DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 18

SYNTHESIS, STRUCTURE VERIFICATION AND GAS CHROMATOGRAPHIC DETERMINATION OF CHLORINATED CATECHOLS AND GUAIACOLS OCCURRING IN SPENT BLEACH LIQUORS OF KRAFT PULP MILLS

BY
J. KNUUTINEN

Academic Dissertation
for the Degree of
Doctor of Philosophy

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University of Jyväskylä, 2024

To my parents

PREFACE

The present investigations were carried out in the Department of Chemistry, University of Jyväskylä, during the years 1979-1984.

I wish to express my sincere thanks to Professor J. Paasivirta for many fruitful discussions and for his co-operation and multifarious help.

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In Jyväskylä, August 1984

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LIST OF ORIGINAL PAPERS

This thesis is based on the following original papers which are referred to in the text by their Roman numerals.

I. J. Knuutinen and I.O.O. Korhonen, Mass Spectra of Chlorinated Aromatics Formed in Pulp Bleaching. 1. Chlorinated Catechols, Org. Mass Spectrom. 18, 438 (1983).
https://doi.org/10.1002/oms.1210181007

II. J. Knuutinen and J. Tarhanen, Limited Methylation of Chlorinated 1,2-Benzenediols to Chlorinated 2-Methoxyphenols, J. Chem. and Eng. Data 26, 347 (1981).
https://doi.org/10.1021/je00025a040

III. J. Knuutinen and I.O.O. Korhonen, Mass Spectra of Chlorinated Aromatics Formed in Pulp Bleaching. 2. Chlorinated Guaiacols, Org. Mass Spectrom. 19, 96 (1984).
https://doi.org/10.1002/oms.1210190210

IV. J. Knuutinen and I.O.O. Korhonen, Gas Chromatographic Separation of Acetylated Chlorinated Phenols, Guaiacols and Catechols on an SE-30 Quartz Capillary Column, J. Chromatogr. 257, 127 (1983).
https://doi.org/10.1016/S0021-9673(01)88162-0

V. J. Knuutinen, J. Tarhanen and M. Lahtiperä, Gas Chromatographic and Mass Spectrometric Analysis of Chlorinated Catechols Occurring in Pulp Bleach Liquors, Chromatographia 15, 9 (1982).
https://doi.org/10.1007/BF02269031

VI. J. Knuutinen, Analysis of Chlorinated Guaiacols in Spent Bleach Liquor from a Pulp Mill, J. Chromatogr. 248, 289 (1982).
https://doi.org/10.1016/S0021-9673(00)87280-5

The mass spectra of acetylated chlorinated catechols and guaiacols are presented in Appendix I.

ABSTRACT

Chlorination stage (C-stage) and extraction stage (E-stage) spent bleach liquors (SBL) from a pine kraft pulp mill and the product from the chlorination of guaiacol (2-methoxyphenol) in aqueous solution were investigated for their content of chlorinated catechols (1,2-benzenediols) and guaiacols (2-methoxyphenols). The compounds were analysed by quartz capillary gas chromatography (GC) and GC-mass spectrometry (GC-MS) of their ethyl or acetyl derivatives. Convenient methods for the synthesis in pure form of model compounds were developed. The most useful methods for the structure verification (NMR and mass spectrometry) are indicated and the GC retention data are summarized. GC and GC-MS were used as main techniques for the identification and determination of the different structural isomers in SBLs. A brief summary is given of the most probable reactions of residual lignin producing chlorinated isomers. Finally note is made of the potential application of the results to the further synthesis of model compounds and to studies of toxicity, degradation, metabolism and off-flavour properties of chlorinated phenolic compounds.

Eight chlorinated catechols were identified in a sample prepared by chlorination of an aqueous solution of guaiacol with chlorine. Only four of these compounds (3,4-dichlorocatechol, 3,4,5-trichlorocatechol, 3,4,6-trichlorocatechol and tetrachlorocatechol) were observed in C-stage SBL. Large amounts (totally ca. 4 ppm) of chlorinated guaiacols were found to be present in E-stage SBL from of a pine kraft pulp mill. 3,4,5-Trichloroguaiacol occurred in the highest concentration (ca. 1.6 ppm), with tetrachloroguaiacol, 4,5-dichloroguaiacol and 4,5,6-trichloroguaiacol as other major components Smaller amounts of 4-chloro-, 5-chloro-, 3,4-dichloro-, 4,6-dichloro- and 3,4,6-trichloroguaiacols were detected.

INTRODUCTION

1. GENERAL INTRODUCTION

Along with cellulose and other carbohydrates, lignin forms part of the basic structure of wood. In the course of the chemical pulping process, the residual lignin gives rise to a brownish colour in the pulp, which can be removed by bleaching with chlorine or some other bleaching chemical. The suitability of chlorine for pulp bleaching was documented in 1868 and still it is the most widely used bleaching chemical. In 1981 the Finnish pulp industry used about 140 million kg of chlorine to bleach a total 2.8 million tons of pulp /1/. Understanding of the behaviour of lignin in chlorobleaching is thus an important problem for laboratory research and engineering process design.

Recent studies have indicated that during chlorobleaching of pulp the lignin macromolecules are degraded to smaller species which have harmful effects on the environment and human health. Among those substances are chlorinated phenolic compounds such as chlorinated phenols, catechols (1,2-benzenediols), guaiacols (2-methoxyphenols), syringols (2,6-dimethoxyphenols) and vanillins (4-hydroxy-3-methoxybenzaldehydes). The total amount of chlorinated phenolics formed in the Finnish pulp industry in 1981 was estimated at some 300 tons /1/. Of especially great concern are chlorinated catechols and chlorinated guaiacols, which have shown to be toxic to fish /2-10/, rat /11/, daphnia magna /10,12/ and other organisms /13,14/. Although spent bleach liquors (SBL) and total mill effluents from the pulp industry have been found toxic /15-17/ and mutagenic /18-21/ by the Ames test, chlorinated catechols and guaiacols themselves have not been proven mutagenic /22-25/. Recently, however, other toxicity studies /26-28/ have indicated that at least some chlorocatechols and chloroguaiacols have highly mutagenic and probably carcinogenic effects. In addition, bioaccumulation properties and enrichment in the food chain have been established for these phenolic substances /5,29-31/.

The first goal of the present investigations was to develop convenient methods for the synthesis in highly pure form of all possible chlorinated catechols and guaiacols. Proton-NMR, carbon-NMR, mass spectrometry and gas chromatography were applied as most suitable structure verification methods. The second goal was to ascertain which of the chlorinated isomers are the most abundant ones in SBL samples from kraft pulp mills. GC and GC-MS were used as main techniques for the identification and determination. A brief summary is provided of the reactions of residual lignin leading to the various chlorinated isomers, the reactions typical of the guaiacylpropane building blocks being used as a model for those of lignin. The main emphasis was placed on bleaching with chlorine (C-stage) and the caustic extraction stage (E-stage) in the pine kraft pulp bleaching process.

2. REACTIONS OF LIGNIN PRODUCING CHLORINATED CATECHOLS AND GUAIACOLS DURING CHLOROBLEACHING

2.1 REACTIONS OF THE GUAIACYLPROPANE BUILDING BLOCKS OF LIGNIN

The lignin molecule is composed of guaiacylpropane building blocks (softwood model, Fig. 1) and undergoes the various reactions typical of this kind of unit /32/. In the formation of chlorinated catechols and guaiacols during the aqueous acid chlorination of residual lignin, the following three reactions A-C (Fig. 1) occur competitively.

A. Aromatic substitution of chlorine into the benzene ring
B. Electrophilic aromatic displacement of the side chain by chlorine
C. Dealkylation (demethylation)

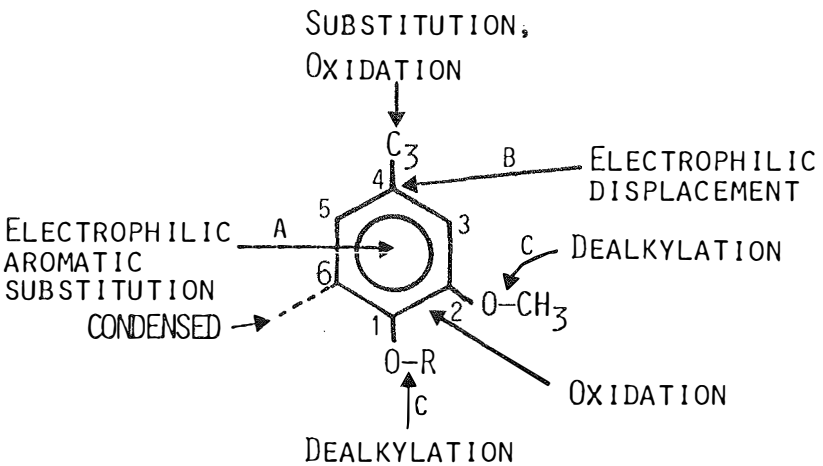


Figure 1. Schematic presentation of the most important reactions of the guaiacylpropane units of lignin during chlorobleaching.

