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The use of carboxymethylcellulose for the tartaric stabilization of white wines, in comparison with other oenological additives

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Summary

The aim of this study was to test the effectiveness of two types of carboxymethylcellulose (CMC), at different doses, for the prevention of tartaric precipitations in two white wines (Pinot Blanc and Chardonnay), in comparison with metatartaric acid and a commercial arabic gum. After the addition of the additives to the wines, the mini-contact test was carried out and the saturation temperature was determined by Ridomi's method. The determination of the saturation temperature was then repeated on the same trials kept at -4 °C for 10 days. Both kinds of CMC caused a significant decrease in tartaric precipitations induced by the addition of potassium bitartrate (KHT) (mini-contact test), by limiting the growth of the added KHT crystals. Their effectiveness increased with the dose, following a hyperbolic trend. The stabilizing effect of the two kinds of CMC, particularly CMC2 (more viscous), was similar to the one of metatartaric acid. Their use must be considered complementary to the cold treatment (chill-proofing).

K e y w o r d s : carboxymethylcellulose, tartaric stability, white wines, mini-contact test, metatartaric acid, arabic gum.

Introduction

The precipitation of potassium bitartrate is the main cause for the formation of sediment in bottled wines. Traditionally, the technological actions carried out for preventing this problem consist in removing by cold treatment (chill-proofing) part of the potassium bitartrate (KHT) present in wines, through the possible addition of crystallization nuclei (exogenous KHT), aimed at accelerating the precipitation of the salt. More recently, the use of electrodialysis was authorized (Moutounet *et al.* 1997). This technique allows the selective removal of ions from the wine (in particular potassium, bitartrate and calcium), working at ambient temperature by an electric field and membranes selective to cations and anions.

Some oenological additives, besides, which limit the growth and/or precipitation of KHT crystals, can be employed for preventing the formation of sediment in bottled wines. The most utilized among these additives is metatartaric acid.

In 2005 the European Community authorized the use of mannoproteins obtained by enzymatic hydrolysis of yeast cell walls. More recently, during the 6th General Assembly, considering the opinion of the "Food Safety" expert group (14th and 15th sessions), the OIV authorized the use of carboxymethylcellulose (CMC) in white wines and in sparkling wines (Resolution OENO 2/2008), though recommending that care should be taken as to potential allergenic risks due to this substance.

The aim of this study was to test the effectiveness of two types of CMC, at different doses, for the prevention of tartaric precipitations in two white wines; at the same time, some comparative trials with metatartaric acid and a commercial arabic gum were carried out.

The stability was measured by a quick test (mini-contact test), currently used in laboratories, and by determining the variation of the saturation temperature of the wines after the cold treatment.

Material and Methods

Two white wines were employed, Pinot Blanc and Chardonnay (2006 vintage), both of them cold-unstable with problems of tartrate precipitations.

For all samples, the following parameters were determined: alcohol, total acidity, pH, potassium, total dry extract (EEC Regulation no. 2676/90), and tartaric acid (Vidal and Blouin 1978). The saturation temperature was calculated using the above-mentioned chemical-physical parameters (Ridomi 1991). The mini-contact test, besides, was carried out: it consists in measuring the variation of electric conductivity ($\Delta\chi$) of a wine, kept in a thermostat at 0 °C under continuous stirring, 10 min after the addition of micronized crystals of potassium bitartrate (Bullio 2002).

E f f e c t i v e n e s s t e s t f o r C M C a t d i f f e r e n t d o s e s : Two kinds of carboxymethylcellulose, with different viscosity grades, were used (Tab. 1): CMC NO30 (CMC1) and CMC ANO30 (CMC2). They were employed at different doses (5-10-15-20 g·hL^{-1}), and all trials were in duplicate.

T e s t f o r t h e c o m p a r i s o n o f t h e d i f f e r e n t a d d i t i v e s : The 2 carboxymethylcelluloses CMC1 and CMC2, both at the dose of 8 g·hL^{-1}, were compared with an arabic gum (Citrogum, Enartis-ESSECO) at the dose of 80 g·hL^{-1}, and with metatartaric acid (8 g·hL^{-1}). All trials were in duplicate.

