Isolation and Identification of the Components of a Commercial Chlordane Formulation[1]

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Technical chlordane, as manufactured in the U.S.A. since 1950, is claimed to be a uniform product. However, its composition is different from earlier preparations (1) and the published literature gives little information about the chemical nature of the various components. In 1952, March (2) isolated chlordene, heptachlor and two isomers of chlordane ($C_{10}H_6Cl_8$) from technical chlordane. Riemschneider (3) reported the presence of four isomers of octachloro-, two of heptachloro- and one each of nonachloro- and decachlorodicyclopentadiene as well as chlordene in technical chlordane manufactured before 1950. Some information about the probable identities of some of the components of currently manufactured

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technical chlordane is reported by Polen (1). This information together with that published in the United States Federal Register or in the U.S.D.A. Research Service Reports is not generally available to the broad scientific community (4).

The gas chromatogram of technical chlordane gives about 14 peaks (1). Since residues of chlordane in various biological materials are likely to be determined by gas chromatography a knowledge of the identities of the compounds represented by these peaks is necessary for the proper interpretation of residue data. This paper reports on the isolation and tentative identification of the components of technical chlordane isolated from a commercial chlordane formulation.

Methods

A 25% chlordane granular formulation supplied by Green Cross in 1967 was used in this study. Sixty grams of chlordane granules were extracted in a Soxhlet apparatus with diethyl ether for 8 hours. Removal of the solvent from the extract gave 16 grams of a pale yellow, viscous oil.

The components of the chlordane-granule extract were separated by gas chromatography on a 5% SE-30 column. Compounds 2,3,6,7,8,9,10, and 13 (Table 1) representing peaks D,E,G,G,H,J,K, and N, respectively, were collected and purified either by crystallization from aqueous ethanol or by rechromatography. Compound 4, representing peak E was isolated by preparative gas chromatography on a 30 ft. x $\frac{1}{4}$ in. column packed with 25% Carbowax 20M supported on acid washed Gas Chrom P. A PYE Autoprep gas chromatograph was used for this purpose. The column and injector temperatures were 190° and 230°C, respectively, and carrier gas flow rate was 100 ml./min.

Partial separation of the components of the extract was also achieved by column chromatography. For this purpose 0.5 g. of the extract was chromatographed on a 1.5 x 45 cm. column packed with 45 g. alumina (Fisher, A-540) and eluted with 1000 ml. purified petroleum ether (b. 30-60°C), followed by 200 ml. acetone. The eluents were collected in 10 ml. fractions and examined by gas chromatography on the SE-30 column. While most of the fractions contained more than one component in appreciable amounts a few contained only one major component which was isolated by gas chromatography on the SE-30 column. Compounds 5,9,10,11, and 12 (Table 1) represented by peaks F,J, K,L, and M, respectively, were isolated by this technique.

Infrared spectra were recorded in micro KBr discs with a Beckman IR-10 instrument equipped with a beam condenser. Mass spectra were recorded with an Associated Electrical Industries MS-12 spectrometer at ambient sample temperature and 70 volts electron energy.

Results and Discussion

The gas chromatogram of the ether extract of chlordane granules (Fig. 1) was identical with that of technical chlordane reported by Polen (1). The various peaks were tentatively identified from their infrared and mass spectra.

Compounds represented by peaks A, C, and I were not identified because of their low concentration.

Peak B is probably due to chlordene. It had the same retention time as that of authentic chlordene.

