

ABSTRACTS

Studies on the Syntheses of the Pyrethrin Analogues and their Biological Activities

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The relationship between chemical structure and insecticidal activity of the pyrethroids is so interesting that the author attempted to synthesize such cyclopropanecarboxylic acids as to give more effective esters with (\pm)-allethrolone.

Some new (\pm)-allethrolone esters of cyclopropanecarboxylic acids were prepared and their insecticidal activities were tested against the common housefly. Most of these esters of the acids showed little activity, but the esters of substituted phenyl cyclopropanecarboxylic acids were more or less toxic. Thereupon, the author synthesized such cyclopropanecarboxylic acids to get some substituted phenyl groups attached to the cyclopropane ring, and tested the insecticidal activities of their esters to clarify the relationship between the toxicity and the substituents on the cyclopropane ring. Among them, (\pm)-allethrolone ester of 2,2-dimethyl-3-(3',4'-methylenedioxyphenyl)-cyclopropane-1-carboxylic acid was found to be more toxic than α -(\pm)-*trans*-allethrin, and the calculated relative effectiveness were 1.48 and 1.21 on the mortality and knockdown activity respectively as compared with α -(\pm)-*trans*-allethrin.

The relationship between stereochemistry and insecticidal activity of the pyrethroids is of great interest and has been prosecuted by many workers. But it is not as yet clear whether this relationship holds for the other pyrethroids type esters of chrysanthemic acid analogues containing substituted phenyl side chains. It seems to be of interest to undertake the elucidation of this problem by dealing with some aryl analogues of chrysanthemic acid. Then, the author undertook the isolation of each geometrical isomers of 2,2-dimethyl-3-(3',4'-methylenedioxyphenyl)-cyclopropane-1-carboxylic acid and the resolution of the more toxic isomer for incorporation with (\pm)-allethrolone to be submitted to insecticidal tests.

2,2-Dimethyl-3-(3',4'-methylenedioxyphenyl)-cyclopropane-1-carboxylic acid was separated into the geometrical isomers and their configurations were achieved. Of the two isomers, the (\pm)-*trans*-acid, which was found 1.75 times in knock-down and 2.36 times in mortality as the (\pm)-*cis*-acid when esterified with (\pm)-allethrolone, was resolved by means of an optically active α -phenylethylamine salt into (+)- and (-)-enantiomers. (1*R*:3*R*)-Configuration was assigned to the (+)-*trans*-acid and (1*S*:3*S*)-configuration to the (-)-*trans*-acid. The bioassay revealed the (\pm)-allethrolone ester with the (+)-*trans*-acid, which belongs to the same optical series as the natural chrysanthemum acid, was the most toxic and was 33.3 times in knock-down and 20.9 times in mortality as toxic as the (-)-*trans*-acid ester against common houseflies, as the case with other pyrethroids.