

Antioxidant Properties of the Hydrophobic Stilbenol Chlorophorin[†]

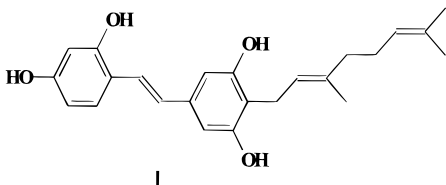
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INTRODUCTION

Extractives from woody plants have the potential for commercial use as free radical scavengers or primary antioxidants. Many phenolic extractives in woody plants exhibit antioxidant properties (Larson, 1988; Huang et al., 1992). Weyerhaeuser Co. once proposed extracting dihydroquercetin from Douglas fir bark followed by oxidation to obtain large amounts of the antioxidant quercetin (Hergert, 1989; Swan, 1989).

Several problems exist with using a plant extractive as an antioxidant for polymers. First, most extractives are relatively immiscible with organic hydrophobic polymers unless chemically modified. Second, most extractives are not thermally stable at temperatures needed to process thermoplastics. Third, most woody tissues contain many different extractives, none of which are present in large amounts, and the total extractive content of wood is usually low (ca. 2–5%). Thus, the isolated yield of a single pure component can be very low. Fourth, some extracts are unsuitable as a plastic additive due to their dark color.

One extractive that is not subject to the above limitations is chlorophorin (4-geranyl-2',4',3,5-tetrahydroxy-*trans*-stilbene), **I**, a relatively hydrophobic stil-



benol. Chlorophorin can be isolated easily in about 5% yield from iroko wood (*Chlorophora excelsa*) (King and Grundon, 1949; Schultz et al., 1995). The presence of phenolic groups in **I** and the observation that finishes on iroko wood will not cure (Norin, 1989) suggest that chlorophorin is an antioxidant.

MATERIALS AND METHODS

Iroko heartwood was extracted with diethyl ether, the solvent removed, and the residue crystallized from toluene to give **I** in 5 wt % overall yield, mp 155–156 °C (King and Grundon, 1949; Harms, 1993; Schultz et al., 1995). The thermal stability of **I** was measured by combined thermal gravimetric analysis (TGA) and differential thermal gravimetric analysis (DTA). A Seiko TG/DTA 220 was used to analyze a 2 mg sample under nitrogen using an empty aluminum sample pan with cap as a reference. The sample was cooled to 16 °C and then heated at 10 °C/min to 240 °C. Below 200 °C, the sample lost <1% of the initial weight. The onset of melting was observed at 148 °C, and the maximum of the melting endotherm occurred at 155 °C. Thus, **I** exhibits sufficient stability to allow melt blending with molten polymers at temperatures between 160 and 200 °C.

Antioxidant properties were first measured using the oxidative stability method of Minn (1991) in which small amounts of an antioxidant, 0.25 wt %, were combined with an oxidizable material and sealed in a vial and the oxygen consumed after a set time was measured. Two oxidizable materials were examined: unstabilized Hercules Ester gum 8D-LT held for 14 days at room temperature and dipentene held for 22 days at room temperature. Two commercial antioxidants, butylated hydroxytoluene (BHT) and tetrakis[methylene(3,5-di-*tert*-bu-

Table 1. Percent Oxygen Consumed by Two Materials with 0.25 wt % of Two Commercial Antioxidants or Chlorophorin as an Additive^a

additive, 0.25 wt %	% O ₂ consumed	material
none	36.9	Hercules Ester gum ^b
BHT	24.8	Hercules Ester gum ^b
tetrakis	23.8	Hercules Ester gum ^b
chlorophorin	17.5	Hercules Ester gum ^b
none	60.7	dipentene ^c
BHT	1.4	dipentene ^c
tetrakis	0.9	dipentene ^c
vitamin E	56.1	dipentene ^c
chlorophorin	0.5	dipentene ^c

^a Vitamin E, a natural lipophilic antioxidant, was also run as a comparison in the dipentene experiment. ^b Unstabilized Hercules Ester gum held at room temperature for 14 days. ^c Dipentene held at room temperature for 22 days.

tyl-4-hydroxyhydrocinnamate)], were used as positive controls. In addition, vitamin E (Aldrich) was used in the dipentene experiment. We (J.M.) have extensively used this method in conjunction with the more common technique of high-pressure differential scanning calorimetry (HPDSC) (Minn, 1985) and have found that the two methods usually give comparable results.

