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FORMATION OF ARYL BENZANTHRONES FROM ANTHRAQUINONE-CATALYSED DEGRADATION OF LIGNIN

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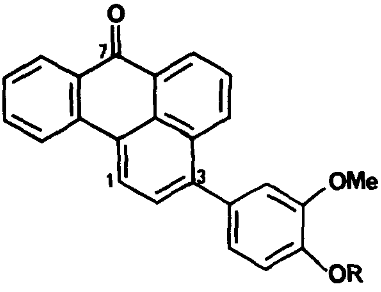
Summary. Anthraquinone-cataylsed pulping of Pinus radiata gives the aryl benzanthrones (1) and (2), their formation involving reaction between anthraquinone and lignin constituents of the wood.

Anthraquinone efficiently catalyses the alkaline pulping of wood, a new process currently of interest to paper manufacture[1]. It acts not only by inhibiting degradation of polysaccharides but also by promoting delignification. Whilst the former action evidently involves terminal oxidation of the polysaccharide by redox reactions, the mechanism of the latter is unknown. This communication provides clear evidence for chemical bonding between anthraquinone- and lignin-related constituents under pulping conditions. Related investigations are being made by other workers[2].

Pinus radiata chips were cooked under standard conditions[1] with 1M-sodium hydroxide at 170° in the presence of anthraquinone (0.1 to 2% of the dry wood). The chloroform-extractable products were subjected to thin layer chromatography. Part of the anthraquinone was recovered together with two new yellow fluorescent compounds. These accounted for 15 and 2% of the anthraquinone originally added and neither was present in liquors from which it had been omitted.

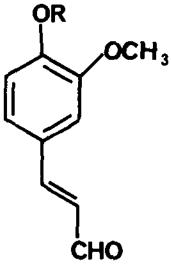
The new compounds $C_{24}H_{16}O_3$, $C_{25}H_{18}O_3$, m.p. 198, 224° respectively, each had an absorption maximum at 424 nm in ethanol. The spectra were qualitatively similar to that of 7H-benz[de]-anthracene-7-one (benzanthrone)[3] but were bathochromically shifted. They were identified as the 3-aryl benzanthrones (1), (2) by syntheses. Thus acid-catalysed condensation of coniferaldehyde (3) and of its methyl ether (4)[4] with 9-anthrone gave the cinnamylidene derivatives (5), (6) (24, 45% respectively). These intermediates efficiently underwent oxidative cyclisation to (1), (2) respectively in boiling 1-chloronaphthalene[5].

Further confirmation of structure, and particularly of substitution of the benzanthrone system at position 3, was provided by spin decoupling. For benzanthrone itself protons 1 and 3 resonated in $CDCl_3$ at $\delta 8.48$, 8.02 respectively, the former conspicuously deshielded by the neighbouring ring[6]. Irradiation at $\delta 7.64$ in the spectrum of (1) caused a similarly deshielded doublet at $\delta 8.54$ (J 8 Hz) to collapse to a singlet. The benzenoid region of the spectrum of (2) was analogous to that of (1).



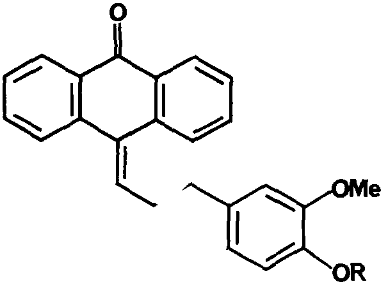
1 R=H

2 R=Me



3 R=H

4 R=Me



5 R=H

6 R=Me

The structures of these benzanthrones require introduction of aryl-C_3 residues, clearly consistent with chemical interaction between anthraquinone- and lignin-related moieties[7,8]. Their combined yield based on the wood, was necessarily small when anthraquinone was used in the catalytic proportions above. However this yield was considerably increased by cooking in the presence of larger proportions of reduced anthraquinone in the form of 10-hydroxy-9-anthrone[9], this reagent being more soluble in the alkaline medium. Under these conditions up to an estimated 10% of the lignin content of the wood has been accounted for as a mixture of (1) and (2).

These observations show that anthraquinone-catalysed pulping can involve not only redox behaviour but also covalent bonding of the catalyst. The oxidation level at which bonding occurs is under continuing investigation, as is the overall mechanism and its relevance to delignification.

Satisfactory elemental analyses and spectra have been obtained for new compounds reported in this work. We are grateful to Australian Paper Manufacturers Limited for helpful discussions and for financial support.

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