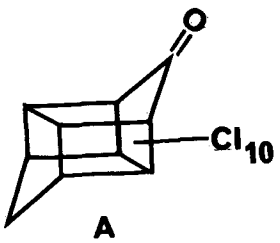
Bull. Environm. Contam. Toxicol. 20, 241-247 (1978)

Identification of Kepone Alteration Products in Soil and Mullet

Arnold P. Borsetti, and John A. G. Roach
Division of Chemistry and Physics, Food and Drug Administration, Washington, DC 20204

The insecticide Kepone (A) (decachloropentacyclo-$(5.3.0.0^{2,6}.0^{3,9}.0^{4,8})$decan-5-one) has been the subject of intensive residue analyses following recent environmental contamination from Kepone production in Hopewell, VA (MURRAY 1976).



A

Many environmental problems have arisen as a result of Kepone's high degree of stability (EATON et al. 1960; GRIFFIN and PRICE 1964; MCBEE et al. 1956). The finding of Kepone homologs in soil and fish (mullet) reported here may suggest a possible pathway for the environmental degradation of this highly persistent pesticide, and may indicate the presence of residue components in addition to Kepone per se that should be considered for inclusion in analyses.

EXPERIMENTAL

Procedure

Soil was collected in the vicinity of the Kepone manufacturing site at Hopewell, VA. Thirty mullet were obtained from the James River south of Hopewell. The mullet were filleted and the fillets were ground to produce a homogeneous composite. A 200 g portion of the soil and a 25 g portion of the ground mullet were extracted and prepared for gas-liquid chromatography (GLC) by an adaptation (CARVER 1976) of the procedure for Kepone in bananas given in the Food and Drug Administration's Pesticide Analytical Manual (PAM) (1974).

0007-4861/78/0020-0241 $01.40

Using this method, the mullet was extracted by blending with isopropanol-benzene, and the extract was transferred to hexane. The hexane was treated with oleum (0% sulfur trioxide in concentrated sulfuric acid). Kepone was extracted from the hexane into aqueous sodium hydroxide; the alkali layer was neutralized and extracted with ethyl ether-petroleum ether. The mixed ether solution was exchanged with benzene. The benzene was reduced in volume and the final solution was adjusted to contain benzene-2% methanol for GLC determination of Kepone.

The soil was Soxhlet-extracted overnight with acetonitrile-water; the extract was diluted with water and then partitioned with ethyl ether-petroleum ether. The mixed ether solution was exchanged with hexane, and the treatment continued as for mullet, beginning with "The hexane was..."

Gas-Liquid Chromatography

The sample extracts were analyzed using a gas-liquid chromatograph equipped with a tritium electron capture detector. Two columns were used: 6' x 4 mm id silanized glass packed with 10% OV-101, and equal parts of 10% OV-101/15% OV-210, respectively, on 80-100 mesh Chromosorb WHP. The column temperature was maintained at 200°C with a nitrogen carrier gas flow of 120 ml/min (PAM 1975). Both samples and Kepone standard solutions were prepared in benzene-2% methanol for GLC and GLC-mass spectrometry (MS).

Mass Spectrometry

Mass spectra were obtained on a Finnigan Model 3300 twin stack mass spectrometer, in both electron impact and chemical ionization modes. A 5' x 2 mm id silanized glass column packed with 3% OV-101 on 60-100 mesh dimethylchlorosilane-treated Chromosorb W was interfaced with the mass spectrometer. Helium carrier gas flow of 25 ml/min was maintained for electron impact, and methane carrier gas at 10-15 ml/min, giving a source pressure of 850-950 μm, was used for chemical ionization.

