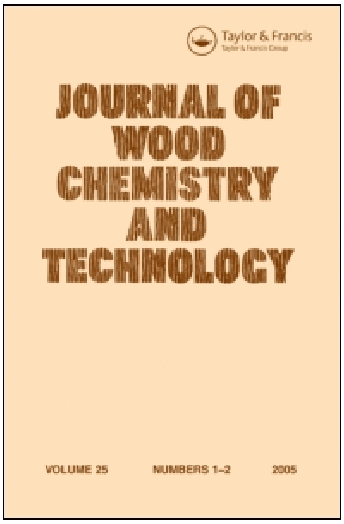

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FORMATION OF 7-KETODEHYDROABIETIC ACID AT THE RADIATA PINE WOOD SURFACE, AND ITS EFFECT ON WOOD YELLOWING

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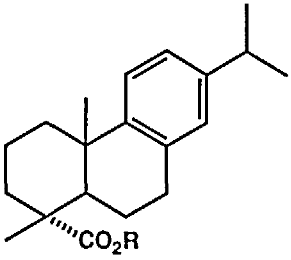
ABSTRACT

Dehydroabietic acid (1), an extractive of radiata pine wood has been shown to undergo light-catalysed oxidation at the wood surface to 7-ketodehydroabietic acid (3), identified by mass spectrometry as the methyl ester (4), and compared with authentic compound. 7-Ketodehydroabietic acid (3) was not generally further oxidised, except in two samples examined which contained a trace amount of 7-ketoabieta-6,8,11,13-tetraen-18-oic acid (7). Consequently, 7-ketodehydroabietic acid (3) accumulated as a major oxidised resin acid product at the radiata pine wood surface when the surface was exposed to air and light. After one year, the compound (3) comprised approximately half of the extractable aromatic ring-C resin acids. Application of synthetic 7-ketodehydroabietic acid (3) to exhaustively methylene chloride extracted radiata pine wood blocks, and exposure of treated and untreated blocks to sunlight did not result in alteration of the yellowing rate of the wood surface.

INTRODUCTION

The chemistry of exposed wood surfaces, and changes in the surface chemistry has received considerable attention, especially with regard to adhesives, and to wood protection[1,2] and recently, as a possible means of determining the age of wood fractures[3]. The study of wood surface chemistry is complicated by changes that can arise through sawing or other machining processes during sample preparation. Non polar extractives can be redistributed during or after surface preparation to become deposited on the surface in concentration higher than in the bulk wood[4]. Extractives can also be mobilised and brought to the surface during kiln drying of wood, whereas ambient air drying results in practically no surface enrichment[5].



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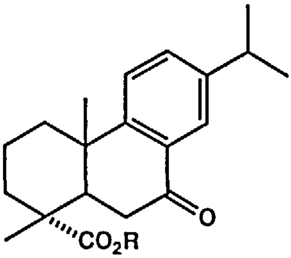
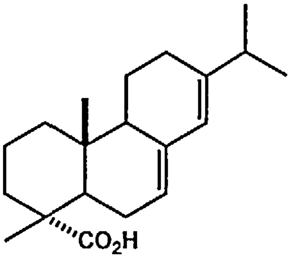
2) R-CH_3



3) R=H
4) R=CH_3



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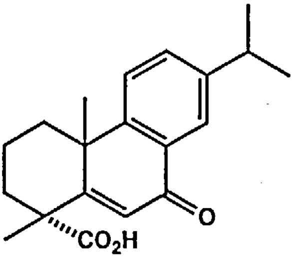

6)

On exposure to air and light, a new wood surface changes physically and chemically. Photochemical reactions proceed rapidly, turning the wood initially yellow, and eventually dark brown or grey at depths of up to 2.5 mm below the surface[6]. These reactions in wood are initiated by phenoxy radicals generated by ultraviolet irradiation[7]. The phenoxy radicals can undergo rearrangement reactions leading to formation of quinones, the simple examples of which being yellow-coloured, contribute to the yellowing of wood.

