

FREE RADICALS FROM CONIFERYL ALCOHOL AND ISOEUGENOL

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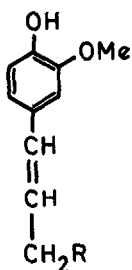
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The formation of lignin is believed to involve the coupling of free radicals formed from the enzymatic oxidation of coniferyl alcohol (Ia) or of polymeric units formed by previous couplings<sup>(1)</sup>. There has been one claim for the observation of the free radical from coniferyl alcohol from an enzymatic oxidation<sup>(2)</sup> (weak esr signal, half-life 45 seconds) but a repetition of this experiment in our laboratory, and in other laboratories<sup>(3)</sup>, was unsuccessful. Theoretical calculations would indicate that this free radical should have approximately equal spin densities on the  $\beta$ , the 5 and the phenolic oxygen positions<sup>(4)</sup>, and models for the structure of lignin have been based on this premise<sup>(1)</sup>.

When coniferyl alcohol or isoeugenol (1b) was photolysed, photolysed with benzophenone as a sensitizer, or photochemically oxidized with ditertiarybutyl peroxide in the presence of the spin trap<sup>(5)</sup> 2-nitroso-2-methylpropane, esr spectra of trapped species were obtained. For each phenol the spectra were invariant under the conditions of formation and consisted of a triplet hyperfine splitting (14.9 G for both phenols) further split into doublets (isoeugenol 2.3G, coniferyl alcohol 2.7G). The doublet splitting is consistent with the spin trap being bound to a saturated carbon atom with a methine hydrogen (range<sup>(5)</sup> 1.5-6G) and the triplet splitting constant being only 0.6G less than the free spin trap also indicates that very little spin delocalization is occurring. Both theory and the analysis of the products of radical oxidation<sup>(1)</sup> would

eliminate the  $\alpha$  position from consideration, hence we assign the observed radicals as those trapped through the  $\beta$  position i.e. structure II.

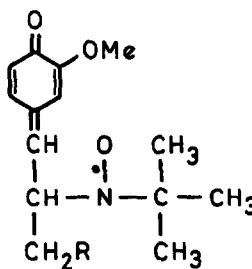
The signal to noise ratio of the esr spectra were 50:1 and no other radical species could be detected. Therefore, unless this is a result of a specific preference on the part of the spin trap, it appears that the  $\beta$  position of the radicals of these phenols is significantly more reactive than the other positions.



(a) R = OH

(b) R = H

(I)



(II)

#### References

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