Peak D is a monochlorinated derivative of the adduct of pentachlorocyclopentadiene and cyclopentadiene. The infrared spectrum of the compound had a strong band at 1595 cm^{-1} due to a Cl-C=C-Cl group and none for a CH_2 group. The mass spectrum gave molecular weight 336 and $C_{10}H_6Cl_6$ as the molecular formula for this compound (5). There were also two

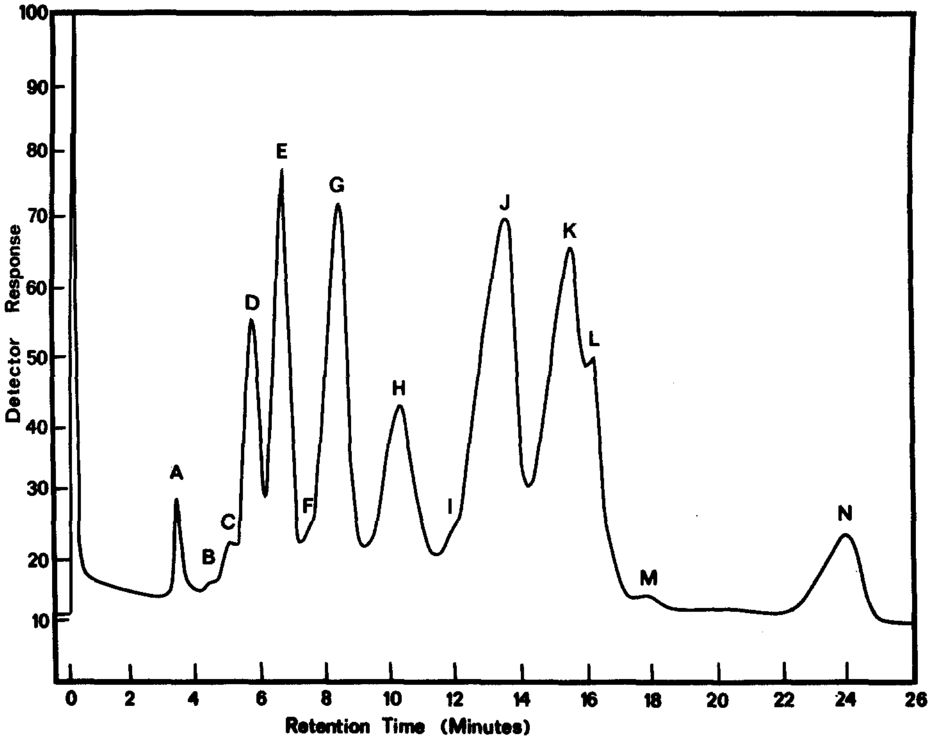
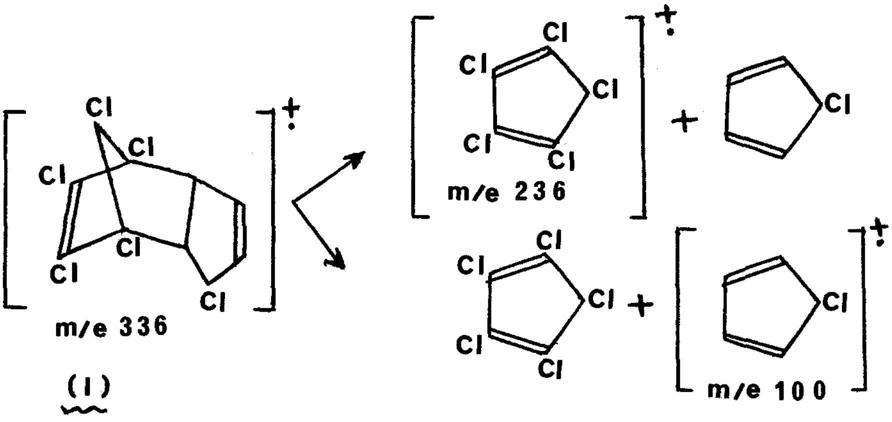


Figure 1. Gas chromatogram of the ether extract of chlordane granules. Column: 5 ft. x 3/16 in. 5% SE-30 on Chromosorb W at 180°C. Injector: 230°C; Detector: 250°C; Helium: 60 ml./min.

major fragments at m/e 100 (base peak) and at m/e 236 due to species containing one and five Cl atoms, respectively. All these data are in agreement with structure I proposed for this compound which agrees with the tentative identification of this peak made by Polen (1).



