

**Table III. Recovery of Chloroform from FW-293**

| Fw-293,<br>$\gamma$ | Chloro-<br>form<br>equiv.,<br>$\gamma$ | Absorbance |                 |               |
|---------------------|--|------------|-----------------|---------------|
|                     |  | FW-293     | Chloro-<br>form | %<br>Recovery |
| 10                  | 3.2                                    | 0.035      | 0.036           | 97.2          |
| 20                  | 6.3                                    | 0.068      | 0.072           | 94.4          |
| 40                  | 12.6                                   | 0.131      | 0.144           | 91.0          |
| 80                  | 25.2                                   | 0.255      | 0.288           | 88.5          |

**Table IV. Reliability of Over-all Method**

| FW-293,<br>$\gamma$ | Absorbance        |
|---------------------|-------------------|
| 10                  | 0.039 $\pm$ 0.001 |
| 20                  | 0.073 $\pm$ 0.003 |
| 40                  | 0.133 $\pm$ 0.002 |
| 80                  | 0.257 $\pm$ 0.003 |

**Table V. Apparent Recovery of FW-293 in Extracts from Valencia Orange Peel**

| Orange<br>Peel, G. | FW-293, P.p.m. |           | %<br>Recovery |
|--------------------|----------------|-----------|---------------|
|                    | Added          | Recovered |               |
| 5                  | 10.0           | 12.5      | 125           |
| 5                  | 10.0           | 10.2      | 102           |
| 25                 | 9.0            | 8.9       | 99            |
| 25                 | 9.0            | 8.8       | 98            |
| 25                 | 4.5            | 4.3       | 96            |
| 25                 | 4.5            | 4.2       | 93            |
| 50                 | 1.0            | 0.8       | 80            |
| 50                 | 1.0            | 1.0       | 100           |
| 50                 | 0.1            | 0.1       | 100           |
| 50                 | 0.1            | 0.1       | 100           |

show that the combination of the stoichiometry of the reaction with alkali and the efficiency of the collection of chloroform afford an average recovery of 93%.

The reliability of the over-all method, shown in Table IV, is equivalent to that for the color development step alone (Table II).

Recovery data obtained at 10, 1.0,

and 0.1 p.p.m. of FW-293 added to the total petroleum ether extractives from Valencia orange peel are shown in Table V and indicate little interference from the orange extractives.

The time required to sweep the liberated chloroform completely from the reaction mixture was established as 20 minutes at 100° C., as shown in Figure 6; sweeping at a room temperature of 30° C. required at least 60 minutes.

**Interferences.** The following materials could contribute colored solutions under the conditions of this procedure (76): methyl chloride, methylene chloride, chloroform, carbon tetrachloride, methyl chloroform, tetrachloroethane, bromoform, or any large molecule capable of liberating these compounds under present conditions. There are currently no known commercial insecticides that will interfere with the present method, including *p,p'*-DDT, *p,p'*-TDE, BHC, and Perthane (ethyl analog of TDE). Petroleum ether extractives from the following crops have been found not to interfere: almonds, apples, grapes, lemons, oranges, peaches, pears, and tomatoes.

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## PESTICIDE DETERMINATION

### Ultraviolet Spectrophotometric Microdetermination of the Acaricide 4,4'-Dichloro- $\alpha$ -(trichloromethyl)-benzhydrol (FW-293)

The *p,p'*-dichlorobenzophenone resulting from the alkaline hydrolysis of the new acaricide, 4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol, or FW-293, may be determined, quantitatively, directly by its absorption at 264 m $\mu$  (molar absorbance index 21,540 in ethyl alcohol) or indirectly by the absorption of its 2,4-dinitrophenylhydrazone in alcoholic alkali at 510 m $\mu$ . In residue applications, chromic anhydride oxidation of extraneous extractives is recommended. Under optimum conditions the method responds to 10  $\gamma$  of FW-293 with 84% efficiency in the presence of citrus peel extractives.

**A**N ANALYTICAL METHOD, based upon the absorption of ultraviolet energy at 264 m $\mu$  by the *p,p'*-dichlorobenzophenone moiety of the acaricide, 4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol,

is presented. A colorimetric method for the microdetermination of this acaricide has been discussed (5).