The reactions B and C are the desirable ones from the chlorobleaching point of view since they are responsible for degrading and solubilizing the residual lignin in the pulp. The reactions A-C account for ca. 50 % of the overall reaction when chlorine and substrate (for example guaiacylethyl carbinol) are reacted in equimolar amounts /33/. The remaining 50 % is mainly due to oxidation reactions, producing compounds such as ortho-benzoquinone derivatives. These may also be intermediate products in the formation of the compounds with catechol structure /33,34/.

Most of the aromatic building blocks of lignin have two (condensed at 6-position; Fig. 1) or three (non-condensed) positions available for substitution /32/. In the guaiacyl-propane unit, every unsubstituted position is activated in varying degree toward electrophilic species. The phenolic

hydroxyl group (R = H; Fig. 1) is more strongly ortho-para directing than the methoxyl group. In general, however, substitution at both 5- and 6- positions has been reported /33,35-37/. When the guaiacylpropane unit is condensed at position 6 it is expected to have a positive influence on the 3- and 5-positions. However, such an influence in directing the entering electrophile is weak in comparison with that of the hydroxyl and methoxyl substituents, and chlorine substitution at 3-position of the guaiacyl building block (Fig. 1) has not been reported.

Chlorination studies with guaiacylethyl carbinol have also indicated that aromatic substitution occurs more extensively than electrophilic displacement of the side chain /33/. In general, the reaction that takes place first is substitution at either the 5- or 6-position of the benzene ring (A, Fig. 1). A second reaction (B; Fig. 1) can occur only when there is a hydroxyl (R = H, Fig. 1) or like group at the 1-position. The degree to which this reaction takes place depends on the nature of the displaceable substituents. For example, an α-hydroxyl or alkyl ether group para to a hydroxyl or methoxy substituent is replaced by chlorine with remarkable ease /34,38/.

2.2. PROPOSED ROUTES TO CHLORINATED GUAIACOLS

Electrophilic aromatic substitution (A; Fig. 1) and electrophilic displacement of the side chain (B; Fig. 1) are the most important reactions producing certain chloroguaiacols (Fig. 2). Almost all units in lignin have been shown to contain a substituent (a linkage) at the 4-position and thus chlorobleaching is expected to give rise to the formation of 4-chloro-isomer (II) by route B (Fig. 3). This compound has previously been shown to be formed by chlorination of guaiacol in organic solvent /39/ and in water solution /40,41/. On the other hand, no evidence has been found for the primary substitution at the 3-position (Fig. 1) of the guaiacylpropane building units. Hence, the only monochlorinated compounds formed in chlorination of the guaiacylpropane building blocks of lignin are the isomer II and 5- and 6-chloro-substituted guaiacylpropane derivatives (Fig. 3),

which can also react further with chlorine, giving rise to the chloroguaiacols VIII, IX, XIV and XV. These compounds have been suggested to be formed in chlorination of guaiacol in aqueous solution and of β-arylether type structure units of lignin /41,42/. Van Buren and Dence /33/ predicted the formation of 4,6-dichloroguaiacol (IX) but did not detect it experimentally. Later, however, it was reported, along with several other chlorinated guaiacols, as a product of alkaline cupric oxide oxidation of the chlorinated oxylignin isolated from red pine kraft spent bleach liquors /43/.

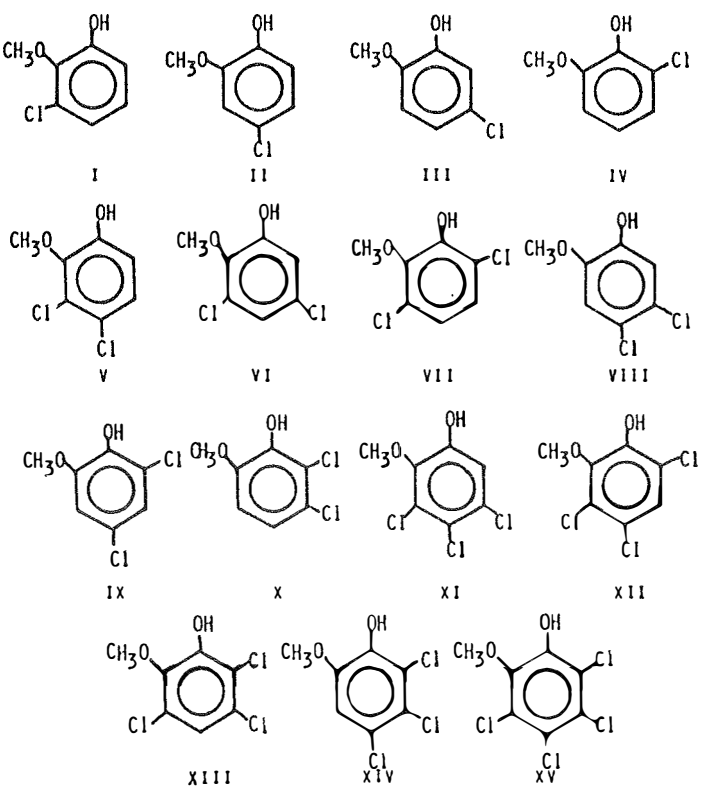


Figure 2. Structures and notation of chlorinated guaiacols (I-XV).

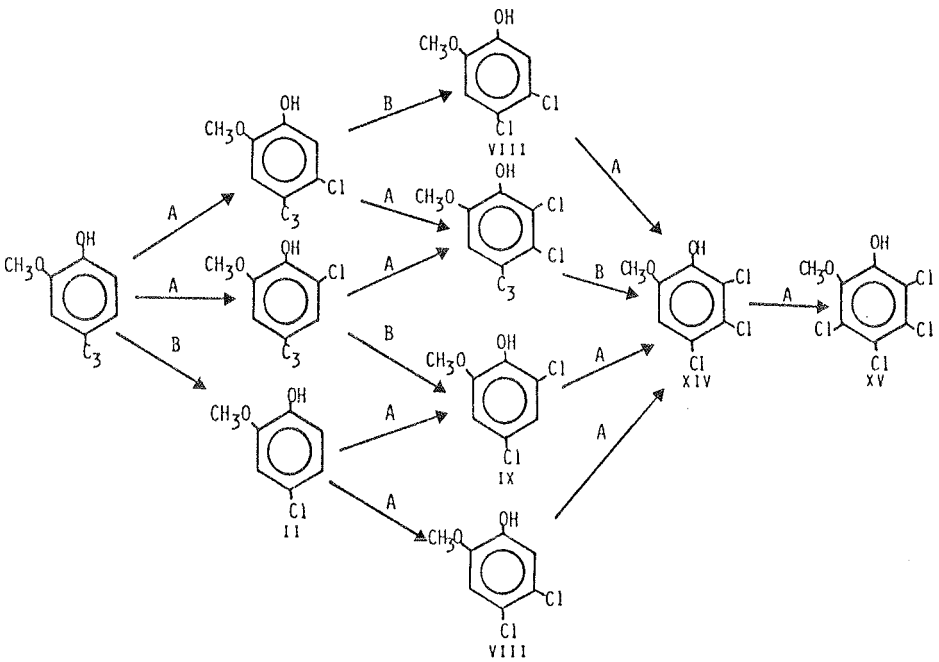


Figure 3. Proposed /33,37/ reactions occurring in chlorination of the guaiacylpropane unit of lignin. A = Electrophilic aromatic substitution; B = electrophilic aromatic displacement of side chain by chlorine.

Polychlorinated guaiacols formed during chlorobleaching have recently been attracting great interest. According to Rogers and Keith /44,45/, the most probable origins for 4,5,6-trichloroguaiacol (XIV) and tetrachloroguaiacol (XV) are the oxidative chlorination of the residual lignin in the brownstock and the chlorination of guaiacol present in the evaporator condensate used as washwater in the mill. 3,4,5-Trichloroguaiacol (XI), on the other hand, is probably formed not by chlorination of guaiacol during chlorobleaching but by dealkylation of chlorinated alkylguaiacols in the pulp slurry /46/. The relative amounts of the isomeric chloroguaiacols XI and XIV have been shown to depend on the pulping and bleaching conditions /47/. In general, the chlorination conditions, such as pH, temperature and chlorine-dosage (and use of chlorine dioxide), have a significant effect on the

structures and quantities of chlorinated phenolic components present in SBLs /6,48-51/. Moreover, if the pulp is well washed and contains no residual free guaiacol or only traces of it, the amount of 3,4,5-trichloroguaiacol (XI) is clearly higher than that of 4,5,6-trichloroguaiacol (XIV) /47/. Finally, the third trichloroguaiacol isomer in SBLs is more probably 3,4,6-trichloroguaiacol (XII) than its isomer (XIII). This supposition is based upon a consideration of the reactions occurring between guaiacylpropane units in lignin and chlorine during the C-stage of bleaching /48/.

