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Isomeric Influence on the Oxidative Coloration of Phenolic Compounds in a Model White Wine: Comparison of (+)-Catechin and (−)-Epicatechin

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The reactions of (+)-catechin and (−)-epicatechin with glyoxylic acid were studied in a model white wine solution. When the reactions were performed in darkness at 45 °C, the (−)-epicatechin concentration decreased more rapidly than that of (+)-catechin, and the (−)-epicatechin sample had twice the 440 nm absorbance of the (+)-catechin sample after the 14 day incubation period. The main pigments generated were identified as xanthylium cation pigments regardless of the isomeric character of the phenolic compound. Using a combination of absorbance and ion current data, the xanthylium cation pigments generated from (−)-epicatechin were found to have combined molar absorptivity coefficients 1.8 times that of the xanthylium cation pigments generated from (+)-catechin. The implication of these results on the development of an index of white wine oxidation susceptibility is discussed.

KEYWORDS: Copper(II); white wine; (+)-catechin; xanthylium cation; (−)-epicatechin; model wine; browning; glyoxylic acid; oxidation

INTRODUCTION

The oxidative spoilage of white wines by both enzymatic and nonenzymatic mechanisms has been the subject of considerable study. The enzymatic process is now well understood (*1*), and methods for the control of oxidative enzymes during the winemaking process have essentially eliminated this spoilage process. The quality defect of random oxidation in white wines has resulted in more emphasis being placed on the nonenzymatic process in recent times. Studies with white wines and model white wine systems have been used in an attempt to unravel the complex chemistry of the nonenzymatic oxidative process.

The indicator commonly used to reflect the extent of oxidation of white wine is an increase in the absorbance at 420 nm (*2*), although 440 nm has been used for model systems containing (+)-catechin (*1*, *3*−*5*). Extensive oxidation leads to an obvious brown color, especially as a result of enzymatic oxidation, whereas a light to dark yellow color tends to be the outcome of nonenzymatic oxidation, especially in model wine systems (*3*, *6*). However, nonenzymatic oxidation will also give brown coloration with prolonged and extensive oxidation. More recently, it has also been demonstrated that the 520 nm absorbance, corresponding to red color, also contributes to the nonenzymatic coloration observed in some white wines (*7*).

Phenolic compounds are the most commonly studied oxidizable substrate in white wine spoilage. Simpson (*5*), in studies on "browning" reactions (30 weeks at 15 °C) and "accelerated browning" reactions (3 weeks at 50 °C), found a significant positive correlation between the total phenolic content and browning, but also reported that monomeric catechin-type compounds and dimeric procyanidin compounds were important indicators of browning susceptibility. Of the monomeric catechins, (−)-epicatechin was more positively correlated ($P < 0.001$) with both browning and accelerated browning than (+)-catechin ($P < 0.01$) (*5*).

However, the phenolic degradation and enhancement in wine color as measured at 420 nm may not necessarily be directly related. Benítez et al. (*8*) examined the effect of ultraviolet and visible radiation on the polyphenolic content of Fino wines. Wine stored in transparent bottles showed a higher level of phenolic degradation over a 45 day exposure compared with that for the same wine stored in a topaz bottle (low transmittance to wavelengths of <500 nm). For example, the (−)-epicatechin concentration decreased from its initial value of 3.78 to 0.35 mg/L (transparent) and to 1.56 mg/L (topaz) after 45 days. Similarly, the (+)-catechin concentration dropped from 5.00 to 0.98 mg/L (transparent) and to 1.75 mg/L (topaz) over the same exposure period. However, and surprisingly, the increase in wine color (absorbance at 420 nm) was more pronounced in the topaz bottles: from an initial absorbance of 0.093 to 0.655 (topaz) and to 0.288 (transparent) (*8*).