The purified crystalline acaricide (melting point 78.5° to 79.5° C.) exhib-

its the ultraviolet spectrum, *A*, shown in Figure 1; the ultraviolet absorption characteristics, *B*, of *p,p'*-dichlorobenzophenone are also shown. Molar absorbance index values for the parent acaricide

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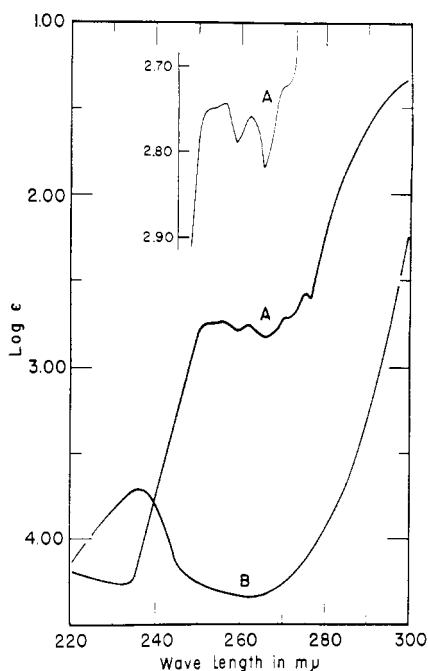


Figure 1. Ultraviolet absorption characteristics of 4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol, A, and *p,p'*-dichlorobenzophenone, B, in 95% ethyl alcohol

in 95% ethyl alcohol are 666 at 265.5  $m\mu$  and 18,640 at 232  $m\mu$ ; in 2,2,4-trimethylpentane the values are 670 at 265.5  $m\mu$  and 19,820 at 232  $m\mu$ . The derived ketone in 95% ethyl alcohol possesses a molar absorbance index value of 21,540 at 264  $m\mu$ .

FW-293 was hydrolyzable under mild conditions to yield, quantitatively, *p,p'*-dichlorobenzophenone. For example, this hydrolysis may be accomplished at room temperature in excess 0.013*M* alcoholic potassium hydroxide, in some commercial samples of acetonitrile, and in alcoholic solutions of ammonia. The resulting ketone can be determined directly by its absorption at 264  $m\mu$  or, if a colorimetric procedure is preferred, by the absorption of its readily formed 2,4-dinitrophenylhydrazone in alcoholic alkali at 510  $m\mu$  (7). Advantage can be taken of the stability of FW-293 in ethyl alcohol solutions to use the "split-blank" procedure (2) to compensate for substrate interferences. For very oily or waxy substrates, an oxidative cleanup procedure (2, 3) is recommended to reduce the bulk of the extracted oils and waxes. This so-called oxidative "total ketone" procedure presumably responds also to other possible metabolic and degradation products of 4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol.

**Reagents.** All chemicals are analytical reagent grade, except where specifically indicated.

Petroleum ether, boiling range 60° to 80° C.

Acidified acetonitrile. Add 1 ml. of

glacial acetic acid to 100 ml. of commercial grade acetonitrile.

Wash solution. Add 1 ml. of glacial acetic acid to 1000 ml. of water.

Light petroleum ether, boiling range 30° to 60° C.

Sodium sulfate, anhydrous.

Glass wool.

Ethyl alcohol, 95%.

Ammonia-ethyl alcohol solution. Add anhydrous ammonia to 95% ethyl alcohol until the concentration exceeds 15 mg. per ml., as determined by titration. Dilute with 95% ethyl alcohol to a concentration of 15.0  $\pm$  0.2 mg. per ml. and store in a tightly sealed bottle.

Sodium hydroxide, 4% solution.

Sodium hydroxide, saturated solution.

Acetic acid, glacial.

Chromic anhydride.

4,4'-Dichloro- $\alpha$ -(trichloromethyl)benzhydrol, melting at 78.5° to 79.5° C. An analytical sample was furnished by Rohm & Haas Co., Philadelphia, Pa.

*p,p'*-Dichlorobenzophenone, melting at 146.3° to 147.1° C.

**Special Apparatus.** Spectrophotometer. Any type that responds satisfactorily at 264  $m\mu$  may be used. A Beckman Model DU was used for the routine analytical procedure; absorption characteristics and reaction rates were determined by use of a Beckman Model DR recording attachment for the Model DU.

Kuderna-Danish evaporative concentrators (2).