2.3. FORMATION OF CHLORINATED CATECHOLS

It has long been known that wood lignin treated with chlorine (or bromine) undergoes a substantial loss of methoxyl content /52-56/. The first postulations of the formation of chlorinated catechols from lignin through demethylation by elemental chlorine have been based on UV-spectroscopy or the determination of methanol liberated in the reaction /33,37,38/. During chlorobleaching chlorine acts as a hydrolysing agent /37,38/ and, indeed, model compound studies have demonstrated that demethylation produces free phenolic hydroxyl groups and methanol /37,40,55,56/. This reaction mainly applies to methyl ethers, but also to other ether ether linkages in lignin /57/.

Of great interest have been the studies on the demethylation reaction of guaiacol remaining in the pulp slurry after the pulping process. In the initial stage of the bleaching (first C-stage), chlorination of residual guaiacol produces several low molecular weight chlorinated components, together with some unknown dimeric and trimeric substances /44,45/. There is some disagreement on the structures of the low molecular weight components. For example, Voss et al. /48/ have reported that the major reaction products are chlorinated catechols, whereas Das et al. /8/ and later Gierer and Sundholm /41/ could not find significant amounts of either catechol or chlorinated catechols in reaction mixtures obtained from guaiacol or glyserolguaiacyl ether. According to Gierer and Sundholm /41/, an oxidative mechanism for the cleavage

reaction gives rise to chlorinated ortho-quinones. The reaction between monochlorinated ortho-quinonoid intermediate products and hydrogen chloride is also a probable route to chlorinated catechols /34/.

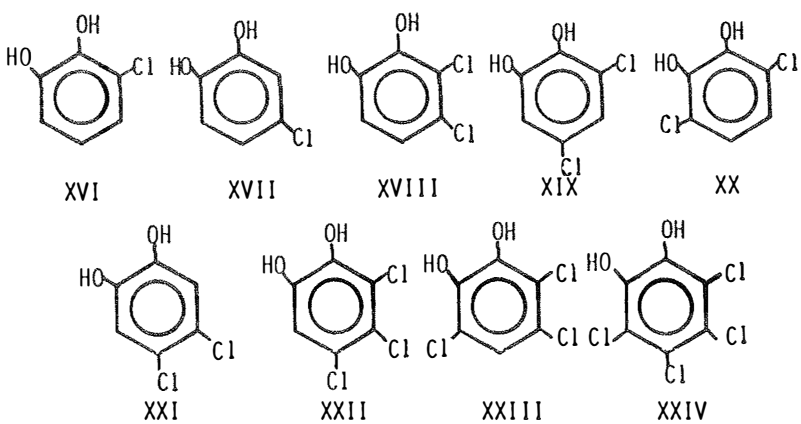


Figure 4. Structures and notation of chlorinated catechols XVI-XXIV.

The contradictory results and partially speculative conclusions referred to above may be due to the differences in the procedures used in sample preparation, as well as to the methods of analysis applied by the different groups. Thus additional experimental work is needed to establish the most probable mechanism or mechanisms for the formation of chlorinated catechols (and chlorinated guaiacols, see Sect. 2.2.) from residual lignin. The present findings concerning the formation of chlorinated isomers are summarised in Sects. 4.3. and 4.4.

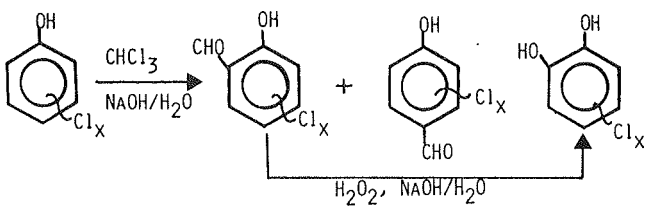
RESULTS AND DISCUSSION

3. SYNTHESIS AND STRUCTURE VERIFICATION OF MODEL COMPOUNDS

3.1. CHLORINATED CATECHOLS

Methods of synthesis and melting points for chlorinated catechols XVI-XXIV (Fig. 4) and their intermediate products (chlorinated salicylaldehydes) are listed in Table I. Routine NMR data are collected to Table II. The detailed description of the mass spectral properties appears in paper I and a summary in Sect. 4.2.

As seen in Table I, most of the compounds studied were prepared by the 'two-step-synthesis' represented by Eq. 1. This procedure was favoured because it yields very pure products with no other chlorocatechol isomers present as impurities.



Equation 1

The well-known Reimer-Tiemann formylation procedure /58/ was applied as follows: The chlorophenol isomer (0.13 mol) was dissolved in a warm solution of 40 g of sodium hydroxide in 40 ml of water. If the resultant phenoxide was not soluble in the reaction mixture, water was added dropwise until the precipitate disappeared. Then 30 g of chloroform was added dropwise while the reaction mixture was warmed at 80 ^{o}C on a water bath. After all the chloroform had been added the mixture was swirled on a boiling water bath for 2 hours. The excess of chloroform was removed from the alkaline solution by steam distillation whereafter the mixture was cooled, acidified to about pH 2 with diluted sulphuric acid and again steam distilled. The precipitate in the steam distillate was

Table I. Synthesis and melting points of chlorinated catechols (XVI-XXIV).[a]

Starting compd.[b]	Intermediate product,[c] Mp °C	Final product, Mp °C
2-Chlorophenol	3-Chlorosalicyl-aldehyde; Mp 53-54 (53.7-54.5; /60/)	XVI; Mp 47-48 (46-48; /61/)
4-Chlorophenol	5-Chlorosalicyl-aldehyde; Mp 98-99 (99-99.5; /60/)	XVII; Mp 90-91 (90-91; /61/)
2,3-Dichloro-phenol	3,4-Dichlorosalicyl-aldehyde; Mp 93-95 (94; /62/)	XVIII; Mp 98-99 (99; /62/)
2,4-Dichloro-phenol	3,5-Dichlorosalicyl-aldehyde; Mp 94-95 (95-96; /59/)	XIX; Mp 84 (84; /63/)
2,5-Dichloro-phenol	3,6-Dichlorosalicyl-aldehyde; Mp 97-98	XX; Mp 111 (109-111; /64/)
Catechol	XVII	XXI;[d] Mp 116 (116-117; /61/)
2,3,4-Trichloro-phenol	3,4,5-Trichloro-salicylaldehyde; Mp 87 (87; /65/)	XXII; Mp 105 (105; /65/)
2,4,5-Trichloro-phenol	3,5,6-Trichloro-salicylaldehyde; Mp 115 (116; /65/)	XXIII; Mp 99-100
Catechol	(XVII, XXI and XXII)	XXIV;[d] Mp 194 (193-194; /66/)

[a] For structures and notation see Fig. 4. [b] Commercial samples. [c] 4-Chloro-non-substituted phenols give rise to a mixture of chlorinated 2- and 4-hydroxybenzaldehydes (see Eq. 1). For their spectroscopic and GC data see Refs. 67-69. [d] The compounds XXI and XXIV were synthesised by the methods presented in Refs. 61 and 66, respectively. Pure XXIV could also be prepared from 2,3,4,5-trichlorophenol by the method presented in Eq. 1.

Table II. NMR data of chlorinated catechols XVI-XXIV.[a]

Compound[a]	^{1}HNMR[b]	^{13}CNMR[c]
XVI	6.50-6.96 (m, 3 H); 8.23 (broad s, 2 OH)	114.8, 120.9, 121.4, 129.1, 142.7, 147.2
XVII	6.57-6.94 (m, 3 H); 8.23 and 8.28 (two singlets,[d] 2 OH)	116.2, 117.1, 120.3, 124.4, 145.1, 147.0
XVIII	6.72-7.03 (q, 2 H); 8.61 (broad s, 2 OH)	114.9, 119.9, 120.7, 123.3, 144.5, 146.1
XIX	6.82-6.91 (q, 2 H); 8.83 (broad s, 2 OH)	115.0, 120.5, 121.6, 124.3, 142.2, 148.0
XX	6.88 (s, 2 H); 8.59 (broad s, 2 OH)	120.0, 121.1, 144.0
XXI	6.99 (s, 2 H); 8.55 (broad s, 2 OH)	117.4, 122.3, 146.1
XXII	6.96 (s, 1 H); 8.22 (broad s, 2 OH)	115.6, 121.2, 121.8, 123.3, 143.6, 146.1
XXIII	7.13 (s, 1 H); 8.92 (broad s, 2 OH)	119.2, 120.2, 121.1, 123.5, 142.7, 145.1
XXIV	9.15 (broad s, 2 OH)	120.1, 123.1, 143.6

[a]For structures and notation see Fig. 4. [b]δ ppm referred to internal standard (TMS); sample concentration: 10 % (w/v) in acetone-d_6; the broad range, the absorptions of aromatic protons; s= singlet, q= quartet, m= multiplet, H= number of protons integrated corresponding to the particular absorptions. [c]Data (except that of XVI) presented in Ref. 70; further information (coupling constants) about the structures of the compounds was obtained from coupled carbon-13 NMR spectra. [d]Resolved hydroxyl proton signals were observed in the spectra of some non-symmetric hydroxybenzenes /71/.

filtered by suction, dissolved in a small amount of diethyl ether and shaken mechanically for 2 hours with twice the volume of saturated sodium bisulphite solution. The resultant white solid was filtered, washed several times with diethyl ether and decomposed by warming the solid on a warm water bath (at 60 ^{o}C) with diluted sulphuric acid for 0.5 hour. Thereafter the reaction mixture was extracted with diethyl ether, the ether layer dried with $MgSO_4$ and the ether removed with a nitrogen gas stream (or distillation). The residue (crude product) was recrystallised from aqueous ethanol giving the pure salicylaldehyde isomer (yields ca. 10-20 %).

