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The effect of pH on esters and quality of Colombar wine during maturation

by

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Der Einfluß des pH-Wertes auf die Ester und die Qualität von Colombar-Wein während der Flaschenreifung

Zusammenfassung. — Der Einfluß verschiedener pH-Werte auf die Esterkonzentration und auf das Ergebnis der sensorischen Qualitätsbeurteilung wurde in Beziehung zur Lagerdauer und -temperatur untersucht. Bei den Acetatestern war, vor allem im niedrigsten pH-Bereich, eine auffälligere Konzentrationsabnahme als bei den Äthylestern zu verzeichnen. Das Diäthylsuccinat nahm zu, insbesondere beim niedrigsten pH-Wert. Die Weinqualität veränderte sich nicht gleichsinnig mit den Konzentrationsverschiebungen bei den Estern. Eine Ursache für diesen Befund könnte im Auftreten eines Reifearomas und dem gleichzeitigen Verschwinden des Sortencharakters zu suchen sein.

Introduction

It is commonly accepted that esters are an important facet of wine quality and flavour. Several research workers stressed the relevant contribution of fatty acid esters in this respect. (Postel *et al.* 1972, Rapp *et al.* 1973, Schreier and Drawert 1974, Marais 1976, unpublished report, Rapp 1977, personal communication).

It is known that ester hydrolysis is accelerated by acids (Glasstone and Lewis 1963) and since wine is an acidic medium, this reaction can be expected to occur in wines. Furthermore, the pH of South African white wines can vary between approximately 3.30 and 3.70 (Marais and Snyman 1978, unpublished data).

Because of the relatively large differences in wine pH values, appreciable differences in ester concentrations due to hydrolysis may occur during wine maturation. When the well-known accelerating effect of high temperatures on chemical reactions and the relatively high ambient temperatures in this country are considered, the influence of pH on this facet of wine quality takes on added importance.

This field of study has received little attention in the past. In view of the importance of the contribution of esters to wine quality and the possible influence of pH upon them, this aspect was investigated further to study the effect of pH and temperature on ester concentrations and wine quality during maturation.

Materials and methods

A Colombar wine made from grapes grown on the experimental farm in the Stellenbosch area served as basic material for this study. The wine was made from free run juice, fermented at 12 °C and bottled with a free sulphur dioxide content of 25 mg/l.

1. pH adjustment and pH groups

The wine was divided into three lots and the pH of two lots were adjusted to obtain the following:

a) pH of the wine without any adjustments (pH 3.32).
b) pH 0.3 units lower than that of the untreated wine. The pH of the wine was decreased to pH 3.02 by the addition of 0.1 n HCl.
c) pH 0.3 units higher than that of the untreated wine. The pH of the wine was increased to 3.62 by the addition of 0.1 n NaOH. Subsequent to this pH adjustment, the wine pH increased slightly to 3.72 and maintained this value throughout the study.

These pH values were regularly checked over the 16 week experimental period and remained constant.

2. Temperature effect

To investigate the influence of pH over a relatively wide range of temperatures, wines of each pH group were stored in rooms at 10, 20 and 30 °C.

3. Stage of analysis and sensory evaluation

Samples were drawn for analysis and evaluation:

I immediately after bottling, as well as
II 3 weeks,
III 7 weeks and
IV 16 weeks after bottling.

Sensory evaluation was carried out by a panel of 13 judges by means of a 9-point scoring system (Tromp 1977).

4. Analysis

Samples were analysed gas chromatographically for 7 major esters by the method of de Vries (1962) as modified by Marais (1976, unpublished report).

Results and discussion

Concentrations of 7 esters as affected by pH, time and temperature are given in Table 1.