**Partition Distribution of FW-293 into Acetonitrile.** A measured volume of filtered petroleum ether (boiling point 60° to 80° C.) stripping solution in a 500-ml. § 24/40 Erlenmeyer flask is evaporatively concentrated on a steam bath through a three-ball Snyder column to less than 50 ml.; then it is transferred to a 500-ml. separatory funnel and shaken for 30 seconds—first with a 50-ml. portion and then with a 5-ml. portion of acidified acetonitrile. The combined acetonitrile extracts are combined in a 500-ml. separatory funnel with 250 ml. of wash solution and extracted for 30 seconds with 150 ml. of light petroleum ether (boiling point 30° to 60° C.); the lower aqueous phase is discarded. The petroleum ether solution is washed with three 25-ml. portions of wash solution, then passed through a Gooch crucible holder, containing a plug of glass wool and 5 grams of anhydrous sodium sulfate, into a Kuderna-Danish evaporative concentrator for the split-blank method (2) or into a 500-ml. § Erlenmeyer flask for the oxidative total-ketone method. The separatory funnel is rinsed with 100 ml. of light petroleum ether, which is also passed through the sodium sulfate into the concentrator or Erlenmeyer flask. For the total-ketone procedure, 2 ml. of saturated sodium hydroxide solution is next added to the combined petroleum ether solutions. For either method, the solution is concentrated in the usual manner to 1 or 2 ml.

**Split-Blank Procedure.** After the above concentrate has been transferred

Table I. Percentage Partition of 4,4'-Dichloro- $\alpha$ -(trichloromethyl)benzhydrol into Acetonitrile from 1.00 Volume of Petroleum Ether

| Comparative Volume Acetonitrile | % in Acetonitrile |
|---------------------------------|-------------------|
| 1.00                            | 90.0              |
| 0.50                            | 71.2              |
| 0.35                            | 48.2              |
| 0.25                            | 58.5              |

Table II. Hydrolysis Rate Constants and Half-Life Values for 4,4'-Dichloro- $\alpha$ -(trichloromethyl)benzhydrol in Ammonia-Ethyl Alcohol Solutions at 30° C.

| Ammonia, Mg./Ml. of Final Solution | Half Life, Min. |
|------------------------------------|-----------------|
| 4                                  | 27              |
| 6                                  | 10              |
| 8                                  | 7               |

to a 10-ml. volumetric flask with 5 ml. of light petroleum ether, it is evaporated to dryness on a steam bath with the ground-glass stopper loosely in place to minimize entrainment losses. Last traces of solvent are removed with the aid of a gentle suction, the residue is dissolved in exactly 4 ml. of 95% ethyl alcohol, and 2 ml. of this solution is pipetted into another 10-ml. volumetric flask and then diluted to volume with ammonia-ethyl alcohol solution. The remaining aliquot is diluted to 10 ml. with ethyl alcohol. After 1 hour, the transmittancy of the ammonia-ethyl alcohol solution is determined at 264  $m\mu$ , using the alcohol solution as a reference solution. A standard curve may be prepared from purified *p,p'*-dichlorobenzophenone (melting point 146.3° to 147.1° C.). However, until interferences from different substrates have been evaluated, it is recommended that a standard curve be prepared from control extractives fortified with purified FW-293, using the exact procedure presented.

**Total-Ketone Procedure.** To the aqueous residue in the Erlenmeyer flask are added 50 ml. of glacial acetic acid and 9 grams of chromic anhydride, with refluxing for 10 minutes. If at this time the solution has a greenish cast, an additional 6 grams of chromic anhydride is added and refluxed for 10 minutes. After cooling, the mixture is transferred to a 500-ml. separatory funnel with 250 ml. of wash solution and 150 ml. of light petroleum ether; this is shaken for 30 seconds and the aqueous layer is discarded. The petroleum ether solution is washed with two 100-ml. portions of wash solution and two 25-ml. portions of 4% sodium hydroxide solution, then passed through a Gooch crucible holder, containing a plug of glass wool and 5 grams of anhydrous sodium sulfate, into a Kuderna-Danish evaporative concentrator.

The separatory funnel is rinsed with 100 ml. of light petroleum ether, which is also passed through the sodium sulfate into the concentrator. After concentration in the usual manner to 1 or 2 ml., the concentrate is transferred to a 10-ml. volumetric flask with 5 ml. of light petroleum ether, then evaporated to dryness on a steam bath with the ground-glass stopper loosely in place to minimize entrainment losses. Next, 5 ml. of 95% ethyl alcohol is added and the mixture is evaporated on a hot plate until the volume is 1 to 2 ml. After the dilution of the concentrate to volume with 95% ethyl alcohol, the transmittancy is determined at 264  $m\mu$ , using a reference solution derived from a control sample which has been subjected to exactly the same cleanup and analytical procedures as the sample itself. A standard curve may be prepared from purified *p,p'*-dichlorobenzophenone (melting point 146.3° to 147.1° C.), but until interferences from different substrates have been evaluated, it is recommended that a standard curve be prepared from control extractives fortified with purified FW-293, using the exact procedure presented.

