16.30
	high	2.60	26.50	17.60
13	low	0.52	2.06	3.61
	high	0.79	2.90	3.63
LSD (P = 0.05)		0.16	0.62[1])	NS

[1]) Between means at 13 weeks. NS at other times.

Results

Experiment 1

Potassium status of vines.

The low-K plants were potassium deficient as indicated by leaf symptoms and the potassium content of petioles (Winkler *et al.* 1974). The values for petiole potassium 3 weeks after flowering were 1.06% and 6.4% for low- and high-potassium plants respectively.

Berry composition.

Potassium: The potassium content (% D.W.) (Table 1) of pericarp tissue from the high- and low-K plants increased for the first three sampling periods, i.e. during the acid accumulating stage of berry development, but during the next stage of development, ripening, it decreased. At all times the pericarp tissue from the high-K plants had a higher K content than that from the low-K plants.

Malate: The malate content of pericarp tissue (Table 1) increased during the acid accumulating stage of berry development. No differences were apparent

Table 2

Changes in acid composition of excised Shiraz berries having different potassium status

Veränderungen in der Säurezusammensetzung isolierter Shiraz-Beeren bei unterschiedlicher Kaliumversorgung

K (% F.W.)	Malate (% F.W.) Initial	Final	Change	Tartrate (% F.W.) Initial	Final	Change
0.17	0.302	0.184	—40%	0.493	0.451	—9%
0.36	0.405	0.314	—22%	0.613	0.563	—8%

between the high- and low-K fruit. However, at 13 weeks, the malate content of the low-K fruit was lower than that of the high-K fruit.

Tartrate: No differences between the tartrate contents of high- and low-K grapes were detected at any time (Table 1).