In the second step of the synthesis the procedure of Dakin /59/ was applied as follows: The crude (or pure) chlorosalicylaldehyde isomer (0.03 mol) and 30 ml 1-M sodium hydroxide solution (0.03 mol) were stirred at 20 ^{o}C for 5 min, after which 10 ml of 3 % H_2O_2 solution was added and the vigorous stirring continued. After a few minutes the temperature of the reaction mixture rose to ca. 40-50 ^{o}C. The stirring was continued and additional drops of peroxide (total amount ca. 0.03 mol) were added during 15 min and the mixture was stirred at room temperature for 0.5 hour. The reaction mixture was then acidified with dilute sulphuric acid solution, and the precipitate that formed filtered and dried at room temperature for 3 hours. In the case of monochlorocatechols, a precipitate did not form and the mixture was extracted twice with diethyl ether, ether was removed and the residue was recrystallised in similar manner as the crude polychlorocatechol precipitates (see above) from hot CCl_4 and finally sublimated at 5 mmHg at 180-200 ^{o}C. Yields were 40-60 %.

3.2. CHLORINATED GUAIACOLS

Methods of synthesis and melting points of chlorinated guaiacols (I-XV) are listed in Table III. Routine NMR data are shown in Table IV. Electron impact mass spectral data are given in paper III and summarised in Sect. 4.2. Most of the compounds studied were synthesised from chlorinated catechols using the limited methylation procedure followed by column

chromatographic separation (paper II). However, this method was not suitable for the separation of 4-chloroguaiacol (II) and 5-chloroguaiacol (III) /72,73/ nor for 3,4,6- and 3,5,6-trichloroguaiacols (XII and XIII). The mixture (ca. 1:1) of XII and XIII was observed, but no suitable solvent system was found for their column (or preparative TLC) chromatographic separation /72-74/. Several attempts to synthesise pure 3,5,6-trichloroguaiacol (XIII) were likewise unsuccessful /75/.

The most convenient technique for the routine separation and purification of chlorinated guaiacols showed to be flash chromatography (FC), first reported by Still et al. /80/. The general FC procedure used in the present study was as follows:

(1) Solvents were chosen that would give good separation and move the desired component(s) to R_F value(s) ca. 0.25-0.45 on an analytical TLC (Kieselgel 60 F_{254}, 5 x 10 cm; layer thickness 0.25 mm; Merck, Darmstadt, FRG). Suitable solvent systems included light petroleum (b.p 40-60 ^{o}C)-ethyl acetate (70/30), chloroform, dichloromethane, dichloromethane-chloroform (90/10) (see Refs. 72 and 73) and various mixtures of n-hexane and acetone.
(2) A glass column of appropriate diameter (e.g. 13 x 4 cm) was selected and filled with 9 cm of dry silica gel (Kieselgel 60, 230-400 mesh; Merck).
(3) The column was eluted with the selected solvent system (see above) and pressure used to remove all air from the silica gel.
(4) The sample (ca. 1.5 g) for example the crude reaction mixture from the limited methylation experiment (paper II), was applied by pipette as ca. 30 % solution in the eluant to the top of the absorbent bed and pressure used to push all of the sample into the silica gel.
(5) The column was refilled with the solvent system and eluted under pressure at a flow-rate of 10 ml/min.
(6) Fractions were collected.

Table III. Synthesis of chlorinated guaiacols I-XV.[a]

Compound[a]	Method[b]	Yield (%)	Mp (°C)
I	LM of 3-chloro-catechol	13	Mp 32 (32; paper II)
II	Chlorination of guaiacol[c]	55	Mp 17 (16-17; /76/)
III	Chlorination of guaiacol acetate[c]	40	Mp 38 (36-37; /76/)
IV	LM of 3-chloro-catechol	18	Mp 54 (54; /76/)
V	LM of 3,4-di-chlorocatechol	10	liquid
VI	LM of 3,5-di-chlorocatechol	12	Mp 64 (63-64; /76/)
VII	LM of 3,6-di-chlorocatechol	20	Mp 70 (paper II)
VIII	Chlorination of guaiacol[d]	75	Mp 72-73 (71.5-73.0; /77/)
IX	LM of 3,5-di-chlorocatechol	15	Mp 66 (64-66; /76/)
X	LM of 3,4-di-chlorocatechol	15	liquid
XI	LM of 3,4,5-tri-chlorocatechol	13	Mp 87 (86.8-87.4; /78/)
XII	Chlorination of VII[d]	40	Mp 103-104
XIII	(-)[e]		
XIV	LM of 3,4,5-tri-chlorocatechol	17	Mp 110 (110; /79/)
XV	LM of tetra-chlorocatechol	23	Mp 120-121 (121.5; /44/)

[a]For structures see Fig. 2. [b]Limited methylation (LM) method presented in paper II; solvent dichloromethane. [c]Chlorination reagent: sulphuryl chloride; solvent: chloroform; temperature 20 °C. [d]Chlorination reagent: chlorine gas; solvent: chloroform; temperature 20 °C. [e]Not available in pure form.

Table IV. NMR data of chlorinated guaiacols I-XV.[a]

Compd.[a]	^{1}HNMR[b]	^{13}CNMR[c]
I[d]	3.88(s, OCH3); 6.90-7.10 (m,3H); 8.35 (broad s,OH)	60.8, 116.2, 121.4, 125.7, 128.3, 144.9, 152.4
II	3.86(s, OCH3); 6.75-7.02 (m,3H); 7.82 (broad s,OH)	56.5, 112.9, 116.8, 121.5, 124.4, 146.6, 149.1
III	3.82(s, OCH3); 6.78-6.93 (m,3H); 8.00 (broad s,OH)	56.3, 113.1, 116.0, 119.9, 126.1, 147.2, 148.1
IV[d]	3.88(s, OCH3); 6.85-7.15 (m,3H); 8.10 (broad s,OH)	56.6, 110.8, 120.3, 120.3, 122.5, 143.9, 149.3
V[d]	3.89(s, OCH3); 6.85-7.35 (q,2H); 8.70 (broad s,OH)	60.9, 116.5, 123.3, 126.0, 127.3, 146.2, 151.0
VI	3.83(s, OCH3); 6.87-6.97 (q,2H); 8.96 (broad s,OH)	60.9, 116.4, 120.8, 129.0, 129.5, 144.2, 152.9
VII[d]	3.92(s, OCH3); 6.90-7.40 (q,2H); 8.90 (broad s,OH)	61.1, 120.6, 121.2, 126.1, 126.9, 145.9, 148.9
VIII	3.89(s, OCH3); 6.99, 7.10 (d,2H); 8.29 (s,OH)	56.7, 114.0, 117.1, 122.1, 123.7, 147.4, 148.3
IX	3.90(s, OCH3); 6.92-7.02 (q,2H); 8.44 (broad s,OH)	56.9, 111.5, 120.8, 121.7, 124.2, 143.0, 149.7
X[d]	3.92(s, OCH3); 6.80-7.10 (q,2H); 8.60 (broad s,OH)	56.8, 111.2, 119.4, 120.4, 124.9, 145.5, 148.0
XI	3.86(s, OCH3); 7.11(s,1H); 9.48 (broad s,OH)	61.0, 117.1, 121.8, 128.6, 128.8, 145.4, 151.2
XII	3.89(s, OCH3); 7.37(s,1H); 9.15(broad s,OH)	61.3, 120.8, 123.2, 126.1, 126.1, 146.8, 147.8
XIII	3.87(s, OCH3); 7.15(s,1H); 8.90(broad s,OH)	61.3, 119.7, 121.1, 126.9, 128.7, 144.5, 149.9
XIV	3.93(s, OCH3); 7.09(s,1H); 8.90(broad s,OH)	57.1, 112.1, 120.4, 123.0, 123.2, 144.5, 148.0
XV	3.90(s, OCH3); 9.78 (broad s,OH)	61.5, 120.8, 122.8, 127.2, 128.3, 145.3, 148.6

[a]For structures and notation see Fig. 2; [b]Running conditions as in Table II. [c]Running conditions as in Ref. 70; further information (coupling constants) about the structures of the compounds was obtained from coupled carbon-13 NMR spectra. [d]Data taken collected from paper II.

