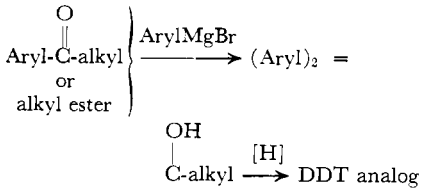
# Insecticidal Properties of Some Topographical Analogs of 1,1-Bis(*p*-chlorophenyl)-ethanol (DMC)

F. A. GUNTHER, R. C. BLINN, and R. L. METCALF

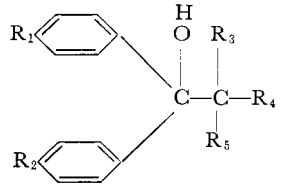
University of California Citrus Experiment Station, Riverside, Calif.

Of a number of systematically substituted 1,1-diphenylmethylcarbinols, 1,1-bis-(*p*-chlorophenyl)-2,2-dichloroethanol and 1,1-bis-(*p*-chlorophenyl)-propanol were as effective as DMC, a commercially established acaricide, against two species of mites. Bioassay data indicate that toxicity of these carbinols is not directly correlatable with van der Waals' attractive forces for an enzyme surface or other interacting surface.

SYNTHESES of a number of topographical analogs of DDT have been mentioned in a preliminary report by Gunther and others (*5*), with the original DDT-chlorine atoms replaced all or in part by hydrogen atoms or methyl groups. Many of the final compounds were prepared according to the following schemes:




Consequently, during the course of this synthetic program, there was made available a secondary series of topographically related compounds, the 1,1-diphenylmethylcarbinols:




R = H, $CH_3$, Cl

The compound $R_1 = R_2$ = Cl and $R_3 = R_4 = R_5$ = H is the well known acaricide DMC, 1,1-bis-(*p*-chlorophenyl)-ethanol. Although Metcalf (*9*) found the related bis-(*p*-chlorophenyl)-methanol to be nearly inactive as an acaricide, it seemed of interest to screen all these carbinols routinely for insecticidal and acaricidal activity. Some of them proved to be effective acaricides in laboratory evaluations. The recent report of Wilson and Barker (*14*) that 1,1-bis-(*p*-chlorophenyl)-2,2-dichloroethanol and -2,2,2-trichloroethanol are highly active acaricides has prompted the present report, for the authors prepared and biologically tested the former compound ($R_1 = R_2 = R_3 = R_4$ = Cl; $R_5$ = H) in February 1951.

### Compounds

In Table I are listed the carbinols according to structural features, their melting points or boiling points, and their carbon-hydrogen analyses. In Table II are listed their ultraviolet maxima and minima as well as their absorptivity indices as additional proof of identity and purity. All ultraviolet spectra were recorded in 2,2,4-trimethylpentane on a Beckman Model DR recording attachment for the Beckman Model DU spectrophotometer.

Because of obvious dehydration during attempted preparations, several carbinols, such as $R_1 = R_3 = R_4$ = H, $R_2 = R_5$ = Cl, and $R_1$ = Cl, $R_2 = R_3 = R_4$ = H, $R_5 = CH_3$, have not been obtained in sufficiently pure form for inclusion in the present report. Presence of the ethylenic dehydration product was readily demonstrable by the quenching of fine structure in the 240- to 280-mμ region.

The absorptivity index values represent compounds purified repeatedly to within 3% agreement between consecutive index values for separate weighings of a given carbinol.

A typical wave length–absorbancy index curve as represented by compound 3295 (Table I) is reproduced in Figure 1.

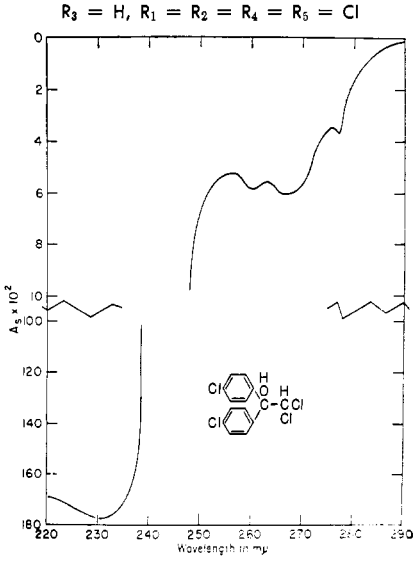
### Bioassay

The carefully purified compounds were evaluated against adult females of *Metatetranychus citri* (McG.), *Tetranychus bimaculatus* Harvey, and *Heliothrips haemorrhoidalis* (Bouché) as residues deposited on mature Valencia oranges by dipping in standard (weight/volume) acetone solutions (*4*, *9*). Five concentrations were used, and the approximate $LC_{50}$ was determined by plotting dosage mortality curves on log-probit paper. The data on larvae of *Culex quinquefasciatus* Say were obtained by adding 1 ml. of standard acetone solution to 100 ml. of water containing the larvae, and the toxicity to *Musca domestica* L. was determined by the topical application of 1-μl. drops of standard acetone solutions to anesthetized female flies (*9*).

