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# Simulating the protective role of bark proanthocyanidins in surface coatings: Unexpected beneficial photo-stabilisation of exposed timber surfaces

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ABSTRACT

Being multifunctional *in planta*, proanthocyanidins extractable from tree bark have been evaluated *in vitro* to provide a protective role to acrylic-based coating resins. These polyflavonoid compounds were assessed as radical and photo-oxidation inhibitors in both native form, and after chemical modification to provide lipophilic character and tailored antioxidant and UV absorption properties. On addition to acrylic and styrene-acrylic co-polymer coatings at typical additive levels (<0.5%) the proanthocyanidins do not inhibit coalescence and cure of the surface coating nor leach from the cured coating. Accelerated weathering and outdoor exposure of acrylic-coated timber revealed modified proanthocyanidins possessing high antioxidant activity were associated with greater coating longevity. Moreover, proanthocyanidins with a high degree of substitution also outperformed synthetic protective agents indicating the inherent UV absorption potential of these materials also contributed this efficacy within the acrylic and styrene-acrylic coating systems. Furthermore, this study has provided an unanticipated finding that the inherent UV absorption and degradation of proanthocyanidins may contribute to the photo-stabilisation and colour stability of the coated timber on weathering.

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## 1. Introduction

In plants, biochemistry affords a variety of compounds for key roles in the health, growth and function of the plant. Polyphenolics such as the proanthocyanidins described in Fig. 1 are secondary metabolites belonging to a class of compounds based on the flavonoid sub-unit obtained *via* the coumarin biochemistry pathway. These polyflavonoid compounds perform various protective roles within the leaf, stem, bark and fruit of plants and trees [1]. Within bark, these polyphenolics provide a core role of protection, mitigating attack from insect, fungal, microbial and oxidation. In leaf and fruit these compounds are additionally involved in ultraviolet absorption and photo-stabilisation [2]. Also classed as condensed tannins, these polyphenolic materials are readily available *via* aqueous extraction of tree bark [3] and have been industrially used to tan leather utilising their inherent ability to complex proteins [4]. Polyflavonoid compounds also possess other attributes such as high antioxidant capacity, and antimicrobial and enzyme inhibition activities suited to nutraceuticals and pharma applications [3].

Similar to the role of tree bark, paints and coatings are applied to exposed timber surfaces to protect the wood against the effects of aging and degradation. The coatings themselves are composed of polymeric components which also require stabilisation to preserve polymer integrity. Paints and coatings usually contain a range of post-polymerization additives to provide functionality and ensure coating performance and longevity, together with protection of the coated substrate [5]. Such additives can range from coalescence aids which effect polymer film formation and adherence to the timber surface to biocides used to inhibit biological growth on the coating surface. Antioxidants and ultraviolet light (UV) stabilisers are other types of additives used in paint and coatings formulations. Their role is to protect the coating polymer from irreversible damage due to oxidation and UV light-induced polymer degradation [6]. Typically, commercial antioxidants tend to be substituted hydroxylated aromatics, whereas those compounds offering UV stability are much more structurally diverse and include hindered amines and phenolics. The inclusion of polyflavonoid materials or condensed tannins in surface coatings has been described for antimicrobial activity [7,8] however, by far their dominant use has been as corrosion and metal surface pre-treatments including steel, aluminium and zinc alloys [9–13]. The affinity for condensed tannins to chelate and bind metal ions is primarily why these compounds have been

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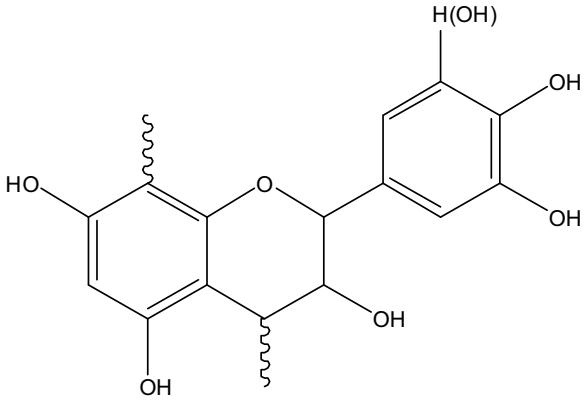


**Fig. 1.** Classed as condensed tannins, proanthocyanidins are oligomeric polyphenols with a chemical structure based on the polyhydroxyl flavonoid sub-unit.

incorporated into metal surface pre-treatments [1,4]. Beyond this specific application, there is little or no information on utilising other inherent flavonoid properties [2] to impart protection to synthetic surface coatings despite their commonality with antioxidant and UV absorbing additives. This report overviews the adaptation of proanthocyanidin functionalities to acrylic-based polymer coatings for the protection of exposed timber surfaces. Adding the proanthocyanidins conferred a protective role, extending the polymer coating performance as well as an unexpected finding of photostabilisation of timber colour on exposure to artificial and natural weathering.

