*Journal of Chromatography*, 291 (1984) 135–144
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,583

# GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC ANALYSIS OF CHLORINATED PHENOXYPHENOLS IN THE TECHNICAL CHLOROPHENOL FORMULATION Ky-5*

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(First received December 2nd, 1983; revised manuscript received January 20th, 1984)

## SUMMARY

The content of polychlorinated phenoxyphenol (PCPP) impurities in the technical chlorophenol formulation Ky-5 (wood preservative) was studied. The phenolic fraction was shown to contain predioxins and isopredioxins, the structures of the components being verified by gas chromatography–mass spectrometry of non-derivatized, methylated and acetylated fractions. 2,6-Dichloro-4-(2,4,6-trichlorophenoxy)phenol and 2,6-dichloro-4-(2,3,4,6-tetrachlorophenoxy)phenol were identified by the comparison of their retention times and the mass spectra of their methyl and acetyl derivatives with those of authentic specimens. The amounts of the above components in Ky-5 were *ca.* 0.8 and 0.2%, respectively. The estimated total amount of PCPPs may be as high as 4–5%. For the formation of various PCPP components three probable routes are postulated, *viz.*, *ortho-*, *meta-* or *para*-elimination of HCl from two chlorophenol molecules during the production of Ky-5.

## INTRODUCTION

Polychlorinated phenoxyphenols (PCPPs) constitute the main impurities in commercial chlorophenol formulations[1–3], which are widely used as bactericides, fungicides, herbicides and wood preservatives. Of special interest are polychlorinated 2-phenoxyphenols (PC2PPs) containing one (or two) chlorine atom(s) in the *ortho*-position with respect to the oxygen of the phenoxy group (predioxins). The compounds with this structure have been shown under certain conditions to undergo ring closure, forming highly toxic polychlorinated dibenzo-*p*-dioxins (PCDDs)[4]. Recently, chlorinated 3- and 4-phenoxyphenols (PC3PPs and PC4PPs) and higher chlorinated 2-phenoxyphenols have also been investigated[5–11]. For example, a commercial pentachlorophenol (PCP) formulation has been shown to contain nonachloro-2-phe-

* For preliminary results, see ref. 3.

0021-9673/84/$03.00 

noxyphenol and nonachloro-4-phenoxyphenol[8]. Rappe and Nilsson[9] also found two octachloro-2PPs with unknown structures in commercial PCP. Amounts as high as 7.5–8% of nonachloro and octachloro isomers in PCP samples have been reported by Deinzer and co-workers[10,11].

In a previous paper[3] we reported the synthesis and analysis of several PC2PPs in the Ky-5 technical chlorophenol formulation, which is one of the most widely used wood preservatives in Finland. The phenolic fraction of Ky-5 was shown to contain at least sixteen PCPPs. This investigation was carried out in an attempt to synthesize new model PCPP substances, to determine the structures of the major PCPP impurities in Ky-5 using gas chromatography (GC) and GC–mass spectrometry (MS) and finally to try to establish the most probable mechanisms for the formation of various PCPP components.

## EXPERIMENTAL

### *Synthesis of model substances*

*4,5,6-Trichloro-2-(2,4-dichlorophenoxy)phenol (I).* This was synthesized by direct chlorination of 5-chloro-2-(2,4-dichlorophenoxy)phenol (commercial product, Giba Geigy) according to Nilsson and Andersson[12] (m.p. 99–100°C; lit[12]. 103.5–104°C).

*4-(2,4,6-Trichlorophenoxy)phenol (II).* A mixture of 2.5 g (6.8 mmol) of 4,4'-dimethoxydiphenyliodoniumtrifluoroacetate[13], 2.2 g (11.0 mmol) of 2,4,6-trichlorophenol, 0.44 g (11.0 mmol) of sodium hydroxide and 50 ml of water was refluxed at 110°C for 2 h. The reaction mixture was cooled and extracted with diethyl ether (3 × 20 ml) and the ether layer was washed with 2 *N* sodium hydroxide solution and water, then dried over sodium sulphate. The ether was evaporated, glacial acetic acid (15 ml) and 47% hydrobromic acid (6 ml) were added to the residue and the mixture refluxed at 110°C for 6 h. After cooling, the mixture was shaken with 20% sodium hydrogen sulphite solution and the precipitate formed was filtered, washed with water and dried at room temperature. The yield of the crude II was *ca.* 65% of theory. The crude product was purified by flash chromatography[14] on silica gel using *n*-hexane–diethyl ether (80:20, v/v) as the solvent system. The yield of II (m.p. 134–135°C) was *ca.* 0.9 g.