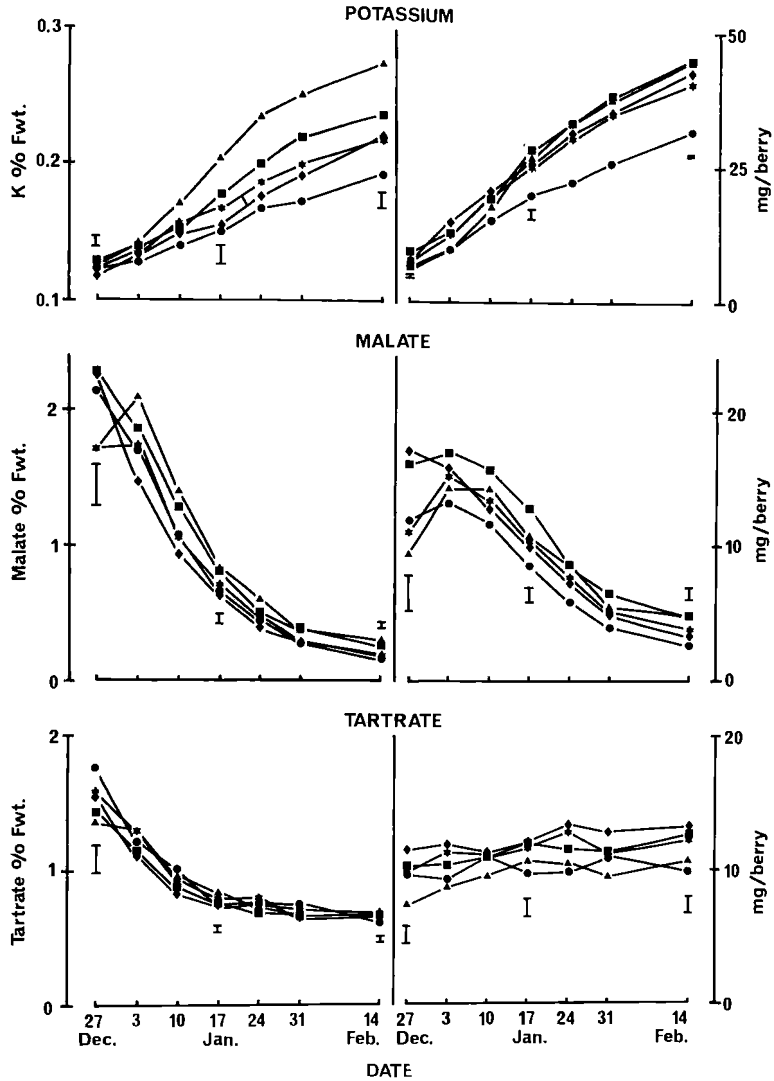

Fig. 1: Changes during ripening in the concentrations (% F.W. and mg/berry) of potassium, malate and tartrate of Sultana berries grown on different rootstocks, 1973—74. The rootstocks were ● own roots, ▲ Dog Ridge, ■ Salt Creek, ✱ 101-14, ♦ Teleki C. The vertical bars indicate the least significant differences (P = 0.05) for the appropriate dates.

Veränderungen der Konzentration (% des Frischgewichtes und mg/Beere) von Kalium, Malat und Tartrat in den Beeren der Sorte Sultana auf verschiedenen Unterlagen, 1973-74. Wurzel: ● = wurzelecht, ▲ = Dog Ridge, ■ = Salt Creek, ✱ = 101-14, ♦ = Teleki C. Signifikanzschwellen für P = 0,05 eingetragen.

Table 3

Potassium contents of petioles from Sultana vines on different rootstocks
Kaliumgehalt in den Blattstielen der Sorte Sultana auf verschiedenen Unterlagen

	Own root	Dog Ridge	Potassium (% D.W.) Salt Creek	101-14	Teleki C
13 November (full bloom)	3.36	2.98	3.85	4.17	3.90
March (after harvest)	2.29	5.30	4.48	3.04	2.96
LSD (P = 0.05)	0.51	0.60	NS	0.63	0.78

Experiment 2

Berries with a low potassium content lost 40% of their malate whereas berries with a high potassium content lost only 22% (Table 2). The changes in tartrate were much less and were not related to the potassium content of the berries.

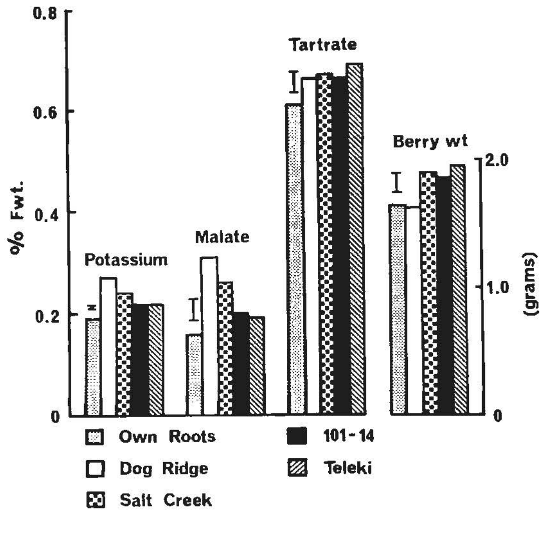

Fig. 2.: Concentration (% F.W.) of potassium, malate and tartrate of Sultana berries grown on different rootstocks at the final harvest 1973—74. The vertical bars indicate least significant differences (P = 0.05).

Konzentration (% des Frischgewichtes) von Kalium, Malat und Tartrat in den Beeren der Sorte Sultana auf verschiedenen Unterlagen, 1973—74 — letzte Ernte. Signifikanzschwellen für P = 0,05 eingetragen.

Experiment 3

Potassium status of the vines.

The values for the potassium content of petioles (Table 3) show that the vines were adequately supplied with potassium (Winkler *et al.* 1974). The potassium content of petioles from vines on 101-14, Teleki C and own roots decreased between flowering and harvest which is the expected behaviour for Sultana vines (Christiansen 1969) whereas the potassium content of petioles from vines on Dog Ridge and Salt Creek increased.

Potassium: The concentrations of potassium in grapes from the different rootstocks were similar at the start of ripening (Fig. 1), but after about two weeks they began to diverge. At the final harvest the ranking in order of decreasing concentration was Dog Ridge > Salt Creek > 101-14 and Teleki C > own roots (Fig. 2). In the second season this ranking was also found in the skin and pulp fractions

(Fig. 3). The proportion of potassium found in the pulp decreased from 70% at the beginning of ripening to 63% at harvest. No differences in the distribution of potassium between skin and pulp were found between grapes from the different stocks.

