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Degradation kinetics of grape skin and seed proanthocyanidins in a model wine system

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ABSTRACT

Catechin (monomer), purified grape skin proanthocyanidin (polymer), and purified grape seed proanthocyanidin underwent monitored accelerated oxidation under continuous oxygenation and UV light, at a constant 20 °C. Compounds were dissolved in model wine solutions with (and without) catechol. Solutions were examined and then contrasted by absorbance measurements, phloroglucinolysis, and subsequent HPLC analysis. Oxidation of these monomers and polymers revealed significant colour changes (measurable increase in colour density). The presence of catechol increased the half-life of catechin, but the opposite was observed for total skin and seed proanthocyanidins. Skin and seed proanthocyanidin degradation half-life decreased with the addition of catechol. In general, based on second order rate reactions, total subunits of seed proanthocyanidin solutions degraded faster than that of skin proanthocyanidin solutions. As expected, there were decreases of measurable phenolics in both monomer and polymer solutions. Under the study conditions, flavanol monomer and polymer oxidation was chiefly dependant upon initial solution concentration.

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1. Introduction

Numerous research reports have shown (Cheynier, 2005, references therein; Jorgensen, Marin, & Kennedy, 2004; Lee, Kennedy, Devlin, Redhead, & Rennaker, 2008), phenolics' importance to red grapes and to the resulting wines made from them. Wine proanthocyanidins (also referred to as tannins, condensed tannins, or flavanol polymers) and colour are important red wine quality factors that can be manipulated by grape growing conditions and wine-making practices. Proanthocyanidins are a high-interest research topic as they play important roles in red wine by stabilizing colour and enhancing mouth-feel, which are critiqued qualities of premium wines (Cheynier, 2005, references therein; Bajec & Pickering, 2008, references therein).

Grape proanthocyanidins are the main group of phenolics found in the skin, seed, and stems of grapes (Cheynier, 2005; Jorgensen et al., 2004; Souquet, Labarbe, Le Guerneve, Cheynier, & Moutounet, 2000; Vidal, Cartalade, Souquet, Fulcrand, & Cheynier, 2002). Once proanthocyanidins have been extracted from their natural source, they undergo a number of reactions, and oxidation is one of them (Cheynier, 2005; Cheynier et al., 2006; Fulcrand, Duenas, Salas, & Cheynier, 2006; Wang, Zhou, & Wen, 2006; Waterhouse & Laurie, 2006). The significance of wine phenolic oxidation and its mechanisms have been well reviewed by others (Fulcrand et al., 2006; Waterhouse & Laurie, 2006). Consumers expect particular organoleptic properties in certain foods (e.g. tea, chocolate, wine, coffee, etc.) that result from oxidised proanthocyanidins (Bajec & Pickering, 2008; Cheynier, 2005; Cheynier et al., 2006; Manach, Wiliiamson, Morand, Scalbert, & Remesy, 2005; Santos-Buelga & Scalbert, 2000; Vidal et al., 2004; Wang et al., 2006). Sensory properties and evaluation of these compounds are ongoing, as purification and analytical methods to identify these compounds become more accessible (Vidal et al., 2002, 2003, 2004).

Any examination of proanthocyanidins is complex and as these compounds alter their structure from their native forms, analysis becomes even more challenging (De Freitas, Glories, & Laguerre, 1998; Es-Safi, Cheynier, & Moutounet, 2003a; Fulcrand et al., 2006; Vidal et al., 2004). Few studies to date have examined the kinetics of grape proanthocyanidins (De Freitas et al., 1998; Jorgensen et al., 2004; Vidal et al., 2002) and due to the intricate nature of wine matrix and the compounds of interest, the topic remains one for further exploration.

The objective of this experiment was to determine the kinetic parameters of catechin, skin proanthocyanidin, and seed proanthocyanidin in model wine system during continuous oxygenation

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and UV light exposure, with and without the presence of catechol (a monomer). This study was initiated to better understand the evolution of polyphenolics.