1. Acetate esters

In general and within a pH group, ester concentrations decreased with both time and temperature. This is especially marked at the longer time intervals. Since the values obtained at 16 weeks (Table 1, IV values) showed the largest effects, these data were normally utilised in preference to all the "time data" to determine general patterns of change. The correlations between the IV values of the individual acetate esters over all pH and temperature values showed high significance indicating that they reacted in a similar manner to pH variations (Table 2). This marked similarity of behaviour was also highly significant even in the values obtained at 7 weeks (Table 1, III) where changes were much smaller than in the IV values (Table 2).

To indicate change patterns, the IV values of the members of low concentration esters (n-hexyl acetate and 2-phenethyl acetate) were adapted to bring them in the same concentration range as i-amyl acetate (Table 1, footnote). By dividing the I

Table 1

Effect of pH on ester concentrations and wine quality of a Colombar wine at several temperatures and time intervals
Einfluß des pH-Wertes auf die Esterkonzentration und die Qualität eines Colombar-Weines bei verschiedenen Temperaturen und Zeitintervallen

Ester mg/l	Time	pH 3.02			pH 3.32			pH 3.72			Average of I samples mg/l	Standard deviation mg/l
		10 °C	20 °C	30 °C	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C		
i-Amyl acetate	I	3.80	3.50	3.98	3.57	3.64	3.86	3.94	3.38	3.45	3.68	0.22
	II	3.53	3.27	2.99	4.10	3.66	3.10	3.74	4.48	3.54		
	III	3.75	2.05	1.00	4.14	3.25	1.60	3.48	3.90	2.93		
	IV	2.50	1.88	0.24	3.43	2.30	0.97	3.15	2.55	1.78		
Ethyl n-caproate	I	1.23	1.21	1.37	1.26	1.27	1.22	1.20	1.14	1.17	1.23	0.07
	II	1.24	1.20	1.31	1.30	1.26	1.18	1.20	1.28	1.21		
	III	1.28	1.06	1.21	1.34	1.24	1.12	1.16	1.21	1.20		
	IV	1.15	1.15	1.12	1.29	1.08	1.15	1.17	1.06	1.14		
n-Hexyl acetate	I	0.32	0.32	0.36	0.34	0.37	0.35	0.32	0.32	0.33	0.34	0.02
	II	0.31	0.28	0.21	0.33	0.32	0.22	0.33	0.32	0.28		
	III	0.28	0.19	0.06	0.31	0.26	0.10	0.31	0.29	0.18		
	IV	0.23	0.16	0	0.30	0.20	0.11	0.29	0.23	0.14		
		(2.49)	(1.71)	(0)	(3.28)	(2.20)	(1.18)	(3.24)	(2.56)	(1.52)		
2-Phenethyl acetate	I	0.89	0.97	0.82	0.84	0.91	0.88	0.86	0.88	1.04	0.90	0.07
	II	0.81	0.85	0.60	0.81	0.81	0.71	0.84	0.80	0.79		
	III	0.69	0.73	0.25	0.76	0.69	0.44	0.79	0.75	0.58		
	IV	0.69	0.50	0.09	0.75	0.65	0.27	0.74	0.81	0.44		
		(2.82)	(2.05)	(0.36)	(3.08)	(2.67)	(1.10)	(3.05)	(3.34)	(1.80)		
Ethyl n-caprylate	I	2.55	3.10	2.67	2.46	2.99	2.89	2.71	2.79	3.56	2.86	0.33
	II	2.86	2.86	3.06	2.65	2.84	3.10	2.93	3.02	2.86		
	III	3.13	3.45	2.72	3.30	2.99	2.76	2.99	2.87	2.62		
	IV	2.62	2.63	2.39	2.27	2.61	2.19	2.54	2.73	1.94		
		(1.13)	(1.13)	(1.03)	(0.97)	(1.12)	(0.94)	(1.09)	(1.18)	(0.83)		
Ethyl n-caprate	I	0.79	0.86	0.73	0.69	0.70	0.69	0.77	0.77	0.96	0.77	0.09
	II	0.82	0.90	0.70	0.76	0.75	0.66	0.81	0.74	0.66		
	III	0.75	0.94	0.58	0.73	0.69	0.50	0.70	0.69	0.54		
	IV	0.76	0.70	0.58	0.79	0.71	0.57	0.65	0.79	0.50		
		(1.21)	(1.12)	(0.92)	(1.25)	(1.12)	(0.90)	(1.04)	(1.72)	(0.79)		
Diethyl succinate	I	0	0	0	0	0	0	0	0	0	—	—
	II	0	0	0.13	0	0	0.06	0	0	0.03		
	III	0	0.09	0.84	0	0.05	0.56	0	0	0.16		
	IV	0.08	0.26	2.29	0.04	0.13	1.00	0.02	0.06	0.55		

