COMMUNICATIONS

Irradiation Studies of Mallard Duck Eggs Material Containing Mirex

Eggs containing Mirex (dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) from mallard ducks (*Anas platyrhychos* l.), fed diets with the insecticide incorporated at levels of 1 and 100 ppm for 25 weeks, were subjected to ultraviolet (uv) and γ irradiation. Seven derivatives were obtained on photolysis and eight derivatives were obtained from γ irradiation. Irradiation products appeared to be mono and dihydro derivatives of Mirex. Structural assignments for two monohydro derivatives and three dihydro derivatives were made on the basis of retention time and mass spectral data.

Irradiation has been shown to degrade chlorinated hydrocarbons. Li and Bradley (1967) applied ultraviolet (uv) irradiation to a stream of milk contaminated with various organochlorines and found all susceptible to photolytic decomposition. Photolysis of aldrin (1,2,3,4,-10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-*endo-exo*-1,4,-5,8-dimethanonaphthalene) in the solid state (Rosen and Sutherland, 1967) and in solution (Henderson and Crosby, 1967; Rosen and Carey, 1968) has also been investigated. Alley et al. (1973) reported the photolytic decomposition of Mirex (dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) in a hydrocarbon solvent with subsequent investigations (Alley et al., 1974a) on identification of the photoproducts as well as studies on photoreduction of Mirex in aliphatic amines (Alley et al., 1974b). Carp et al. (1972a,b) studied the effect of γ irradiation of aldrin in hydrocarbon and lipid solutions. This study encompasses the photolytic and γ irradiation of egg tissues containing naturally occurring Mirex.

Irradiation studies on chlorinated hydrocarbons generally yield hydrogen derivatives of the parent compounds. With Mirex, mono and dihydro isomers are formed with the pentacyclodecane nucleus of Mirex remaining intact. Exact structural assignment of monohydro and dihydro derivatives of Mirex from irradiation studies is somewhat complicated since NMR, infrared, and mass spectral data do not furnish conclusive evidence to distinguish among the three nonequivalent positions on the pentacyclodecane skeleton. Unambiguous syntheses of mono and dihydro derivatives of Kepone (Dilling et al., 1967; Alley et al., 1973, 1974a) with subsequent chlorination to corresponding mono and dihydro derivatives of Mirex and comparison of these products with photoproducts of Mirex has led to structural elucidation of two monohydro derivatives and one dihydro derivative of Mirex.

MATERIALS AND METHODS

Eggs containing 233 ppm of Mirex from mallards fed at the 100-ppm level were homogenized in a Waring Blendor for 5 min. Fifty-gram quantities of the homogenate were introduced into each of 10 whirl packs and placed about symmetrically in a 2-l. beaker. The beaker was introduced into a constant temperature irradiation chamber equipped with a ^{60}Co source whose activity was 1140 rads/min calculated by the Fricke Dosimetry Method (Weiss, 1952) and corrected on the basis of the half-life for ^{60}Co of 5.24 years.

Two whirl packs were withdrawn at calculated intervals to yield dosages of 1, 2, 3, and 4.5 Mrads, respectively. Four samples of 2 g each were weighed from each whirl pack giving a total of eight samples for each dosage. After treatment the samples were stored at 4°C until time for analysis.

Table I. Retention Time Data for Uv and γ Irradiation Products of Mirex

Peak no.	Retention time rel to Mirex, 10% DC 200, 195°C
1	0.30
2	0.32
3	0.37
4	0.42
5	0.48
6	0.51
7	0.65
8[a]	0.75
9	1.00

[a] Obtained in γ radiation study only.

Table II. Mirex Residues Remaining after Uv Radiation for 24 and 48 hr at 24°C

Control, ppm	24 hr, ppm	48 hr, ppm
2.48 ± 0.05	2.04 ± 0.04	1.60 ± 0.07

Photolytic studies were carried out on eggs from Mallards fed at the 1-ppm level. Two-gram quantities of a homogenate of eggs containing 2.48 ppm of Mirex were weighed into 12 50-ml beakers and subjected to uv irradiation at ambient temperature (24°C) for 24 and 48 hr. The uv source was a General Electric Germicidal Lamp, 18 in. in length and 1 in. in diameter. Uv output at 253.7 nm was 3.6 W or 760 μW/cm^2 at the surface of the samples. The source was positioned 6 in. above the samples being irradiated. From the homogenate, six samples were subjected to uv irradiation for 24 hr and six samples were irradiated for 48 hr.