2. Materials and methods

2.1. Purification of skin and seed proanthocyanidins

Grape samples (*Vitis vinifera* cv. Pinot noir) were harvested from OSU experimental vineyard (Alpine, OR, USA) two weeks prior to véraison (mid-August) in 2006. Berries were collected at what Bogs et al. (2005), considered maximum proanthocyanidin containing stage: slightly larger than pea size, hard, and green with no pink colouration in any of the berries. The immature clusters were picked, placed in a cooler filled with ice, and transported to laboratory (within two hours of picking). Upon arrival at the laboratory the berries were immediately fractionated into skins and seeds. These samples were used for fractionation, extraction, and purification of skin and seed proanthocyanidins; the details were as described in Kennedy and Jones (2001). Resulting purified freeze-dried skin and seed proanthocyanidins were stored at −80 °C for further experiments.

2.2. Reagents, chemicals, standards, and gases

All chemicals (ammonium formate, formic acid, ethanol, catechin, catechol, phloroglucinol, acetic acid, acetonitrile, etc.) used in this study were obtained from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). All solvents and chemicals for this investigation were analytical and high performance liquid chromatography (HPLC) grade. Oxygen (extra dry) and nitrogen (ultra high purity) gases were purchased from Norco Inc. (Nampa, ID, USA).

2.3. Proanthocyanidin oxidation system and sample preparation

All monomers and polymers were dissolved in model wine solutions (total 25 ml) consisting of the following: 20 mM ammonium formate, 14% ethanol (v/v), adjusted to pH 3.5 with formic acid. Model solutions of skin proanthocyanidins were dissolved at a concentration of 2 g/l, without and with catechol (two equal molar). Seed proanthocyanidin and catechin concentrations were determined based on the catechol amount required for skin proanthocyanidin, so the two equal molar ratio remained the same. A microscale photochemical reactor assembly with quartz well (Ace Glass Inc., Vineland, NJ, USA) was used to carry out the controlled oxidation experiment, as originally designed by Penn and Orr (1989). A PS-1 model UV lamp (5.5 W, 5.4 cm, 115 V/60 Hz, lamp current 18 mA, Ultra-Violet Products, Ltd., Upland, CA, USA) was placed in the reactor. Oxygen gas was continuously bubbled through a gas-washing bottle, fitted with a gas diffusion tube (both obtained from Ace Glass Inc.) containing the model wine solution (made as described previously), into the reaction mixture. Reaction mixtures were maintained at 20 °C by a circulating water bath (Isotemp 3013, Fisher Scientific Inc., Pittsburgh, PA, USA), pumping chilled water through double walled assembly for the duration of each reaction.

The different phenolic solutions (six total combinations; catechin, catechin + catechol, skin proanthocyanidin, skin proanthocyanidin + catechol, seed proanthocyanidin, and seed proanthocyanidin + catechol) were oxidised in the photochemical reaction assembly under continuous oxygenation and UV light as described in the previous section. Samples for oxidation measurements were taken during each treatment at eight intervals over the 15,360 s period (samples taken at time = 0, 240, 480, 960, 1920, 3840, 7680, and 15,360 s). Two aliquots from each time point sample were immediately dried under a gentle nitrogen stream with a N-evap 112 nitrogen evaporator (Organomation Associates Inc., Berlin, MA, USA) with the water bath temperature set to 40 °C. One dried sample from each time point later underwent phloroglucinolysis (as described), while the other was retained for monomer corrections. These steps did not deviate from the previously described methods (Kennedy & Jones, 2001; Lee et al., 2008).

2.4. Absorbance measurements, phloroglucinolysis, and HPLC analysis

Absorbances at 280, 420, and 520 nm were conducted using a SpectraMax M2 microplate reader (Molecular Devices Corp., Sunnyvale, CA, USA). Absorbances were auto-corrected for a one-cm pathlength cell value.