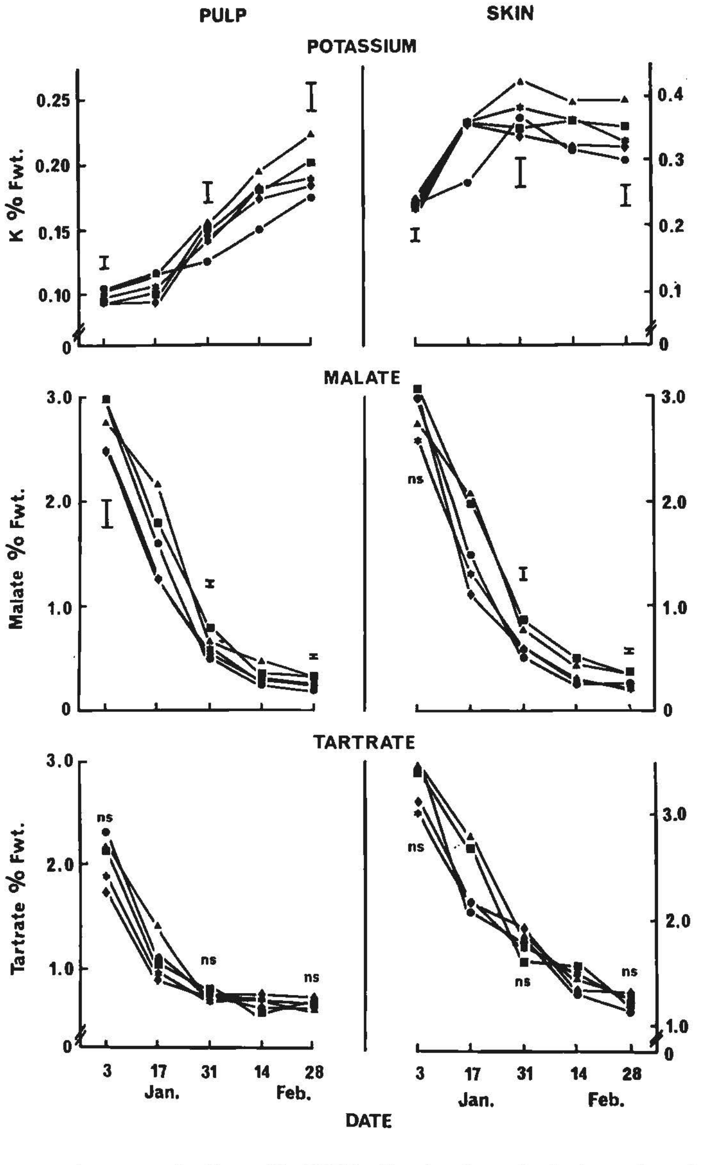

Fig. 3.: Changes in concentrations (% F.W.) of potassium, tartrate and malate in pulp and skins of Sultana berries grown on different rootstocks, 1974—75. Symbols as for Figure 1.

Veränderungen der Konzentration (% des Frischgewichtes) von Kalium, Tartrat und Malat in Beerenfleisch und -häuten der Sorte Sultana auf verschiedenen Unterlagen, 1974—75. Symbole wie in Abb. 1.

Malate: The concentration of malate (Fig. 1) in berries from Salt Creek, Teleki C and own roots fell rapidly from the first time of sampling and in berries from 101-14 and Dog Ridge from the second. The concentrations at harvest were about one-tenth of their maximum values. Berries from Dog Ridge and Salt Creek had the highest concentrations and own roots the lowest (Fig. 2). These rankings were found in the second season in both skin and pulp (Fig. 3).

The changes in malate per berry (Fig. 1) show that no appreciable loss of malate occurred until about the 10th January. Thus the initial rapid fall in malate concentration was due to berry growth and not to malate degradation. At the final harvest Dog Ridge and Salt Creek had the highest malate content on both a berry and a fresh weight basis, and Teleki C and own roots had the least. Relatively more malate was lost from Teleki C and own roots than from Dog Ridge and Salt Creek. Most of the malate was lost during the period of rapid malate degradation which began on 10th January and finished about three weeks later (Fig. 1).

