A Photoisomerisation Product of Dieldrin

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Roburn (1) reported on the presence of an unknown compound on grass which had been treated with dieldrin and subjected to sunlight. He also showed that the same compound was produced by ultraviolet irradiation of dieldrin on a glass plate.

We have prepared a quantity of this material either by irradiating a solution of dieldrin as described by Bird, et al, (2) or by depositing a thin layer of dieldrin on a sheet of filter paper and irradiating it for 30 minutes with an ultraviolet lamp (2537 Å). The conversion products were extracted with 1:1 v/v hexane/acetone mixture and then applied to preparative thin layer chromatoplates, coated with silica gel H 254. The plates were developed with 1:4 acetone/hexane mixture, and the separated bands were located by u.v. light. The band of the major conversion product was scraped from the plate and extracted from the gel with diethyl ether. Further purification was achieved by chromatography through a silica gel column using hexane/benzene 1:4 as eluant. Recrystallization of the product from ethanol gave a product with a melting point of 188°C.

Using Apiezon L as the stationary phase the retention time of

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the conversion product (relative to dieldrin) was 4.5 as reported by Roburn; the relative retention times (dieldrin=1) on silicone SE 30, Oronite polybutene 128, QF 1, and neopentyl glycol succinate were 2.6, 4.3, 9, and 20 respectively.

We confirm Roburn's observation that the product is more polar than dieldrin by its behaviour on reversed phase paper chromatography. The R_f values for dieldrin and the photoconversion product on thin layer chromatography were as follows:

TABLE 1

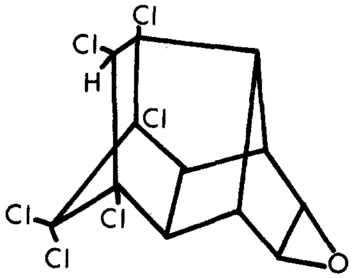
R_f values of dieldrin and photochemical conversion product

Compound	Absorbent	
	Silica Gel (a)	Alumina H (b)
Dieldrin	0.93	0.55
Photoconversion product	0.55	0.46

Developing solvents: (a) 4:1 (v/v) cyclohexane/acetone: (b) 6:1 (v/v) cyclohexane/propanol.

Microanalysis, mass spectrum and molecular weight determinations indicate that the compound is an isomer of dieldrin. Inspection of the infrared spectrum of the conversion product shows that the absorption bands at 6.25 u and 6.81 u, attributable to the dichlorethylene and methylene groups respectively in dieldrin, are absent. The absorption bands attributed to the epoxide group in dieldrin at 8.02, 11.8, and 12.05 u are missing or have been displaced; the appearance of new bands at 8.88 u and 10.57 u may indicate the presence of an oxygen ring with more than 3 members. The NMR spectrum of the conversion product confirms the absence of a methylene group and indicates the presence of a CHCl group. These observations indicate that a bridge has been formed in the conversion product between the CH_2 bridge and the Cl-C=C-Cl group in dieldrin, but the evidence regarding the oxygen function in the conversion product is ambiguous: the infrared spectrum indicates the absence of a carbonyl or hydroxyl group and it is tentatively concluded that an oxygen ring system is still present. This ring system may be unchanged 1-2 oxide or a larger ring. However, the presence of a larger ring necessitates the shift of a carbon-carbon link with the formation of an endo-endo structure. Triphenyl phosphine has been reported to be a specific reagent for the conversion of 1:2 epoxides to the corresponding ethylene derivatives but neither dieldrin nor the conversion product reacts with this reagent. A study of the cracking pattern of dieldrin, endrin and the conversion product indicates that the pattern of relative abundance ratios of the breakdown products of the conversion product is similar to that of dieldrin (an endo-exo compound) and quite different from that of endrin (an endo-endo compound). This observation indicates that the conversion of the endo-exo ring fusion in dieldrin under the influence of light to an endo-endo fusion product is unlikely.

It is tentatively concluded that the structure of the conversion product is:



Both dieldrin and the photoconversion product react with anhydrous hydrogen bromide in dioxan to give bromo-hydrins. Both bromo-hydrins are converted back to the original compounds on treatment with alcoholic potash. Once again these reactions are not specific for 1:2 oxide ring systems.

Since the conversion product is formed by the action of sunlight on dieldrin, it was considered essential to obtain evidence of the occurrence of this compound in the environment as a result of current agricultural practice. Direct applications of dieldrin to the edible foliage of plants is uncommon and in this preliminary survey we have concentrated attention upon those crops in which residues of dieldrin have been found in the past. Animal experiments indicate the conversion product has lipophilic properties and specimens or animal fats have also been analysed. In order to assess the overall dietary intake of man, two samples of cooked meals (corresponding to 24 hour samples) have been analysed,

TABLE 2

Concentration of photoconversion product of dieldrin in the environment

Nature of Sample	Number of Specimens	Average concentration of photo conversion product ppm	Lower limit of detection, ppm	Dieldrin content ppm
English mutton fat	2	(a) none detected (b) 0.004	0.001	0.07
Australian mutton fat	1	none detected	0.0001	0.01
Argentine corned beef fat	2	(a) 0.0018 (b) none detected	0.002	0.16 0.015
Crude & refined edible oils & fats	8	none detected	0.004 - 0.05	0.05
Whole cooked meals	2	none detected	0.001	0.02
Human fat	10 (pooled)	none detected	0.0005	0.4
Butter	2	none detected	0.001	0.04
Cooked meats	2	none detected	0.001	0.008
Milk	1	none detected	0.001	0.006
Shag eggs	62 (pooled)	none detected	0.0001	2.1
Potatoes	2	none detected	0.005	0.04
Soil	2	none detected	0.01	0.12
Forage beet foliage	1	0.02	0.01	0.09
Forage beet	1	none detected	0.008	0.005

and the pooled body fat from 10 people has also been analysed.

A pooled sample of shag eggs (corresponding to 62 eggs) was included in the specimens as the dieldrin residues in these eggs are higher than those found in the majority of birds eggs.

Apart from the English mutton samples, Argentine beef fat, and the foliage of forage beet, the photoconversion product could not be detected in any of the samples examined. The identity of the component in these samples, estimated as the photoconversion product, requires confirmation.

The results of this preliminary survey of the concentration of the photoconversion product of dieldrin in the human diet indicate that this compound is occurring, if at all, in very small amounts in the environment. The failure to find any of the compound in the bulked sample of human fats, even at a level of less than 0.0005 ppm, also indicates that the concentrations of this compound in the environment are very small. The ratio of the concentration of dieldrin to that of the photoconversion product varies from 16:1 to 1000:1. It is concluded, therefore, that the possible conversion of dieldrin by sunlight to an isomer is not significantly increasing the overall residues arising from the use of aldrin and dieldrin.

1. J. ROBURN, Chem. and Ind., 1963, 1555.
2. C. W. BIRD, R. C. COOKSON, and E. CRUNDWELL, J. Chem. Soc., 1961, 4809.