Table 1 (continued)

Wine quality %	Time	pH 3.02			pH 3.32			pH 3.72		
		10 °C	20 °C	30 °C	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C
Sensory evaluation after TROMP (1977)	I	65	69	67	66	69	71	70	68	63
	II	67	65	66	68	71	71	78	74	69
	III	65	67	66	73	70	69	63	67	70
	IV	69	75	75	76	67	75	74	69	70

I: Immediately after bottling.
II: 3 weeks after bottling.
III: 7 weeks after bottling.
IV: 16 weeks after bottling.

Bracketed numbers: Adapted values
I n-Hexyl acetate and I 2-phenethyl acetate in relation to I i-amylacetate values.
Hexyl acetate values IV × 11.02.
2-Phenethyl acetate IV values × 4.10.
I Ethyl n-caprylate and I ethyl n-caprate in relation to I ethyl n-caproate values.
Ethyl n-caprylate IV values × 0.43.
Ethyl n-caprate IV values × 1.59.

values of n-hexyl acetate and 2-phenethyl acetate into the I values of i-amyl acetate, adjustment factors were obtained. The values at time IV were then multiplied with the relevant adjustment factors. The initial I values and the averaged adjusted IV values of the acetate esters were plotted against time for each pH and temperature value.

These data are shown in Fig. 1. It is clear that pH has a marked effect on the rate of decrease in ester concentration in the wine; in fact, the lower the pH the faster these decreases. Furthermore, this influence is accentuated by an increase in temperature. The effect of low pH (3.02) and relatively high temperature (30 °C) showed practically complete loss of acetate esters after 16 weeks. At lower temperatures, pH influence was clearly not as marked but it was nevertheless evident that the lower pH was still more effective than the higher in decreasing ester concentrations.

2. Ethyl esters

From the data in Table 1 it is clear that decreases in ethyl esters were largest in the IV values as in the case of the acetate esters. Correlations were consequently determined between the IV values of the individual members of this ester group (Table 2). Significance at the 95 % confidence level was established only between ethyl caprylate and caprate. The differences which occurred here were often within the range of the standard deviation (Table 1) and consequently statistical significance was difficult to establish. Nevertheless, the general pattern of change of the ethyl esters appeared similar with respect to magnitude and direction and adapted values were again employed, as for the actetate esters (Table 1, footnote). The initial and averaged final values are plotted in Fig. 2.

The changes in this group of esters were considerably smaller than that of the acetate esters. Furthermore, the decreases within each pH group were to all intents practically similar for the ethyl esters. Individually the caprate ester did tend to show slightly larger decreases but these appeared to be more strongly influenced by temperature (30 °C) than by pH (Table 1).

3. Succinate ester

Initially there were no determinable amounts of diethyl succinate in the wines of any of the pH groups (Table 1). However, it increased with time and after 16 weeks diethyl succinate was present in all samples (Table 1). From these data it was shown that pH manifested a marked effect on its formation; the higher the pH the less succinate is formed. Moreover, within a pH group, the higher the temperature, the higher the succinate concentration at a given time. A low pH combined with a high temperature was by far the most effective in bringing about increases in this ester.

