Photodecomposition of Pyrethrin I, Allethrin, Phthalthrin and Dimethrin

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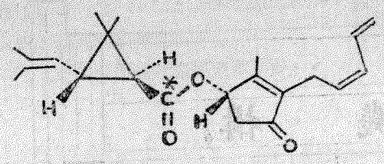
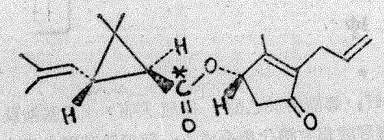
The insecticidal esters in pyrethrum extract are unstable, converting to non-inseoticidal products on exposure to air and sunlight or ultravioletlight. The natural esters and their synthetic analogs, such as allethrin, phthalthrin and dimethrin, are nonpersistent insecticide chemicals partly as the result of their ease of photodecomposition. It is necessary to understand the photochemistry of pyrethroids in order to predict conditions for their use or to devise modifications in structure necessary to achieve an appropriate degree of persistence in insect control. The available chemical information on the photodecomposition of pyrethroids relates primarily to the constituents of pyrethrum extract and, in no case, identifies the decomposition products. The slow progress in this important area of research is the result of the complex nature of the chemistry involved and the lack of adequate procedures for detecting, separating, and determining the products encountered.

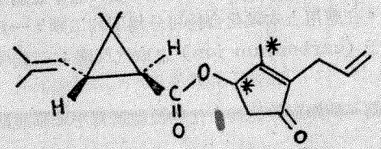
Studies were made on the phctcdecomposition of pyrethrin I (I), phthal--thrin (Ⅲ), allethrin (Ⅱ) and dimethrin (Ⅳ), the rate of decomposition decressing in the order listed and eaeh pyrethroid yielding at least 11 products. The photo-decomposition products probably are esters based on the fact that different products are obtained from the four pyrethroids when each pyrethroid is identically labeled with carbon-14 in the d-trans-chrysanthemimate moiety and that, in the case of allethrin and phthalthrin, identical products are obtained from separate preparations labeled with carbon-14 in the acid and in the alcohol moieties. Thus, hydrolysis does not appear to be a major photochemical reaction for pyrethroids. Based on work with pyrethrin I and allethrin, the alcohol moiety of pyrethroids prcbably suffers phctcchemical attack, but the chemical reactions involved are nct known. The phctochemical changes in the acid moiety of each of the fcur pyrethroids are the same and they involve 1) stepwise oxidation of the trans-methyl grcup cf the iscbutenyl moiety to the respective alcohol, aldehyde, and csrboxylic acid derivatives, 2) cxidation of the iscbutenyl dcuble bond to a keto derivative, 3) rupture of this double bond to yield esters of trans--caronic acid, and 4) cther attack resulting in at least six additional modifications of the acid moiety, It is clear that preparation of pyrethroids of improved photostability requires the use of acid and alcohol moieties which are less susceptible to photodecomposition than those in the four pyrethroids studied.



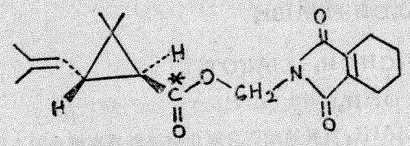
Pyrethrin I-acid-C^{14} (I)



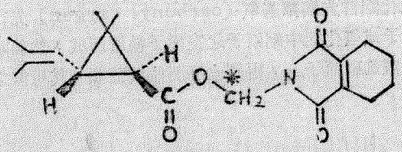
Allethrin-acid-C^{14} (Ⅱ)



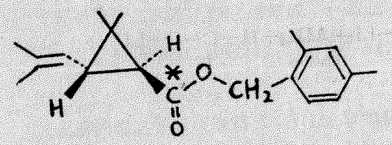
Allethrin-alcohol-C^{14} (Ⅱ)



Phthalthrin-acid-C^{14} (Ⅲ)



Phthalthrin-alcohol-C^{14} (Ⅲ)



Dimethrin-acid-C^{14} (Ⅳ)

〔註〕本文係本院藥學系植物化學兼任教授陳玉麟博士(國立臺灣大學農學院農業化學系教授)最近出國講學在美國加州大學 (university of california, Berkeley, California) 所作研究工作之論文摘要。詳細全文現投稿於美國化會學 Journal of Agricultural and Food chemistry, 預定於1939年間出刊。