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Enhancement of red wine colour by pre-fermentation addition of copigments

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Abstract

The effects of pre-fermentation additions of catechin and caffeic acid to musts were investigated. The cultivar Listan negro, a major red grape grown in the Canary Islands, was used for these studies. The addition of catechin at 120 mg/l resulted in only 10% enhancement in wine colour (AU at 520 nm) after fermentation, while caffeic acid, at the same level, enhanced the wine colour by 60%. These results appear to be the first report of such a significant increase in wine colour achieved by pre-fermentation treatments with natural grape constituents, supporting the view that red wine colour is generally limited by the levels of cofactors for copigmentation rather than by the level of anthocyanins alone. This demonstrates the importance of non-pigment composition in establishing red wine colour and the influence of initial must composition.

Keywords: Copigmentation; Red wine; Colour; Copigment precursors; Caffeic acid

1. Introduction

Copigments are colourless substances which can form a coloured cluster with colourless forms of anthocyanins (Baranac, Petranoviv & Dimitric-Markovic, 1996, 1997a,b,c; Brouillard, Mazza, Saad, Albrecht-Gary & Cheminat, 1989). This copigmentation is widespread in nature. The colour changes in fruit, vegetables and flowers may be caused by these reactions between anthocyanins and various organic compounds present in higher plants (Asen, Stewart & Norris, 1972; Davies & Mazza, 1993; Mistry, Cai, Lilley & Haslam, 1991). Anthocyanins are not naturally red, but show a red colour when in an acid solution, as in wine. At a typical red wine pH of 3.5, about 6% of free anthocyanins change into the red form. So, when certain phenols, which are not pigments, are added, they may form a cluster (stack) with free colourless anthocyanins, increasing the colour of the wine. Moreover, these copigments can exert a strong stabilizing effect on the colour of anthocyanins (Brouillard & Dangles, 1994; Brouillard et al., 1989).

The copigmentation reaction in anthocyanins was first reported by Robinson and Robinson (1931), and subsequently studied in model solutions. When a copigment is added to an acid aqueous solution of anthocyanin, it produces an increase in colour intensity due to the formation of coloured clusters (Baranac et al., 1996, 1997a,b,c; Brouillard et al., 1989; Davies & Mazza, 1993; Liao, Cai & Haslam, 1992; Mistry et al., 1991).

The copigmentation equilibrium could be written:

$$\text{Free anthocyanins} + \text{Copigmentation cofactors} \Longleftrightarrow \text{Copigmented anthocyanins}$$

An increase in the concentration of cofactors leads to colour intensification, since it displaces colourless free anthocyanins in favour of coloured forms. In the maceration of red musts, the greater or lesser presence of these copigments in the grape may notably influence the extraction of anthocyanins, as this study shows.

Copigments include a large variety of structurally unrelated compounds, such as flavonoid and non-flavonoid

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phenols, amino acids and organic acids (Brouillard et al., 1989).

The object of the present study was to investigate the copigmentation effect of caffeic acid and catechin on anthocyanins and wine colour. Both catechin and caffeic acid are natural grape constituents, although most caffeic acid is found in grapes as its tartaric acid ester, caftaric acid. This study has increased our knowledge of colour extraction and the influence of non-pigment composition on the colour of red wine.

2. Materials and methods

2.1. Grapes and winemaking procedure

The grape cultivar used for this study was Listan negro, a major red grape of *Vitis vinifera* grown on the Canary Islands, harvested at maturity during the 1996 season in the north of the island of Tenerife. Wines were elaborated at the experimental wine-production centre at the University of La Laguna. The grapes were destemmed and crushed and the must was then mixed and divided into three batches in 50-l containers. These were control samples and prefermentation additions of 120 mg/l each of caffeic acid (Fluka Chemie AG. ref. 60020) and (+) catechin (Fluka Chemie AG. reference 22110) were made.

