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Research Note

Model wine solutions: Caffeic acid is not an important factor in colour and composition changes during red wine aging

JOHANNA BAKKER, A. PICINELLI, P. BRIDLE and C. GARCIA-VIGUERA*

S u m m a r y : The effect of caffeic acid and SO_2 on the interaction between malvidin 3-glucoside, (+)-catechin and acetaldehyde was investigated in model wine systems. Reactions were monitored by HPLC, spectrophotometry and tristimulus colorimetry. Caffeic acid had only a marginal effect on the reactions involving the other components in these model wine solutions.

K e y w o r d s : model wines, anthocyanins, acetaldehyde, catechin, SO_2, caffeic acid, HPLC, colour measurements.

Introduction: Caffeic acid and its derivatives (e.g. *trans*-caffeoyltartaric acid and chlorogenic acid) are known to have an important role in the enzymic and the non-enzymic oxidative browning reactions in white wines and also during the first stages of oxidative browning in grape musts (CHEYNIER *et al.* 1988; CILLIERS and SINGLETON 1989; CILLIERS and SINGLETON 1990 a; CHEYNIER and MOUTOUNET 1992). In studies using both caffeoyltartaric acid (caftaric acid) and caffeic acid, the non-enzymic reaction was enhanced, both at pHs approaching neutrality and at higher temperatures (CILLIERS and SINGLETON 1989, 1990 a), although slow oxidation of caffeic acid was observed at pH 4. Thiols, such as gluthatione, increase oxygen uptake in combination with *o*-dihydroxyphenols (CILLIERS and SINGLETON 1990 b) and can also react rapidly with caftaric acid quinones, to yield 2-S-glutathionylcaffeic acid. After depletion of thiols, the caftaric *o*-quinones oxidise other phenolic compounds (CHEYNIER and MOUTOUNET 1992). Hence once caftaric quinones have been formed, enzymically or non-enzymically, they can induce coupled oxidation of catechin to catechin *o*-quinone, which in turn, reacts rapidly with hydroquinones to form condensation products (CHEYNIER *et al.* 1989).

Caffeic acid is an important non-flavonoid phenolic constituent in wines, reported as occurring at levels of ca. 5 mg/l (AMERINE and OUGH 1980), although we have found up to 37 mg/l in red wines analysed in our laboratory. Research has focused on the effect of caffeic acid on oxidation and browning of white wines or white wine models, but there appear to be no studies on the possible interaction of caffeic acid in condensation reactions occurring in model red wine solutions. Hence, it was of interest to investigate any additional effect produced by caffeic acid in the presence of some principal contributors to red wine colour, malvidin 3-glucoside, (+)-catechin and acetalde-hyde. The possible inhibitory effect of SO_2 on these reactions in red wines was also considered.

Materials and methods: All materials were obtained commercially, except for malvidin 3-glucoside which was isolated and purified in our laboratory by semi-preparative HPLC of a *Vitis vinifera* grape skin extract.

Model solution components were dissolved in a sterilised wine medium of potassium bitartrate (0.02 M, pH 3.7) containing ethanol (10 % v/v) to give the following final concentrations: malvidin-3-glucoside 0.21 mM (0.11 mg/ml), (+)-catechin 0.53 mM (0.15 mg/ml), caffeic acid 0.53 mM (0.10 mg/ml), acetaldehyde 0.90 mM (0.04 mg/ml) and using sodium metabisulphite solutions, SO_2 0.90 mM (0.06 mg/ml). Different experimental mixtures were prepared, filtred (0.45 µm sterile membrane filters) and kept in screw-top vials as follows: M: malvidin-3-glucoside (control), MC: malvidin-3-glucoside and (+)-catechin, MF: malvidin-3-glucoside and caffeic acid, MCA: malvidin-3-glucoside, (+)-catechin and acetaldehyde, MCF: malvidin-3-glucoside, (+)-catechin and caffeic acid, MCS: malvidin-3-glucoside, (+)-catechin and SO_2, MFA: malvidin-3-glucoside, caffeic acid and acetaldehyde, MFS: malvidin-3-glucoside, caffeic acid and SO_2, MCFAS: malvidin-3-glucoside, (+)-catechin, caffeic acid, acetaldehyde and SO_2.

All the samples were allowed to react in the dark at room temperature and were analysed in duplicate over a period of 150 d.

Changes in the colour and composition of the test solutions were followed using HPLC, spectrophotometry and tristimulus colour measurements (CIELAB 76) (BAKKER *et al.* 1993). SO_2 (free and total) was measured by ion chromatography and total acetaldehyde was determined enzymatically.

Results and discussion: Results reported previously in the absence of caffeic acid (PICINELLI *et al.* 1994) were confirmed in this work, and comments are made here only on changes in solutions containing caffeic acid.