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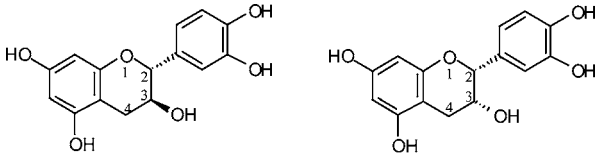

Figure 1. Structures of the diastereoisomers (+)-catechin and (–)-epicatechin.

Oxidative processes for white wine phenolic compounds have been studied extensively in model systems in an attempt to understand the chemistry of the oxidative coloration of white wines. A mechanism for the production of yellow xanthylium pigments from (+)-catechin and glyoxylic acid (formed by the oxidative cleavage of tartaric acid) has been described (*9*, *10*). Iron(II) and copper(II) were found to increase the extent of xanthylium pigment production (*3*, *6*, *11*, *12*). A specific mediating role played by copper(II) was reported to be enhancement of the bridging of (+)-catechin molecules by glyoxylic acid (*4*).

Acetaldehyde is well-known to bridge catechin-type phenolic compounds to give a colorless ethyl-bridged dimer (*13*), similar to the carboxymethine-linked dimer formed as an intermediate compound in the production of xanthylium cations (*10*). A comparison of the acetaldehyde bridging of both (+)-catechin and (−)-epicatechin has been reported, and the (−)-epicatechin/acetaldehyde reaction was observed to be faster than the equivalent reaction with (+)-catechin at pH values of ≤3.0 (*14*).

(+)-Catechin and (−)-epicatechin are diastereoisomers, differing only in the geometry at carbon-3 (**Figure 1**). This work was undertaken to compare the extent of xanthylium pigment formation in the presence of glyoxylic acid. The aim was to seek evidence from model systems for the observation by Simpson (*5*) that (−)-epicatechin is more positively correlated with browning than (+)-catechin. It was intended that the outcomes of this study would provide a better link between the oxidation of phenolic compounds in model systems and the browning processes observed in white wines.

MATERIALS AND METHODS

Reagents and Apparatus. All glassware and plastic ware were soaked for at least 16 h in 10% nitric acid (BDH, AnalaR) and then rinsed with copious amounts of grade 1 water (ISO 3696). Solutions and dilutions were prepared using grade 1 water. Potassium hydrogen tartrate (>99%) and L-(+)-tartaric acid (>99.5%) were obtained from Sigma. (+)-Catechin monohydrate (Sigma, 98%) and (−)-epicatechin (Sigma, 95%) were used without further purification.

Absorbance measurements and spectra were recorded on a μQuant Universal microplate spectrophotometer (Biotek Instruments) with the software KC4 v 3.0 (Biotek Instruments). The absorbance measurements were recorded at 440 nm and spectra recorded from 200 to 600 nm.

The LC-DAD experiment was conducted on a Waters 2690 separation module run by Millenium^{32} software and connected to a Waters 2996 photodiode array detector. The column used was a reverse phase Wakosil C18RS column of particle size 5 μm and 250 × 2 mm with a guard column of the same type. The LC-DAD analyses were carried out as described previously (*6*).

LC-MS experiments were conducted on a SpectraSYSTEM LC run by Xcalibar software with a P4000 sample pump, a UV6000LP UV detector, and a Finnigan AQA quadrapole MS with an electrospray source. The same column was used as in LC-DAD experiments. The LC-MS experiments were carried out in the positive ion mode, with an ion spray voltage of 3 kV and an orifice voltage of 10 V, and in the negative ion mode, with an ion spray voltage of −3 kV and an orifice voltage of −30 V. In experiments investigating fragmentation products, the orifice voltages were increased to 80 V and −80 V in the positive and negative ion modes, respectively. Simultaneous wavelength detection at 278 and 440 nm was performed. The same column, solvent conditions, and flow rate were used as for LC-DAD experiments. The sample injection was 20 μL.