## 2. Experimental section

### 2.1. Materials

An acrylic coating resin Setaqua 6704 together with two styrene-acrylic copolymer coatings Viscopol 6191 and 6756 were sourced from Nuplex Ltd (New Zealand). These formulations were obtained as the base resin coating only and contain no post-polymerisation additives. Each coating formulation was used as received. Commercial antioxidant and UV stabilisers Chimasorb™ 90 and Tinuvin 292 were also obtained from Nuplex Ltd. The native tannin (HWT) was a proanthocyanidin containing spray dried extract obtained from the hot water extraction of *Pinus radiata* bark [14]. This extract is generally composed of 10% carbohydrate material and 90% proanthocyanidins where the degree of polymerization of this polyflonoid component typically ranges 3–13 units. From this HWT extract the tannin esters and ethers were prepared according to published procedures to give tannin acetate (TanAc), tannin laurate, tannin maleate (TanMal), tannin maleate acetate (TanMalAc) and sodium tannin methylcarboxylate (TanMC) described elsewhere [15–17].

### 2.2. Antioxidant assay

The 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonic acid) radical cation ($ABTS^{\bullet+}$) decolorisation assay was a modified method described by Gülçin et al. [18]. Using a 7 mM solution of ABTS the $ABTS^{\bullet+}$ radical was generated by mixing 5 ml of this solution with 88 μl of 140 mM $K_2S_2O_8$. The $ABTS^{\bullet+}$ solution was diluted with either 1:1 ethanol:water (hydrophilic samples) or 8:2 acetone:water (lipophilic samples) to achieve an absorbance of $0.70 \pm 0.02$ at 734 nm. Trolox standards were also prepared to give final concentrations in the range of 2.5–20 μM. Approximately 5 mg of Trolox was dissolved in 10 ml 1:1 ethanol:water or 8:2 acetone:water before this stock solution was diluted to give concentrations ranging from 31.3 to 250 μg/ml. Similarly, the various tannin samples were prepared in 1:1 ethanol:water (hydrophilic samples) or 8:2 acetone:water (lipophilic samples) to concentrations of approximately 62.5–125 μg/ml. To six quartz cuvettes was added 4 ml of $ABTS^{\bullet+}$ working solution and the cuvettes were placed in a multicell reader within a Cary 300 Bio UV–vis spectrophotometer using an absorbance at 734 nm. The cuvettes were incubated at 30 °C and the time zero (0 min) absorbance readings were recorded. The standard or sample solution (80 μl) was added to each cuvette and the solutions mixed and then measured precisely after 6 min. The percentage inhibition of the absorbance of the $ABTS^{\bullet+}$ was calculated from the Trolox calibration curve as per [18].

### 2.3. Modification of coatings

For each modified coating, either the commercial additives or a proanthocyanidin-based modifier was typically added at 0.2% loading w/w on wet emulsion. The commercial additives were added as an aqueous slurry by first adding this material to a minimum amount of water. For proanthocyanidin-based modifiers, each was initially dissolved in a small amount of polyethylene glycol (PEG 400) as *ca.* 20% solutions. The PEG solutions were then added to the base resin which was stirred sufficiently to allow the PEG solution addition without coagulating the coating. For the HWT and TanMalAc additives, each was also added at a rate of 0.4% to the styrene-acrylate copolymer resins with the 0.2% and 0.1% samples obtained by dilution with further coating formulation.

### 2.4. Application and evaluation of coatings

The preparation of coated substrates, artificial weathering and coating assessments were conducted according to the AS/NZS1580 standard. Dressed, untreated radiata pine clears ($280 \times 60 \times 10$ mm) were used as the wood substrate and sanded (150 grit) prior to coating application. Coated wood substrates were also prepared by pre-coating an exterior grade white acrylic coating onto these substrates. The base resin and modified coatings were applied directly to the wood at an overall application rate of *ca.* 50–75 g/m$^2$. Two coats were applied per specimen (both sides) and achieved by initially applying the first coat with a second coat applied at least 2 h later. The coated specimens were then end-sealed with the exterior white acrylic coating to limit moisture and water ingress. Overall, at least 5 specimens were prepared for each modified coating sample (1 reference, 2 accelerated weathering, 2 outdoor exposure). All specimens were placed in a sealed box and stored away from any light until testing.

### 2.5. Accelerated weathering

Samples were exposed to artificial weathering conditions using a QUV accelerated weather tester made by Q Panel Lab Products. Protocols for AS/NZS1580 483.1 were followed where both UV (8 h) and condensation (4 h) cycles were undertaken at 45 °C for up to 4000 h. UV exposure was achieved through the use of UVA-340 lamps at an irradiance of 0.89 W/m$^2$. Two specimens were used per sample, with specimens each having two exposure areas ($50 \times 80$ mm). Specimens were rotated every 250 h to ensure even exposure to QUV conditions. At this time specimens were photographed and colour measurements and coating evaluations undertaken.

### 2.6. Outdoor exposure

Two specimens per sample were randomly mounted at 45° in a support frame which was North facing at a test facility in Rotorua,

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