

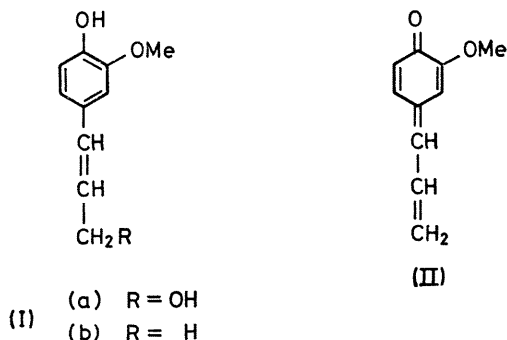
Flash Photolysis of Coniferyl Alcohol

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Summary Flash photolysis of coniferyl alcohol gives rise to a long-lived transient assigned a quinone methide structure.

It is generally accepted that lignin is derived from the enzymatic polymerization of a mixture of *p*-coumaryl alcohols rich in coniferyl alcohol (Ia). The mechanism, which is thought to involve phenoxy-radicals derived from the *p*-coumaryl alcohols, has been inferred mainly from the structure of the dilignols isolated by interrupting the laboratory polymerization of coniferyl alcohol at an early stage.¹



The reports that phenols, in general, give rise to phenoxy-radicals upon photolysis,^{2,3} and that coniferyl alcohol may be polymerized to yield artificial lignin,⁴ suggest that photolysis of coniferyl alcohol should result in the formation of its phenoxy-radical. In an attempt to produce and characterise the phenoxy-radical from coniferyl alcohol we have studied the photochemistry of coniferyl alcohol.

We now report that photolysis of coniferyl alcohol in various solvents does not apparently yield the phenoxy-radical, but gives instead a long-lived transient which absorbs near 350 nm (Figure) and whose lifetime is unaffected by the presence of atmospheric oxygen. A transient

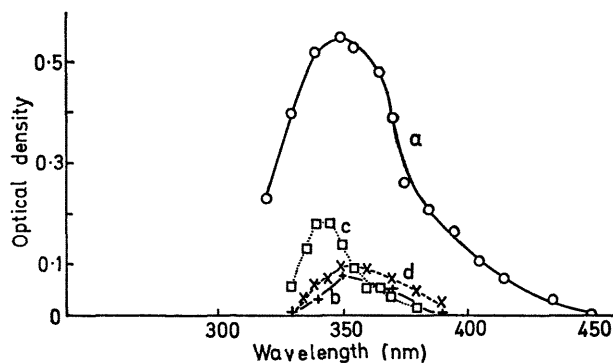


FIGURE. Transient absorption spectra obtained upon flash photolysis of coniferyl alcohol in (a) water, (b) ethanol, (c) carbon tetrachloride, and of isoeugenol in (d) water. Delay time = 0.1s.

of similar lifetime and spectrum is also observed upon photolysis of the related *p*-vinyl substituted phenol, isoeugenol (Ib) in water or in ethanol (Figure). These transient spectra are virtually identical with that assigned by Pew *et al.*⁵ to the quinone methide (II), obtained upon enzymatic dehydrogenation of eugenol, and we believe that we are observing the same species here. In agreement with this assignment we find that the transient observed upon flash photolysis of coniferyl alcohol behaves like a typical quinone methide in its reaction with acid.⁶ Its rate of reaction in acetic acid (first-order rate constant K_1

= 0.4 s^{-1}) is much greater than its rate of reaction in water ($K_1 = 10^{-3} \text{ s}^{-1}$).

Flash photolysis of coniferyl alcohol in the very polar solvents, water or acetic acid, gives a yield of quinone methide (II) which is at least five times that observed upon photolysis of coniferyl alcohol in ethanol or of isoeugenol in any of these solvents (Figure). This dramatic change in

reactivity with solvent may indicate an ionic mechanism for the formation of the quinone methide (II) from coniferyl alcohol. On the other hand, the same transient absorption, slightly shifted to the blue, is also observed upon flash photolysis of coniferyl alcohol in carbon tetrachloride, a solvent in which ionization should be suppressed.

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¹ K. Freudenberg in 'Lignin Structure and Reactions,' Advances in Chemistry Series, ed. R. F. Gould, American Chemical Society, Washington, D.C., 1966, vol. 59.

² E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, 1961, **57**, 1885.

³ E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2016.

⁴ K. Freudenberg and H. Dietrich, *Chem. Ber.*, 1953, **86**, 1157.

⁵ J. C. Pew, W. J. Connors, and A. Kunishi, in 'Chimie et Biochimie de la Lignine, de la Cellulose et des Hemicelluloses. Actes du Symposium International de Grenoble, Juillet 1964,' Imprimeries Réunies, Chambéry, 1965, pp. 229—245.

⁶ K. Freudenberg in 'Constitution and Biosynthesis of Lignin,' Springer-Verlag New York Inc., 1968, p. 94.