*2,6-Dichloro-4-(2,4,6-trichlorophenoxy)phenol (III).* A 0.4 g (1.4 mmol) amount of II was dissolved in 30 ml of glacial acetic acid and chlorine was passed through the reaction mixture at 20°C. The chlorination reaction was controlled directly by GC (SE-54 quartz capillary column). After all the substrate had reacted, the mixture was treated with 20% sodium hydrogen sulphite solution and water and the precipitate formed was filtered and dried. The crude III was recrystallized from *n*-hexane, giving 250 mg (*ca.* 50%) of pure III (m.p. 128–129°C).

*4-(2,3,4,6-Tetrachlorophenoxy)phenol (IV).* The same procedure used for the preparation of II, with 2,3,4,6-tetrachlorophenol as substrate, yielded IV containing some 4-(pentachlorophenoxy)phenol impurity as a result of contamination of the substrate with PCP. The yield of IV (m.p. 147–152°C) was *ca.* 40%.

*2,6-Dichloro-4-(2,3,4,6-tetrachlorophenoxy)phenol. (V)* A mixture of 150 mg of IV dissolved in glacial acetic acid and a 1.0 *M* solution of chlorine in acetic acid (5–10 ml) was allowed to react at room temperature for 4 h, then 10 ml of 20%

sodium hydrogen sulphite solution and water (100 ml) were added and the precipitate formed was filtered, washed with water and dried, yielding 150 mg of crude V (82%). The product was purified by recrystallization from glacial acetic acid. The melting point of V containing traces of 2,6-dichloro-4-(pentachlorophenoxy)phenol was 135–145°C.

*4-(Pentachlorophenoxy)phenol (VI) and 2,6-dichloro-4-(pentachlorophenoxy) phenol (VII).* These were synthesized in the same manner as IV and V. After recrystallization from *n*-hexane–benzene (80:20, v/v) the melting points of VI and VII were 186–187°C (lit.[15] 170°C) and 184–185°C, respectively.

*5-Chloro-2-(pentachlorophenoxy)phenol (VIII).* Equimolar amounts of hexachlorobenzene and 4-chloroguaiacol (9.4 mmol) were refluxed with potassium carbonate (5.0 g) in N,N-dimethylformamide (40 ml) for 2 h. After cooling, water was added to the reaction mixture and the mixture was extracted with diethyl ether. The ether layer was dried over sodium sulphate and evaporated to dryness. The residue was demethylated with boron tribromide by the procedure of Kolonko *et al.*[15]. The crude VIII was purified by flash chromatography followed by recrystallization from *n*-hexane–benzene (80:20, v/v) giving 1.2 g of pure VIII (m.p. 137–138°C).

*4,5,6-Trichloro-2-(pentachlorophenoxy)phenol (IX).* This was prepared in high yield by prolonged chlorination of VIII in chloroform with excess of chlorine and a iodine crystal as a catalyt. Evaporation of the solvent resulted in IX (m.p. 175–177°C).

*3-(Pentachlorophenoxy)phenol (X), 4,6-dichloro-3-(pentachlorophenoxy)phenol (XI) and 2,4,6-trichloro-3-(pentachlorophenoxy)phenol (XII).* The procedure used for the preparation of VIII with 3-methoxyphenol as a starting compound yielded pure X (yield *ca.* 30%; m.p. 135–136°C); lit.[15] 134°C). Further chlorination of X in glacial acetic acid gave XI (m.p. 150–152°C) by the procedure described for V. Prolonged chlorination of XI with iodine catalyt yielded XII (m.p. 140–142°C).

The structures of compounds I–XII were also confirmed by $^{1}H$ and $^{13}C$ NMR and mass spectrometry. The results will be published elsewhere.