The purity of the fractions separated by FC method was checked by GC /81/. The structures of the components were confirmed by TLC (R_F-values and characteristic colour reactions /72,73/), GC-MS or MS using direct inlet (paper III). The final structure verification was performed by ^{13}CNMR spectroscopy (Table IV) /82/.

The above FC method was shown to be suitable for the separation and purification of chlorinated guaiacols I, IV, V-XI, XIV and XV. However, no suitable solvent system was found for separation of the positional isomers XII and XIII nor II and III /72,73/. The best yields (best recovery in the FC experiment) were obtained for 3,6-dichloroguaiacol (VII), 4,5-dichloroguaiacol (VIII) and tetrachloroguaiacol (XV) which were synthesised from the corresponding symmetric chlorinated catechols.

In summary, FC provided a rapid and easy method for the preparative separation and purification of most chlorinated guaiacols requiring only moderate resolution ($\Delta R_F > 0.1$). Where higher resolution was required, preliminary purification by the FC technique allowed simplified high-resolution separations. The method may also be useful for prepurifications before high pressure liquid chromatographic (HPLC) separations, allowing a savings in expensive HPLC columns.

4. GC AND GC-MS DETERMINATION OF MODEL COMPOUNDS IN SBLs

4.1. GC SEPARATION

Convenient analysis of isomeric chlorinated catechols and guaiacols present in SBLs and other multicomponent samples demands a rapid, simple, selective and sensitive analytical method. At present, quartz capillary GC and GC-MS provide a capability for detection, identification and determination of specific components in waste waters containing extremely complex mixtures of organic constituents. The selectivity of the GC and GC-MS methods can be increased by simultaneous use of polar and non-polar quartz capillary columns, making it important to know the retention behaviour of the model substances in both polar and non-polar stationary phases.

A non-polar SE-30 quartz capillary column has been shown

to be suitable for the separation of chlorinated guaiacols /81/ and catechols /83/ without their prior derivatization. Success of the direct GC and/or GC-MS analysis of these compounds depends, however, on effective clean-up procedures to remove possible interferring substances, e.g. high molecular weight phenolic components. Derivatization in conjunction with other clean-up procedures was found useful for the analysis of this work. For this purpose the most appropriate derivatization techniques were ethylation (paper V and Ref. 84), acetylation after separation /84/ or the 'in situ acetylation' first reported by Voss et al. /51/. All ethylated chlorinated catechols can be separated on a non-polar stationary phase as recorded in paper V. A non-polar stationary phase is not suitable for separation of all ethylated chloroguaiacols /84/. Nor do polar or non-polar columns resolve all acetylated chlorinated guaiacols /84/. However, an SE-30 quartz capillary column allows the simultaneous separation of the most probable chlorinated catechols and guaiacols (and chlorinated phenols) to be formed as chlorination products of lignin during chlorobleaching of pulp (paper IV).

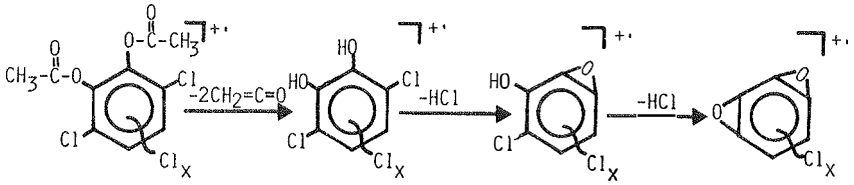
4.2. MS PROPERTIES

The electron impact (EI) mass spectra and the most characteristic fragmentation pathways of chlorinated catechols and guaiacols are presented in papers I and III. The mass spectra of the corresponding acetyl derivatives are given in App. I. The important features of the spectra may be summarised as follows:

The losses of ketene (or ethylene) molecules from acetylated (or ethylated) chlorocatechol and chloroguaiacol molecular ions give rise to the stabile chlorocatechol and guaiacol molecular ions. These ions further fragment, following principally the fragmentation pathways presented in paper I and III.

Isomeric chlorinated catechols and especially chlorinated guaiacols are difficult to distinguish on the basis of their EI mass spectra. Some characteristic fragmentations were nevertheless observed in the spectra of chlorocatechol isomers

and also their ethyl (paper V) and acetyl (App. I) derivatives. The most characteristic disparities are due to the primary or secondary elimination of the HCl molecule (epoxide and diepoxide ion formation, see paper I) (Eq. 2).



Equation 2

This HCl elimination was not observed with chlorinated guaiacols and their acetyl derivatives. The mass spectra of isomeric chloroguaiacols as well as of 3,4- and 3,5-dichlorocatechols were found to be very similar. It is very important therefore that pure authentic reference compounds and their GC retention data are available for reliable GC and/or GC-MS analysis of the positional isomers of I-XIV, XVIII and XIX.

4.3. CHLORINATED CATECHOLS IN SBL

Chlorinated catechols were analysed as their ethyl derivatives in C-stage SBL from a kraft pulp mill and in the product from chlorination of guaiacol in water solution (paper V). The results are presented in Fig. 5 and can be summarised as follows:

Chlorination of guaiacol in aqueous solution was found to give rise to chlorinated catechols and minor amounts (total amount less than 0.1 %) of chlorinated guaiacols. This result is in good agreement with that of Voss *et al.* /48/ but in disagreement with the findings of Gierer and Sundholm /41/ (see Sect. 2.3.). As recorded in Fig. 5, 3,4,5-trichlorocatechol (XXII) and 3,4-dichlorocatechol (XVIII) were here found as main chlorocatechols, along with smaller amounts of 4,5-dichlorocatechol (XXI), 3,5-dichlorocatechol (XIX), 3,4,6-trichlorocatechol (XXIII) and tetrachlorocatechol (XXIV). Both monochlorocatechols (XVI and XVII) were also identified in

small amount by mass chromatography (paper V).

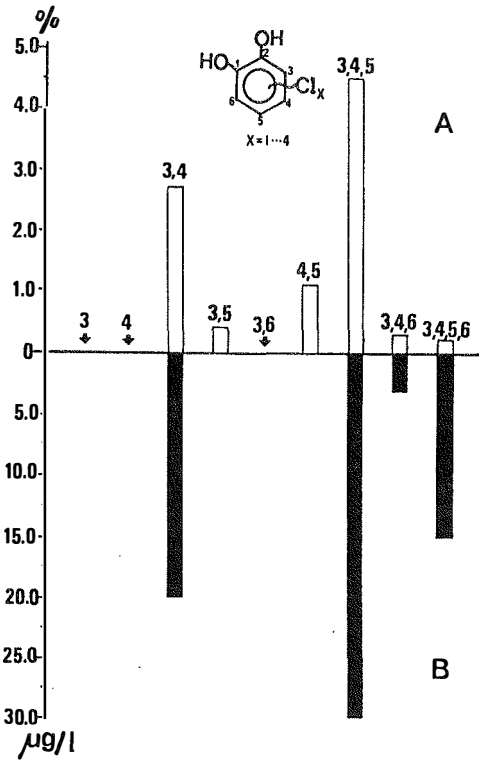


Figure 5. Chlorinated catechols (paper V); A. detected in product from chlorination of guaiacol in aqueous solution (% from starting compound) and B. detected in C-stage SBL (µg/l). The numbers indicate chlorinated positions.

As can be seen in Fig. 5, 3,4,5-trichlorocatechol (XXII), 3,4-dichlorocatechol (XVIII) and tetrachlorocatechol (XXIV) constituted the main chlorocatechols in C-stage SBL. The compound XXII was also identified as the major chlorocatechol in several E-stage SBLs, total mill effluents and water samples analysed at other times in our laboratory. On the other hand, monochlorocatechols (XVI and XVII) and dichlorocatechols (XIX and XXI), which were identified in the product formed by chlorination of guaiacol in water solution (Fig. 5)

were not detected at above 1 µg/l level in the SBL sample. This may be partly due to their lability (possible formation of chlorinated ortho-benzoquinones /85/) in water solution. The perhaps more stable 3,4,6-trichlorocatechol (XXIII), the ethyl derivative of which is also more sensitive to electron capture detection, was detected at above 1 µg/l level in C-stage SBL (paper V).

4.4. CHLORINATED GUAIACOLS IN SBL

Chlorinated guaiacols were analysed as their acetyl derivatives in E-stage SBL from a pine kraft pulp mill (paper VI). The amounts of structural isomers identified are illustrated in Fig. 6.