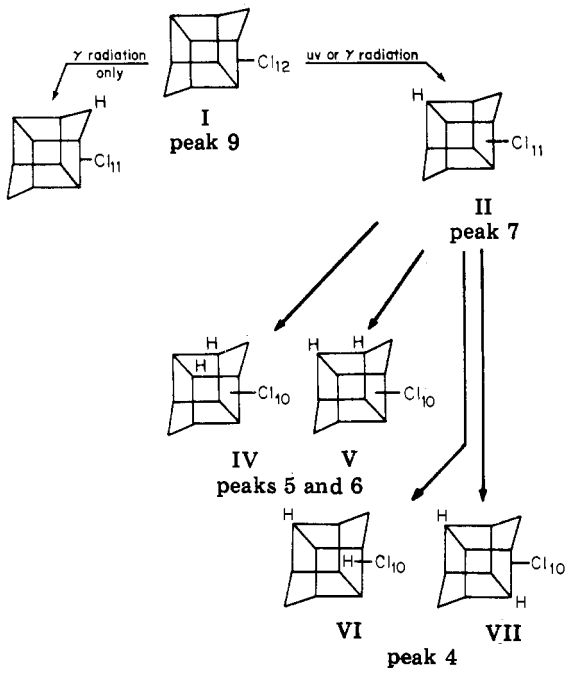
All irradiated samples as well as controls were subjected to extraction and cleanup according to the method of Cummings et al. (1966). Appropriate dilutions were made for quantitation of unreacted Mirex. Controls were samples of the homogenate which were not irradiated and therefore contained only Mirex. Gas chromatographic analysis of the controls after cleanup gave only the peak for Mirex. It was assumed that new peak formation, as uv and γ irradiation time increased, was caused by Mirex degradation. Mass spectral evidence from new peak formation with a concomitant decrease in Mirex concentration demonstrated that this assumption was valid.

Retention time data of irradiation products were obtained on a Perkin-Elmer Model 810 gas chromatograph equipped with an electron capture detector (column 6 ft × 1/8 in. i.d.; 10% DC 200 on 80–100 mesh Chromosorb

Table III. Mirex Residues Remaining after Various Dosages of γ Radiation

Control, ppm	1 Mrad, ppm	2 Mrad, ppm	3 Mrad, ppm	4.5 Mrad, ppm
232.89 ± 12.84	206.99 ± 7.63	163.52 ± 4.80	130.96 ± 3.14	85.45 ± 1.41

Scheme I. Schematic Diagram of the Irradiation Products of Mirex



W; 195°C). Retention times for photo and γ irradiation products are given in Table I.

Combined gas chromatography–mass spectrometry was employed to identify the photolytic and γ irradiation products of Mirex. The mass spectrometer was a Hitachi-Perkin Elmer, Model RMS 4, with an electron bombardment source. The electron ionizing potential was set at 80 V. Mass spectra were scanned magnetically from approximately a mass-to-change ratio of 400 to 12.

RESULTS AND DISCUSSION

Degradation data are presented in Tables II and III for the photolytic and γ irradiation studies. Photolysis caused a 36% decrease at 48 hr whereas γ irradiation at 4.5 Mrad caused a 64% loss in Mirex. A linear relationship existed in loss of Mirex with respect to time for both uv and γ irradiation studies.