### Discussion

From the data in Table III it is apparent that all the carbinols were less than 0.01 times as toxic as DDT to *Musca domestica*, *Culex quinquefasciatus*, and *Heliothrips haemorrhoidalis*. Conversely, however, certain of the carbinols such as numbers 282, 4526, 3295, 4538, 6120, and 6118 were effective acaricides. The most active compounds were number 282, 1,1-bis-(*p*-chlorophenyl)-ethanol or DMC, number 3295, 1,1-bis-(*p*-chlorophenyl)-2,2-dichloroethanol, and number 4538, 1,1-bis-(*p*-chlorophenyl)-propanol. The last two compounds were approximately as effective as DMC, a commercially established acaricide, and are worth further investigation. In these tests the outstanding acaricide was FW-293, 1,1-bis-(*p*-chlorophenyl)-2,2,2-tri-

Figure 1. Wave length–absorbancy index curve from a 2,2,4-trimethylpentane solution of compound 3295

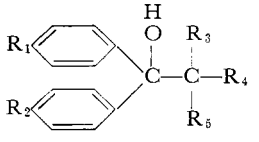


chloroethanol, which is also available commercially.

The aromatic substituents appear to have had a pronounced effect on the acaricidal activity of the carbinols, which was in the approximate order *p,p'*-dichloro>*p*-chloro-*p'*-hydrogen>*p*-chloro-*p'*-methyl>*p,p'*-dimethyl>unsubstituted->*p*-methyl-*p'*-hydrogen. With substitution in the aliphatic portion of the carbinol molecule, the differences in activity appeared to be in the order trichloromethyl > methyl > dichloromethyl>ethyl>isopropyl. The quantitative bioassay data in Table III indicate, however, that both ends of the molecule are important and interdependent in exerting the total biological action. Such an arrangement is therefore without real significance in predicating acaricidal activity of untested compounds.

When the attempt is made to plot the negative logarithms of the $LC_{50}$ value against the sum of the logarithms of the van der Waals attractive forces of the five substituent groups in question (*5*), straight-line plots are not obtained. This indicates that with these insects and mites (Table III) the carbinols tested are not interacting simply and as intact molecules with a proteinlike substance, such as an enzyme, as the primary process (*5*). The transport from outside the

**Table I. Carbinols Tested for Insecticidal and Acaricidal Activity**




| Compound No. | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | M.P., °C. | Calculated, % C | Calculated, % H | Calculated, % Cl | Found, % C | Found, % H | Found, % Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4449 | H | H | H | H | H | 80.3–81.3 | 84.65 | 7.10 | ... | 85.1 (*7*)[a] | 7.1 (*7*) | ... |
| 282 | Cl | Cl | H | H | H | 68.9–70.1 | 62.93 | 4.53 | ... | 62.9 (*3*) | 4.5 (*3*) | ... |
| 4531 | H | H | H | H | Cl | 64.4–65.0 | 72.26 | 5.63 | 15.69 (*8*) | ... | ... | 15.58 (*8*) |
| 4525 | H | H | H | Cl | Cl | 96.1–96.8 | 62.93 | 4.53 | 26.58 (*1*) | ... | ... | 26.65 (*1*) |
| 4526 | H | Cl | H | Cl | Cl | 80.1–80.5 | 55.74 | 3.68 | ... | 55.95 | 3.92 | ... |
| 3295 | Cl | Cl | H | Cl | Cl | 108.1–108.8 | 50.03 | 3.00 | ... | 50.25 (*10*) | 3.25 (10) | ... |
| 4527 | H | $CH_3$ | H | Cl | Cl | 61.8–62.8 | 64.06 | 5.02 | ... | 64.47 | 5.36 | ... |
| 4535 | H | H | H | H | $CH_3$ | 93.4–94.4 | 84.85 | 7.60 | ... | 85.54 (*6*) | 7.30 (*6*) | ... |
| 6116 | H | H | H | $CH_3$ | $CH_3$ | 53.9–54.9 | 84.91 | 8.02 | ... | 84.5 (*11*) | 7.8 (*11*) | ... |
| 6117 | H | H | $CH_3$ | $CH_3$ | $CH_3$ | ...[b] | 84.98 | 8.39 | ... | ... (*2*) | ... (*2*) | ... |
| 4539 | $CH_3$ | $CH_3$ | H | H | $CH_3$ | 41.8–42.8 | 84.98 | 8.39 | ... | 84.82 | 8.74 | ... |
| 6119 | $CH_3$ | $CH_3$ | H | $CH_3$ | $CH_3$ | 96.3–97.3 | 84.98 | 8.72 | ... | 84.9 (*12*) | 8.7 (*12*) | ... |
| 4538 | Cl | Cl | H | H | $CH_3$ | ...[c] | 64.07 | 5.02 | ... | 64.56 | 5.13 | ... |
| 6120 | Cl | $CH_3$ | H | H | $CH_3$ | ...[d] | 73.70 | 6.57 | ... | 73.26 | 6.63 | ... |
| 6118 | Cl | Cl | H | $CH_3$ | $CH_3$ | 113.8–114.8 | 65.10 | 5.46 | ... | 65.26 (*13*) | 5.58 (*13*) | ... |
| FW-293[e] | Cl | Cl | Cl | Cl | Cl | 78.5–79.5 | ... | ... | ... | ... | ... | ... |