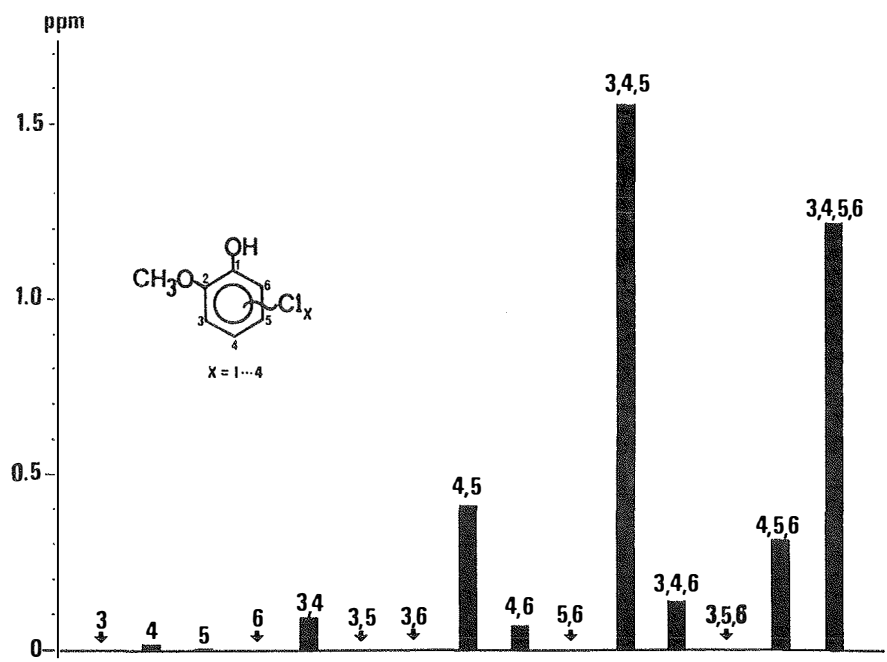


Figure 6. Chlorinated guaiacols (ppm) in E-stage SBL of a kraft pulp mill (paper VI). The numbers indicate chlorinated positions.

As can be seen in Fig. 6, the sample investigated contained detectable amounts (above 1 µg/l level) of nine chlorinated guaiacols. 3,4,5-Trichloroguaiacol (XI) was present in highest concentration (ca. 1.6 ppm), with tetrachloroguaiacol (XV), 4,5-dichloroguaiacol (VIII) and 4,5,6-trichloroguaiacol (XIV) present as other major components. These same main components were also identified in several total mill effluents analysed later in our laboratory. Small amount of 3,4-dichloroguaiacol (V), 4,6-dichloroguaiacol (IX), 3,4,6-trichloroguaiacol (XII) and both monochloroguaiacols (II and III) were also detected. All the above results agree well with the findings reported by Kovacs et al. (see Ref. 88).

CONCLUSIONS AND SIGNIFICANCE OF RESULTS

Before the present study was begun, several papers had appeared on the synthesis and analysis of chlorinated catechols and guaiacols in various liquors from the pulp industry. Now, for the first time, results achieved using a complete series of analytical chlorocatechol and guaiacol standards have been described. The present qualitative and quantitative results agree reasonably well with those reported previously /4,7,86,88-92/. The lack of agreement among different investigators on the concentrations and the number of positional isomers in SBLs is due not only to actual differences in chlorobleaching processes but also to the procedures selected for the analysis of compounds. In most earlier studies, certain problems (identification, separation and quantitation) remained unsolved due to the lack of pure model substances and adequate standards for GC and GC-MS work. The new synthetical, analytical and spectroscopic information contained in the present report thus provides a firmer basis for chlorocatechol and chloroguaiacol studies in the future. The results obtained can be expected to find application in the following areas:

1. Synthesis of model compounds

Limited methylation of chlorinated catechols (paper II) followed by FC purification provides highly pure chlorinated guaiacols. Extremely high purity of model substances are essential for toxicity studies and quantitative determiminations, for example. The same procedures can be applied to the preparation of other lignin model substances, such as chlorinated syringols, vanillins and some dimeric and polymeric phenolic substances.

Chlorinated catechols, guaiacols and their intermediate products, chlorinated 2- and 4-hydroxybenzaldehydes, are important starting compounds in the synthesis of other chemicals found or suggested to be present in SBLs. For example, chlorinated p-hydroxybenzaldehydes can be oxidized to chlorinated p-hydroquinones. Some of these substances (2,6-dichloro-4-hydroxybenzaldehyde and 2,6-dichlorohydroquinone) have been identified in SBLs /6,7/. Chlorinated catechols are easily converted to chlorinated veratroles (1,2-dimethoxybenzenes), which are important metabolites of chlorinated guaiacols /93,94/. Further, chlorinated o-benzoquinones, which can be prepared from chlorinated catechols, have previously been suggested to occur in SBLs /8/. In addition, chlorinated catechols and guaiacols are useful starting compounds in the synthesis of chlorinated dimeric and polymeric aromatics which occur in technical chlorophenol formulations /78,95/, pyrolysis products of PCB /96/ and also SBLs.

2. Studies on degradability and metabolism

Tetrachlorocatechol has been shown to be a metabolite of pentachlorophenol /97/. Similarly, other chlorinated catechols may occur in the environment as metabolites of other chlorophenols though also as metabolites of chlorobenzene and phenoxyacid herbicides /98-101/. Enzymatic degradation of 4-chloro- and 3,5-dichlorocatechols has been reported by Bollag et al. /102/. Thus, systematic study on the enzymatic biodegradability of all chlorinated catechols and guaiacols, especially those occurring in largest concentrations in SBLs (paper V and VI), needs to be carried out in order to evaluate

their persistency in nature and health risk in the environment /103/.

3. Toxicity studies

Pure chlorocatechol and guaiacol model substances can provide valuable chemical material for studies on the toxicity and mutagenicity /104/ and the persistency of the mutagenicity of these compounds in the environment /105/. Together with the analytical methods developed for their determination they can assist the identification of mutagenic substances in SBLs, discovery of the mechanism of their formation in pulp bleaching, development of methods to avoid their formation and possible hazardous effects, and finally, the development of better new systems to detoxify bleached mill effluents /1,106/.

4. Odour and taste problems

Taste panel evaluations are frequently used as an effective means of measuring the off-flavour of fish exposed to pulp mill effluents /88,107,108/. Although chlorophenolic compounds have been reported to have an unpleasant taste and odour even in very low concentration /109/, recent studies indicate that the chlorinated catechols and guaicols present in SBLs plausibly do not contribute an off-odour to recipient waters /88/. The odour threshold for most chlorinated catechols have been reported /88/, but no data are available for 3,4-di- and 3,5-dichlorocatechols, 3,4,6-trichloro-catechol, 5-chloroguaiacol or 3,4,6-trichloroguaiacol.

In summary, highly pure chlorocatechol and guaiacol model substances such as synthesised here are of great assistance to the development of new systems for testing and hazard evaluation of chlorophenolic chemicals in the environment /110/ and can assist the discovery of convenient routine methods of controlling the contamination of the environment with these chemicals.

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PAPER I

https://doi.org/10.1002/oms.1210181007

PAPER II

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PAPER III

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PAPER IV

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PAPER V

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PAPER VI

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APPENDIX I

MASS SPECTRA OF ACETYLATED CHLORINATED CATECHOLS AND GUAIACOLS

Acetylated chlorinated catechols

The electron impact mass spectra of acetylated chlorinated catechols are assembled in Fig. 1. As in the spectra of acetylated chlorinated guaiacols, the abundance of the molecular ion peak is relatively weak. The base peak $(M-CH_2CO-CH_2CO)^{+\cdot}$ (ion $A^{+\cdot}$) is formed by the losses of two ketene molecules from the molecular ion. The other abundant ions are $(A-CHO)^+$, $(A-Cl)^+$, $(A-HCl)^{+\cdot}$, $(A-HCl-HCl)^{+\cdot}$, $(A-HCOOH)^{+\cdot}$ and $(A-CHO-HCl)^+$. For structure determination of positional isomers, the $(A-HCl)^{+\cdot}$ and $(A-HCl-HCl)^{+\cdot}$ ions are the most informative.

Acetylated chlorinated guaiacols

Fig. 2 illustrates the mass spectra of acetylated chlorinated guaiacols. The abundance of the molecular ion peak is weak in all cases, the most typical fragments occurring at m/z M-42, M-57, M-85 and M-121. The loss of ketene constitutes the base peak, following the subsequent or simultaneous losses of a methyl radical, carbon monoxide and hydrogen chloride, i.e., $(M-CH_2CO-CH_3-CO-HCl)$. The peak at m/z M-78, $(M-CH_2CO-HCl)^{+\cdot}$, does not appear in the spectra of acetylated chloroguaiacols and thus only M-93 $(M-CH_2CO-CH_3-HCl)^+$ and M-92 $(M-CH_2CO-CH_3-Cl)^{+\cdot}$ are characteristic for structure verification of monochloroguaiacol isomers (peak at m/z 107 in the spectra of acetylated 3- and 6-chloroguaiacols).