Table 2

Correlations between ester concentrations in a Colombar wine over a range of pH values and temperatures

Korrelationen zwischen den Esterkonzentrationen eines Colombar-Weines. Die Daten für die verschiedenen pH-Werte und Temperaturstufen wurden zusammengefaßt

Esters	2-PEA IV	HA IV	i-AA IV	HA III	2-PEA III	EC_8 IV	EC_{10} IV
i-AA IV	0.950**	0.989**	—	—	—	—	—
HA IV	0.949**	—	—	—	—	—	—
DES IV	—0.925**	—0.910**	—0.897**	—	—	—	—
i-AA III	—	—	—	0.957**	0.839**	—	—
HA III	—	—	—	—	0.926**	—	—
EC_6 IV	—	—	—	—	—	—0.397 NS	0.135 NS
EC_8 IV	—	—	—	—	—	—	0.723*

i-AA: i-Amyl acetate.
HA: n-Hexyl acetate.
2-PEA: 2-Phenethyl acetate.
EC_6: Ethyl n-caproate.
EC_8: Ethyl n-caprylate.
EC_{10}: Ethyl n-caprate.
DES: Diethyl succinate.

III: 7 weeks after bottling.
IV: 16 weeks after bottling.

*: Significant at 95 % confidence level.
**: Significant at 99 % confidence level.
NS: Not significant.

Table 3

Influence of pH in a Colombar wine on esters and wine quality over time and range of temperatures. Analysis of variance of Table 1 data

Einfluß des pH-Wertes auf die Ester und die Qualität eines Colombar-Weines. Die Daten für die verschiedenen Zeitintervalle und Temperaturstufen wurden zusammengefaßt. Varianzanalysen der Daten aus Tabelle 1

pH	i-AA mg/l	HA mg/l	2-PEA mg/l	EC_6 mg/l	EC_8 mg/l	EC_{10} mg/l	DES mg/l	SE %
3.02	2.71	0.23	0.66	1.21	2.84	0.76	0.31	68
3.32	3.13	0.27	0.71	1.22	2.75	0.69	0.15	71
3.72	3.36	0.28	0.78	1.18	2.80	0.71	0.07	70
LSD	0.59	0.05	0.12	0.06	0.26	0.08	0.35	3.40

Abbreviations of esters see Table 2.
SE: Sensory evaluation (wine quality).
LSD: Lowest significant difference ($P \leqslant 0.05$).

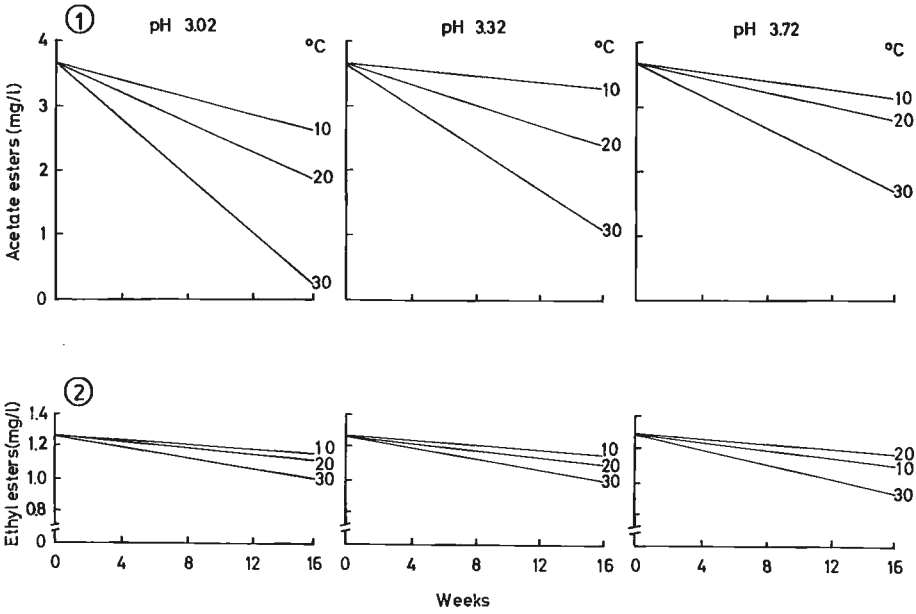

Fig. 1: Decrease in adapted averages of summed i-amyl acetate, n-hexyl acetate and 2-phenethyl acetate ester concentrations in a Colombar wine over 16 weeks at three temperatures for pH values of 3.02, 3.32 and 3.72.