(I)

Peak E is mainly heptachlor and probably an isomer of chlordane ($C_{10}H_6Cl_8$). The material collected by gas chromatography on the SE-30 column and purified by crystallization had melting point and infrared and mass spectra identical with those of authentic heptachlor. But another compound (No. 4, Table 1) was isolated in very small quantity by preparative gas chromatography on the Carbowax column. The retention time of this compound on the SE-30 column was identical with that of authentic heptachlor. The infrared spectrum of compound no. 4 indicated the presence of Cl-C=C-Cl (1595 cm^{-1}) and CH_2 (1430 cm^{-1}) groups in the molecule. The mass spectrum gave molecular weignt 406 and $C_{10}H_6Cl_8$ as the molecular formula for this compound. According to Polen (1) also this peak is represented by heptachlor and an isomer of chlordane.

TABLE 1

Components of a commercial chlordane formulation

Compd. No.	Probable identity and method of isolation
1B*	Chlordene
2D	Chlordene analog. GLC on SE-30
3E	Heptachlor. GLC on SE-30 & cryst. m.p. 95°C
4E	Chlordane isomer. GLC on Carbowax m.p. 168-70°C
5E	Chlordane isomer. Column chromatog.
6G	Heptachlor isomer. GLC on SE-30
7G	Chlordane analog. GLC on SE-30 & cryst. m.p. 135-37°C
8H	Chlordane isomer. GLC on SE-30
9J**	γ-chlordane. GLC on SE-30, m.p. 106-7°C
10K**	α-chlordane. Column chromatog. & GLC, m.p. 108-9°C
11L	Chlordane analog. Column chromatog.
12M	Chlordane isomer. Column chromatog.
13M	Nonachlor isomer. Column chromatog.
14N	Nonachlor. GLC & cryst. 164-5°C

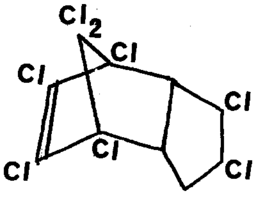
*Letters refer to peak no. in Fig. 1.

**Reference samples supplied by Velsicol Corporation.

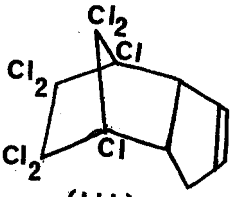
Peak F is probably an isomer of chlordane (compound no. 5, Table 1). The infrared spectrum of the compound indicated the presence of Cl-C=C-Cl and CH_2 groups in the molecule. The mass spectrum gave molecular weight 406 and $C_{10}H_6Cl_8$ as the molecular formula for this compound. It also gave a fragment at m/e 270, strongly suggesting that this compound is an isomer of chlordane (II). Polen did not identify the compound represented by this peak (1).

Peak G is probably due to an isomer of heptachlor and an octachlorodicyclopentadiene (compound no. 6 and 7, respectively, Table 1). The infrared spectrum of the sample collected from the SE-30 column and presumably containing both the components had a strong band at 1595 cm^{-1} due to Cl-C=C-Cl and a weak band at 1435 cm^{-1} due to a CH_2 group. The mass spectrum gave an apparent molecular weight 370 and $C_{10}H_5Cl_7$, as the molecular formula for this compound. It also gave major fragments at m/e 100 (base peak) and m/e 270, same as authentic heptachlor. This would indicate that this compound is probably an isomer of heptachlor. The mass spectrum was taken at ambient sample temperature and it appears that this isomer of heptachlor vaporized more readily than the other compound present in the sample. The weak band at 1435 cm^{-1} in the infrared spectrum was due to the other component, which had a strong band in this region.