Wines were made by standard local winemaking procedures. Sulphur dioxide (40 mg/l) was added as metabisulphite, the length of extraction was three days and the fermentation temperature 24°C. At the end of alcoholic fermentation, malolactic fermentation was periodically checked. When both had finished, all wines were racked, another 40 mg/l of sulphur dioxide was added as metabisulphite, and the wines were stored in glass containers. All the wines were bottled on 15 December 1996.

2.2. Analytical methods

Ultraviolet and visible spectrophotometric determinations, using spectra from 380 to 780 nm were carried out periodically with a Lambda 11 Perkin Elmer spectrophotometer.

Free anthocyanins were analysed by bleaching with bisulphite (Ribereau-Gayon & Stonestreet, 1968). Total anthocyanins (WCA), polymeric pigments (PPC), and total phenolics A_{280} were determined (Somers & Evans, 1977).

3. Results and discussion

Visible spectra of wines were registered at 30, 90 and 210 days after fermentation had stopped. Fig. 1 shows spectra on the 30th day for three wines. At that stage, the addition of catechin at 120 mg/l resulted in a mean of only 13% enhancement in wine colour (AU at 520 nm) while that of caffeic acid, at the same level, enhanced the wine colour by 60%, on average. These values changed with time, the differences being reduced

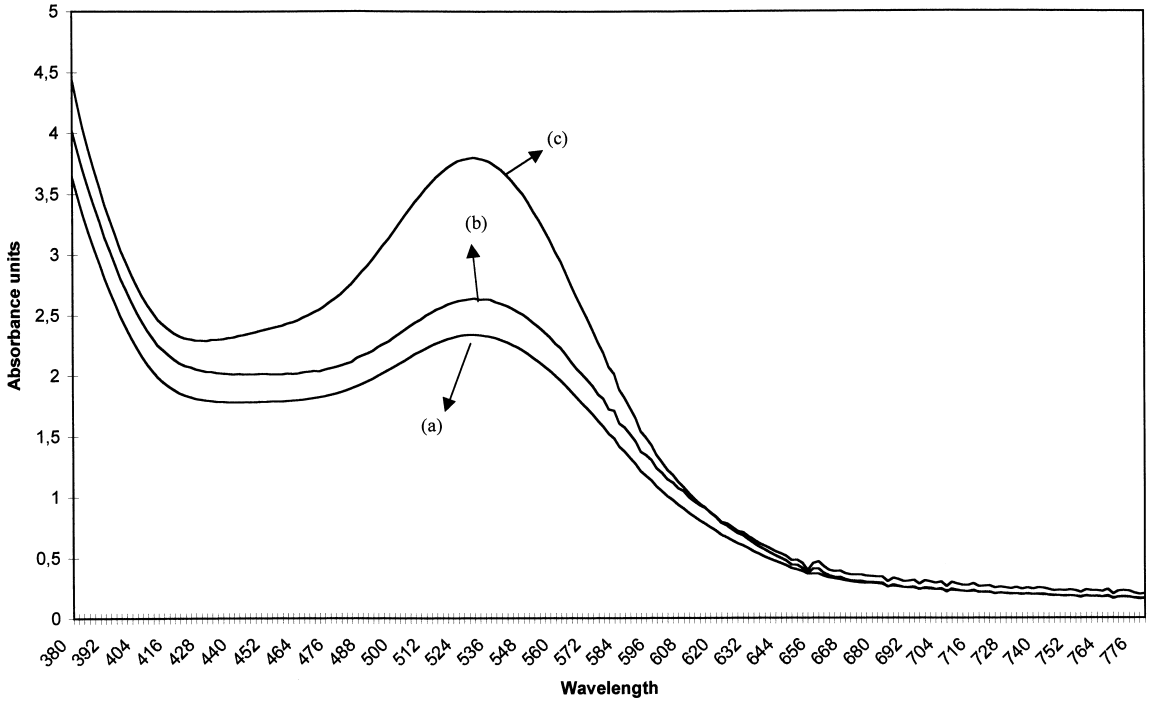

Fig. 1. Visible absorption spectra at 30th day. (a) control sample; (b) catechin addition; (c) caffeic acid addition. Path length 1 cm.