[a] Italic numbers in parentheses refer to literature cited.
[b] $n_D^{20}$ = 1.5746; Bateman and Marvel (*2*) reported $n_D^{20}$ = 1.5748.
[c] $n_D^{20}$ = 1.5920.
[d] $n_D^{20}$ = 1.5802.
[e] Courtesy Rohm & Haas Co.

**Table II. Principal Ultraviolet Absorption Maxima and Minima and Molar Absorptivity Indices of Carbinols in 2,2,4-Trimethylpentane Solution**

(See Table I for coded structures of compounds)

| Compound No. | Ultraviolet Absorption, λ Max. | Min. | Max. | Min. | Max. | Min. | Absorptivity Indices λ, mμ | λ, mμ |
|---|---|---|---|---|---|---|---|---|
| 4449 | 264.5 | 262.5 | 258.5 | 255 | 252.5 | 240 | 395/258.5 | 317/252.5 |
| 282 | 276 | 273.5 | 267.5<br>260.5 | 263<br>251 | 227.5<br>224 | 225.5 | 720/267.5 | 20,600/227.5 |
| 4531 | 264.5 | 263 | 258.5 | 255 | 252.5 | 240 | 425/258.5 | 335/252.5 |
| 4525 | 269<br>265.5 | 268<br>264 | 263<br>259 | 262<br>255 | 253<br>220 | 244.5 | 452/259 | 11,150/220 |
| 4526 | 265<br>262.5 | 264<br>261.5 | 259<br>253 | 255 | 228 | 250 | 495/259 | 15,140/228 |
| 3295[a] | 277 | 275 | 266.5 | 263 | 260.5 | 256.5 | 600/266.5 | 21,200/231 |
| 4527 | 263.5 | 261.5 | 259.5 | 248.5 | 224.5 | ... | 509/259.5 | 12,430/224.5 |
| 4535 | 265 | 263 | 258.5 | 255.5 | 253 | 241 | 452/258.5 | 380/253 |
| 6116 | 265 | 264 | 259 | 255.5 | 253.5 | 245.5 | 437/259 | 373/253.5 |
| 6117 | 270.5 | 269.5 | 264.5 | 263<br>255.5 | 258.5<br>253 | 238 | 413/264.5 | 473/258.5 |
| 4539[b] | 274 | 271 | 265 | 261.5 | 224.5 | 248 | 710/265 | 14,520/224.5 |
| 6119[c] | 275 | 272 | 266 | 262.5 | 226.5 | 251 | 750/266 | 13,560/226.5 |
| 4538 | 276.5 | 274 | 268<br>254 | 265<br>226.5 | 228.5<br>225 | 252.5 | 889/268 | 20,000/228.5 |
| 6120 | 273<br>268 | 272<br>267 | 265<br>260.5 | 262.5 | 224.5 | 250 | 791/265 | 17,080/224.5 |
| 6118[d] | 277 | 275 | 269 | 265 | 230.5 | 257.5 | 867/269 | 18,780/230.5 |
| FW-293 | 276<br>271.5 | 275<br>270 | 265.5<br>258.5 | 263 | 232 | 255.5 | 669/265.5 | 19,820/232 |

[a] Additional strong absorption maximum at 231 mμ.
[b] Additional strong absorption maximum at 259.5 mμ.
[c] Additional strong absorption maximum at 260.5 mμ.
[d] Additional strong absorption maximum at 262 mμ.