*Preparation of standards and Ky-5 samples*

*Methylation with dimethyl sulphate.* A 1–3 mg amount of each model PCPP substance was dissolved in 2 ml of 8% sodium hydroxide solution. A small amount of acetone was added to increase the solubility of the compound. Dimethyl sulphate (50 μl) was added and the mixture was allowed to stand for 1 h with occasional shaking. The methylated compounds were extracted into diethyl ether. Before GC and GC–MS analysis, the sample was diluted (concentrated) to 5 ml and 0.5 ml in *n*-hexane, respectively. A 50 mg amount of Ky-5 (Kymi/Kymmene Co.; wood preservative containing 2,3,4,6-tetrachlorophenol and 2,4,6-trichlorophenol as its main components) was methylated with 200 μl of dimethyl sulphate as described above.

*Acetylation with acetic anhydride.* A 1–3 mg amount of each PCPP compound (50 mg of Ky-5) was dissolved in 2 ml of acetone and 1 ml of 0.1 *M* potassium carbonate solution and shaken with 100 μl (200 μl) of redistilled acetic anhydride. After standing for *ca.* 2 h the mixture was treated as described above.

*Apparatus and operating conditions*

An Orion Analytica Micromat HRGC 412 gas chromatograph equipped with a flame-ionization detector and an SE-52 quartz capillary column (25 m × 0.3 mm I.D.) was used for GC experiments. The carrier gas was helium at a flow-rate of *ca.*

1 ml/min. The injector and detector temperature was 250°C. The column temperature was increased from 60 to 280°C at 10°C/min and then held for 15 min.

MS investigations were carried out using a Varian-MAT 212 mass spectrometer equipped with a Varian Series 3700 gas chromatograph and an SE-54 quartz capillary column (20 m × 0.3 mm I.D.). The capillary interface and ion source temperatures were 230 and 300°C, respectively. The mass spectra were recorded at 70 eV from mass number 50 up to 450.

## RESULTS AND DISCUSSION

The GC retention times of model compounds I–XII (Fig. 1) are given in Table I. The total ion current chromatograms of acetylated and methylated phenolic fraction of Ky-5 and the proposed structures of PCPP impurities are shown in Fig. 2. The mass spectra of the most prominent components in acetylated Ky-5 sample are illustrated in Fig. 3. Examples of the mass spectra of methylated PCPP substances

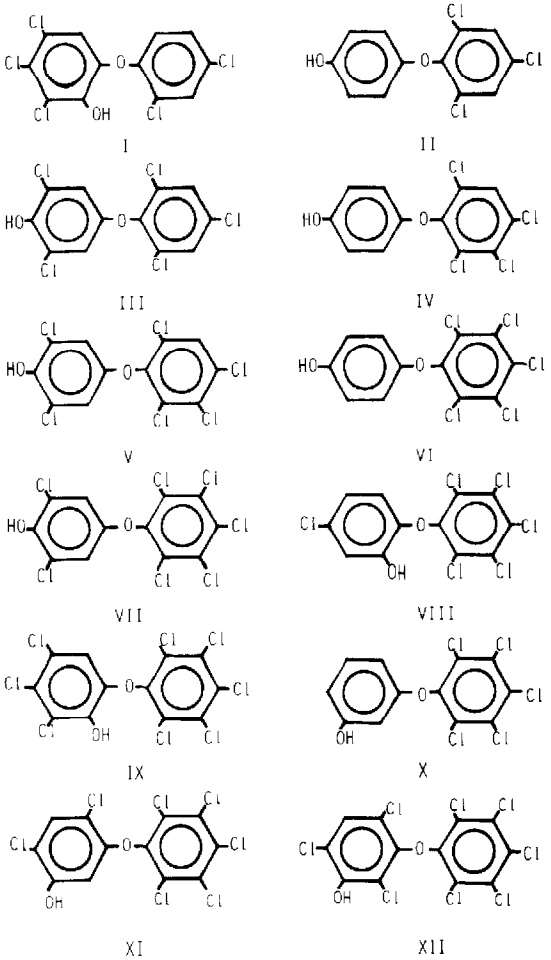


Fig. 1. Structures and notation of compounds studied.