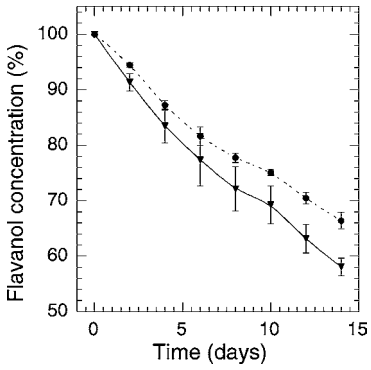

Figure 2. Change in concentrations of (+)-catechin (●) and (–)-epicatechin (▼) during their reaction with glyoxylic acid. Ratio of glyoxylic acid (0.25 mM) to phenolic compound (0.50 mM) was 0.5:1.0. Error bars indicate 95% confidence limits.

To confirm that the total xanthylium cation concentration was indeed proportional to the total ion current, solutions of xanthylium cation were injected into the LC-MS (positive ion mode) at injection volumes of 0, 5, 10, 15, and 20 μL (in triplicate). This was performed for both sets of xanthylium cations derived from (+)-catechin and (−)-epicatechin. In both cases the r^2 correlation between xanthylium cation concentration and total ion current at *m*/*z* 617 was >0.9907.

Reactions. The winelike solution was prepared by adding 0.011 M potassium hydrogen tartrate and 0.008 M tartaric acid to aqueous ethanol (12% v/v, 2 L) and stirring overnight at room temperature. The pH of the winelike solution was 3.2 ± 0.1. (+)-Catechin or (−)-epicatechin (0.5 mM) was added to this solution immediately prior to the commencement of an experiment. The addition of 0.25 mM glyoxylic acid (Aldrich, 98%) was made to 150 mL in 250 mL Schott bottles with screw-top lids. The samples were held in darkness at 45 °C, and the sample bottles were opened only on measurement days. All samples were prepared in triplicate, and the plotted data are the mean of the replicates with the error bars representing the 95% confidence limits.

RESULTS AND DISCUSSION

In this work, glyoxylic acid was added to winelike solutions containing either (+)-catechin or (−)-epicatechin at a mole ratio of 0.5 glyoxylic acid to 1 phenolic compound. This ratio was consistent with the ratio of glyoxylic acid and (+)-catechin required to form one xanthylium cation pigment.

Comparison of Reactivity of (+)-Catechin and (−)-Epicatechin in the Presence of Glyoxylic Acid. Figure 2 plots the loss of (+)-catechin and (−)-epicatechin in the presence of glyoxylic acid over the time course (14 days) of the reaction. With the chromatographic conditions employed, both (+)-catechin and (−)-epicatechin can be detected at 280 nm, with (+)-catechin eluting at 46 min and (−)-epicatechin at 57 min. The comparative loss of the phenolic reactants was assessed by recording the decrease in the respective peak areas, as (+)-catechin and (−)-epicatechin have similar molar absorptivities at 280 nm (*15*), which has also been observed for the phloroglucinol derivatives of these phenolic compounds (*16*). The loss of (−)-epicatechin was 1.2 times faster than for (+)-catechin, with average rates of degradation of 15.5 ± 0.7 and 12.5 ± 0.7 μM/day, respectively. This faster loss of (−)-epicatechin is consistent with the reported observations of Es-Safi et al. (*14*) for acetaldehyde reactions with the same two monomeric phenolic compounds. The data of Es-Safi et al. (*14*) suggested that at pH 2.2, 2.5, and 3.0, the reaction rates of the two phenolic compounds with acetaldehyde were much the same

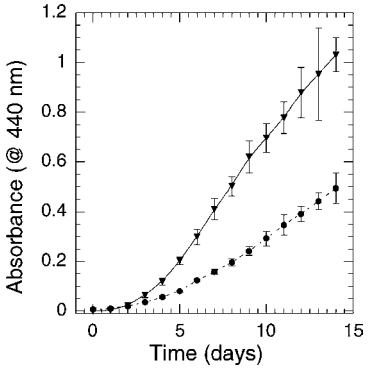

Figure 3. Absorbances at 440 nm for (+)-catechin/glyoxylic acid (●) and (–)-epicatechin/glyoxylic acid (▼) solutions throughout the 14 day reaction period. Error bars indicate 95% confidence limits.