The two compounds representing this peak on crystallization from ethanol gave a crystalline product (compound no. 7, Table 1). The infrared spectrum of the crystalline product had a strong band due to CH_2 group and none due to Cl-C=C-Cl group. The mass spectrum of the compound gave molecular weight 406, $C_{10}H_6Cl_8$ as molecular formula and no evidence of any retro-Diels-Alder decomposition product. These data strongly suggest that this compound is probably an analog of chlordane (III). According to Polen (1) peak G is represented by isomers of the adduct of hexachlorocyclopentadiene and cyclopentadiene which does not agree with the mass spectroscopic data.



(II)



(III)

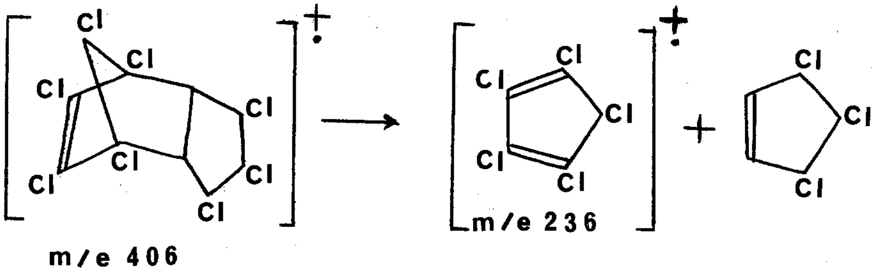
Peak H is probably due to an octachlorodicyclopentadiene. The infrared spectrum of the compound indicated the presence of Cl-C=C-Cl and CH_2 groups. The mass spectrum gave molecular weight 406 and

$C_{10}H_6Cl_8$ as molecular formula. It also showed ions due to successive loss of Cl or HCl fragments and no major fragment at m/e 270. According to Polen also this peak represents a chlordane analog (1).

Peak J is due to *gamma*-chlordane, called *alpha*-chlordane by March (2). The compound represented by this peak had melting point and infrared and mass spectra identical with those of the *endo*-*cis* isomer of chlordane.

Peak K is due to *alpha*-chlordane, called *beta*-chlordane by March (2). The compound represented by this peak had melting point and infrared and mass spectra identical with those of the *endo*-*trans* isomer of chlordane. Polen (1) also identified peaks J and K as *gamma*- and *alpha*-chlordane, respectively.

Peak L is probably an octachlorodicyclopentadiene. The infrared spectrum of the compound represented by this peak indicated the presence of Cl-C=C-Cl and no CH_2 group in the molecule. The mass spectrum gave a molecular weight 406 and $C_{10}H_6Cl_8$ as molecular formula. The mass spectrum also gave a fragment at m/e 236 indicating a C_5HCl_5 species. These data agree with structure **IV** proposed for this compound. However, according to Polen (1) this peak is due to a nonachlor ($C_{10}H_5Cl_9$) which disagrees with the mass spectroscopic data.



(IV)

Peak M is probably due to an isomer of chlordane (major component) and an isomer of nonachlor. Polen did not identify the compounds represented by this peak (1). The mass spectrum of the compounds representing this peak gave an apparent molecular weight 440 and molecular formula $C_{10}H_5Cl_9$. But the fragment at m/e 405 (M-Cl) did not have isotope distribution pattern consistent with a $(C_{10}H_5Cl_8)^+$ ion. The peaks at m/e 406,408,410,412 and 414 were stronger than those at m/e 405,407,409,411, and 413, respectively, indicating a parent ion at m/e 406 and corresponding to the formula $C_{10}H_6Cl_8$.

Peak N is due to a nonachlor. The infrared spectrum of the compound indicated the presence of Cl-C=C-Cl and no CH_2 group in the molecule. The mass spectrum was identical with that of nonachlor, reported by Damico and Barron (6).

Commercial chlordane formulations, as they are manufactured today, probably contain chlordene, one hexachloro-, two heptachloro-, eight octachloro-, and two nonachlorodicyclopentadienes. Attempts are being made to synthesize some of these compounds so that additional proofs of their structure can be obtained.

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