TABLE I

RETENTION TIMES OF PCPPs IN GC EXPERIMENTS

For GC–MS conditions, see Experimental.

| *Compound No.* | *Retention time (min)* | | |
|---|---|---|---|
| | *Phenolic form* | *Methyl derivative* | *Acetyl derivative* |
| I | 24.7 | 23.7 | 24.3 |
| II | 20.9 | 20.2 | 21.6 |
| III | 23.0 | 22.6 | 23.8 |
| IV | 23.1 | 22.3 | 23.8 |
| V | 25.6 | 24.9 | 26.6 |
| VI | 25.8 | 24.6 | 26.6 |
| VII | 29.0 | 26.1 | 30.3 |
| VIII | 26.5 | 26.1 | 27.2 |
| IX | 35.0 | 32.5 | 33.9 |
| X | 25.5 | 24.0 | 25.4 |
| XI | 29.0 | 28.6 | 29.5 |
| XII | 32.9 | 31.2 | 33.6 |

are presented in Fig. 4. Schemes illustrating the probable routes of formation of the main PCPP impurities in Ky-5 are given in Fig. 5.

*MS of PCPPs*

The molecular ion peak of acetylated PCPPs is weak, whereas the peak indicating the primary loss of a ketene molecule from the molecular ion is the most abundant in the spectra of all PCPP compounds studied, corresponding principally to the molecular ion ($A^{+\cdot}$) of the non-derivatized PCPPs. In general, the most characteristic fragments of acetylated PCPPs are due to the formation of the ions $(A-Cl)^+$, $(A-HCl)^{+\cdot}$, $(A-2Cl)^{+\cdot}$, $(A-HCl-COCl)^+$ and $(A-HCl-COCl-COCl)^{+\cdot}$. The greatest disparity between the spectra of PC2PPs and PC4PPs is due to the hydroxy hydrogen transfer rearrangement in the PCPP molecular ion[3,16]. This rearrangement occurs only in the molecular ion of PC2PPs and thus it gives directly the number of chlorine atoms on each phenyl ring of PC2PPs. Instead of this characteristic fragmentation, with PC4PPs (spectra III, E and V, Fig. 3) and PC3PPs the cleavage of the ether linkage give rise to the formation of a chlorinated phenyl cation (*e.g.*, the peak at *m/z* 179 in the spectrum of III, Fig. 3).

As seen above, it is difficult to distinguish PC4PPs and PC3PPs by means of their acetyl derivatives by MS. However, great disparities between the spectra of methylated PCPPs have been observed[9,17]. As can be seen in Fig. 4, methylated PC4PPs show a intense fragment ion $(M-15)^+$ resulting from the primary loss of a methyl radical. The positive charge formed can be stabilized by the non-bonding electron pair on the phenyl oxygen. This type of resonance stabilization is not possible in PC3PPs and thus the main fragmentation of PC3PPs is due to the primary loss of two $Cl^{\cdot}$. In principle, PC2PPs could be stabilized in the same manner, but in the spectra of PC2PPs the M – 15 peak generally occurs with low abundance. On the