Purified skin and seed proanthocyanidins, along with the oxidisation reaction samples were subjected to phloroglucinolysis (acid-catalysis in the presence of excess phloroglucinol), prior to HPLC injection (Kennedy & Jones, 2001). A HP1100 system equipped with a DAD was used to analyse the samples (Agilent Technologies Inc., Palo Alto, CA, USA). Analysis was performed as previously described by Kennedy and Jones (2001) with the exception of the analytical column employed (two sequentially connected Onyx Monolithic C_{18} columns; Phenomenex Inc., Torrance, CA, USA); the identical procedure with alterations can be found in Lee et al. (2008). Peaks were monitored at 280, 320, and 520 nm. Injection volume was 20 μl. All peaks were identified based on retention time, spectra, and known previous identifications (Jorgensen et al., 2004; Lee et al., 2008). All values were expressed as catechin. Mean degrees of polymerization (mDP), yield conversion, % molar proportion, and galloylation rate calculations have been well documented in previously published work (Kennedy & Jones, 2001; Kennedy & Taylor, 2003; Lee et al., 2008).

3. Results and discussion

3.1. Purified skin and seed proanthocyanidin: starting material composition

Composition summary of the purified proanthocyanidin fractions are listed in Table 1. Freeze-dried skin proanthocyanidins had an estimated total molecular weight of 5797 g/mol, an estimated average subunit molecular weight of 295 g/mol, 19.6 mDP, and a 95.6% conversion yield. Freeze-dried seed proanthocyanidins had an estimated total molecular weight of 3247 g/mol, an estimated average subunit molecular weight of 309 g/mol, 10.5 mDP, and a 87.0% conversion yield. Skin proanthocyanidins were higher in molecular weight, mDP, and conversion yield compared to the purified seed proanthocyanidins, as noted in previous studies (Jorgensen et al., 2004; Kennedy & Taylor, 2003). Phloroglucinolysis of the skin proanthocyanidins yielded (−)-epigallocatechin (EGC), (+)-catechin (C), (−)-epicatechin (EC), (−)-epicatechin-3-*O*-gallate (ECG) extension subunits, and C terminal subunits. Phloroglucinolysis of the seed proanthocyanidins yielded C, EC, ECG as extension subunits and C, EC, and ECG as terminal subunits. Based on molar proportion, the main extension subunits in skin proanthocyanidins were EC (62.0%) and EGC (28.6%). The main extension subunits in seed proanthocyanidins were EC (71.4%) and ECG (11.1%), again based on % molar proportion. The composition of the 'Pinot noir' skin and seed proanthocyanidins did not diverge from previous reports (Jorgensen et al., 2004; Kennedy & Taylor, 2003).

3.2. Spectrophotometric measurements

Colour density ($A_{420} + A_{520}$) of all solution mixtures increased with time (Fig. 1). Skin proanthocyanidin + catechol mixture exhib-

Table 1
Total skin and seed purified proanthocyanidin and subunits composition analysed by phloroglucinolysis and HPLC. All subunits were expressed as catechin.

Fraction	mDP	Extension subunits (% molar proportion)				Terminal subunits (% molar proportion)		
		EGC	C	EC	ECG	C	EC	ECG
Skin proanthocyanidin	19.6	28.6	2.4	62.0	1.8	5.1	na	na
Seed proanthocyanidin	10.5	na	7.9	71.4	11.1	4.4	2.1	3.0

mDP, mean degrees of polymerization; EGC, (−)-epigallocatechin; C, (+)-catechin; EC, (−)-epicatechin; ECG, (−)-epicatechin-3-*O*-gallate; na, not applicable.

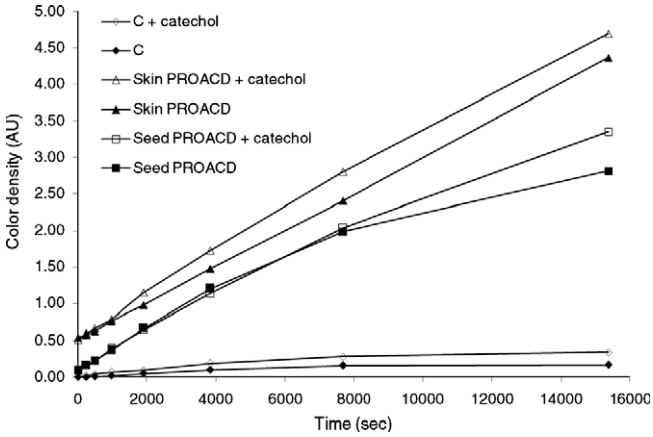

Fig. 1. Colour density (A_{420} + A_{520} in absorbance units; AU) of the flavanol solutions undergoing oxidation over time (n = 8). Solid data points indicate flavanol solutions without catechol. Hollow data points indicate flavanol solutions with a two equal molar catechol addition. Proanthocyanidin abbreviated PROACD.

