原　著

Studies on Pyrethroidal Compounds* Part IV. Thermal Behavior of Furamethrin. Yasuo Abe, Nobushige Itaya, Yoshio Fujita and Noboru Muramoto (Research Department, Pesticides Division, Sumitomo Chemical Co., Ltd., Takatsukasa 4-2-1, Takarazuka City, Hyogo, Japan) Received Sept. 26, 1973. *Botyu-Kagaku*, 39, 1, 1974.

1. ピレスロイド系化合物の研究（第4報）フラメスリンの熱挙動

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フラメスリンの熱安定性を，その主用途である電気蚊取器の使用時加熱温度120-200°Cにおいて検討した．フラメスリンの主な熱分解生成物として，菊酸，ピロシン，δ-ラクトンおよび2種の不飽和アルデヒドの構造を明らかにし，それらの生成経路について考察した．

フラメスリンを含有する電気蚊取マットからの加熱揮散物，およびフラメスリンを含有する蚊取線香の燃煙物を昇温ガスクロマトグラフィーで検討したところ，フラメスリンの熱分解生成物は検出されなかった．

Pyrethroids, such as pyrethrins and allethrin, have been widely used as domestic insecticides in the form of smoke from burned mosquito coil or fume from mat electrically heated at temperature ranging over 120-180°C. Thus, it is important to consider the thermal stability and the thermal decomposition of pyrethroids, to predict conditions for their use, and to ensure safe usage.

There have been some studies about pyrolysis of pyrethrins, allethrin, pyrethrin-I and proparthrin,[1-5] but no report on the thermal behavior of highly insecticidal furamethrin, 5-propargyl-2-furylmethyl chrysanthemate.[6]**

Present report deals with the identification of compounds derived from furamethrin by heating in atmosphere and the way of formation thereof is proposed. The vapor from an electric fumigator and the smoke of burned mosquito coil containing furamethrin in practical use are investigated by gaschromatography.

Materials and Methods

Furamethrin (I) : Furamethrin used was the preparation of a technical grade manufactured by Sumitomo Chemical Co., Ltd. Purity 84.9%, ratio of *cis/trans*=20/80. Anti-oxidant (di-*tert*-butylhydroxytoluene) was added at 1 wt%. Technical furamethrin was recrystallized 10 times from methanol: water (11 : 1, v/v), yielding pale yellow solid. The solid was submitted to TLC on silicic acid, using *n*-hexane : ethyl acetate (5 : 1, v/v) as developing solvent. Obtained colorless solid gave only one spot on TLC and one peak on GLC. Ratio of *cis/trans* isomer= 5/95.

Preparation of authentic samples :

(a) Pyrocin (V) ; *d, l-trans*-Chrysanthemic acid was refluxed for 5 hr under nitrogen current.[7] Mp 58-59°C (recrystallized from petroleum ether).

(b) *cis*-Dihydrochrysanthemo-δ-lactone (VI) ; Synthesized from *d, l-cis, trans*-chrysanthemic acid.[8,9] Mp 51-52°C (recrystallized from *n*-hexane).

(c) 5-Formyl-2-furylmethyl chrysanthemate (II) ; Chrysanthemic acid (34.5g ; 0.21 mole) and triethylamine were dissolved in dimethylformamide (70m*l*). 5-Chloromethylfurfural diethylacetal (44g; 0.20 mole) dissolved in dimethylformamide (30m*l*) was added to the mixture with stirring and allowed to stand overnight at 50°C. The reaction mixture was dissolved in ether (500m*l*). The ether solution was washed with 5% sodium bicarbonate (200m*l* × 4) and dried over sodium sulfate and the solvent was evaporated to yield a dark brown viscous liquid (39.7g).

The liquid was dissolved in ether (200m*l*),

* Part III, *Botyu-Kagaku*, 37, 102 (1972).

** Furamethrin is a new synthetic pyrethroid, which is also known as prothrin, pynamin-D® and D-1201.

followed by washing with 6% hydrochloric acid (70ml×2). The solvent was distilled away to give a brown viscous liquid (27.4g). The liquid was chromatographed on silicic acid column with *n*-hexane : ethylacetate (6 : 1, v/v) as eluent, yielding pale yellow solid (13.9g). The solid was recrystallized from *n*-hexane to give colorless powder. Mp 54.0-55.0°C (corrected). Found: C, 69.91; H, 7.56. Calcd. for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. MW 276.32. MS m/e : 276 (M^+). IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1728 (O-C=O), 1683 (=C-CHO), 1525 (C=C), 1190, 1149 (-CO-O-), 748, 802 (furan). NMR $\delta_{TMS}^{CCl_4}$: 9.62 (1H, singlet, -CHO), 7.12 (1H, doublet, J = 3.5 cps, =C-H), 6.54 (1H, doublet, J = 3.5cps, =C-H), 5.08(2H, singlet, O-CH_2-C), 4.87 (1H, double multiplet, J = 8.0cps, =C-H), 2.01 (1H, double doublet, J = 5.2, 8.0 cps, C-H), 1.70 (6H, doublet, J= 1.0 cps, -CH_3×2), 1.36 (1H, doublet, J=5.2 cps, C-H), 1.24 (3H, singlet, -CH_3), 1.14 (3H, singlet, -CH_3).