Whereas the involvement of flavanoids, stilbenes and other polyphenols[8,9,10] in wood surface discolouration has been studied, the role of diterpene resin acids has not been reported. This is not the case for wood pulps, where resin acids residual in bleached sulphite pulps are known to contribute to brightness reversion[11]. Formation of oxidised resin acids, such as 7-ketodehydroabietic acid (3) from air oxidation of dehydroabietic acid (1) at the wood surface would be expected to alter its light absorption properties, since 7-ketodehydroabietic acid (3), having a benzyl ketone function, absorbs over the range 250-302 nm[12]. Aromatic carbonyl compounds can act as photochemical initiators[13], and some have been identified as assuming a major role in the photochemical yellowing of lignin in both wood and pulp[14].

The question of any effect of 7-ketodehydroabietic acid (3) on the yellowing of radiata pine wood was therefore raised and examined. This paper describes the oxidation of dehydroabietic acid (1) to 7-ketodehydroabietic acid (3) at the freshly exposed radiata pine sapwood surface, and the yellowing rate of radiata pine wood blocks exposed to light, and treated with 7-ketodehydroabietic acid (3) compared with that of untreated, and solvent-extracted wood.

RESULTS AND DISCUSSION

A representative gas chromatogram (flame ionisation detector) of a methylated extract of a wood surface sample is shown in Figure 1. The peaks of interest are n-hexadecane internal standard (peak 1), methyl dehydroabietate (2) (peak 2) and methyl 7-ketodehydroabietate (4) (peak 3). Since both methyl dehydroabietate (2) and methyl 7-ketodehydroabietate (4) fragment on electron ionisation in the mass spectrometer to give $[M-75]^+$ ions as base peak in their mass spectra, selected ion monitoring mass spectrometry of the ions m/z 239 for methyl dehydroabietate (2), and m/z 253 for methyl 7-ketodehydroabietate (4) could be used to clearly identify and quantify the compounds of interest in the derivatised radiata pine wood extracts. The use of n-hexadecane as an internal standard, and monitoring ions m/z 57 and m/z 226 allowed compensation for variability in ion detection between samples. An example of the analysis carried out by gas chromatography selected ion monitoring mass spectrometry is shown in Figure 2. A plot of the ratio of m/z 253 to m/z 239 integrals *vs* the logarithm of time of exposure of the radiata pine wood surface is shown in Figure 3. This plot clearly shows that dehydroabietic acid (1) is oxidised over time to 7-ketodehydroabietic

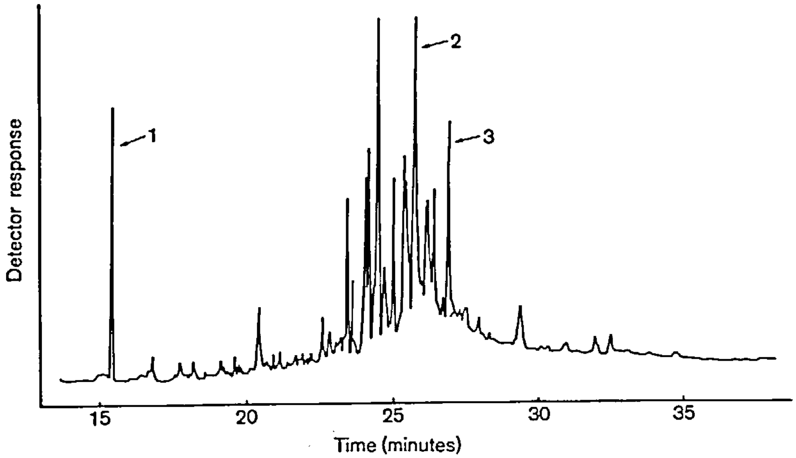

FIGURE 1 - Gas chromatographic analysis of methylated radiata pine wood surface extract