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Table 1

Physico-chemical composition of the 2 kinds of CMC used in the trial

CMC	Viscosity (cP) in a 1% solution	Degree of substitution (DS)	Average molecular weight	Degree of polymerization	pH	Turbidity		% Humidity
						in water	at pH 2.5	
NO30	9	0.6 – 0.9	80000	360	6.71	2.5	4.6	10.58
ANO30	12	0.7 – 0.95	140000	600	7.47	3.8	4.0	4.97

After the addition of the additives, the parameter $\Delta\chi$ (mini-contact test) as well as the concentration of tartaric acid and potassium were determined, and the saturation temperature was calculated according to Ridomi's method (Ridomi 1991). The analytical controls were then repeated on the wines filtered through 0.45 µm syringe filters after the cold treatment (10 d at -4 °C in a glycol thermostatic bath).

Statistical analysis: The data related to the effectiveness of CMC at different doses was processed with two-factor ANOVA, separately for each wine: the factors "dose" (5 levels) and "kind of CMC" (3 levels) were studied. The data related to the comparison of the different additives was processed with one-factor ANOVA (factor = kind of additive). Tukey's test was used for the multiple comparison test among the trials (SPSS 1999).

Results

Effect of 2 kinds of CMC at different doses (1st experiment): Tab. 2 reports the physical-chemical composition of the Chardonnay and Pinot Blanc wines used for the trial. Pinot Blanc had a lower saturation temperature than Chardonnay, in spite of its higher content of potassium and tartaric acid. 'Pinot', in fact, had a lower pH and, above all, a lower alcoholic degree than Chardonnay: this increases the solubility product of KHT at a given temperature (Usseglio-Tomasset and Bosia 1982).

Tab. 3 reports the mean content of potassium and tartaric acid, as well as the mean values of the saturation temperature of the control and of the treated theses, soon after the addition of CMC. The addition of CMC, as expected (Ribéreau-Gayon *et al.* 2003), did not modify the content of potassium and tartaric acid nor the saturation temperature of the wines. The effect of the addition of two kinds of CMC, at different doses, on the tartaric precipitations was evaluated before cooling by the mini-contact test, and after cooling (-4 °C for 10 d) by measuring both the decrease of the content of potassium and tartaric acid, and the decrease of the saturation temperature. The data were processed by a complete two-factor ANOVA; the studied factors were the dose (5 levels) and the type (2 types) of CMC.

Table 2

Physico-chemical composition of the wines used for the first experiment

	Chardonnay	Pinot Blanc
pH	3.48	3.29
Titratable acidity (g·L^{-1})	5.05	5.30
Alcohol (%)	13.28	12.48
Tartaric acid (g·L^{-1})	2.04	2.22
Potassium (mg·L^{-1})	790	838
$\Delta\chi$ (µS·cm^{-1})	86	111
T_{sat} (°C)	22.3	21.7

Fig. 1 shows the results of the mini-contact test (mean values of the $\Delta\chi$ parameter) before cooling. With this test, the effect of CMC on the slowdown of the growth of KHT crystals (induced homogeneous nucleation) is evaluated by quantifying the amount of precipitated KHT salts. The test consists in the estimation of the KHT salts that precipitate after the addition of 4 g·hL^{-1} of finely micronized KHT (crystallization nuclei), by measuring the variation of conductivity ($\Delta\chi$ parameter) at 0 °C.

The $\Delta\chi$ values are significantly lower in treatments added with CMC than in controls; this depends on the higher losses of KHT salts by precipitation in the control treat-

Table 3

Mean content (n = 4) of tartaric acid and potassium, and mean values (n = 4) of the saturation temperature for the control and for the tests added with different doses of CMC before the cold treatment. 1st experiment. The p-values for the effect of the dose derive from a complete two-factor ANOVA (dose and kind of CMC)

	Control	D5	D10	D15	D20	p-value
Chardonnay						
T_{sat} (°C)	22.25	21.85	22.20	22.10	22.48	0.70
Tartaric acid (g·L^{-1})	2.04	2.12	2.12	2.14	2.22	0.26
Potassium (mg·L^{-1})	790	779	786	778	766	0.413
Pinot Blanc						
T_{sat} (°C)	21.7	19.9	20.3	19.9	19.4	0.436
Tartaric acid (g·L^{-1})	2.22	2.09	2.14	2.08	2.03	0.40
Potassium (mg·L^{-1})	838	805	801	802	788	0.178

