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High-Pressure Liquid Chromatographic Separation of *o,p'*- and *p,p'*-Dicofol and Their Dichlorobenzophenone Degradation Products

J. Kvalvåg*, Y. Iwata, and F. A. Gunther
Department of Entomology, University of California, Riverside, Calif. 92521

The thermal decomposition of p,p'-dicofol [Kelthane, 4-chloro-α-(4-chlorophenyl)-α-(trichloromethyl)benzenemethanol] to p,p'-dichlorobenzophenone on gas chromatographic columns was demonstrated by GUNTHER et al. (1962). Although BLACK et al. (1971) succeeded in reducing the decomposition by proper selection of column packing material, it is still an inconvenient way to obtain reliable analytical results. The work of WESTLAKE et al. (1966) to clarify the confusion caused by the similarity in gas and thin-layer chromatographic behavior exhibited by o,p'-dicofol and heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene) was continued by OTT et al. (1966) to give a method for the determination at ambient temperature of the two p,p'-compounds by oscillopolarography after thin-layer chromatographic preparation.

The improvements in high-pressure liquid chromatographic equipment that have taken place in this decade have made liquid chromatography into a highly versatile tool for pesticide analysis at ambient temperature. Conditions for the separation of the two dicofol and two dichlorobenzophenone isomers by this technique are given here.

MATERIALS AND METHODS

Instruments. The Waters Associates liquid chromatograph consisted of a septum injection system, two Model 6000 reciprocating pumps, and a Model 660 solvent flow programmer. The column used was a 0.5 m x 2.2 mm i.d. stainless steel tube dry-packed with Bondapak^R C_{18} ODS on 37-50 μm diameter Corasil silica. The detector was a tunable wavelength Perkin-Elmer Model LC-55 combined UV/VIS spectrophotometer equipped with a micro flow-cell. The output was connected to a recorder operating in the 0-100 mv range; chart speed was 1.3 cm/min. Full-scale recorder deflection represented 0.2 absorbance units.

Reagents. Commercial spectroquality dioxane, analytical reagent quality acetone, and redistilled water were used after degassing under reduced pressure.

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*Current address: Chemical Research Laboratory, Agricultural University of Norway, P.O. Box 31, N-1432 Ås-NLH, Norway.

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Analytical conditions. The detector wavelength setting was 240 nm, with output in absorbance units. A 10-µl solution containing 1.0 µg of each of *o,p*'- and *p,p*'-dichlorobenzophenone or 5 µl containing 3.0 µg of the technical acaricide (Kelthane 40MF emulsifiable concentrate) was injected by the stop flow technique. A flow of 2.0 ml/min was started from an initial condition of 90% Solvent A (water containing 1.2% acetone) and 10% Solvent B (dioxane). The amount of dioxane was increased linearly to 80% over 12 min.

RESULTS AND DISCUSSION

Figure 1 shows the peak shapes and separation obtained for a mixture of one µg each of *o,p*'- and *p,p*'-dicofol and *o,p*'- and *p,p*'-dichlorobenzophenone when using the described liquid chromatographic conditions. The use of 1.2% acetone in the water was found to reduce the baseline drift accompanying the increasing amount of dioxane in the eluting solvent mixture. Thus, acetone can be used in reverse-phase chromatography to counteract baseline drift of a spectrophotometric detector in the same way SNYDER and SAUNDERS (1969) used carbon disulfide and other compounds with early UV-cutoff when the UV-absorbance of the eluting phase changed in the course of a solvent programmed run in normal-phase chromatography.

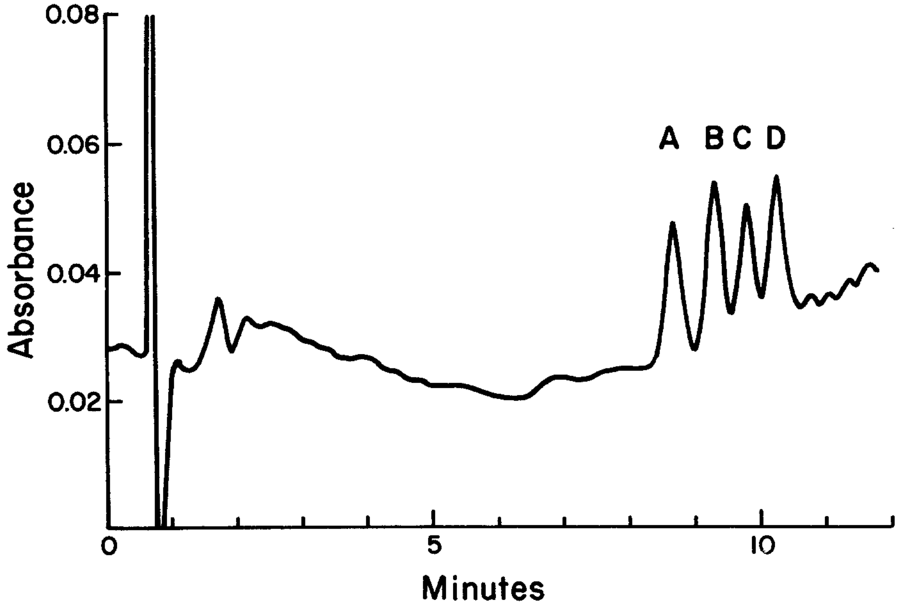

Figure 1. Liquid chromatographic separation of one µg each of A = *o,p*'-dichlorobenzophenone, B = *p,p*'-dichlorobenzophenone, C = *o,p*'-dicofol, and D = *p,p*'-dicofol.