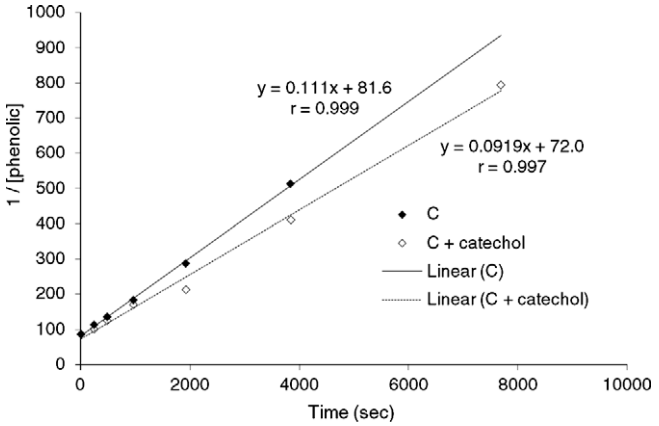

Fig. 2. Evolution of catechin (C), and C with catechol (two molar equivalent), dissolved in model wine under continuous oxygenation and UV light exposure. Phenolic concentration units were in mM. Solid data points indicate flavanol solutions without catechol. Hollow data points indicate flavanol solutions with a catechol addition.

ited the most drastic increase in colour density (0.52 AU at time zero and 4.65 AU at the end of the reaction). The presence of catechol increased colour density of all the flavanol monomer and polymer solutions compared to their counterparts without a catechol addition (Fig. 1). An increase in A_{520} for all monomer and polymer solutions indicated that these oxidised compounds have potential contributions to the red colour in wine. Visually, all proanthocyanidin solutions were initially faint yellow in colour but were reddish-brown in hue at the end of the reaction (15,360 s), as observed by others (Clark, 2008; Es-Safi et al., 2003a; Es-Safi, Cheynier, & Moutounet, 2003b; Lutter, Clark, Prenzler, & Scollary 2007; Tanaka, Mine, Inoue, Matsuda, & Kouno, 2002). These newly formed pigments could be xanthylium salts, as such a formation has been demonstrated with cleaned-up flavanols (Clark, 2008). Both catechin solutions also underwent a visual colour change, but not as intense as the four proanthocyanidin solutions. The A_{280} for all solutions increased steadily up to 7680 s (difference in change ranging from 1.34 to 1.95 AU), but with very little absorbance change from 7680 s to 15,360 s. C solution had the only A_{280} that decreased after the 7680 s time point.

3.3. Oxidation of the monomer and total subunit of skin and seed proanthocyanidin solutions

Under these study conditions the decrease in peak area obtained by HPLC showed most monomer, extension subunits, and terminal subunits disappeared with time. C with, and without, catechol followed second order reaction kinetics (Fig. 2). The half-life of C + catechol solution was increased compared to oxidation of C itself. The half-life of C alone was 770 s, but 930 s with the addition of catechol, though both solutions' half-lives were shorter than those of proanthocyanidins (Table 2). As C disappeared (in both C and C + catechol solutions), a new peak appeared with a retention time close to that of EC that was below the quantification range and only present in samples taken between 240 and 3840 s. EC peaks in some of the oxidised C and C + catechol solutions were likely the epimerization of C under our experiment conditions. The opposite of this trend (C $t_{1/2}$ < C + catechol $t_{1/2}$) was observed in both total subunits of proanthocyanidin mixtures, where skin or seed proanthocyanidin exclusive solutions had slightly longer half-lives compared to their counterparts with added catechol. Monomers disappeared faster than polymers (Figs. 2 and 3; Table 2).