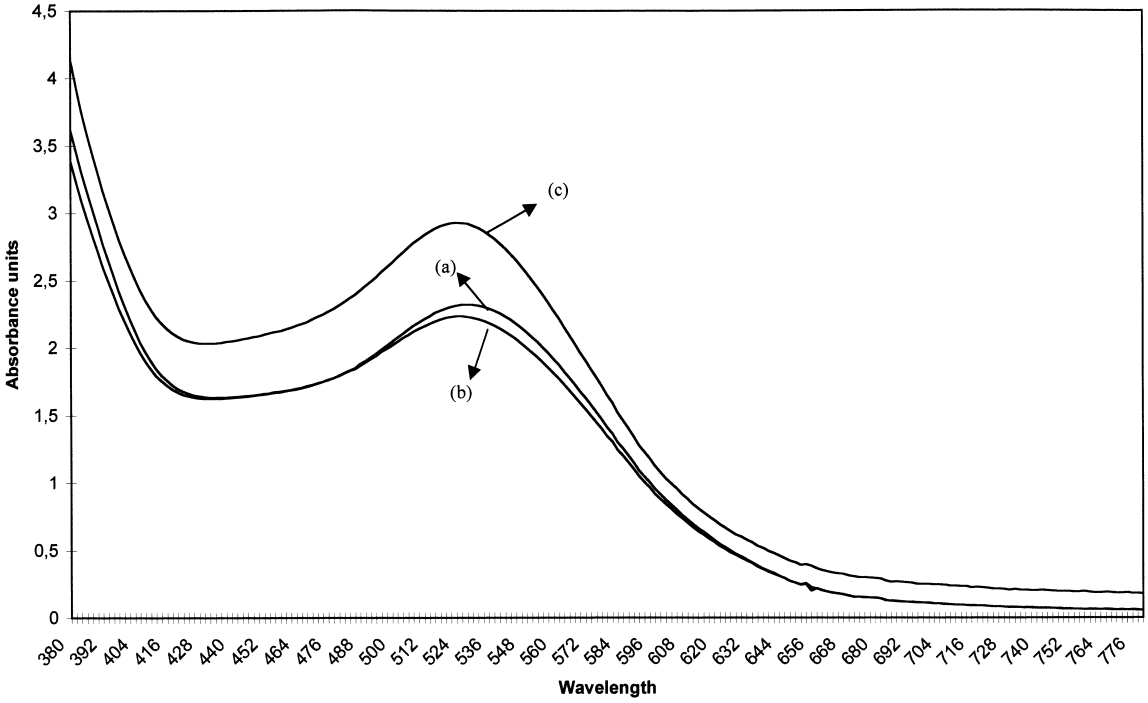

Fig. 2. Visible absorption spectra at 210th day (a) control sample; (b) catechin addition; (c) caffeic acid addition. Path length 1 cm.

