[Contribution from the Entomology Research Branch, Agricultural Research Service, United States Department of Agriculture]

# Allethrin. Synthesis of Four Isomers of *cis*-Allethrin

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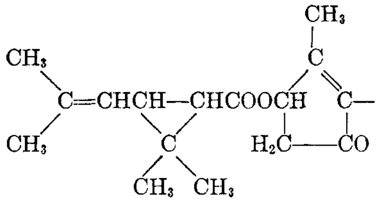
Allethrin, a commercially produced insecticide of the pyrethrin type, is a mixture of eight possible isomers. The four *trans* isomers have been described previously. To complete the series, the four *cis* isomers have now been prepared. These forms are now being investigated for relationships between isomerism (optical and geometric) and insecticidal properties.

Allethrin, a synthetic insecticide of the pyrethrin type developed in 1948[2,3] is being produced commercially[3,4] to supplement supplies of imported pyrethrum and is used chiefly in aerosol bombs and fly sprays.

Because of optical and geometric isomerism, allethrin, which is a mixture of esters of *dl-cis-* and *dl-trans*-chrysanthemum monocarboxylic acids with *dl*-allethrolone, can be considered as consisting of eight optically active stereoisomers or four racemic isomers. One of the racemic isomers, *alpha-dl-trans*-allethrin, was isolated in crystalline form by Schechter, *et al.*[5] The four optical isomers having *trans*-chrysanthemum monocarboxylic acid components have been described and the composition of the *alpha-dl-trans* isomer has been established.[6]



ALLETHRIN

The present article describes the preparation of the four optically active isomers of the *cis*-chrysanthemum monocarboxylic acid series. The preparation of these isomers involved the resolution of *dl*-allethrolone as described in our previous article[6] into *d*- and *l*-allethrolones and their acylation with *d-cis-* and *l-cis*-chrysanthemum monocarboxylic acids (*via* the acid chlorides). The resolution of the *dl-cis* acid was accomplished by the method of Campbell and Harper.[7] The esters were prepared by acylating the resolved allethrolones, employing the optically active *cis*-chrysanthemum monocarboxylic acid chlorides in benzene-pyridine.

These optically active allethrin isomers will permit studies to be made of the relationships of optical and geometric isomerism of the allethrin molecule to insecticidal toxicity and synergism, the results of which will be reported elsewhere.

## EXPERIMENTAL

*d- and l-Allethrolones. d*-Allethrolone, b.p. 125–128°/0.5 mm., $[\alpha]^{25}_{D}$ +8.6° (no solvent), and *l*-allethrolone, b.p. 101–109°/0.05 mm., $[\alpha]^{25}_{D}$ −8.7° (no solvent), were prepared as described previously[6] and showed the same rotations.

*d- and l-cis Chrysanthemum monocarboxylic acids.* The *d-cis* acid had b.p. 100–104°/0.4 mm., m.p. 50–51°, $[\alpha]^{23}_{D}$ +60.3° (supercooled, no solvent), $[\alpha]^{27}_{D}$ +59.5° (supercooled, no solvent), $[\alpha]^{24}_{D}$ +83.0° (*c*, 1.75 in chloroform), and a second lot had b.p. 89–94°/0.03 mm., $[\alpha]^{29}_{D}$ +59.3° (supercooled, no solvent). The *l-cis* acid had b.p. 95°/0.12 mm., m.p. 50–51°, $[\alpha]^{26}_{D}$ −59.2° (no solvent), $[\alpha]^{26}_{D}$ −86.3° (*c*, 1.97 in chloroform). Campbell and Harper[7] give b.p. 95°/0.1 mm., m.p. 41–43°, $[\alpha]^{20}_{D}$ +83.3° (*c*, 1.034 in chloroform) for the *d-cis*-acid, and m.p. 41–43°, $[\alpha]^{19}_{D}$ −83.3° (*c*, 1.555 in chloroform) for the *l-cis*-acid.

TABLE I

Optically Active Esters of Allethrolone with *cis*-Chrysanthemum Monocarboxylic Acid

| Allethrin Components | | | | | $[\alpha]^{25}_{D}$ | | | |
|---|---|---|---|---|---|---|---|---|
| Allethrolone | *cis*-Acid | B.p., °C. | Mm. | $n^{25}_{D}$ | Kerosene[a] | No solvent | Analysis[b] C | H |
| *d* | *d* | 142–148 | 0.25 | 1.5080 | + 5.6 | +13.5 | 74.79 | 8.47 |
| *l* | *l* | 135–140 | 0.05 | 1.5070 | − 5.5 | −14.8 | 75.08 | 8.59 |
| *d* | *l* | 144–146 | 0.1 | 1.5074 | −19.7 | −19.4 | 74.59 | 8.84 |
| *l* | *d* | 147–148 | 0.1 | 1.5076 | +19.1 | +19.0 | 75.19 | 8.57 |

[a] *c* = 16 in purified kerosene (Deobase). [b] Calc'd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67.

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[1] Retired in 1952.

[2] Schechter, Green, and LaForge, *J. Am. Chem. Soc.*, **71**, 3165 (1949).

[3] Roark, *U. S. Bur. Ent. and Plant Quar., E-846* (1952); Roark and Nelson, *U. S. Dept. of Agriculture, ARS-33-12* (1955).

[4] Sanders and Taff, *Ind. Eng. Chem.*, **46**, 414 (1954).

[5] Schechter, LaForge, Zimmerli, and Thomas, *J. Am. Chem. Soc.*, **73**, 3541 (1951).

[6] LaForge, Green, and Schechter, *J. Org. Chem.*, **19**, 457 (1954).

[7] Campbell and Harper, *J. Sci. Food Agr.*, **4**, 189 (1952).

*Acid chlorides.* The optically active acids were converted to acid chlorides in the usual manner by employing a 20% excess of thionyl chloride in 2 to 3 volumes of low-boiling petroleum ether. The solution was allowed to stand overnight at room temperature under a reflux condenser protected by a drying tube, and the solvent and excess thionyl chloride were removed under reduced pressure. The acid chlorides were distilled in a high vacuum employing a Dry Ice-cooled receiver. They boiled at about 76–78°/0.03 mm. If the distillation is carried out at water-pump pressure, the esters prepared from the acid chlorides will not have the correct optical rotation.[8] This matter is being investigated.

*Optically active esters.* The acylations of the allethrolones with the acid chlorides were all performed in benzene-pyridine solution in the manner described[6] for the esters of the *trans* series, except that no excess of acid chloride was used. The quantities employed in a typical experiment were 4.35 g. (0.0286 mole) of the allethrolone, 5.34 g. (0.0286 mole) of the acid chloride, 3.2 ml. of pyridine, and 50 ml. of benzene.

The properties of the four esters are given in Table I. The final esters were distilled in a high vacuum, small foreruns and residues in each case being discarded. The yields of distilled esters were 80–85%.

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(8) A. Zimmerli, Benzol Products Co., suggested distilling the acid chlorides in a high vacuum.