The disappearance of the total, extension, and terminal proanthocyanidin subunits were modelled through second order kinetics (Table 2; Fig. 3). At the concentrations tested, the proanthocyanidin mixtures estimated reaction rate for the disappearance of these compounds varied upon total subunits of proanthocyanidin reaction rate; seed proanthocyanidin (18.2×10^{-5} mM^{-1} s^{-1}, r = 0.990) degraded the fastest followed by seed proanthocyanidin + catechol (13.9×10^{-5} mM^{-1} s^{-1}, r = 0.995), skin proanthocyanidin + catechol (9.01×10^{-5} mM^{-1} s^{-1}, r = 0.991), and finally skin proanthocyanidin ($8.40x10^{-5}$ mM^{-1} s^{-1}, r = 0.994). Seed proanthocyanidins (both with and without catechol) degraded faster than their skin proanthocyanidin counterparts. The addition of catechol affected the rate kinetics for all extension and terminal subunits of both proanthocyanidins (Table 2), and will be discussed in a later section.

These findings were different from Jorgensen et al. (2004), where they reported that 'Pinot noir' under their experimental conditions (oxidised under basic solutions and exposed to the air) skin proanthocyanidin degraded first, followed by seed proanthocyanidin, with seed proanthocyanidin + monomer solutions last. They reported that their degradation also followed a second rate order reaction. The observed discrepancies between these studies might be due to the different conditions utilised to oxidise these compounds, and to the different initial concentrations of the proanthocyanidin solutions. Jorgensen et al. (2004) used 10 g/l of

Table 2
Photochemical reaction rates (k in 1/mM·s), half-lives ($t_{1/2}$ in seconds), and correlation coefficients (r) of purified proanthocyanidins (PROACD) dissolved in model wine solution with and without catechol. Catechol additions were at two molar equivalent. $N = 8$ data points per sample.

		Total PROACD	Extension subunits				Terminal subunits		
			EGC	C	EC	ECG	C	EC	ECG
Skin PROACD	k	$8.40 \cdot 10^{-5}$[a]	$49.5 \cdot 10^{-5}$[a]	[b]	$12.6 \cdot 10^{-5}$[a]	$320 \cdot 10^{-5}$[a]	[b]	na	na
	$t_{1/2}$	2262	1801	[b]	2211	2216	[b]	na	na
	r	0.994	0.975	[b]	0.981	0.973	[b]	na	na
Skin PROACD + catechol	k	$9.01 \cdot 10^{-5}$[a]	$61.5 \cdot 10^{-5}$[a]	[b]	$10.5 \cdot 10^{-5}$[a]	$217 \cdot 10^{-5}$[a]	[b]	na	na
	$t_{1/2}$	1935	1137	[b]	2450	4329	[b]	na	na
	r	0.991	0.991	[b]	0.996	0.997	[b]	na	na
Seed PROACD	k	$18.2 \cdot 10^{-5}$[a]	na	$173 \cdot 10^{-5}$[a]	$24.4 \cdot 10^{-5}$[a]	$119 \cdot 10^{-5}$[a]	[b]	[c]	$284 \cdot 10^{-5}$[a]
	$t_{1/2}$	1690	na	1870	1701	2302	[b]	[c]	3436
	r	0.990	na	0.976	0.993	0.997	[b]	[c]	0.956
Seed PROACD + catechol	k	$13.9 \cdot 10^{-5}$[a]	na	$114 \cdot 10^{-5}$[a]	$21.9 \cdot 10^{-5}$[a]	$140 \cdot 10^{-5}$[a]	[b]	[c]	$255 \cdot 10^{-5}$[a]
	$t_{1/2}$	1568	na	1958	1341	1482	[b]	[c]	2920
	r	0.995	na	0.994	0.991	0.979	[b]	[c]	0.990

EGC, (−)-epigallocatechin; C, (+)-catechin; EC, (−)-epicatechin; ECG, (−)-epicatechin-3-*O*-gallate; na, not applicable.
[a] Followed second order kinetics. Units for second order reaction constants are 1/mM·s.
[b] Indicate reactions that did not have r values equal or greater than 0.950 and did not follow first nor second order rate reactions.
[c] Not enough material present to monitor and calculate values for.