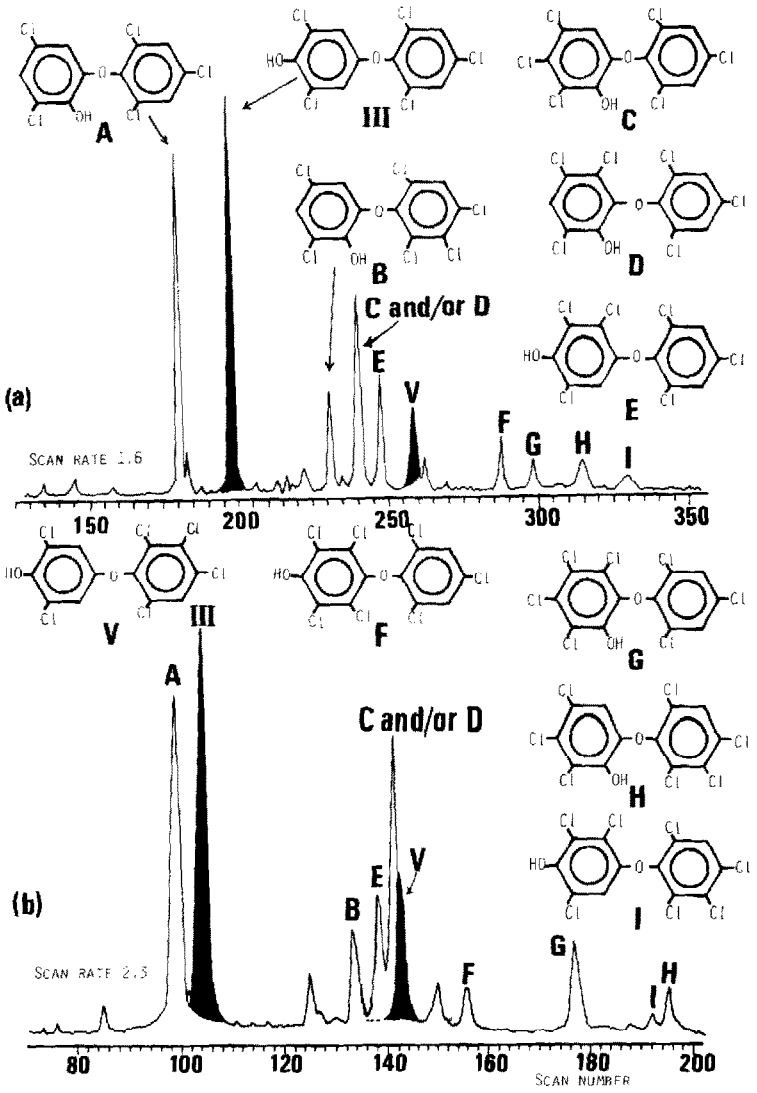


Fig. 2. Total ion current chromatogram of (a) acetylated and (b) methylated Ky-5 sample. For GC MS conditions see Experimental.

other hand, the primary loss of $CH_3Cl$ (M − 50) is generally more favourable and the fragmentation M − 50 is observed instead of the primary loss of a methyl radical.

*PCPPs in Ky-5*

The identification of various PCPP components in Ky-5 was based on the mass spectral characteristics (see above) and GC data (Table I) of the reference substances, and also the proposed formation routes presented in Fig. 5. As can be seen in Fig. 2, Ky-5 contains both predioxins and isopredioxins, as reported previously[3]. Two PC4PPs (III and V; Fig. 2) were identified by means of GC and MS as their non-