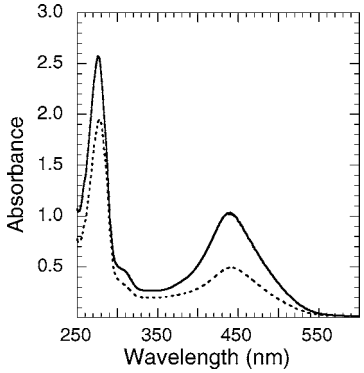

Figure 4. UV–visible spectra of (+)-catechin/glyoxylic acid solution (- - -) and (–)-epicatechin/glyoxylic acid solution (—) after 14 days of reaction.

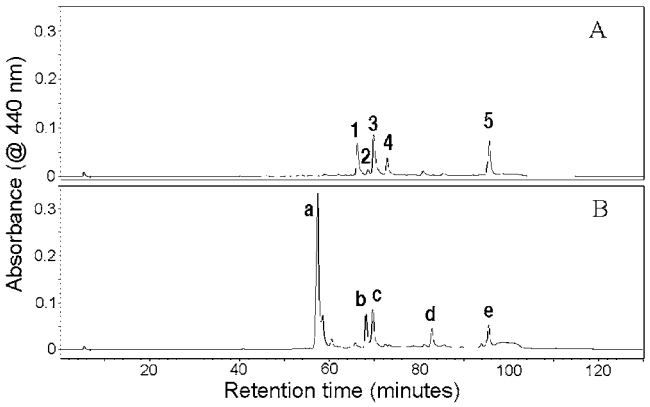

Figure 5. LC-DAD chromatograms (440 nm) for the (+)-catechin/glyoxylic acid solution (**A**, peaks 1–5) and the (–)-epicatechin/glyoxylic acid solution (**B**, peaks a–e) after 14 days of reaction.

throughout the reaction, whereas at pH 3.5 and 4.0 the reaction was faster for (−)-epicatechin compared to (+)-catechin, ∼1.2 times faster when 60% of the (−)-epicatechin remained in the system. In the present study, only one pH value (3.2, modeling white wine conditions) was used, and this falls within the two groups of pH values as categorized by Es-Safi et al. (*14*). However, in the study by Es-Safi et al. (*14*), different reagent mole ratios were adopted, namely, an acetaldehyde-to-flavanol ratio of 46:1 compared to the glyoxylic acid to flavanol ratio used of 0.5:1 in the current study.

The different reaction rates of the phenolic compounds could be due to either the differing stereochemical conformation of the phenolic compounds or alternatively trace metal contamination of the phenolic compound. However, it is unlikely that this trace metal contamination would be sufficiently high to achieve the difference in phenolic compound degradation observed in **Figure 2**. For instance, the presence of 0.6 mg/L copper(II) (*6*) or 1.0 mg/L iron(II) (*3*) was found to decrease the catechin concentration of model wine systems by <1.5% over similar time periods as in **Figure 2**. Furthermore, the addition of 0.1 mg/L copper(II) in a model wine system containing both catechin and glyoxylic acid resulted in only a further 1% increase in the loss of catechin compared to a solution without added copper(II) (*4*).

Figure 3 presents the evolution of the absorbance at 440 nm for model wine systems containing either (+)-catechin or (−)-epicatechin together with glyoxylic acid. It is obvious that the reaction system containing (−)-epicatechin results in a much higher absorbance at 440 nm. After the 14 day reaction period (**Figure 3**), the ratio of absorbance values for the (−)-epicatechin to (+)-catechin reaction systems is 2.1 ± 0.3 and the overall rates of increase in absorbance intensity were 0.074 ± 0.005 and 0.035 ± 0.004 absorbance unit/day, respectively.