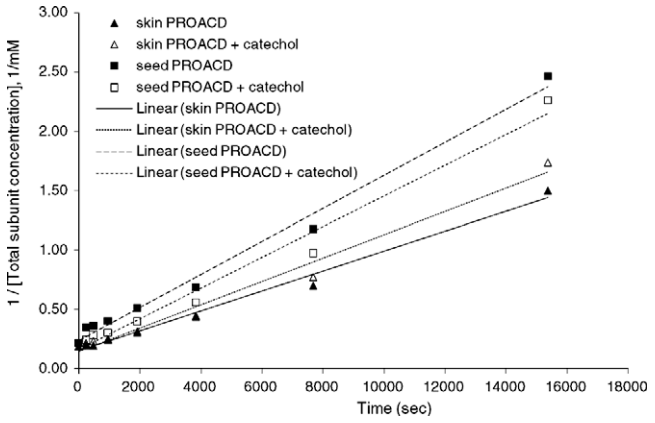

Fig. 3. Evolution of skin and seed proanthocyanidin (PROACD) solutions with, and without catechol (2.0 M equivalent), under continuous oxygenation and UV light exposure. Solid data points indicate flavanol solutions without catechol. Hollow data points indicate flavanol solutions with two equal molar equivalent catechol addition.

both proanthocyanidin fractions, which was well above the concentrations used in this study. Bors and Michel (1999) observed second order decay kinetics in most of the flavanols they tested as well.

Catechol was chosen as the addition monomer for this simplified oxidation experiment due to its simple *o*-diphenol structure. At experiment final time points ~30% of the starting catechol (monitored by HPLC) was still present (for all phenolic solutions), indicating there was enough available catechol, although degradation/hydrolysis products that evolved into catechol could have contributed to this concentration.

3.4. Oxidation of extension and terminal subunits

In the skin proanthocyanidin solutions (both, with and without catechol present), C terminal and extension subunits did not degrade in zero, first, nor second order reactions, which might have been due to additional C subunits produced during the oxidation process or EC epimerizing. The monomer C solution alone, and the formation found in seed proanthocyanidin solutions, followed a second order reaction as indicated in Fig. 2 and Table 2. It is interesting to note the change in reaction rate when C is incorporated into a larger molecule, compared to its degradation as a monomer.

From the skin proanthocyanidin extension subunits, ECG disappeared first, followed by EGC, and then by EC. This order of disappearance did not alter with the addition of catechol, but the catechol did slow the degradation of the EC and ECG extension subunits compared to the skin proanthocyanidin + catechol solutions. ECG extension subunits might have degraded the fastest due to the initially low concentration found in the skin proanthocyanidin fraction (1.8% based on molar proportion; Table 1), since the reaction rate depended on initial concentration of the solution.

From the seed proanthocyanidin solutions, ECG terminal units degraded the most rapidly, followed by C extension subunits, ECG extension subunits, and EC extension subunits. With the addition of catechol this order changed slightly: ECG extension subunits and C extension subunits changing their positions with respect to degradation speed. Interestingly, there was a vast difference in the reaction rate between the seed C extension subunits and the seed EC extension subunits, which was likely due to the higher initial concentration of EC extension subunits (Table 1). Again, C terminal subunits from both seed proanthocyanidin solutions did not follow zero, first, or second order rate reaction.

3.5. Conversion yield, mDP, estimated molecular weight, and gallolyation rate

In all proanthocyanidin mixtures (with or without catechol), conversion yield of the polymers gradually declined as expected, and by the end of the oxidation period conversion yield had dropped to ~10%. This was similar to what Jorgensen et al. (2004) and Salas, Fulcrand, Meudec, and Cheynier (2003) observed in their oxidation experiments with techniques similar to those of this study (cleavage of the proanthocyanidins followed by HPLC).