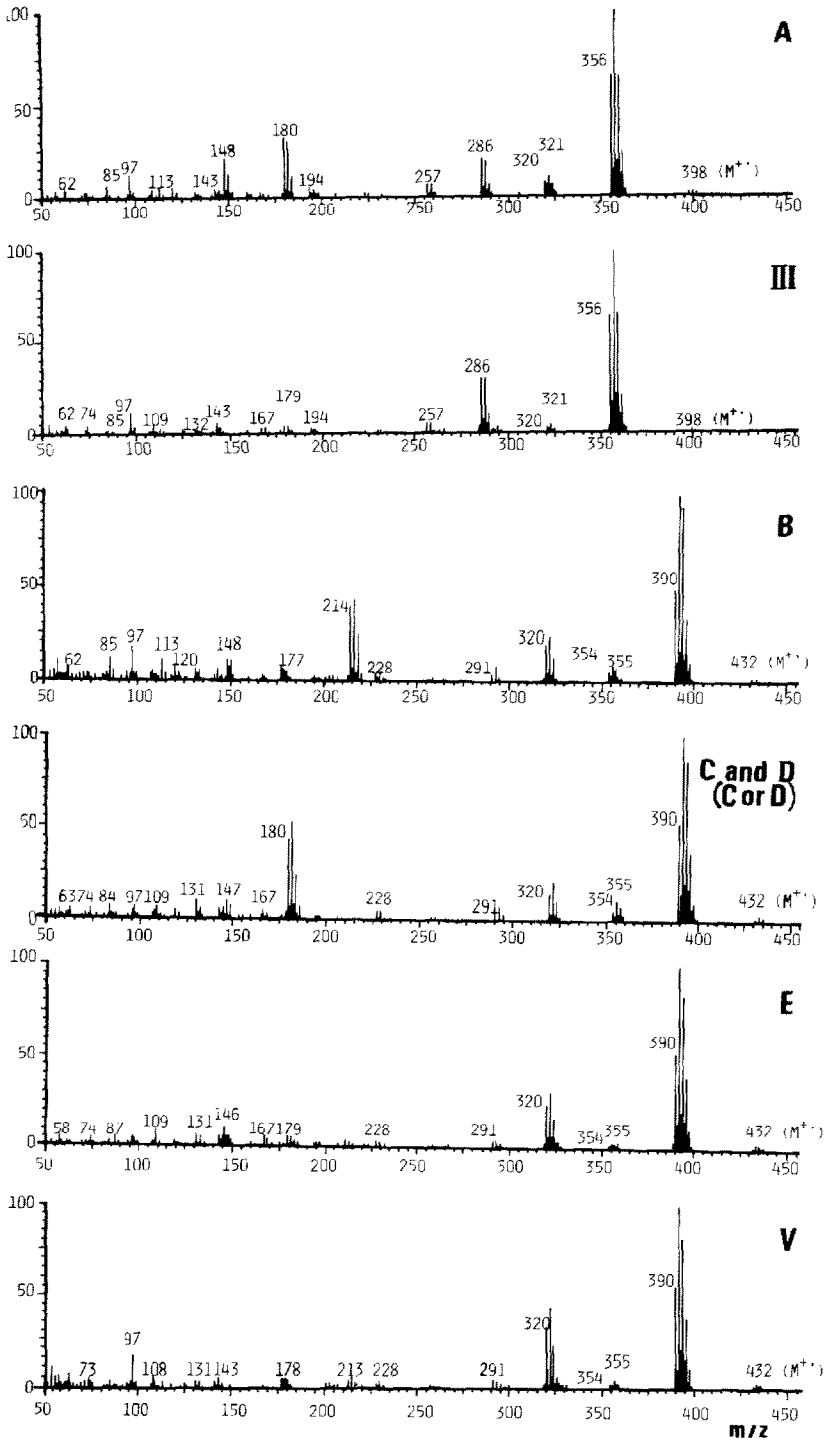


Fig. 3. Electron impact mass spectra of PCPPs in acetylated Ky-5 sample (Fig. 2).