If the products of the (−)-epicatechin/glyoxylic acid reaction were the same as that for the (+)-catechin/glyoxylic acid reaction, apart from the expected stereochemical differences, the faster loss of (−)-epicatechin would give rise to an enhanced absorbance of only ∼1.2, compared to the observed enhancement of ∼2.1. Two alternative explanations then need to be considered: either the products of the respective reactions are considerably different or the diastereoisomeric relationship of the reactant phenolic compounds is influencing the relative molar absorptivities of the two products.

Identification of Reaction Products. It has been established that products of the reaction between (+)-catechin and glyoxylic acid in winelike solutions are xanthylium pigments (*12*). The UV−visible spectrum of xanthylium pigments derived from (+)-catechin is characterized by a maximum absorbance at 440 nm and a shoulder at 310 nm together with a peak at 278 nm (*9*), corresponding to the catechin component of the xanthylium cation. **Figure 4** presents the UV−visible spectra for the (−)-epicatechin/glyoxylic acid and (+)-catechin/glyoxylic acid systems. It is obvious that the spectra are essentially identical, except that the absorbance values at 310 and 440 nm for the (−)-epicatechin/glyoxylic acid system are around double those for the (+)-catechin/glyoxylic acid system (compare **Figure 3**). These observations present prima facie evidence for the formation of xanthylium pigments in the (−)-epicatechin/glyoxylic acid system and that these pigments are the main compounds responsible for absorbance in the visible region.

The LC-DAD (440 nm) chromatograms of the (−)-epicatechin/glyoxylic acid and (+)-catechin/glyoxylic acid systems at day 14 reaction period are compared in **Figure 5**. Peaks 1−4 (**Figure 5A**) of the (+)-catechin/glyoxylic acid system represent different isomers of the xanthylium pigments that have been previously identified (*4*, *17*). Peak 5 is the ethyl ester of the xanthylium pigment; the absorbance maxima of this peak is at 460 nm rather than 440 nm (*18*). With the (−)-epicatechin/glyoxylic acid system (**Figure 5B**), the LC-DAD (440 nm) chromatogram shows three distinct peaks (a−c) with intensity ratios different from those observed for the (+)-catechin-derived xanthylium pigments. Two peaks (d, e) eluted later, with the retention time of peak e close to that for the esterified xanthylium pigment formed in the (+)-catechin system (**Figure 5A**).

UV−visible spectra extracted from the LC-DAD chromatogram of the (−)-epicatechin/glyoxylic acid system for each of the peaks a−c show the spectral characteristics of xanthylium pigments noted above and as in **Figure 4**: a peak maximum at

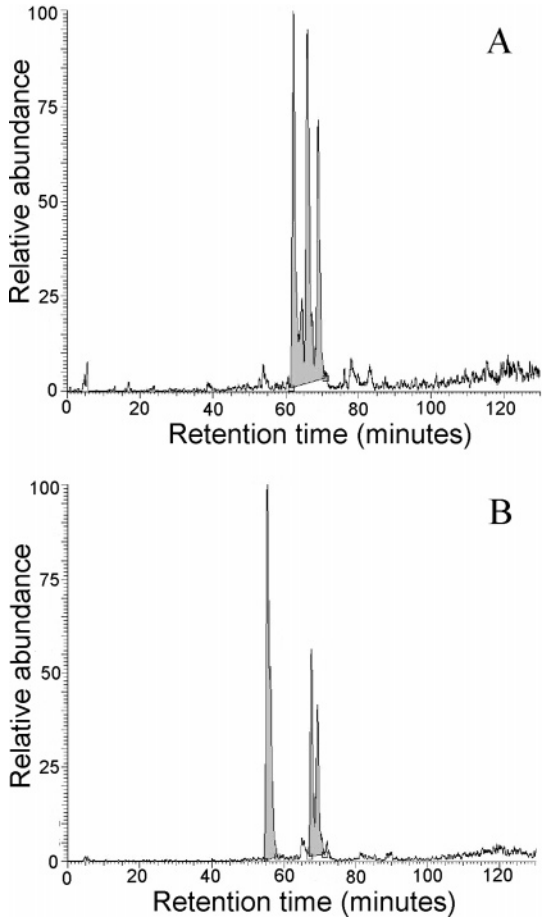

Figure 6. LC-MS ion chromatograms (*m*/*z* 617) for the (+)-catechin/glyoxylic acid solution (**A**) and the (–)-epicatechin/glyoxylic acid solution (**B**) after 14 days of reaction.

