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COMMISSION ON TERMINAL PESTICIDE RESIDUES

IUPAC Reports on Pesticides (2)

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TERMINAL RESIDUES OF ORGANOCHLORINE INSECTICIDES

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CHLORDANE

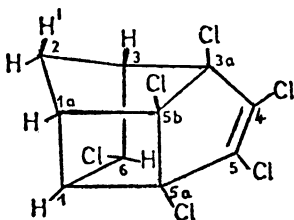
The chemical composition of the multicomponent technical chlordane and elucidation of some of its components has had considerable attention in the recent period. Cochrane and Greenhalgh (1) have separated technical chlordane into twenty-six peaks by temperature-programmed gas chromatography. Components were identified by combined gas chromatography-mass spectrometry (GLC-MS). Four GLC columns were used to overcome peak overlap and to determine known constituents quantitatively. The structures of a number of other components were tentatively identified including three peaks which indicated the presence of epoxy compounds, presumably derived from aerial oxidation of the technical product.

In a study of the analysis of technical chlordane by gas chromatography and mass spectrometry, Sovocool et al. (2) made partial or complete structure identifications for approximately forty-five constituents which they isolated.

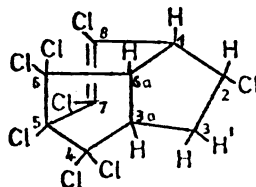
Many of these compounds are simple Diels-Alder adducts of cyclopentadiene and hexachlorocyclopentadiene, with further chlorine additions or substitution. A series of adducts derived from tetra- and pentachlorocyclopentadiene, followed by further chlorination, has been identified.

Sovocool et al. differ with the interpretation of Cochrane and Greenhalgh which concludes that oxygen-containing compounds have been formed. Instead they postulate that certain unidentified components result, during manufacture, from extraction of a Cl_2C radical from chloroform which they presume is used as a solvent in the process. (Chloroform is in fact not used in the commercial preparation of technical chlordane.) These authors also hypothesized the presence of "reduced" chlordanes and heptachlors but did not succeed in matching their observed fragmentation patterns and GLC properties with those of known dihydroheptachlors or dihydrochlordene.

Further studies are reported on the structure of Compound C and Compound K (3,4). Compound C is an isomer of chlordene ($\text{C}_{10}\text{H}_2\text{Cl}_6$) formed by rearrangement of isochlordene and is considered to be 3a,4,5,5a,6-hexachloro-1a,2,3,3a,5a,5b-hexahydro-1,3-methano-1H-cyclobuta[cd]pentalene (I). Compound K is a formal isomer of chlordane ($\text{C}_{10}\text{H}_6\text{Cl}_8$) which is formed by chlorination of alpha-chlordene via a Wagner-Meerwein-rearrangement. The proposed structure for Compound K, based largely on X-ray data, is 2,4,4,5,6,6,7,8-octachloro-octahydro-1,5-ethenopentalene (II).



(I) Compound "C"



(II) Compound "K"

Recent reports on the monitoring of human adipose tissue in the United States indicate wide spread residues of heptachlor epoxide, oxychlordane and trans-nonachlor (5,6). Heptachlor epoxide and oxychlordane are each reported at frequency in excess of 90% of the samples and at levels approximating 0.1 ppm. Quantitation of nonachlor appears to be uncertain and is done primarily by MS methods rather than through GLC.

Analysis of adipose tissue of Canadians present a similar picture (7). Oxychlordane, trans-nonachlor and heptachlor epoxide occur at an incidence in excess of 97% and fairly uniformly at levels between about 0.04 to 0.07 ppm. Whilst all the foregoing reports on the residues in human adipose tissue claim confirmation of the findings, Atallah et al. (8) report observations indicating that routine monitoring by GLC analytical techniques are likely to respond to several substances which act as "masqueraders" for oxychlordane, heptachlor epoxide and trans-nonachlor if these methods alone are used.

The conversion of trans-nonachlor to oxychlordane has been reported in the rat (9). When rats were given diets containing 50, 100, or 200 ppm technical chlordane or 10 or 100 ppm of trans-nonachlor for fourteen days, oxychlordane was found in the adipose tissue of the rats fed either technical chlordane or nonachlor. Rats were fed 200 ppm of technical or 100 ppm of trans-nonachlor for fourteen days and sacrificed 0, 14, 28, 56, and 112 days post insecticide feeding. They showed intact chlordane residues after 56 and 112 days that were lower than the residues of oxychlordane. However, the residues of trans-nonachlor were never greater than those of oxychlordane, which is the major metabolite of both chlordane isomers and trans-nonachlor. It was concluded that in the rat, trans-nonachlor is not as good an indicator of chlordane exposure as oxychlordane. However, the apparent ubiquitous occurrence of trans-nonachlor in human adipose tissues suggests that human metabolism of chlordane insecticide is substantially different from that in the rat. The latter statement is based upon comparison of the relative retention levels of the three metabolites which were observed in the rat and the apparent relative levels in EPA human monitoring reports.

The state of the art of analysis of human tissue for chlordane residues appears to be uncertain. The residue profiles reported in monitoring human adipose tissue are incongruous with patterns of residues in test animals under controlled conditions. While the possibility exists that human metabolism is substantially different from that of the rat and hence generates a grossly different residue pattern, that theory is weakened by the likelihood of analytical artifacts in routine monitoring giving misleading information as observed by Atallah et al. Further research on the validity of analysis of residues in human tissue is needed.

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