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Detection of Mirex in the Presence of Polychlorinated Biphenyls

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Mirex has reportedly been found in fish extracts, which also contained polychlorinated biphenyls (PCB) (KAISER 1974). Gas-liquid chromatographic (GLC) detection of mirex in this combination is hindered by its coelution with a major PCB component.

Because of the well-documented omnipresence of PCB, and increasing interest in mirex as an environmental contaminant, a study was undertaken to develop procedures for the rapid GLC determination of mirex in the presence of PCB. A simple chromous chloride reduction, following the technique developed (CHAU, 1970a; CHAU, 1970b; CHAU and COCHRANE, 1971a; CHAU et al., 1971b; CHAU, 1972a; CHAU and WILKMSON, 1972b) yielded products from mirex which are eluted in an area of the chromatogram free of PCB components. Mirex was selectively dehalogenated, whereas the aromatic PCB were unaffected by the reagent. The result was similar to the photochemical reduction procedure developed (LEWIS et al. 1975).

MATERIALS AND METHODS

Frozen ocean perch fillets were blended for 5 min in a Waring Blendor to a paste consistency. To a 50-g portion of this paste, we added 150-µg Aroclor 1260 and 50-µg mirex. To a second 50-g portion, we added 150-µg Aroclor 1260; a third portion contained 50-µg mirex, and a final 50-g portion was analyzed without additions. Each portion was remixed and then blended for 5 min with 10-g sodium sulfate plus 200-mL acetonitrile and filtered. After adding 200-mL water, the filtrate was extracted with 100-mL hexane. The hexane extract was washed first with 40 mL of 1:1 mixture of 20% oleum:concentrated sulfuric acid and then with 25 mL of 2:1 mixture of 20% oleum:concentrated surfuric acid (FDA Pesticide Analytical Manual Vol. II). The extract was dried with sodium sulfate, concentrated to about 10 mL, placed onto a 2X14-cm Florisil (activated for 5 h at 135°C) column, and eluted with 200 mL of 6% (v/v) ethyl ether in hexane. This eluant was concentrated to an appropriate volume (about 0.1 mL), using a stream of dry nitrogen, and a portion analyzed at 230°C on a 1.8 m x 2-mm GLC column containing 10% DC-200 and 15% QF-1 on 80/100 acid-washed chromosorb W to give chromatograms before reduction by the chromous chloride treatment.

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The remaining concentrate was transferred to a 15-mL conical test tube and further evaporated to near dryness. While a vigorous stream of dry nitrogen excluded air from the conical tube, 2-mL dimethylformamide and 1-mL of chromous chloride solution were added, and the tube was stoppered and secured by a spring clamp and immediately immersed in water at 100° for 45 min, after which it was immediately extracted with 5-mL hexane. The hexane extract was concentrated to an appropriate volume and analyzed on the above column.

RESULTS AND DISCUSSION

Chromatograms before reduction of fish and mirex, fish and Aroclor, and fish, mirex, and Aroclor demonstrated the coelution of mirex with a major component of Aroclor (Figs. 1-B,C,D). Chromatograms of these same samples after reduction (Figs. 1-F,G,H)

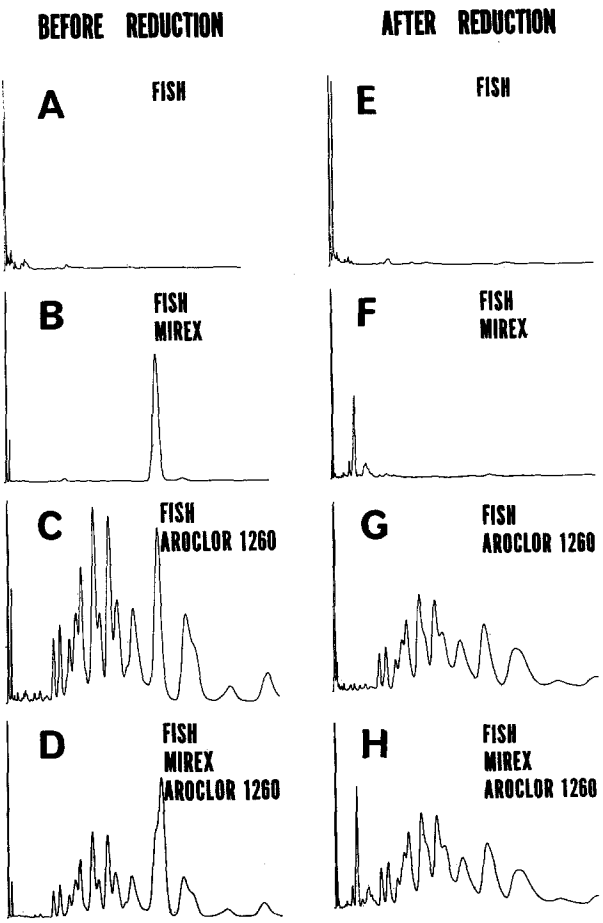

FIG 1

with chromous chloride showed the presence of the mirex-reduction products in the early window of Aroclor 1260. The extent of reductive dechlorination, and, therefore, the pattern of reduction products was highly dependent on both the temperature and duration of the reaction. The reaction of Aroclor 1260 with chromous chloride does not produce reduction products which elute in the normal Aroclor 1260 window. The final paired graphs clearly demonstrated the detection of mirex in the presence of Aroclor 1260.

An investigation is currently underway to determine the structure of the major mirex reduction product under these conditions. This technique has not been applied to Aroclor other than type 1260. Different reaction conditions may be required to produce mirex reduction products which will be eluted in component-free regions of these Aroclors.

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