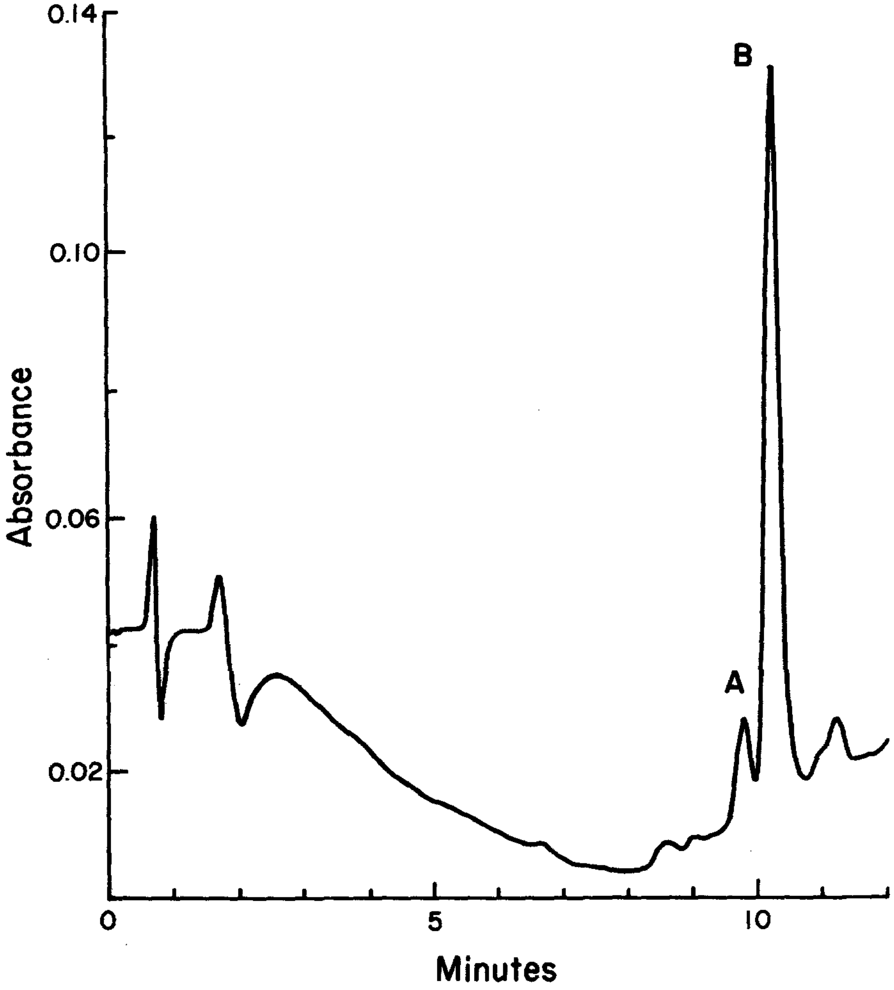

Figure 2. Liquid chromatogram of A = o,p'-dicofol and B = p,p'-dicofol in Kelthane 40MF emulsifiable formulation.

The packing material of the column was a relatively coarse material of particle size 37-50 μm in diameter and the separation of p,p'-dichlorobenzophenone and o,p'-dicofol proved difficult. The described flow program and flow rate represent optimum conditions for the separation. The use of the coarse material for column packings gives a column with less separation capability than the increasingly used packings with particle size of 10 μm in diameter. When a separation can be achieved, however, by means of a column filled with coarse material, it is advantageous since column efficiency is less affected by the extraneous materials in the environmental samples injected onto it.

Figure 2 shows the liquid chromatogram obtained for Kelthane 40MF emulsifiable concentrate. The isomeric o,p'-dicofol is the most abundant impurity that can be detected. The retention value of heptachlor is about twice that of the compounds shown.

REFERENCES

BLACK, R. F., C. P. KURTZ, and H. BAUM: J. Assoc. Offic. Anal. Chem. 54, 1237 (1971).

GUNTHER, F. A., J. H. BARKLEY, R. C. BLINN, and D. E. OTT: Pestic. Res. Bull., Stanford Res. Inst. 2, 2 (1962).

OTT, D. E., F. E. HEARTH, and F. A. GUNTHER: Bull. Environ. Contam. Toxicol. 1, 181 (1966).

SNYDER, L. R. and D. L. SAUNDERS: J. Chromatog. Sci. 7, 195 (1969).

WESTLAKE, W. E., R. T. MURPHY, and F. A. GUNTHER: Bull. Environ. Contam. Toxicol. 1, 29 (1969).