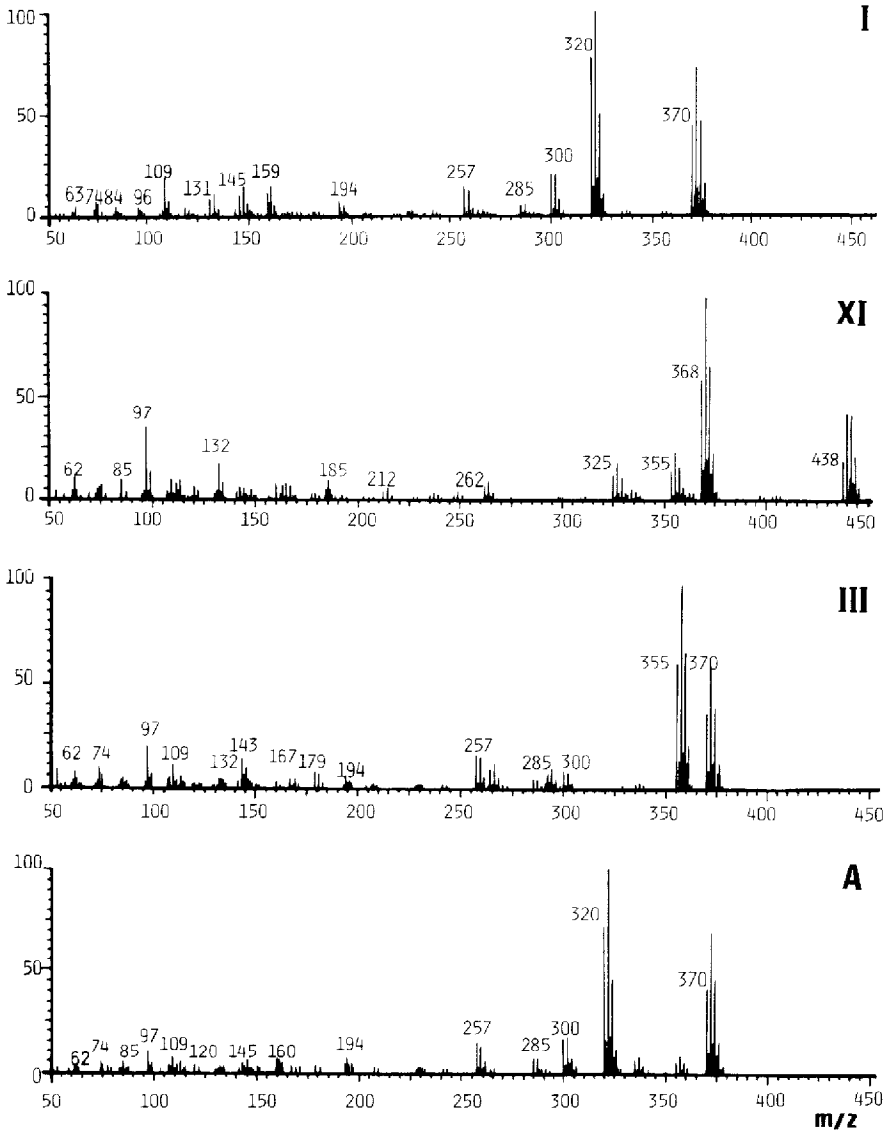


Fig. 4. Electron impact mass spectra of methylated PCPPs.

derivatized, methylated and acetylated forms. Amounts as high as *ca.* 0.8 and 0.2% were observed for compounds III and V, respectively. The estimated total amount of PCPPs in Ky-5 is suggested to be *ca.* 4–5%.

It seems evident that the main PCPPs in commercial chlorophenol formulations are formed through *ortho-*, *meta-* or *para*-elimination of HCl molecules (Fig. 5) from two monomeric chlorophenol molecules. For example, 2,6-dichloro-4-(2,4,6-trichlorophenoxy)phenol (III) is formed from two 2,4,6-trichlorophenol molecules by *para*-elimination (Fig. 5). Correspondingly, *ortho*-elimination is expected to produce 4,6-dichloro-2-(2,4,6-trichlorophenoxy)phenol (peak A in Fig. 2). On the

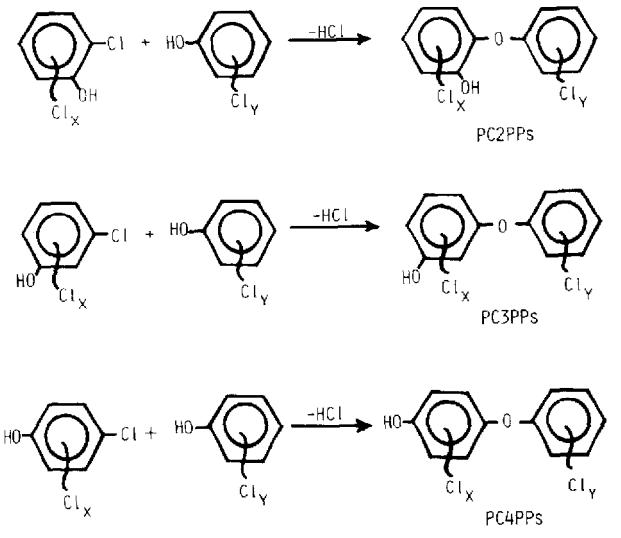


Fig. 5. Proposed routes for formation of PCPPs.

other hand, PC3PPs (formed by *meta*-elimination of HCl) were not observed in Ky-5. Similar structural assignments based on MS and Fig. 5 were made for the other PCPPs (A–I, Fig. 2) in Ky-5.

## CONCLUSIONS

A reliable GC–MS method has been devised for verifying the structures of various PCPP components. The model compounds synthesized and their mass spectrometric properties and GC retention times can be used succesfully for analysis of environmental samples contaminated with chlorophenols and their probable PCPP impurities. The formation routes producing PCPPs (HCl elimination during chlorination of phenol in Ky-5 production) can be applied in studies on the formation of PCPPs and related substances, *e.g.*, in the destruction of materials containing chlorophenolic compounds and also in chlorobleaching of pulp. The present results are also of practical importance for prospective synthetic and analytical investigations for developing syntheses of new dimeric and polymeric chlorinated aromatics.

## ACKNOWLEDGEMENTS

This work was supported financially by the Foundation for Research on Natural Resources in Finland and the Maj and Tor Nessling Foundation.

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