440 nm and a shoulder at 310 nm. Peaks d and e were characteristic of the ethyl ester of the xanthylium cation: a peak maximum at 460 nm and a shoulder at 310 nm.

The mass chromatogram for each peak was recorded, in both positive and negative ion modes to provide further evidence that peaks a−c in **Figure 5B** are xanthylium pigments formed from (−)-epicatechin. The mass chromatogram for peak a demonstrated *m*/*z* 617 (positive ion mode) and 615 (negative ion mode) values corresponding to the xanthylium pigments (*12*). When the positive ion mass chromatogram was searched for *m*/*z* 617 values, the pattern of peaks found (**Figure 6B**) is identical to that observed in the LC-DAD (440 nm) chromatogram (**Figure 5B**). For comparison, the *m*/*z* 617 mass chromatogram for the (+)-catechin/glyoxylic acid system is shown in **Figure 6A**, the four peaks corresponding to peaks 1−4 in the LC-DAD chromatogram (**Figure 5A**).

The mass chromatographic study was repeated but with increased fragmentation of the *m*/*z* 617 ions to allow comparison between the fragmentation patterns of the xanthylium cations derived from (+)-catechin and (−)-epicatechin. For the (+)-catechin-derived xanthylium cations, peaks 1−4 (**Figure 5A)**, the fragmentation ions at *m*/*z* 465, 447, 421, and 313 in the postive ion mode were observed and their formation included a retro-Diels−Alder fission (465 *m*/*z*) and decarboxylation with this fission (*m*/*z* 421) as described by Es-Safi et al. (*17*). The *m*/*z* 447 was probably a dehydration of the *m*/*z* 465 ion and the *m*/*z* 313 ion resulting from two retro-Diels−Alder fissions. In the negative ion mode, the two main fragments ions were *m*/*z* 571 and 419, the former resulting from decarboxylation of the

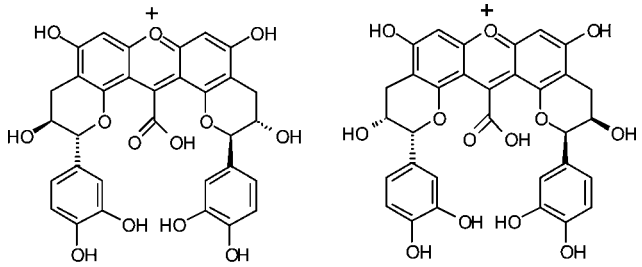

Figure 7. Comparison of xanthylium cations formed from (+)-catechin and (–)-epicatechin. These particular isomers are formed from glyoxylic acid bridging at position 8 of either (+)-catechin or (–)-epicatechin.

xanthylium cation and the latter from both decarboxylation and retro-Diels−Alder fission (*17*). For the (−)-epicatechin-derived xanthylium cations exactly the same fragmentation patterns were observed for peaks a−c (**Figure 5B**) in both the positive and negative ion modes of the mass chromatogram.

Clearly, the (−)-epicatechin/glyoxylic acid system produces xanthylium pigments analogous to those formed from the (+)-catechin/glyoxylic acid system. The different retention times of the xanthylium cations in the two reaction systems will be a consequence of the diastereoisomeric relationship between the products. The observation of three, rather than four, peaks and the differing peak intensities in the (−)-epicatechin/glyoxylic acid system compared to the (+)-catechin/glyoxylic acid may well be the consequence of either the coelution of xanthylium pigment isomers or the preferential formation of certain isomers. One isomeric form of each of the (+)-catechin and (−)-epicatechin-derived xanthylium cations is shown in **Figure 7**.