RESULTS AND DISCUSSION

GLC of the sample extracts (Fig. 1) indicated the presence of Kepone in both the soil and fish at levels of 60 and 0.56 ppm, respectively. In addition, 2 other peaks were detected in the chromatogram from soil; one of these peaks also appeared in the chromatogram from mullet extracts. The identities of the compounds causing these GLC peaks were of interest because they had survived the stringent treatment with fuming sulfuric acid and sodium hydroxide used to isolate Kepone from the sample matrix. MS analysis of these additional peaks indicated that they were caused by 9-chloro and 8-chloro homologs of Kepone (Fig. 2). The chromatographic characteristics of these compounds

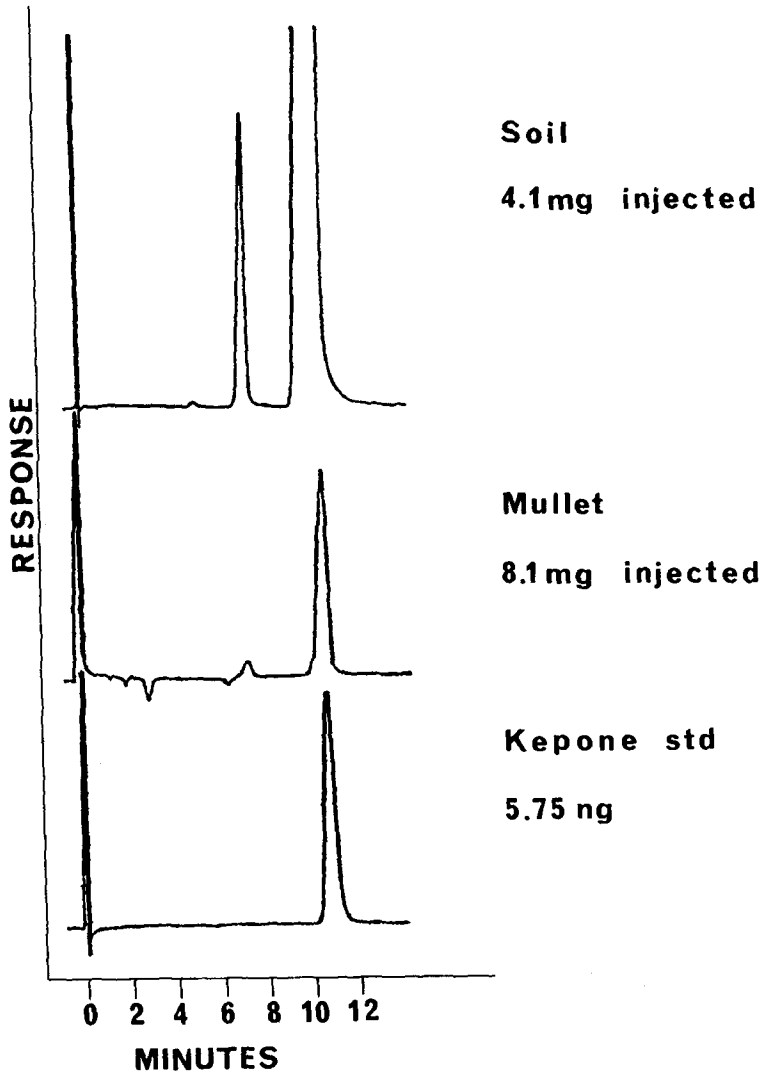


FIG. 1. Kepone standard and sample chromatograms obtained using 10% OV-101 on 80-100 mesh Chromosorb WHP.