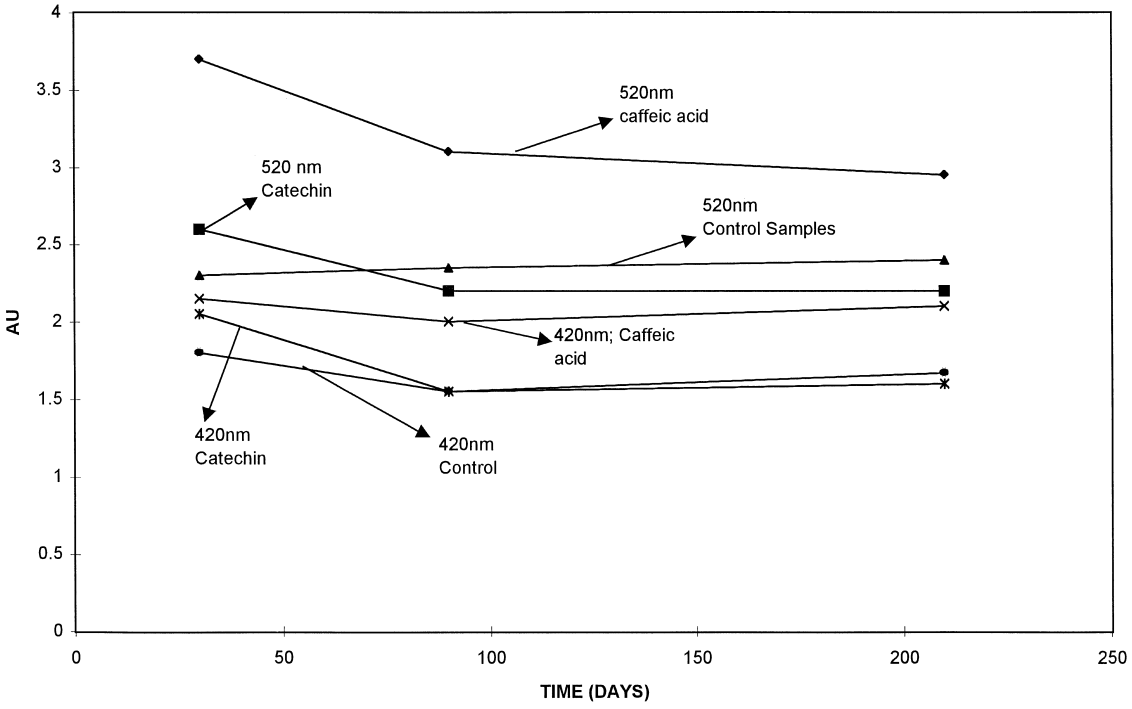

Fig. 3. Evolution of absorbances values at 520 and 420 nm.

(Fig. 2). In this way, the samples with caffeic acid reached 33% enhancement after 90 days and 23% after 210 days. The absorbance, at 520 nm, of samples with catechin, decreased to 8% less than control samples. The effect of catechin addition, after 90 days, was a reduction in wine colour, while the caffeic addition maintained an enhancement.

This phenomenon has been observed in model solutions (Liao et al., 1992) where the rate of colour change depends on the particular copigment employed. In the current experiment, the change with time affected absorbance at 520 nm more than at 420 nm (Fig. 3). Control wine remained more stable.

Table 1
Pigments in wines with and without copigments

Wine[a]	Time (days after end of fermentation)	Anthocyanins by bisulphite bleaching (mg/l)	Polymeric pigments (AU)	Total anthocyanins (AU)	A_{280}
CF	30	145	1.60	12.0	48
CT	30	162	1.17	11.9	43
CW	30	130	1.2	10.0	39
CF	210	79	1.71	7.9	41
CT	210	65	1.50	7.2	40
CW	210	45	1.43	6.3	31

[a] CF, wine with caffeic acid addition; CT, wine with catechin addition; CW, control wine.

These results demonstrate the importance of non-pigment composition on red wine colour. The caffeic acid content in a must seems to have a notable effect on colour extraction. There are really two effects, the first is to enable more pigment to be dissolved. The second is that the copigmented anthocyanins provide more colour than if they were in their free form. There are probably other flavonoid and non-flavonoid phenols in the must able to affect anthocyanins, not only due to formation of polymeric pigments, but also by copigmentation (Brouillard & Dangles, 1994).

Table 1 shows some analytical determinations at 30 and 210 days after fermentation had finished.

Typical spectrophotometric analyses do not adequately explain the differences due to copigmentation. This fact has been studied in California wines (Boulton, 1996).

4. Conclusions

Caffeic acid clearly appears to contribute to young wine colour, as its addition before fermentation enhanced colour extraction.

The addition of catechin leads to a slight decrease in colour with aging of wine. These results suggest the importance of copigmentation phenomena in red wines, and the capacity of initial must composition to exert a greater effect than is attributable to the contacting and extraction procedures alone.

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