**Table III. Bioassay Data for Carbinols**

| Compound No.[a] | ΣLog $K_0'$[b] | —Log $LC_{50}$ *Metatetranychus citri* | —Log $LC_{50}$ *Tetranychus bimaculatus* | —Log $LC_{50}$ *Heliothrips haemorrhoidalis* | $LC_{50}$, P.P.M., *Culex quinquefasciatus* | Topical $LD_{50}$, γ/G., *Musca domestica* |
|---|---|---|---|---|---|---|
| 4449 | 0.00 | 0.16 | 0.00⁻ | 0.05 | 10–100 | >500 |
| 282 | 1.00 | 0.82 | 1.22 | 0.03 | 10 | >500 |
| 4531 | 0.50 | 0.30 | 0.47 | 0.54 | 10–100 | >500 |
| 4525 | 1.00 | 0.00⁻ | 0.00⁻ | 0.00⁻ | 10 | >500 |
| 4526 | 1.50 | 0.70 | 0.70 | 0.55 | 1–10 | >500 |
| 3295 | 2.00 | 0.82 | 1.05 | 0.85 | 1–10 | >500 |
| 4532[c] | 1.00 | 0.00⁻ | 0.00⁻ | 0.00⁻ | 10–100 | >500 |
| 4527 | 1.39 | 0.05 | 0.00⁻ | 0.70 | 1–10 | >500 |
| 4535 | 0.39 | 0.22 | 0.07 | 0.09 | 10–100 | >500 |
| 6116 | 0.78 | −0.08 | 0.17 | 0.29 | 10–100 | >500 |
| 6117 | 1.11 | 0.22 | 0.22 | 0.09 | 10–100 | >500 |
| 4539 | 1.11 | 0.27 | 0.17 | −0.15 | 10 | >500 |
| 6119 | 1.56 | 0.00⁻ | 0.00⁻ | 0.00⁻ | 1–10 | >500 |
| 4536[d] | 0.89 | 0.17 | 0.27 | 0.20 | 1–10 | 500 |
| 4538 | 1.39 | 0.75 | 1.05 | −0.08 | 1–10 | >500 |
| 6120 | 1.28 | 0.66 | 0.33 | 0.00⁻ | 1–10 | >500 |
| 6118 | 1.78 | 0.60 | 0.62 | 0.00⁻ | 1–10 | >500 |
| *p,p'*-DDT | 2.50 | 0.00⁻ | 0.00⁻ | 3.00 | 0.01–0.1 | 1.65 |
| FW-293 | 2.50 | 1.70 | 1.80 | 0.30 | ... | ... |

[a] See Table I for coded structures of compounds.
[b] See (*5*); this value represents sum of logarithms of van der Waals attractive forces of five substituent groups, with H = 1.00.
[c] Compound 4532 ($R_1 = R_3 = R_4 = H$, $R_2 = R_5 = Cl$) may be of questionable purity; b.p. 140–4°/1.5 mm. (not listed in Table I).
[d] Compound 4536 ($R_1 = R_3 = R_4 = H$, $R_2 = Cl$, $R_5 = CH_3$) may be of questionable purity (not listed in Table I).

cuticle to the site of action (*5*) may be the limiting mechanism in this study.


### Acknowledgment

The authors wish to thank R. B. Carlson and Marion McMahon for invaluable laboratory assistance, and the Rohm & Haas Co. for a purified sample of the acaricide FW-293.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**PESTICIDE FORMULATION**

# Hydroquinone and Its Derivatives as Stabilizers for Pyrethrum and Allethrin


**ALAN BELL**

**Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.**

**GEORGE S. KIDO**

**Insecticide Testing Laboratory, Wisconsin Alumni Research Foundation, Madison, Wis.**


INSECTICIDAL PREPARATIONS CONTAINING PYRETHRUM deteriorate with age and deterioration is hastened by exposure to air, heat, and sunlight. For these reasons, a stabilizer is desired to maintain reasonably good keeping qualities. In this work, hydroquinone and four of its derivatives were incorporated into pyrethrum dusts and tested as stabilizers. Two of the compounds were also studied as stabilizers for allethrin, which is closely related to some of the components of pyrethrum. The insecticidal, active components of pyrethrum are pyrethrins I and II and cinerins I and II, to which allethrin is closely related.

The stability of pyrethrum, which has been the subject of numerous investigations, is dependent on the physical state of the formulation. Fine dust mixtures and ground or pulverized pyrethrum flowers lose insecticidal activity more rapidly than whole flowers (*22*).

Moreover, artificially prepared dusts consisting of pyrethrum extracts combined with inert diluents lose activity more rapidly than ground pyrethrum flowers (*19, 21*), partly because more surface is exposed. Gnadinger and others