Similarly, peaks d and e (**Figure 5**) both displayed signals at *m*/*z* 645 in the positive ion mode and *m*/*z* 643 in the negative ion mode, consistent with their assignment as xanthylium cation ethyl esters. Furthermore, the fragmentation patterns of the ethyl esters of the xanthylium cations (peak 5, **Figure 5A**, and peaks d and e, **Figure 5B**), albeit derived form either (+)-catechin or (−)-epicatechin, were also identical. In the positive ion mode both esters gave fragment ions at *m*/*z* 493, 447, and 341, whereas in the negative ion mode both esters gave fragment ions at *m*/*z* 597, 445, and 339. In the positive ion mode *m*/*z* 493 most likely corresponded to the retro-Diels−Alder fission and *m*/*z* 447 (and *m*/*z* 445 in the negative ion mode) to retro-Diels−Alder fission with both decarboxylation, including loss of esterification, and dehydration, whereas the *m*/*z* 341 (and *m*/*z* 339 in the negative ion mode) corresponded to two retro-Diels−Alder fissions.

Figure 8 shows the change in total peak areas by LC-DAD for the xanthylium cations during the reaction period, that is, peaks 1−4 for the (+)-catechin-derived xanthylium cations (**Figure 5A**) and peaks a−c for the (−)-epicatechin-derived xanthylium cations (**Figure 5B**). As expected, more intense xanthylium cation peaks are detected in the (−)-epicatechin/glyoxylic acid system than in the (+)-catechin/glyoxylic acid system. Furthermore, the increase in xanthylium cation peak area (**Figure 8**) reflected the profile for the increase in the 440 nm absorbance of the respective reaction systems (**Figure 3**), confirming that the xanthylium cations were the main pigments absorbing at 440 nm in both reaction systems (**Figure 5**).

Comparison of (+)-Catechin and (−)-Epicatechin Reaction Products. The UV−visible, LC-DAD, and LC-MS data show that (−)-epicatechin in the presence of glyoxylic acid dimerizes to form xanthylium pigments analogous to those obtained when (+)-catechin is the reactive phenolic compound, although the diastereoisomeric relationship between the two

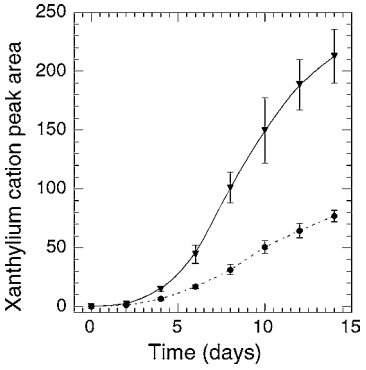

Figure 8. Combined peak areas (LC-DAD 440 nm) of xanthylium cations in the (+)-catechin (●) and (–)-epicatechin systems (▼) during the 14 day reaction period. Error bars indicate 95% confidence limits.

monomeric phenolic compounds is retained in the bridged dimers formed in the reaction process. The diastereoisomeric difference between the phenolic compounds results in an increased loss of (−)-epicatechin compared to (+)-catechin (**Figure 2**); however, this difference is not sufficient to fully explain the 440 nm absorbance ratio of 2.1 for the (−)-epicatechin to (+)-catechin samples (**Figure 3**). Given that the xanthylium cations are the compounds that are the main contributors to the absorbance at 440 nm (**Figure 5**), this demonstrates that the molar absorptivities of the (−)-epicatechin-derived and (+)-catechin-derived xanthylium cations must be different. It is well established that the different spatial geometries of diastereoisomers can produce differences in spectral properties (*19*).