Fig. 2: Decrease in adapted averages of summed ethyl caproate, ethyl caprylate and ethyl caprate ester concentrations in a Colombar wine over 16 weeks at three temperatures for pH values of 3.02, 3.32 and 3.72.

Abb. 1: Abnahme der Gesamtkonzentration (angepaßte Mittelwerte) von i-Amylacetat, n-Hexylacetat und 2-Phenyläthylacetat eines Colombar-Weines im Verlauf von 16 Wochen bei drei Temperaturen und den pH-Werten 3,02, 3,32 und 3,72.

Abb. 2: Abnahme der Gesamtkonzentration (angepaßte Mittelwerte) von Äthylcapronat, Äthylcaprylat und Äthylcaprinat eines Colombar-Weines im Verlauf von 16 Wochen bei drei Temperaturen und den pH-Werten 3,02, 3,32 und 3,72.

To summarize, three discrete groups of esters based on pH effect, emerged. The first group viz. the ethyl esters generally showed relatively small changes and were not markedly pH dependent. Changes in this group showed no significant effect of pH (Table 3). The second group viz. the acetate esters, were pH dependent and significant decreases in the ester concentrations occurred as shown by the markedly lower values in the pH 3.02 group in relation to those of the pH 3.72 group (Table 3). The diethyl succinate ester was classed in the third group and showed increasing trends with decrease in pH, the inverse of that of group two. Although the differences were not significant the trends were nevertheless clear and consistent (Table 3).

4. Wine quality

It has been found that both the acetate and ethyl esters correlated significantly with wine quality in 4 months old Colombar wines made under standard conditions (Marais 1976, unpublished report). Under the conditions of this study i.e. where pH

and temperatures were varied, marked and dissimilar ester changes occurred and could consequently have influenced wine quality dissimilarly. From the sensory evaluation data in Table 1 there were indications that quality tended to improve especially at 16 weeks in the two lower pH groups. In the sensory evaluation it was noted that bottle maturation bouquet developed in these wines. In effect, the important wine quality factor, bouquet, underwent changes from a varietal to a matured character, resulting in no clear and consistent relationship between ester concentrations and wine quality.

It has been reported that dimethyl sulphide is an important contributor to bottle maturation bouquet (DU PLESSIS and LOUBSER 1974, LOUBSER and DU PLESSIS 1977). Its possible formation in the wines of this study could consequently overshadow ester influence and effect inconclusive relationships in this respect. The data in Table 3 show that significant decreases occurred in all the acetate esters with lower wine pH, yet sensory evaluation differences in wine quality were insignificant.

The overall evaluation of this study on Colombar wines indicates a marked complexity where contra-effects tended to balance out pH effect on wine esters and quality. Nevertheless, pH effect was shown to be important. Furthermore, this study has also indicated marked temperature effects on ester concentrations which could be important in the warmer wine producing countries. It is clear from this work that further investigations are necessary, especially with regard to more clearly defined sensory evaluation in terms of varietal and maturation bouquet. In this respect varietal character appears to be of importance and further studies which cover this and temperature aspects are at present being undertaken.

Summary

The effect of several pH values upon esters and quality of a Colombar wine was studied at various times and temperatures. The decreases of the acetate ester concentrations were considerably more marked than that of the ethyl esters, especially at the low pH. Increases in diethyl succinate occurred, especially at the low pH. Wine quality did not follow a trend similar to that of the esters. The appearance of a maturation bouquet simultaneously with the disappearance of varietal character appeared to be possible cause for this finding.

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