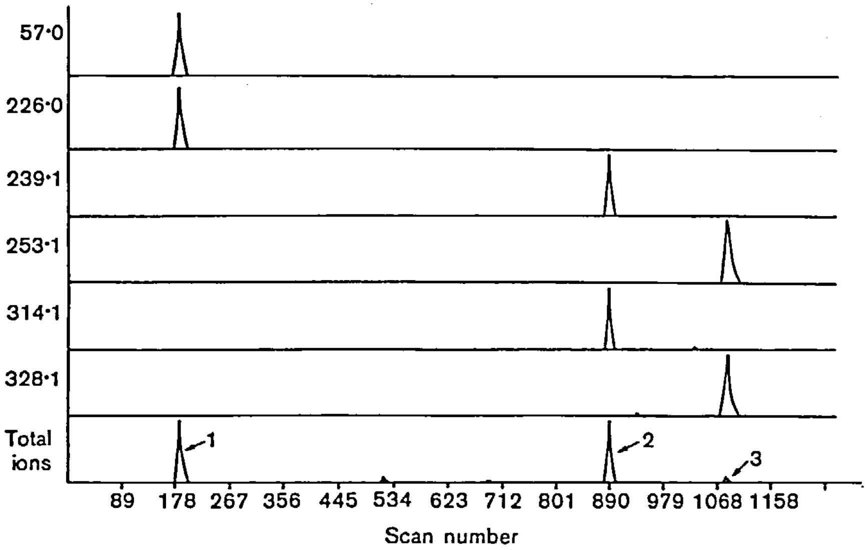

FIGURE 2 - Gas chromatographic - selected ion monitoring mass spectrometric analysis of methylated radiata pine wood surface extract

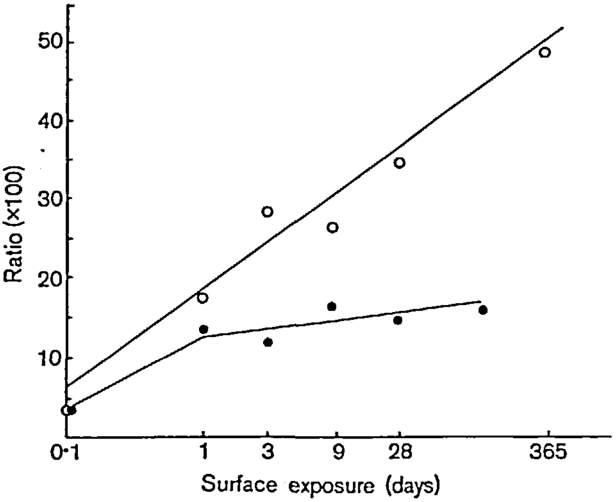

FIGURE 3 - Plot of ratio of methyl 7-ketodehydroabietate to methyl dehydroabietate in radiata pine wood surface *vs* time of surface exposure to air and light. o = exposed to light, • = kept in dark.

acid (3) at the radiata pine wood surface, and that the reaction is promoted by the wood surface having been exposed to light.

For wood kept in the dark, an initial increase in the yield of 7-ketodehydroabietic acid (3) was observed for the first day of surface exposure, possibly as a result of the wood surface preparation. Thereafter, the conversion of dehydroabietic acid (1) to 7-ketodehydroabietic acid (3) was slow (Figure 3).

It is stressed that the ratios measured are not for a true surface, but for a volume of wood having a small finite depth (c 1 mm), and that the concentration of 7-ketodehydroabietic acid (3) at the true surface may be considerably higher than these data show.

Dehydroabietic acid (1) itself is formed from oxidation of diene resin acids, such as abietic acid (5) on their exposure to air[15]. The initial concentration (c. 0.045%,[16] of dehydroabietic acid (1) in a small, finite depth of wood surface would therefore be expected to increase at one rate (k_1) and to be converted to

7-ketodehydroabietic acid (3), at another rate (k_2). The observed (Figure 3) fast initial rate of production of 7-ketodehydroabietic acid (3) suggests that the available dehydroabietic acid (1) is rapidly oxidised within three days of exposure of the wood surface to air and light (i.e. $k_2 > k_1$). After that, the formation of 7-ketodehydroabietic acid (3) proceeds more slowly, governed by the rate of formation of dehydroabietic acid (1) from diene resin acids.

No products resulting from further oxidation of 7-ketodehydroabietic acid (3) such as the 6-hydroxy or 6-keto derivatives (the latter are yellow-coloured) nor their corresponding lactones[17] could be identified in any of the radiata pine wood surface extracts analysed. Two samples, however, were shown by mass spectrometry to contain trace amounts (< 0.1% of the methyl dehydroabietate (2) ion current) of 7-ketoabieta-6,8,11,13-tetraen-18-oic acid (6), possibly formed by rapid dehydration of an intermediate 6-hydroxy-7-ketodehydroabietic acid. Therefore, after a long period of time, 7-ketodehydroabietic acid (3) would become the dominant resin acid at the exposed wood surface, when the surface had also become darkened and yellowed.

