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Short Note

Reaction of a Lignin Model Dimer with Chlorine and Chlorine Dioxide

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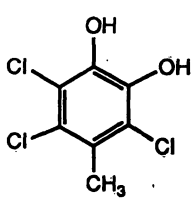
Introduction

The high mass material produced during pulp bleaching with chlorine-containing bleaching agents is a complex mixture which is difficult to characterize. Analytical and spectroscopic studies have shown the material has a low aromatic content and contains numerous polar functional groups such as carboxylic acid and hydroxyl groups (Lindström and Österberg 1984; Österberg and Lindström 1985). Recent studies also suggest the molecular weight average may be considerably lower than previously thought because association effects occur during some of the analytical techniques used in molecular weight determination (Jokela and Salkinoja-Salonen 1992). A variety of lignin-type materials have been reported to exhibit molecular association in various solvents so this phenomenon is not new (Glasser and Sarkanen 1969). In addition, the high mass material has been shown to be capable of binding low mass fragments which are difficult to remove (O'Connor and Voss 1992). Although further studies will provide more information on the nature of the high mass material, it is apparent that other complementary approaches would be valuable in determining the structure, behaviour and environmental fate of this material.

One approach to the study of this material is to use model compounds which have similar structural features. Recently it was found that successive treatment of 4-methyltrichlorocatechol **1** and 4-methylguaiacol **2** with Cl_2 and NaOH gave the dihydroxytetrachlorocyclopentenecarboxylic acid **3** (McKague and Reeve 1992). The formation of a polar product containing both hydroxyl and carboxylic acid groups is consistent with reports concerning the functional groups present in high mass material. Dimers and trimers of compounds like **3**, but having a higher carbon to chlorine ratio, may have properties similar to that of the high mass material.

Dimeric model compounds whose structures were consistent with information available on the structure of residual kraft lignin and which could be converted to non-aromatic dimers by succesive treatment with Cl_2 and NaOH were desired for this work. According to the literature, the β-aryl ether linkages which remain in residual lignin are resistant to alkali cleavage and the lignin is more condensed (Gellerstedt *et al.* 1988; Gierer 1985). NMR studies also indicate that there appears to be a surprisingly large number of saturated carbons in the side chain (Gellerstedt and Robert 1987).

The dimer **4** was chosen for this study. Since this dimer does not have substituents on the α– or γ-carbon-atoms which could become involved in neighbouring group participation, cleavage of the β-aryl ether



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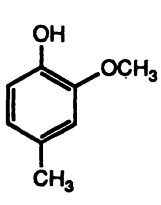

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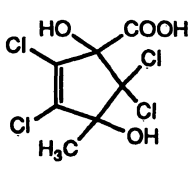

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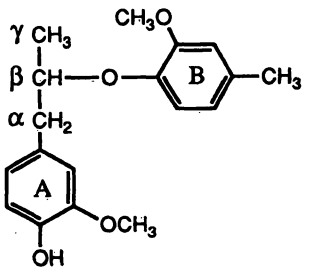

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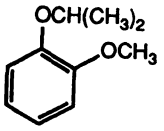

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