Experimental details

Five milligrams of the compound was dissolved in 2 ml of K_2CO_3 solution. 50 µl of acetic anhydride was added and the mixture shaken for 5 min. The acetyl derivative formed was extracted into 2 ml of n-hexane and 1 µl of the hexane layer was used for GC-MS.

The mass spectra (at 70 eV) were recorded on a Varian MAT-212 mass spectrometer with sample inlet from a Varian Series 3700 gas chromatograph equipped with an SE-30 quartz capillary column (25 mm x 0.25 mm I.D).[2] The capillary interface and ion source temperatures were 230 and 300 °C, respectively. The scan time used was 1.5 sec per mass decade.

References and notes

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2. The acetylated 3,4,6- and 3,5,6-trichloroguaiacols were not separated on the non-polar stationary phases such as SE-30, SE-54, OV-101 and SP-2100. Successful separation was obtained with a polar OV-351 quartz capillary column (25 m x 0.30 mm I.D).

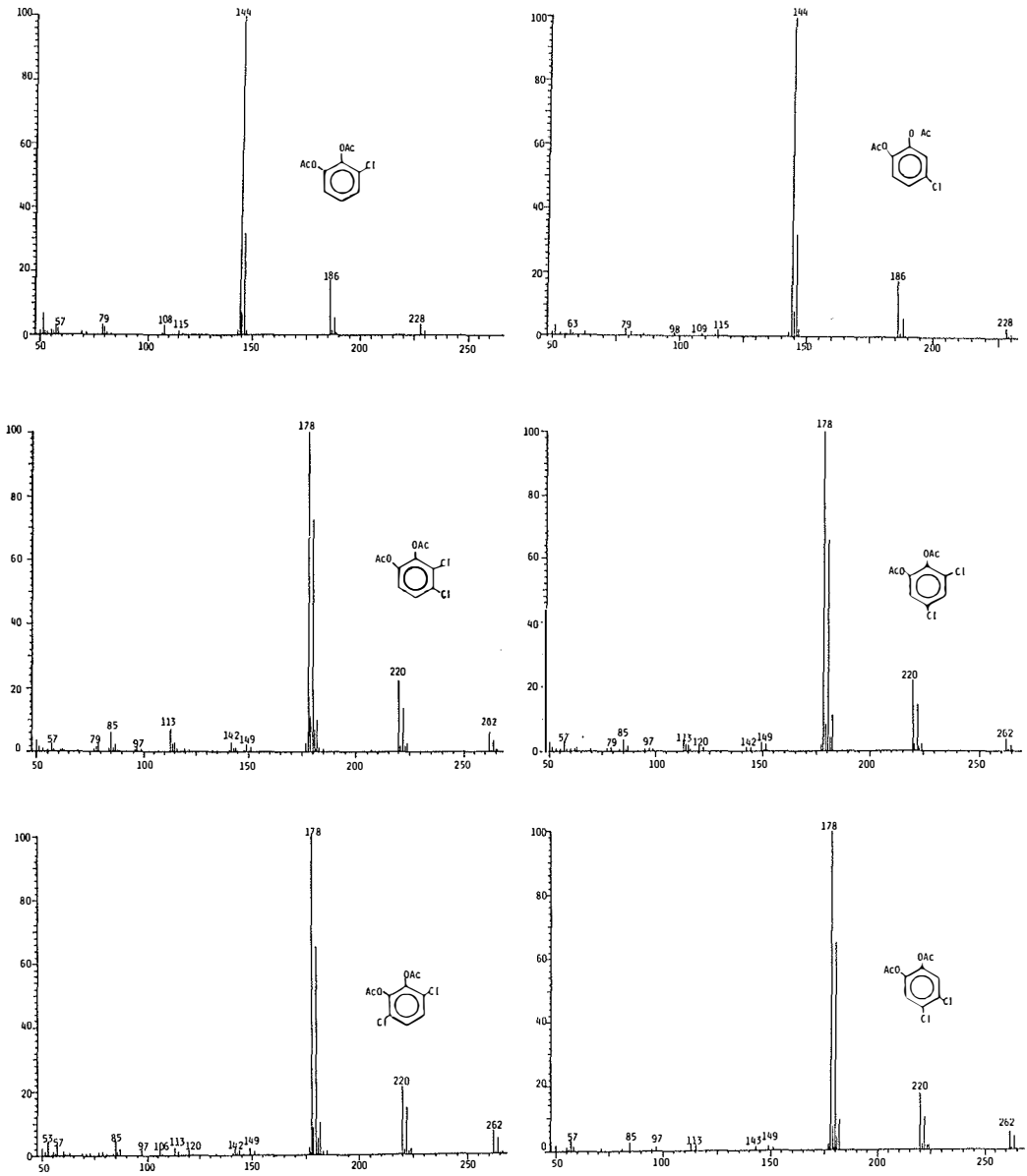

Figure 1. Electron impact mass spectra of acetylated chlorinated catechols.

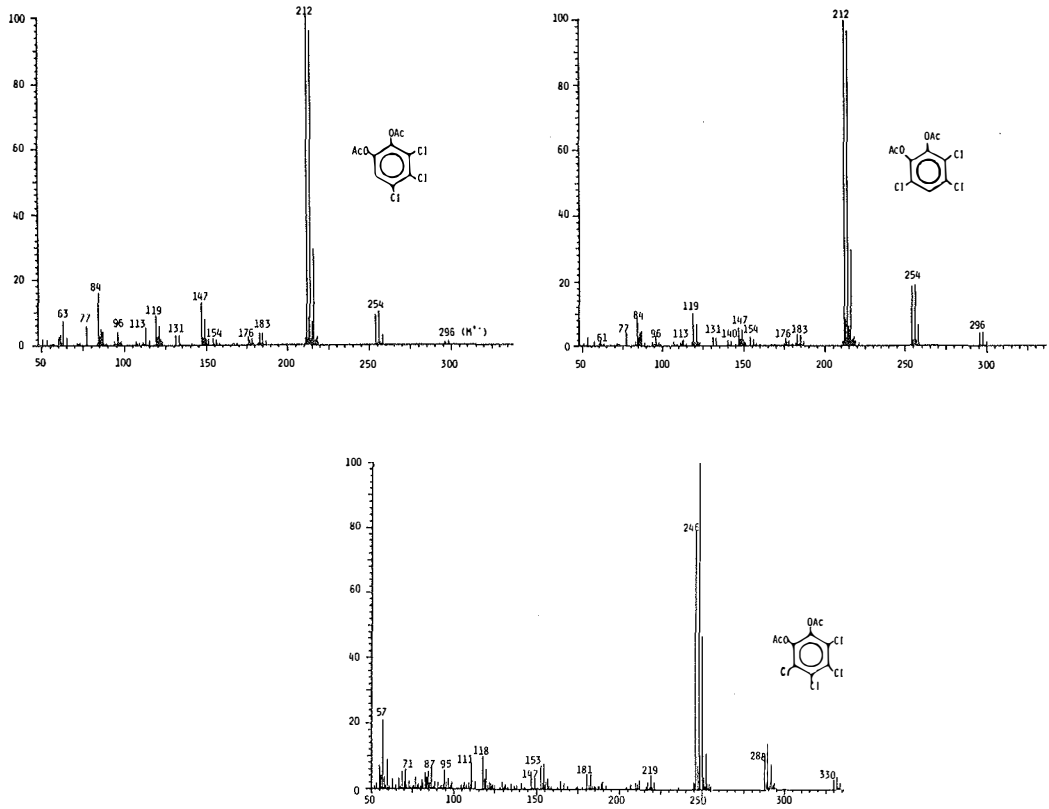

Figure 1. (continued)