Potential applications as a polyolefin antioxidant were explored using DSC under an oxygen atmosphere as described by Collins and Wendlandt (1982). Various concentrations of **I** were mixed with low-density polyethylene (LDPE, Aldrich) by dissolving both LDPE and **I** in xylene at 120 °C, recovering the mixture by casting a film on a glass plate, and evaporating the solvent under vacuum at 80 °C overnight. Bis-BHT [4,4'-methylenebis(2,6-di-*tert*-butylphenol)] at 0.1 wt % served as a positive control. The sample was heated in a DSC from 20 to 220 °C at 100 °C/min and then held at 220 °C. The time required for onset of polymer degradation as indicated by a rapid exotherm when the antioxidant was consumed was measured. Similar experiments were run using high-density polyethylene (HDPE, Aldrich) with either no antioxidant or 0.5 wt % **I** added as described above.

RESULTS AND DISCUSSION

Chlorophorin (**I**) moderated the oxidation of unstabilized Hercules Ester gum and dipentene as indicated by the relative percent oxygen consumed in Table 1. For each material, the controls (no additive) consumed significant oxygen, indicating that rapid oxidation occurred. The addition of BHT or tetrakis at 0.25 wt % reduced the oxygen consumption. A greater reduction in oxygen consumption was obtained by adding 0.25 wt % **I**, indicating that at moderate temperatures the natural extractive exhibited better antioxidant properties than the two commercial antioxidants. Vitamin E in the dipentene experiment performed poorly at 22 days.

The time to degradation onset for LDPE containing various amounts of **I** is shown in Table 2. Higher levels of **I** increased the apparent stability of LDPE, indicating that **I** has antioxidant properties. When compared with bis-BHT at the same level, however, **I** is apparently only about two-thirds as effective as bis-BHT. Since these tests were run at temperatures above the decomposition temperature of **I**, thermal degradation could be contributing to a rapid consumption of chlorophorin.

Table 2. Time to Degradation Onset for LDPE and HDPE As Measured by DSC under an Oxygen Atmosphere

polymer	additive, wt %	onset time, min
LDPE	chlorophorin, 0.01	0.75
LDPE	chlorophorin, 0.05	3.72
LDPE	chlorophorin, 0.1	6.32 ^a
LDPE	chlorophorin, 0.5	24.29
LDPE	bis-BHT, 0.1	9.87 ^b
HDPE	none	16.75
HDPE	chlorophorin, 0.5	49.21

^a Average of two runs. ^b Average of three runs.

The possible application of **I** in HDPE was explored, and the results are reported in Table 2. The relatively long period required to promote the onset of degradation for the control sample indicated that the polymer already contained a stabilizer. Addition of **I** to HDPE lengthened the onset time, which demonstrated that **I** may exhibit synergistic properties when used in conjunction with other antioxidants.

The preliminary experiments reported above suggest that **I** exhibits antioxidant properties approximately comparable to commercial antioxidants and is thermally stable up to 200 °C. The hydrophobic nature of this stilbenol as compared to most extractives in woody plants should enhance its compatibility with thermoplastics. Unfortunately, **I** is reported to cause "strong allergic reactions" (Norin, 1989), and iroko dust is an irritant (King and Grundson, 1949), which suggests that **I** should not be used in materials in which prolonged direct human contact can occur without bioactivity studies.

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