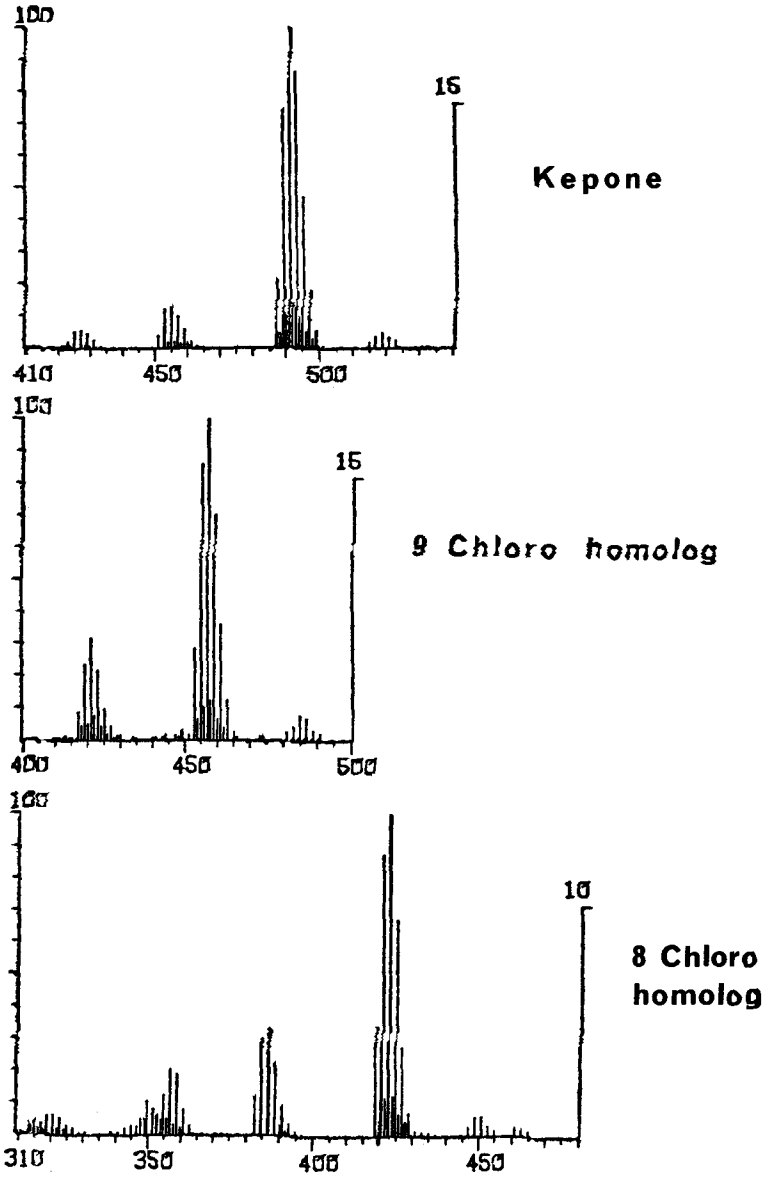


FIG. 2. Mass spectra of Kepone and its 9-chloro and 8-chloro homologs obtained using GLC/MS (chemical ionization mode).

TABLE I

GLC characteristics of Kepone and Kepone homologs

Compound	ng ½ FSD[a]	RR_A[b]	
		10% OV-101[c]	10% OV-101/15% OV-210[d]
8-Chloro homolog	ND[e]	1.31	1.55
9-Chloro homolog	ND	1.90	2.03
Kepone	5	2.70	2.68

[a]FSD = full scale deflection.

[b]RR_A = retention time relative to aldrin.

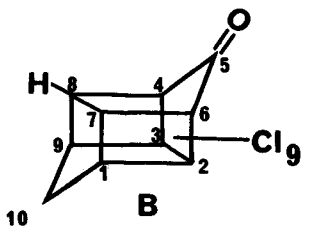
[c]RR_A for p,p'-DDT = 3.03.

[d]RR_A for p,p'-DDT = 3.25.

[e]ND = not determined. No reference compound available.

were determined using GLC parameters for organochlorine pesticides and an electron capture detector as described in PAM (1975). These data are presented in Table I.

Further interpretation of the MS fragmentation pattern of the 9-chloro homolog indicated that the proton is in 1 of 4 equivalent positions beta to the carbonyl. This conclusion was based on the observation of major fragmentation corresponding to $C_5Cl_5^+$, $C_5Cl_5H^+$, $C_5Cl_4O^+$, and $C_5Cl_3HO^+$ ions. Of the 4 possible monohydro isomers of Kepone, only a proposed structure such as B could give the observed ions on fragmentation.