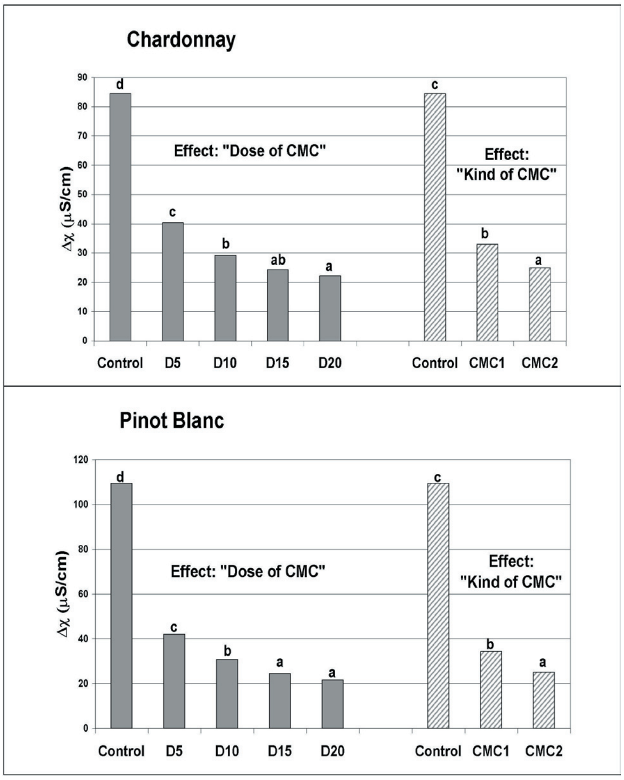

Fig. 1: Mean values (n = 4) of $\Delta\chi$ in the treatments added with different doses of CMC (Effect of the dose of CMC: Control = 0 g·hL^{-1}; D5 = 5 g·hL^{-1}; D10 = 10 g·hL^{-1}; D15 = 15 g·hL^{-1} and D20 = 20 g·hL^{-1}), and mean values (n = 8) of $\Delta\chi$ in the control and in the treatments added with 2 kinds of CMC (Effect of the kind of CMC). 1st experiment. Different letters ($P \leq 0.05$), indicate significant statistical difference separately for the 2 studied factors (dose and kind of CMC).

ments.It is reported (Gerbaux 1996) that KHT crystals, in presence of CMC, grow slower and change their morphology. Their shape becomes flatter because they lose 2 of the 7 faces, changing their dimensions. CMC molecules, negatively charged at wine pH, interact with the electropositive surface of the crystals, where potassium ions are accumulated. The slower growth of the crystals and the modification of their shape are caused by the competition between CMC molecules and bitartrate ions for binding to the KHT crystals (Cracherau *et al.* 2001).

The values of $\Delta\chi$ also changed with the dose and the type of CMC (Fig. 1). They decreased by increasing the dose of CMC. The treatment with added 5 g·hL^{-1} (D5 trial) could be significantly distinguished from the other treatment (added with 10, 15 and 20 g·hL^{-1}), with a higher value of $\Delta\chi$ than the fixed stability threshold of 30 µS·cm^{-1} (Bullio 2002). The treatment added with 10 g·hL^{-1} (D10), only for 'Pinot Blanc', resulted in significant distinguishment from D15, while D15 and D20 were similar for both wines. Concerning the type of CMC, CMC2 showed a better stabilizing effect (lower value of $\Delta\chi$) than CMC1. No significant interactions between the two factors (dose and kind of CMC) were observed. The wines were kept for 10 d at -4 °C. The losses of potassium and tartaric acid (data not reported), as well as the consequent decrease of the saturation temperature, depended on the amount of KHT that precipitated in each wine. After cooling, only for Pinot Blanc, the control was significantly different from all the other treatments with CMC, because of the larger decreases of the saturation temperature (Fig. 2); no effect on KHT precipitations was observed by increasing the doses of CMC from 5 to 20 g·hL^{-1}.