Therefore, to show that the difference within **Figures 3** and **5** could be explained by the molar absorptivities of the products, the overall ratio of molar absorptivity for the different xanthylium cations was calculated using LC-MS. **Figure 6** presents the *m*/*z* 617 ion chromatograms for the (+)-catechin/glyoxylic acid (**A**) and (−)-epicatechin/glyoxylic acid (**B**) systems after 14 days of the accelerated oxidation process. From these chromatograms, it is possible to calculate the total ion current for all peaks corresponding to *m*/*z* 617. The xanthylium pigments formed from both (+)-catechin (*9*, *20*) and (−)-epicatechin are positively charged and therefore do not need to acquire a charge during the electrospray process. Hence, structural differences should not influence ionization efficiencies and the ion currents are anticipated to reflect the concentration of the various xanthylium cations. As the LC-MS system also had a DAD, the total absorbance for peaks 1−5 (**Figure 5A**) and peaks a−c (**Figure 5B**) could also be calculated. Given these data, the ratio of the relative molar absorptivity coefficients of the (+)-catechin-derived and (−)-epicatechin-derived xanthylium cations was calculated using the Beer−Lambert Law as

$$\epsilon_e/\epsilon_c = (A_e c_c)/(A_c c_e)$$

where A, ϵ, and c refer to the absorbance, molar absorptivity coefficient, and concentration, and the subscripts c and e refer to (+)-catechin and (−)-epicatechin, respectively.

From the mass chromatograms, the concentration of xanthylium cation, c, will be proportional to the total ion current, I

$$c = r \times I$$

where r is a constant; then

$$\epsilon_e/\epsilon_c = (A_e I_c)/(A_c I_e)$$

Consequently, the ratio of molar absorptivity coefficients is

$$\epsilon_e/\epsilon_c = (A_e I_c)/(A_c I_e) = 1.8 \pm 0.1$$

providing evidence that the xanthylium cations generated by (−)-epicatechin had a collective molar absorptivity that was 1.8 times that of the (+)-catechin-derived xanthylium cations. Given that the rate of loss of (−)-epicatechin was 1.2 times faster than that for (+)-catechin (**Figure 2**) and that the main pigment generated had 1.8 times the molar absorptivity in the (−)-epicatechin system, this is consistent with a total 440 nm absorbance in the (−)-epicatechin/glyoxylic acid system 2.1 times that of the (+)-catechin system (**Figure 3**).

It is instructive to compare the results of this work with the observations reported by Simpson (*5*) in his study on oxidative browning of white wine. The high positive correlation reported by Simpson between browning and the wine's (−)-epicatechin concentration is most probably a reflection of the ability of (−)-epicatechin to generally react more quickly with aldehydes and, as with glyoxylic acid, its ability to generate xanthylium pigments with greater 440 nm absorbance than found for (+)-catechin.

From an enology perspective, the results of this study suggest that the establishment of an index of white wine oxidation, based on the total phenolic content of the wine alone, is unlikely to succeed. The phenolic composition of white wines depends on a range of factors including seasonal growing conditions and grape- and wine-processing technologies. Goldberg et al. (*21*), in a survey of white wines, found that the concentrations of catechin were generally higher than those of epicatechin. In comparison, in a study of the phenolic composition of Champagnes, Chamkha et al. (*22*) reported that the (−)-epicatechin concentration was 1.15 mg/L in the 2000 vintage and 0.5 mg/L in the 2001 vintage compared with (+)-catechin concentrations of 0.71 and 2.2 mg/L in the respective vintages. These data show that not only the relative amount but also the ratio of (−)-epicatechin to (+)-catechin varies from vintage to vintage. Given the difference in 440 nm absorbances observed for the oxidation products of these two diastereoisomeric phenolic compounds used in this work, an oxidation index will require knowledge of the distribution of the various phenolic compounds that can lead to coloration as a result of oxidation.

ABBREVIATIONS USED

LC-DAD, high-performance liquid chromatography with photodiode array detector; LC-MS, liquid chromatography with mass spectrometry; UV, ultraviolet.

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