However, there appears to be no observable effect of 7-ketodehydroabietic acid (3) in either accelerating or retarding the rate of yellowing of radiata pine wood when the compound was applied to the wood surface, and the surface then exposed to sunlight. A plot of the mean chroma (b*, or amount of yellow colour component of the wood sample surface) *vs* time of exposure is shown in Figure 4. Regardless of the treatment received by the wood surface, all surfaces began to become yellowed after approximately 2000 minutes of sunlight exposure, and thereafter, increased in surface yellowing at similar rates. A similar family of curves was obtained for the mean value quantifying darkening of the wood (L*, or colour density on a white-grey-black scale).

It is concluded therefore, that accumulation of 7-ketodehydroabietic acid (3), arising from light catalysed air oxidation of dehydroabietic acid (1) at the radiata pine wood surface, occurs concomitantly with the onset of wood yellowing, but the compound appears not be to involved directly in initiation or acceleration of the yellowing process chemistry.

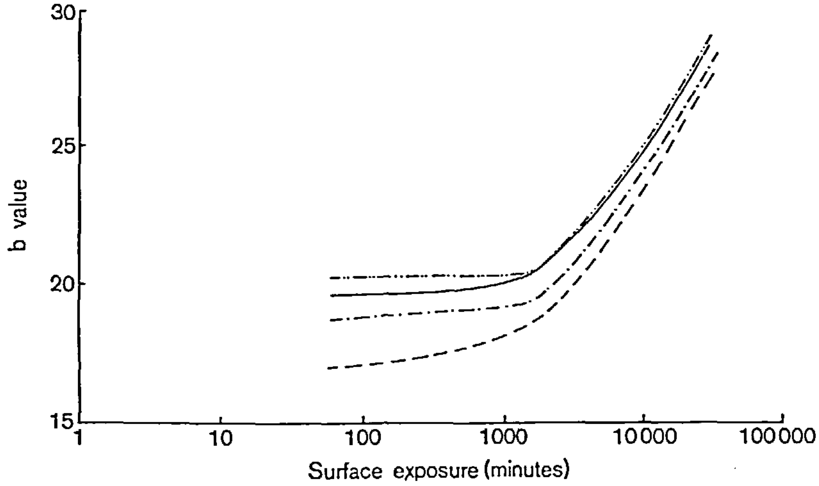

FIGURE 4 - Plot of radiata pine wood surface yellow colour (b*, chroma) *vs* time of surface exposure to light.

——— = control
—·— = CH_2Cl_2 extracted
– – – = 7-ketodehydroabietic acid, 0.5 ratio
—··— = 7-ketodehydroabietic acid, 0.2 ratio.

EXPERIMENTAL

Wood Material

One piece of air-dried radiata pine sapwood 200 x 50 x 600 mm, flatsawn, was cut into eight equal portions and the freshly exposed surfaces allowed contact with air for 1, 3, 9 and 28 days. Half the pieces of wood were kept in the dark, the other half were exposed to daylight. All pieces were kept at approximately 12% moisture content. A similar piece of air-dried radiata pine sapwood which had been kept exposed to normal daylight for approximately 1 year was cut in half longitudinally. The inside faces of this were used to provide a zero exposure time sample, and the outside faces for a sample representing long term exposure.

After exposure, an approximately 1-mm-thick sample was machined from the surface using a planer, and the wood shavings were collected.

Extraction and Derivatisation

A 1 g sample of each of the shavings was added to dichloromethane (100 ml, freshly distilled) containing n-hexadecane (50 mg) as internal standard. After soaking the shavings for 24 h, the extract was filtered, and concentrated at 30°C using a rotary evaporator. The residue was treated with a small excess of ethereal-ethanolic diazomethane and allowed to stand at 20°C for 5 minutes. Excess of diazomethane was removed using a current of dry N_2, and the clear solution made up to 250 ml using dichloromethane.

Analysis

Samples were analysed by gas chromatography - mass spectrometry (GCMS). The separation was carried out using a 10 m x 0.2 mm SE-30 fused silica open tubular capillary column with helium carrier gas having a mean linear velocity of 30 cm s^{-1}. The purged-splitless injector was at 220°C, and the GCMS interface (open-split type) at 250°C. The column was programmed from 50°C to 250°C at 5°C min^{-1} and then held at 250°C for 10 minutes. The mass spectrometer was operated in electron ionisation mode, using 70 eV, 300 μA electron energy, and an ion-source temperature of 200°C. Methyl dehydroabietate (2) was detected by monitoring ions of m/z 314 and 239, methyl 7-ketodehydroabietate (4) by ions of m/z 328 and 253, and n-hexadecane by ions of m/z 226 and 57. Dwell times of 50 ms were used.