#### Comments on Procedures

The partition distribution of 4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol from petroleum ether (boiling point 60° to 80° C.) into acidified acetonitrile is shown in Table I.

The rates of hydrolysis of FW-293 in various concentrations of ammonia in 95% ethyl alcohol are listed in Table II.

The table shows that the ultraviolet procedure gives virtually a quantitative conversion into the benzophenone in the time specified.

With the split-blank procedure (2) the method is specific for FW-293, as only

**Table III. Typical Recoveries of 4,4'-Dichloro- $\alpha$ -(trichloromethyl)benzhydrol by the Split-Blank Method**

| Added,<br>$\gamma$ | Recovered |      |
|--------------------|-----------|------|
|                    | $\gamma$  | %    |
| 23                 | 18        | 78.3 |
| 37                 | 27        | 73.0 |
| 37                 | 34        | 92.0 |
| 115                | 102       | 88.7 |
| 115                | 104       | 90.3 |
| 115                | 102       | 88.7 |
| 218                | 188       | 86.4 |
| 218                | 183       | 84.1 |

**Table IV. Typical Recoveries of 4,4'-Dichloro- $\alpha$ -(trichloromethyl)benzhydrol from Citrus Peel Extractives by the Total-Ketone Procedure**

| Added    |        | Recovered |        |    |
|----------|--------|-----------|--------|----|
| $\gamma$ | P.p.m. | $\gamma$  | P.p.m. | %  |
| 20       | 0.1    | 15        | 0.075  | 75 |
| 100      | 1.0    | 88        | 0.88   | 88 |
| 100      | 1.0    | 86        | 0.86   | 86 |
| 500      | 10.0   | 400       | 8.0    | 80 |
| 500      | 10.0   | 455       | 9.1    | 91 |

compounds which are very susceptible to hydrolysis with accompanying increase in absorptivity at 264  $m\mu$  will respond; also, minor interferences are automatically compensated. Only substances which absorb by themselves or which are very easily hydrolyzed to substances which strongly absorb ultraviolet energy will interfere.

The ultraviolet absorption characteristics of FW-293 and *p,p'*-dichlorobenzophenone are reproduced in Figure 1. A calibration curve for *p,p'*-dichlorobenzophenone prepared by the present procedure conforms to Beer's law from 10 to

280  $\gamma$  at 264  $m\mu$ . The split-blank procedure has an over-all efficiency of 73 to 92%, based upon recovery of *p,p'*-dichlorobenzophenone (Table III).

The total-ketone procedure will respond to most compounds having a



type structure, which

includes many of the probable metabolic and degradation products of 4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol. The total-ketone procedure has an over-all efficiency of 75 to 91%, based upon recovery of *p,p'*-dichlorobenzophenone from citrus peel extract (Table IV). Residues of FW-293 on and in citrus fruits determined by this procedure, as well as by the colorimetric (5) and total-chloride procedures, are presented in another paper (4).

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## INSECTICIDE SYNERGISM

### Mode of Action of Di-(*p*-Chlorophenyl)-(Trifluoromethyl)-Carbinol, as a Synergist to DDT Against DDT-Resistant Houseflies

The recently described di-(*p*-chlorophenyl)-(trifluoromethyl)-carbinol is a very active synergist to DDT for DDT-resistant houseflies and its mode of action has now been studied. The carbinol is absorbed rapidly through the fly cuticle and is fairly stable inside the fly body. The action of minute doses is felt over a period of many days. In vivo, the carbinol inhibits the dehydrochlorination of DDT by DDT-dehydrochlorinase but it also inhibits the penetration of DDT through the fly cuticle. As the compound counteracts its own synergistic activity, an optimum ratio of synergist to DDT exists for maximum effect.

**D**IARYL-(TRIFLUOROMETHYL)-CARBINOLS, of the general formula (*p*-XC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>.C(OH).CF<sub>3</sub> have recently been reported to be very active as DDT

synergists, when applied topically to resistant houseflies (1, 2, 15). The activity of the most potent member of the group, the di-(*p*-chlorophenyl)-(tri-

fluoromethyl)-carbinol, surpasses that of a related compound, 1,1-bis-(*p*-chlorophenyl)-ethanol (DMC), whose mode of action has been described in detail

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