The concentrations of malate in skin and pulp from the same berries were similar (Fig. 3). This is of interest because of the known effects of temperature on malate loss and the temperature differential between skin and interior of the berry. The proportion of malate in the pulp of berries from own rooted vines fell from 80% at the start of ripening to 72% at the final harvest. In the others it remained at about 80% throughout ripening.

Tartrate: The concentration of tartrate (% F.W.) fell rapidly during early ripening (Fig. 1). This rapid fall was due to berry growth because tartrate per berry increased slightly (Fig. 1) during ripening. Differences in tartrate concentration apparent early in ripening had disappeared by the 17th January and after this tartrate concentrations were similar in fruit from all stocks.

The concentration of tartrate was greater in skins than in pulp (Fig. 3); at the final harvest it was almost double. There were no differences between rootstocks. The proportion of tartrate in the pulp tended to fall during ripening, the mean values being 71% and 67% for the first and last samples respectively.

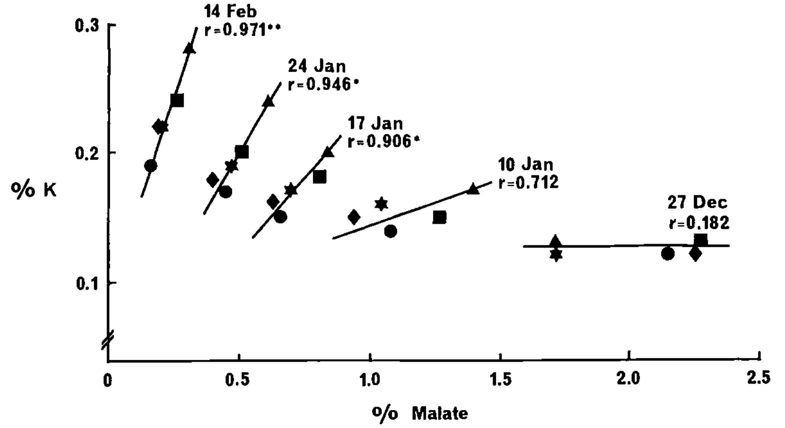

Fig. 4.: Correlations between potassium and malate at different times during the ripening of Sultana berries grown on different rootstocks 1974—75. Symbols as for Figure 1.

Korrelation zwischen Kalium und Malat zu verschiedenen Reifezeitpunkten in den Beeren der Sorte Sultana auf verschiedenen Unterlagen, 1974—75. Symbole wie in Abb. 1.

Relationship between potassium and malate: A positive correlation between potassium and malate became apparent as ripening progressed (Fig 4) and became statistically significant on 17th January. This was about the time that malate degradation began to play a major part in reducing malate concentration.

Table 4

Titratable acidity and pH of ripe Sultana berries grown on own roots (OR), Dog Ridge (DR), Salt Creek (SC), 101—14 and Teleki C (T). The grapes were harvested on February 14, 1974 and February 28, 1975

Titrierbare Säure und pH reifer Beeren der Sorte Sultana auf eigener Wurzel (OR), Dog Ridge (DR), Salt Creek (SC), 101-14 und Teleki C (T). Traubenernte am 14. Februar 1974 und am 28. Februar 1975

Year	Berry fraction	Titratable acidity (% F.W.)						pH					
		OR	DR	SC	101-14	T	LSD (P = 0.05)	OR	DR	SC	101-14	T	LSD (P = 0.05)
1974	Entire	0.62	0.70	0.67	0.64	0.61	0.05						
1975	Pulp	0.47	0.53	0.55	0.48	0.50	0.04	3.63	3.79	3.76	3.65	3.67	0.10
	Skin	0.76	0.87	0.84	0.75	0.76	0.07	3.61	3.75	3.70	3.67	3.43	0.08

B e r r y w e i g h t : Berries on Dog Ridge and own roots were the same size and were smaller than the others (Fig. 2). In the second season, berries on Dog Ridge were smaller than those on own roots which, in turn, were smaller than the others.