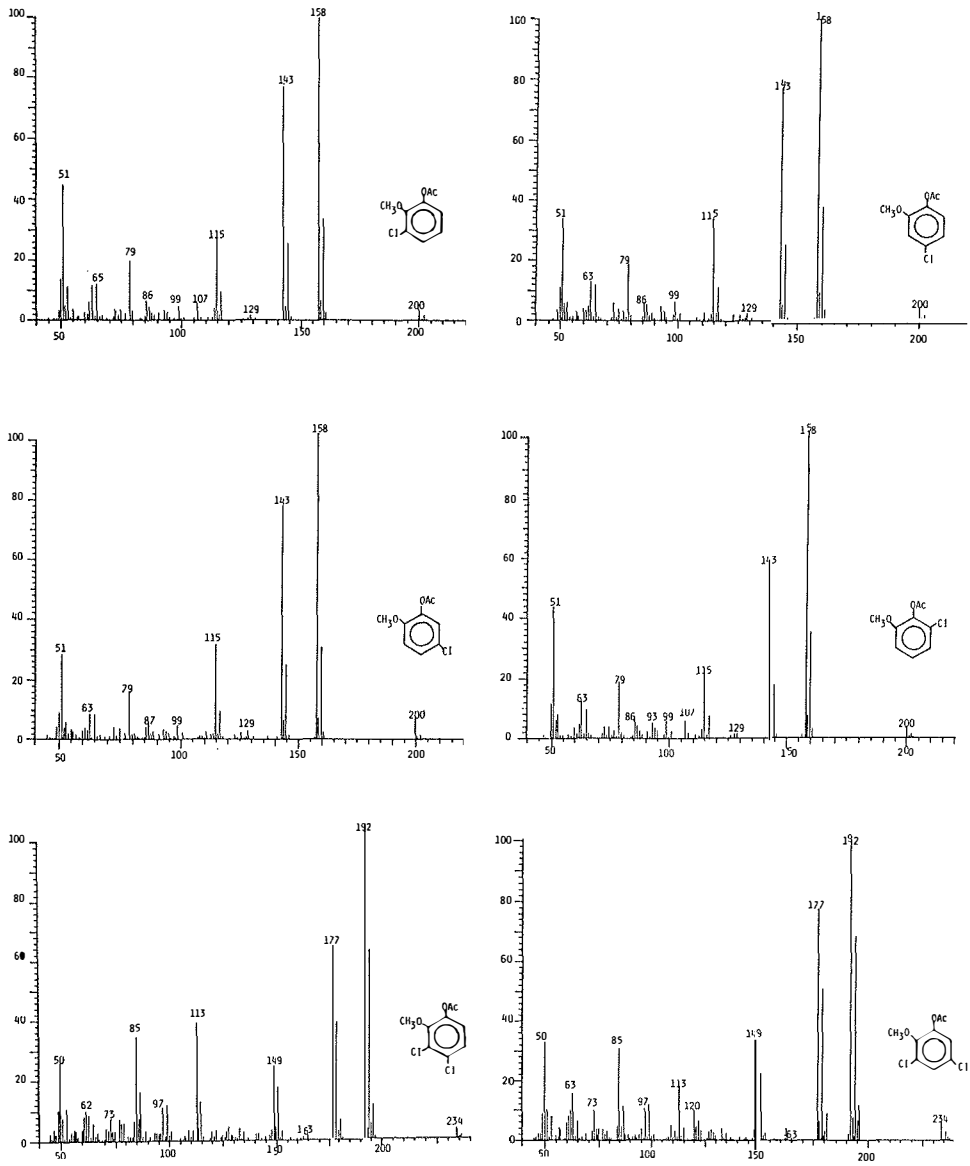

Figure 2. Electron impact mass spectra of acetylated chlorinated guaiacols.

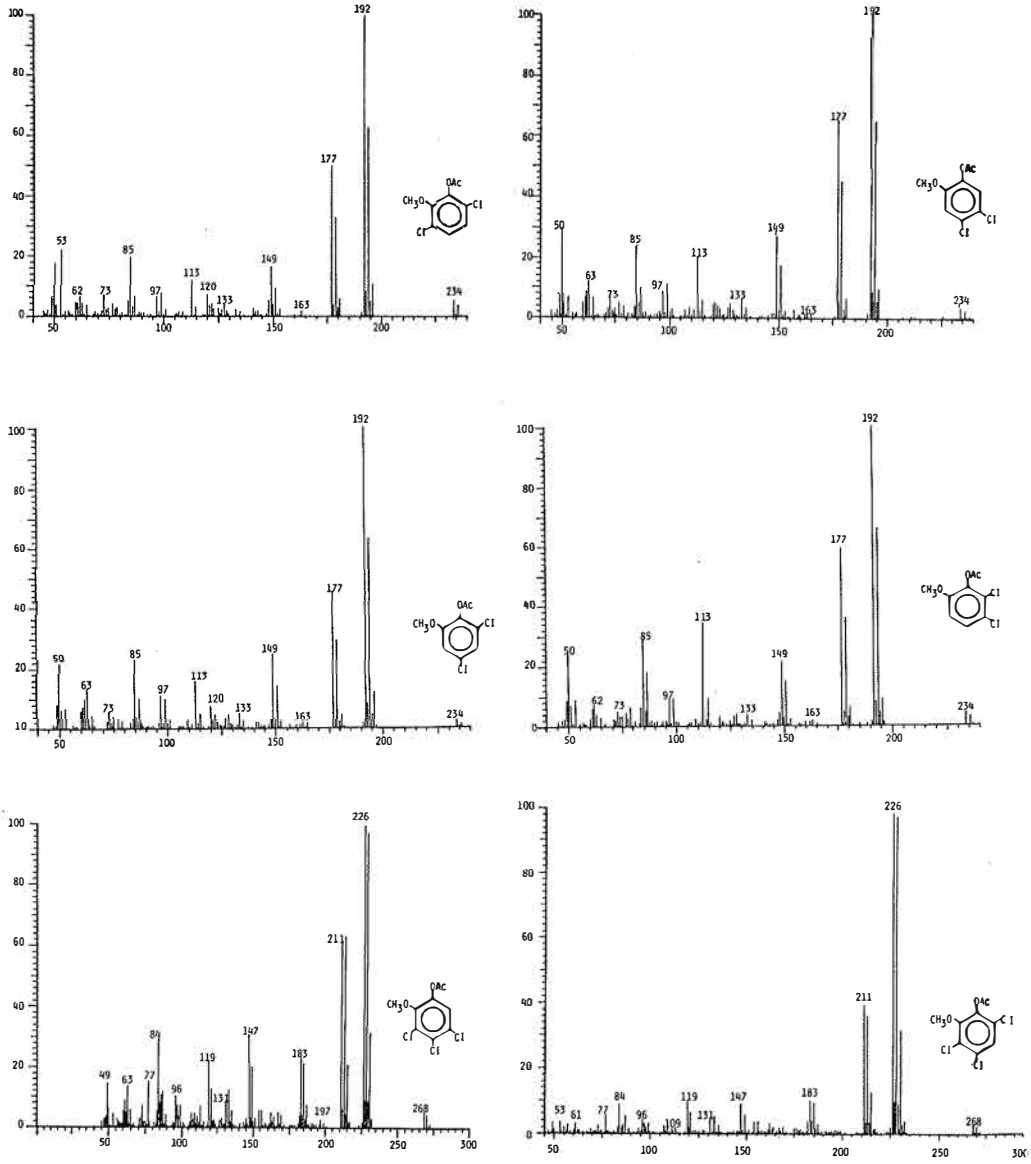

Figure 2. (continued)

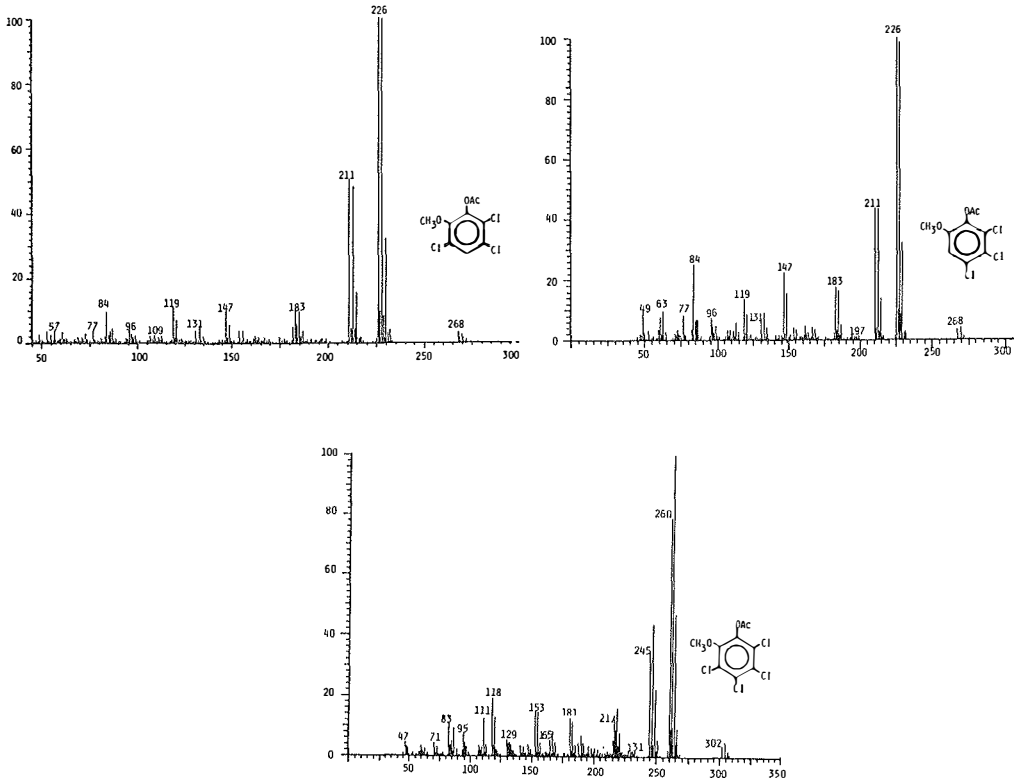

Figure 2. (continued)