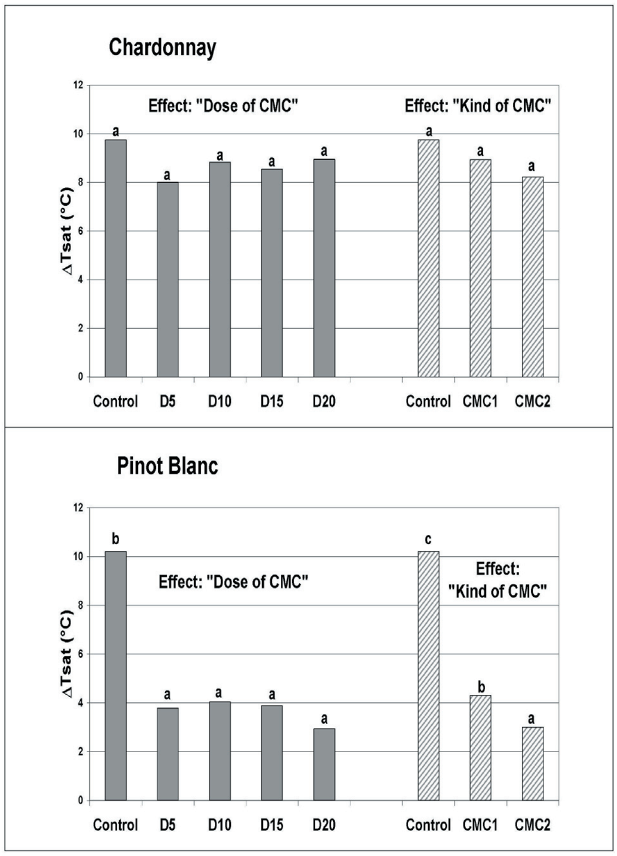

Fig. 2: Mean variation (n = 4) of the saturation temperature (ΔT_{Sat}) after 10 d at -4 °C in the treatments added with different doses of CMC (Effect of the dose of CMC: Control = 0 g·hL^{-1}; D5 = 5 g·hL^{-1}; D10 = 10 g·hL^{-1}; D15 = 15 g·hL^{-1} and D20 = 20 g·hL^{-1}), and mean variation (n = 8) of the saturation temperature (ΔT_{Sat}) in the control and in the treatments added with 2 types of CMC (Effect of the kind of CMC). 1st experiment. Different letters indicate significant statistical difference ($P \leq 0.05$), separately for the 2 studied factors (dose and kind of CMC).

Effect of CMC in comparison with other additives (2nd experiment): The second half of the experiment concerned the study of the effect on the tartaric stability of the two types of CMC, both of them at the dose of 8 g·hL^{-1} (CMC1 and CMC2 treatments), in comparison with metatartaric acid (8 g·hL^{-1}, MTA treatments) and with an arabic gum (Citrogum, Enartis) added at the dose of 80 g·hL^{-1} (AG treatments).

The second experiment was carried out with the same wines, Chardonnay and Pinot Blanc, two months after the first experiment. The changes in wine composition, in comparison with the first experiment (control wine in Tab. 3), were the natural consequence of wine evolution during aging.

Tab. 4 reports, separately for Chardonnay and Pinot Blanc, the mean content of potassium and tartaric acid, as well as the mean values of saturation temperature and of $\Delta\chi$

for the different theses before cooling. The different additives did not modify the values of saturation temperature, but the treatments were distinguished from the control by the $\Delta\chi$ parameter. According to this last index, all the additives had a stabilizing effect on the tartaric precipitations. Statistically significant differences among the treatments, due to the additives, were also observed: on average, $\Delta\chi$ decreased in the order of AG > 2 types of CMC > MTA (the lowest).

Tab. 5 reports the variations of the content of potassium and tartaric acid, as well as the variations of saturation temperature after cooling. The decrease of saturation temperature after cooling was significantly higher for the control than for the other treatments. Only for Chardonnay, significant differences among the treatments were observed: the decrease of saturation temperature was lower (higher tartaric stability) for the wines with added MTA and CMC2 than for those with added CMC1 and arabic gum.

Discussion and Conclusion

The storage conditions at cold temperature (T° = -4 °C for 10 d) were the same used in a previous work (Maujean *et al.* 1985) regarding the determination of the super-saturation field of a white wine, when treated with different clarifying products, or filtered, or when metatartaric acid was added. After cooling, for all the treatments, the decrease of the content of tartaric acid and potassium, as well as the decrease of saturation temperature, were observed. During the first experiment, which regarded wines with a high degree of instability (saturation temperatures above 20 °C), the precipitation of KHT was important after cooling, both in the controls and in the treatments added with CMC. In this case, some differences between the wines were observed: unlike Pinot Blanc, for Chardonnay the addition of CMC did not have any significant effect on the losses of KHT by precipitation. The values of the saturation temperature after cooling disagreed with the results of the mini-contact test, which, on the contrary, indicated the reaching of the stabilization threshold in the treatments added with more than 5 $g \cdot hL^{-1}$ of CMC, for both wines.