The caffeic acid concentration in solutions MF, MCF, MFA and MFS did not change significantly during 150 d, indicating that if caffeic acid quinones had been formed, they would have oxidised the catechin or malvidin 3-glucoside by coupled oxidation, and themselves revert back to hydroquinones. Coupled oxidation of caffeoyltartaric acid *o*-quinones with catechin has been reported previously (CHEYNIER *et al.* 1989).

Fig. 1 shows that catechin and caffeic acid both individually increase the rate of loss of malvidin 3-glucoside. The loss of malvidin 3-glucoside was only marginally faster in model MF compared to M, indicating the caffeic acid did not have a significant oxidative effect on malvidin 3-glucoside. The loss of malvidin 3-glucoside in MCF was marginally faster than in model MC, indicating a possible coupled oxidation of caffeic acid with catechin under these conditions, thus enhancing the anthocyanin loss.

Institute of Food Research, Reading Laboratory, Reading, UK.
* Permanent address: CEBAS-CSIC Apdo Correos, E-30080 Murcia, Spain

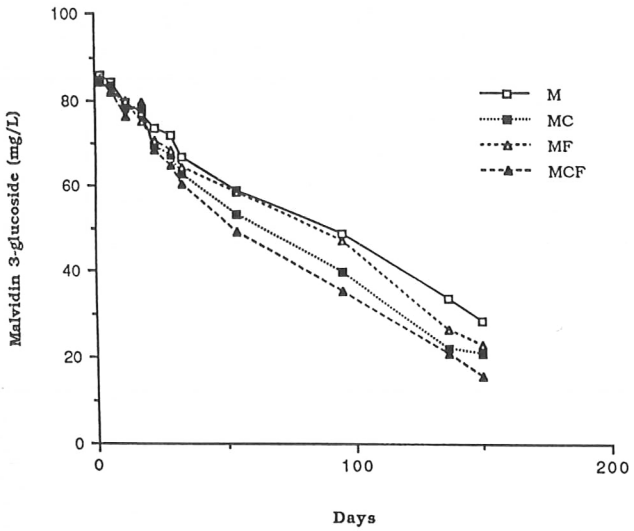

Fig. 1: Loss of malvidin 3-glucoside in solutions M, MC, MF and MCF (Abbreviations see "Materials and methods").

Fig. 2 shows that SO_2 reduces the loss of malvidin 3-glucoside in the presence of the caffeic acid, e.g., compare MF with MFS. The smaller loss of malvidin 3-glucoside in MCS compared to MC agrees with our previous data (PICINELLI *et al.* 1994). The presence of acetaldehyde (MFA) increases the loss of malvidin 3-glucoside compared to MF, possibly due to a reaction of acetaldehyde with malvidin 3-glucoside.

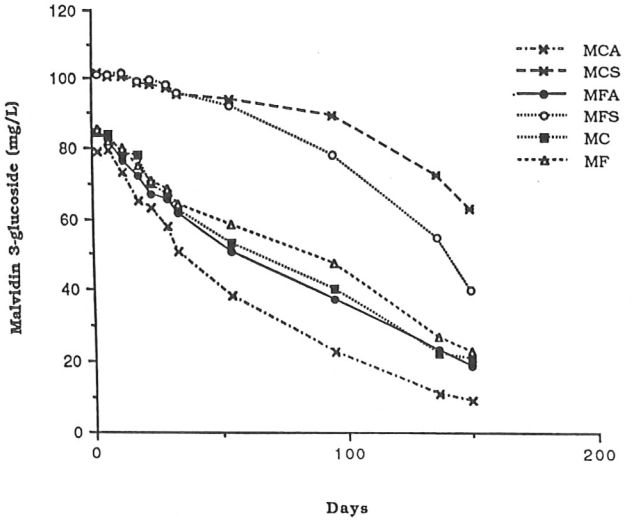

Fig. 2: Loss of malvidin 3-glucoside in solutions MC, MF, MCA, MCS, MFA and MFS (Abbreviations see "Materials and methods").

The formation of two new wine pigments A and B after 29 d (GARCIA-VIGUERA *et al.* 1994) was delayed in the presence of caffeic acid and SO_2 (MCFAS). Pigment B appeared after 54 d and A after 137 d. Compounds analogous to A and B formed from caffeic acid, instead of catechin, are unlikely to be found, since a centre of net negative charge is not feasible on the caffeic acid molecule. Caffeic acid quinones formed would only be expected to oxidise the catechin present, by coupled oxidation, and possibly be involved in the formation of condensation products (CHEYNIER *et al.* 1989).

Caffeic acid had no additional effect on the colour quality, expressed as hue angle and chroma, of the malvidin control or on the rate of browning of malvidin 3-glucoside with catechin (data not shown).

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