H = 2,3,7 or 8

Similar reasoning has been used by other investigators in identifying this compound (ALLEY et al. 1974; IVIE et al. 1974). Analysis of the MS fragmentation for the 8-chloro homolog did not provide a clear structural assignment. Major fragments corresponding to $C_5Cl_3HO^+$ and $C_5Cl_5H^+$ ions, however, strongly suggest a symmetrically substituted compound.

Analysis of the mullet sample indicated the presence of the same 9-chloro homolog, although no 8-chloro homolog was detected. Since suitable reference compounds were not available, the amount of the 2 homologs was approximated, based on response of the elctron capture detector to Kepone. Assuming a GLC response similar to that of the homologs, the approximate levels of the 9-chloro and 8-chloro homologs in the soil would be 1.0 and 0.01 ppm, respectively. Approximately 0.04 ppm 9-chloro homolog was estimated in the mullet.

The results of previously reported experiments on the photolysis of Kepone suggest that the homologs found in these samples were produced by photodegradation of the Kepone contaminating the Hopewell, VA, location. ALLEY et al. (1974) and HARDIN (1976) reported that photolysis of Kepone under laboratory conditions produced the same 9-chloro and similar 8-chloro homologs to those identified here. IVIE et al. (1974) have shown that, under photolytic conditions, the pesticide Mirex ($C_{10}Cl_{12}$), which possesses the same basic structure as Kepone and is also a persistent compound, is converted to Kepone and to the 9-chloro homolog reported here. Of more direct importance Mirex has recently been shown to degrade to Kepone under environmental conditions (CARLSON et al. 1976), a finding which emphasizes the need to determine the fate of Kepone. However, it remains to be shown whether a photolytic reaction actually plays an important role in the environmental degradation of Kepone. Until this is proven, other possible sources of the homologs must include some metabolic pathway or simply some impurity in the plant production of Kepone.

ACKNOWLEDGMENTS

The authors thank Richard Carver and Louis Carson, Food and Drug Administration, for preparing the samples prior to GLC and GLC-MS determination; Terryl Farrell, Food and Drug Administration, for providing the soil sample; and Robert Huggett, Virginia Institute of Marine Science, Gloucester Point, VA, for providing the mullet samples.

REFERENCES

ALLEY, E.G., B.R. LAYTON and J.P. MINYARD, JR.: J. Agric. Food Chem. 22, 442 (1974).

CARLSON, D.A., K.D. KONYHA, W.B. WHEELER, G.P. MARSHALL and R.G. ZAYLSKIE: Science 194, 939 (1976).

CARVER, R.A.: Division of Chemistry and Physics, Food and Drug Administration, Washington, D.C., unpublished communication (1976).

EATON, P., E. CARLSON, P. LOMBARDO, and P. YATES: J. Org. Chem. 25, 1225 (1960).

PESTICIDE ANALYTICAL MANUAL, Vol. II, Decachloro-octahydro-1,3,4-metheno-2H-cyclobuta [cd] pentalen-2-one, Food and Drug Administration, Washington, DC (Dec. 1974).

PESTICIDE ANALYTICAL MANUAL, Vol. I, Sec. 331A,B, Food and Drug Administration, Washington, DC (July 1975).

GRIFFIN, G.W. and A.K. PRICE: J. Org. Chem. 29, 3192 (1964).

HARDIN, N.F.: Food and Drug Administration, New Orleans, LA, private communication (1976).

IVIE, G.W., H.W. DOROUGH and E.G. ALLEY: J. Agric. Food Chem. 22, 933 (1974).

MCBEE, E.T., C.W. ROBERTS, J.D. IDOL and R.H. EARLE: J. Am. Chem. Soc. 78, 1511 (1956).

MURRAY, C.: Chem. Eng. News (Feb. 2, 1976).