During the second experiment, when the wines had a lower degree of instability (mean saturation temperature: 16-17 °C), the losses of KHT were less important than in the first experiment and, for both wines, all the additives caused the decrease of the losses of potassium and tartaric acid after cooling. Only for Chardonnay, a relationship was observed between the results of the mini-contact test ($\Delta\chi$) and the losses of KHT by precipitation. After cold stabilization at -4 °C, the mean differences in the values of satu-

Table 4

Mean content (n = 2) of tartaric acid and potassium, temperature of saturation and $\Delta\chi$ for the control and for the treatments added with different additives before the cold treatment. 2nd experiment. Different letters indicate significant statistical difference ($P \leq 0.05$). In the column "Sign." the symbols *, **, *** and n.s. indicate significance at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$, and not significant, respectively

	Control	CMC1	CMC2	MTA	AG	Sign.
Chardonnay						
T_{sat} (°C)	15.85	15.50	14.90	15.30	15.40	n.s.
Tartaric acid ($g \cdot L^{-1}$)	1.58	1.55	1.51	1.52	1.53	n.s.
Potassium ($mg \cdot L^{-1}$)	642 b	638 ab	623 a	651 bc	658 c	*
$\Delta\chi$ ($\mu S \cdot cm^{-1}$)	79.5 d	19.0 c	14.0 b	6.5 a	19.0 c	***
Pinot Blanc						
T_{sat} (°C)	17.6	17.7	17.6	17.9	17.6	n.s.
Tartaric acid ($g \cdot L^{-1}$)	1.58	1.55	1.51	1.52	1.53	n.s.
Potassium ($mg \cdot L^{-1}$)	707	720	721	723	725	n.s.
$\Delta\chi$ ($\mu S \cdot cm^{-1}$)	111.0 d	19.0 b	16.5 b	9.5 a	28.0 c	***

Table 5

Mean variations (n = 2) of the content of tartaric acid and potassium, temperature of saturation and $\Delta\chi$ for the control and for the treatments with different additives after the cold treatment (T° = - 4 °C for 10 d). Different letters indicate significant statistical difference ($P \leq 0.05$). In the column "Sign." the symbols *, **, *** and n.s. indicate significance at $p \leq 0.05$, $p \leq 0.01$, $p \leq 0.001$, and not significant, respectively

	Control	CMC1	CMC2	MTA	AG	Sign.
Chardonnay						
ΔT_{sat} (°C)	5.15 c	4.15 b	2.90 a	3.27 a	3.90 b	*
Δ Tartaric acid ($g \cdot L^{-1}$)	0.41 b	0.28 a	0.26 a	0.25 a	0.31 a	**
Δ Potassium ($mg \cdot L^{-1}$)	69.5 d	64.0 cd	20.0 a	37.0 ab	46.0 bc	**
Pinot Blanc						
ΔT_{sat} (°C)	6.15 b	3.60 a	3.20 a	2.50 a	3.10 a	*
Δ Tartaric acid ($g \cdot L^{-1}$)	0.38 b	0.24 ab	0.24 ab	0.14 a	0.18 a	*
Δ Potassium ($mg \cdot L^{-1}$)	119.5 b	60.0 a	35.0 a	39.0 a	51.0 a	n.s.

ration temperature between the control and the treatments added of CMC and MTA (8 g·hL^{-1} for both), were, respectively, 2.2 °C and 2.8 °C. It was calculated (Maujean *et al.* 1985), for the addition of 5 g·hL^{-1} of metatartaric acid in a white wine, an increase of its super-saturation field of about 2.5 °C.

The two carboxymethylcelluloses, particularly the most viscous (CMC2), and metatartaric acid had a similar effect on the tartaric stabilization of white wines. The use of these products, considering their effect on the super-saturation field, is always advised in previously cold treated wines having medium to low values of saturation temperature (below 13-14 °C).

For wines with a medium degree of instability, also the use of an arabic gum (Citrogum) showed a positive effect on the prevention of tartaric precipitations. This result should be verified by comparative studies with other types of arabic gums.

The evaluation by the cold test of the stabilizing power of the additives is not comparable with the results of the mini-contact test that, on the whole, overestimates the effect of the additives. This, probably, depends on the fact that the mini-contact test is based only on the evaluation of the effect on the induced nucleation; too short, besides, is the duration of the step of precipitation of the KHT crystals.

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