Average mDP during the entire reaction duration ranged from 17.8 for seed proanthocyanidin solutions to 29.7 for skin proanthocyanidin + catechol solutions, showing active changes in molecule size during reactions. They could increase, decrease, and increase again (Fig. 4) throughout the reaction in each proanthocyanidin solution, indicating that the proanthocyanidins analysable by our study method underwent dynamic changes in molecule size under these conditions. The mDP calculation was based on detecting new formations of recently identified compounds (Bors, Foo, Hertkorn, Michel, & Stettmier, 2001; Drinkine, Lopes, Kennedy, Teissedre, &

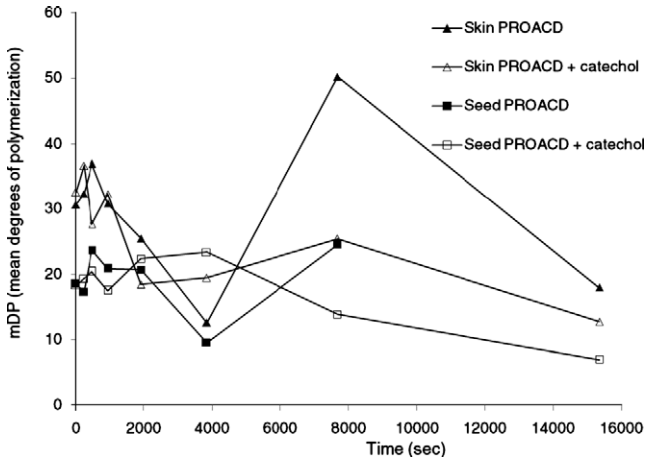

Fig. 4. Solution mean degrees of polymerization (mDP) at time points ($n = 8$) when samples were drawn and analysed. Solid data points indicate flavanol solutions without catechol. Hollow data points indicate flavanol solutions with the two equal molar catechol addition. Proanthocyanidin abbreviated PROACD.

Saucier, 2007; Es-Safi et al., 2003a; Guyot, Cheynier, Souquet, & Moutounet, 1995; Tanaka, Kondou, & Kuono, 2000; Tanaka et al., 2002); particular configurations of proanthocyanidins that can undergo phloroglucinoysis, which is structure specific (Kennedy and Jones, 2001). If these new formations do not have an interflavonoid bond, or if the interflavonoid bond is not easily accessible (De Freitas et al., 1998; Tanaka et al., 2000), they do not undergo phloroglucinolysis and were subsequently not accounted for in the results.

Vidal et al. (2002) also observed little change in mDP within their proanthocyanidin model wine solutions (monitored over 53 days at 30 °C). Though Jorgensen et al. (2004) saw a drastic decrease in mDP in skin and seed proanthocyanidin solutions oxidised under alkaline conditions.

Only a 1–2% increase was observed in the proportion of the galloylated subunits (molar proportion of ECG extension and terminal subunits compared to total subunits), from time zero until the end of the reaction period. In seed proanthocyanidin solutions, maximum gallolyation rates were (4% gallolyation rate) between the range of 1920 and 7680 s, but at the final sampling point they were still only 1–2% higher than the initial gallolyation rate. This slight increase in gallolyation rate was probably due to other non-gallolyated subunits disappearing faster, under study conditions.

The intricacy of oxidative decomposition compounds are a challenge to understand and difficult to analyse. Despite utilising purified compounds, skin and seed proanthocyanidin oxidation study is complicated by the formation of complex new structures that are not analysable by phloroglucinolysis or HPLC. Additional work using a HPLC-mass spectrometer might make it possible to identify some of these newly formed compounds. This study demonstrated the suitability of controlled accelerated oxidation for future proanthocyanidin oxidation studies.

4. Conclusion

Under the oxidation conditions tested in this study, skin and seed proanthocyanidin oxidation was dependant upon the initial concentration of the material. Seed proanthocyanidin (although tested at a lower concentration than skin proanthocyanidin) oxidised more rapidly compared skin proanthocyanidin, which may have been due to seed proanthocyanidin being less bulky in size (smaller mDP value). Catechol addition slowed the degradation rate of C and total seed proanthocyanidin, but not total skin proanthocyanidin.

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