Calculation of Results

Ion currents for m/z 239, 253, 226 and 57 were integrated. To calculate the ratio of methyl 7-ketodehydroabietate (4) to methyl dehydroabietate (2) in each sample, the ratio of the integrals for m/z 253:239 was determined. To allow for variation in mass spectrometer performance between samples, the ratios were normalised using the ratio of ions m/z 57:226 for n-hexadecane internal standard. (This ratio is made = 10.0). A factor of 2 is introduced to account for the difference in ion-current intensity of m/z 253 in methyl 7-ketodehydroabietate (4) (19.5%) and m/z 239 in methyl dehydroabietate (2) (38%) mass spectra. The ratio of methyl 7-ketodehydroabietate (4) to methyl dehydroabietate (2) is given by:

$$\text{Ratio} = \frac{m/z\ 253\ \text{integral}}{m/z\ 239\ \text{integral}} \times \frac{m/z\ 226\ \text{integral}}{m/z\ 57\ \text{integral}} \times \frac{10}{1} \times \frac{2}{1}$$

For each sample this value was plotted *vs* log number of days' wood surface exposure.

Exhaustive extraction of radiata pine sapwood blocks

Four air-dried sapwood blocks (230 x 60 x 8 mm, density 480 kg/m^3) were placed in a large diameter Soxhlet apparatus, and extracted with methylene chloride for 12 h. The extract was concentrated, and the weight of extractive determined. The blocks were subjected to a further three extractions, such that the residue from the last extraction was very small (<5%) compared with the weight of the initial extract. The total extract obtained was 2.66 g or 1.25% of the dry weight of the wood which is the expected extractive yield from radiata pine sapwood[16]. At this point, it was considered that the wood blocks had been exhaustively extracted. Before use in the yellowing rate experiments, a new wood surface was exposed by planing approximately 1 mm from the block face.

7-ketodehydroabietic acid (3)

Oxidation of methyl dehydroabietate (2) with chromium trioxide in glacial acetic acid, followed by column chromatographic isolation of methyl 7-ketodehydroabietate (4), and its subsequent alkaline hydrolysis provided a sample of 7-ketodehydroabietic acid (3), as a nearly colourless gum, characterised by its spectroscopic properties[12].

Application of 7-ketodehydroabietic acid (3) to wood surfaces, and their exposure to sunlight

A solution of 7-ketodehydroabietic acid (3) (10 mg) was prepared using methylene chloride (10 ml). To the solvent-extracted radiata pine wood surfaces was applied

(i) 1.1 ml of solution, spread as evenly as possible over the surface (230 x 60 mm), to provide an amount of the keto-acid (3) on the surface equivalent to a ratio of the keto-acid (3) to dehydroabietic acid (1) of 0.2 (Figure 3). This amount is derived using the following argument. A 1 mm deep "surface" of the wood sample was 230 x 1 x 60 mm^3, or 13.8 cc. Using the wood density of $\rho = 0.48$, the surface contained 6.624 g wood substance, of which c 0.1%, or c 6.6 mg was dehydroabietic acid (1), when the surface was freshly prepared. The amount of 7-ketodehydroabietic acid (3) to apply was derived from $\frac{x}{6.6-x} = 0.2$.

(ii) 2.2 ml of the 7-ketodehydroabietic acid (3) solution, similarly evenly applied to the wood surface, as above, to provide an amount of keto-acid (3) equivalent to a ratio of 7-ketodehydroabietic acid (3) to dehydroabietic acid (1) of 0.5 (Figure 3).

The treated wood blocks, together with untreated, and solvent-extracted wood blocks were exposed to exterior daylight. The blocks were set at approximately 45°, facing NW.

Wood block colour measurement

The colour of the surface of the wood blocks was quantified using a Minolta CR-100 chroma meter. The colour was measured at three points on each block, and the means for the surface darkening value (L*), the hue (a*) and the chroma (b*) recorded over a 500 hour period. The chroma value was plotted against the logarithm of time (minutes) the wood surface was exposed to light.

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