A c i d i t y : At the final harvest in both years grapes on Dog Ridge and Salt Creek had higher acidities than grapes on the other stocks (Table 4).

Acidity was higher in skins than in pulp for all stocks.

p H : The pH of pulp and skin extracts of fruit from all stocks increased during ripening and at the final harvest (Table 4), the values for grapes from Dog Ridge and Salt Creek were higher than the others.

Discussion

The relationship between potassium and malate was established during ripening, i.e. the acid loss stage of berry development and not, surprisingly, during the acid accumulating stage. The similarity of the results from the different experimental approaches suggests that there may be a causal relationship between potassium and malate in ripening grapes. The fact that it was established when malate was being degraded makes it unlikely that it could be due to acid synthesis in response to the greater cation uptake as has been proposed for the direct relationship between potassium and organic acids in the tomato (Hobson and Davies 1971). A more likely explanation is that it is due to an effect of potassium on membrane permeability.

There is general agreement that membrane permeability increases in ripening fruits (Sacher 1973), and Vickery and Bruinsma (1973) reported an inverse relationship between potassium and tonoplast permeability in the ripening tomato fruit. From considerations of cell anatomy, it is thought that most of the malate in grape berries is located in the vacuole. It is proposed that tonoplast permeability regulates in some way the malate concentration at the conclusion of the rapid acid loss phase of ripening.

Temperature, the chief environmental factor affecting malate concentration in ripe grapes (Winkler *et al.* 1974), may exert its effect in the same way. Ruffner *et al.* (1976) suggested an involvement of membrane permeability in the regulation of malate concentration in ripe grapes when they were unable to explain effects of temperature on malate concentration by shifts in activities of enzymes involved in malate degradation.

Support for the idea that environmental factors which influence acid concentration in ripe grapes act through a common mechanism, comes from data which describe effects of different treatments on acid concentrations in grapes during ripening (Peynaud and Maurié 1956, Kliewer *et al.* 1967, du Plessis 1968, Kliewer and Lider 1970, Kliewer 1971). These data show that the effect of the different treatments (temperature, shade or season) is on the level to which the concentration of malate is reduced at the end of the period of rapid acid loss. Subsequently, the concentration declines slowly until ripeness but treatments appear to have no further effect.

The experiment with excised berries suggests that potassium may modify the effect of temperature on the malate concentration of ripe grapes. This interaction could account for some of the unexpectedly high acid levels found sometimes when grapes ripen at high temperatures (Amerine 1956, Peynaud and Maurié 1956, du Plessis 1968).

Grapes with the higher potassium content had a higher titratable acidity and pH. The higher acidity may be accounted for by the higher malate content of these grapes. The higher pH was probably related to the higher potassium and to the greater proportion of malic acid which is a weaker acid than tartaric.

The higher potassium and malate content and pH of grapes grown on Dog Ridge and Salt Creek than of those grown on their own roots raises the possibility that *V. champini* stocks may not be suitable for wine grapes in some situations. These would be in the hotter grape-growing regions where high pH associated with a high malate content is undesirable on grounds of wine stability (AMERINE 1956, CIRAMI 1973), or where the potassium content of the grapes is already excessively high (SOMERS 1975). Effects of these stocks on wine grapes and wine quality is being examined.

Summary

The relationship between potassium and malate and tartrate in grape berries was investigated in fruit from Shiraz vines grown in the glasshouse and from field-grown Sultana vines. The potassium content of Shiraz berries was varied by varying the potassium supply and that of the Sultana berries by use of rootstocks.

No relationship between potassium and malate or tartrate during the acid accumulating stage of berry development was found. However, a direct relationship between potassium and malate developed during ripening. No relationship between potassium and tartrate in ripe berries was seen. A possible causal relationship between potassium and malate concentrations in ripe grapes is discussed.

Ripe Sultana grapes grown on the *Vitis champini* rootstocks, Dog Ridge and Salt Creek, had higher potassium and malate contents, higher titratable acidity and higher pH values than grapes grown on their own roots. Values for grapes grown on 101-14 and Teleki C stocks were intermediate. The enological significance of these results is discussed.

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