Structural assignments for the mono and dihydro derivatives of Mirex are outlined in Scheme I. Peak 7 (II), the major photolytic and γ irradiation product of Mirex, gave a retention time which was identical with that of the major photoproduct furnished by Alley from his photolysis of Mirex. Unambiguous structural assignment of II, 1,2,-3,4,5,5,6,7,9,10,10-undecachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.-$0^{4,8}$]decane, was made (Alley et al., 1974a) by photolysis of Kepone (decachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]-decan-5-one) to its monohydro isomer with subsequent chlorination to the corresponding monohydro derivative of Mirex. The mass spectrum of II is consistent with these findings since major ion clusters appear at m/e 270 ($C_5Cl_6^+$), m/e 235 ($C_5Cl_5^+$), and m/e 236 ($C_5Cl_5H^+$). Peak 8 (III), 1,2,3,4,5,5,6,7,8,9,10-undecachloropentacyclo[0.-$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane, was obtained during γ irradiation only. Its mass spectrum and retention time were identical with an authentic sample prepared by Alley by chemical reduction and subsequent chlorination of Kepone to the monohydro derivative of Mirex. Alley et al. (1974b) more recently obtained this product from photoreduction of Mirex in triethylamine.

Peaks 5 and 6 were obtained by both uv and γ irradiation and found to be isomeric. Isotope clusters at m/e 270 ($C_5Cl_6^+$), m/e 236 ($C_5Cl_5H^+$), m/e 202 ($C_5Cl_4H_2^+$), and m/e 201 ($C_5Cl_4H^+$) indicated that the parent compounds were unsymmetrical dihydro derivatives of Mirex, i.e., both hydrogens substituted on the same cyclopentadiene. The isotope cluster at m/e 202 ($C_5Cl_4H_2^+$) seemed to be the parent fragment representing the most intense ion cluster. Since Alley et al. (1973) demonstrated that the monohydro derivative was a precursor of the dihydro derivative, peaks 5 and 6 must have been derived from II. The dihydro derivatives from III may be eliminated as possibilities since III was obtained during γ irradiation only. Possible structures consistent with mass spectral data are structures IV and V.

Peak 4 (VI or VII) was obtained on uv and γ irradiation. The retention time for VI or VII was consistent with that of a dihydro derivative furnished by Alley from photolysis of Mirex in cyclohexane. Alley et al. (1974a) more recently showed that VI or VII was identical with a dihydro photoproduct of Kepone after chlorination with phosphorus pentachloride. The mass spectrum of VI or VII demonstrated that the molecule was purely symmetrical since major isotope clusters appeared at m/e 236 ($C_5Cl_5H^+$) and m/e 201 ($C_5Cl_4H^+$). No mass spectra were obtained on peaks 1, 2, and 3 since they were not present at detectable levels for mass spectral analyses.

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LITERATURE CITED

Alley, E. F., Dollar, D. A., Layton, B. R., Minyard, J. P., Jr., *J. Agric. Food Chem.* **21**, 138 (1973).
Alley, E. G., Layton, B. R., Minyard, J. P., Jr., *J. Agric. Food Chem.* **22**, 442 (1974a).
Alley, E. G., Layton, B. R., Minyard, J. P., Jr., *J. Agric. Food Chem.* **22**, 727 (1974b).
Carp, A. E., Liska, B. J., Ziemer, P. L., *Bull. Environ. Contam. Toxicol.* **7**, 321 (1972a).
Carp, A. E., Liska, B. J., Ziemer, P. L., *Bull. Environ. Contam. Toxicol.* **7**, 331 (1972b).
Cummings, J. G., Zee, K. T., Turner, V., Quinn, F., *J. Assoc. Off. Agric. Chem.* **49**, 354 (1966).
Dilling, W. L., Braendlin, H. P., McBee, E. T., *Tetrahedron* **23**, 1211 (1967).
Henderson, G. C., Crosby, D. G., *J. Agric. Food Chem.* **15**, 888 (1967).
Li, C. I., Bradley, R. C., Jr., *J. Dairy Sci.* **50**, 944 (1967).
Rosen, J. D., Carey, W. F., *J. Agric. Food Chem.* **16**, 536 (1968).
Rosen, J. D., Sutherland, D. J., *Bull Environ. Contam. Toxicol.* **2**, 1 (1967).
Weiss, J., *Nucleonics* **10**, 28 (1952).

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