(d) 5-(2'-Formylethenyl)-2-furylmethyl chrysanthemate (III); Vinyl magnesium chloride (3.3g; 0.038 mole) in tetrahydrofuran (15g) was added to 5-formyl-2-furylmethyl chrysanthemate (8.5g; 0.031 mole) in tetrahydrofuran (20g) with stirring at 0°C. The mixture was allowed to stand overnight at room temperature, then poured into ammonium chloride with ice and extracted with ether. The solvent was removed from the dried (over Na_2SO_4) extract to give 5-(1'-hydroxy-2'-propenyl)-2-furylmethyl chrysanthemate (11.3g, crude).

Phosphorus tribromide (6g ; 0.022 mole) in absolute ether (50ml) was added to the prepared 5-1'-hydroxy-2'-propenyl)-2-furylmethyl chrysanthemate in absolute ether (100ml) with stirring at 0°C, and the mixture was kept overnight at room temperature.

The mixture was treated with 40% potassium carbonate. Chloroform (100ml) was added to the dried ether fraction (over K_2CO_3), then which was concentrated to 100ml. The concentrate was refluxed with activated manganese dioxide (30g) at 75°C during 7hr. After filtration, the solvent was evaporated to yield a dark brown liquid (28.0g). The crude liquid was purified by silica gel chromatography, eluted witn *n*-hexane:ethyl acetate (6.1, v/v), to give pale yellow liquid. Found: C, 62.82; H, 6.89. Calcd. for C_{18} $H_{22}O_4$: C, 71.5; H, 7.33. MW 302.36. MS m/e: 302(M^+). IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1791, 1730 (O-C=O), 1681 (C=C-C=C-CHO), 1630 (C=C), 1186, 1152 (-CO-O-C), 850, 795 (furan) NMR $\delta_{TMS}^{CCl_4}$: 9.54 (1H, doublet, J=7.2 cps, -CHO), 7.10 (1H, doublet, J=15.6 cps, -CH=), 6.52 (1H, double doublet, J = 7.2, 15.6 cps, =CH-), 5.01 (2H, singlet, -O-CH_2-), 4.83 (1H, double multiplet, J = 7.8 cps, -CH=), 1.70 (6H, doublet, J = 1.0 cps, CH_3-×2), 1.24 (3H, singlet, CH_3-), 1.14 (3H, singlet, CH_3-). (e) 5-Propadienyl-2-furylmethyl chrysanthemate (PDC); To 5-propargyl furfurylalcohol (20g ; 0.15 mole) dissolved in ethanol (100ml), 10% sodium hydroxide (50ml) was added, followed by stirring at room temperature for 5 hr. After concentration, the residue was dissolved in toluene (100ml), and mixed with triethylamine (30g), Chrysanthemoyl chloride (30g; 0.16 mole) in toluene was added to the solution with stirring at 30-40°C for 3 hr. After addition of 15% hydrochloric acid (40ml), the mixture was extracted with toluene (100ml). The extract was washed with 1% sodium hydroxide, 1% hydrochloric acid and then saturated sodium chloride solution. The dried extract (over Na_2SO_4) was mixed with silica gel (50g) and aluminum oxide (50g). After filtering the mixture, filtrate was concentrated to give pale yellow liquid. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1942 (C=C=C), 1725 (-COO-), 1150 (CO-O-C), 856 (=C=C(H)-H), 789 (furan). NNR $\delta_{TMS}^{CDCl_3}$: 6.28 (1H, doublet, J = 2.7 cps, =C-H), 6.15 (1H, doublet, J=2.7 cps, =C-H), 5.99 (1H, doublet, J=7.0 cps, C=C=CH-), 5.14 (2H, doublet, J=7.0 cps, $C=CH_2$), 4.97 (2H, singlet, O-CH_2-C), 4.85 (1H, multiplet, =C-H), 2.10 (1H, multiplet, C-H), 1.72 (6H, singlet, -CH_3×2), 1.40 (1H, multiplete, C-H), 1.25 (3H, singlet, CH_3-), 1.10 (3H, singlet, CH_3-).

Heating of compound : The compound (4-5g) was placed in a 100ml round-bottomed flask equipped with a reflux condenser. The flask was covered with aluminum foil to shelter light, and heated in a silicone oil bath. Vapor through condenser was trapped in methylene chloride or 2,4-dinitrophenylhydrazine solution.

Chromatography:

(a) Thin layer chromatography (TLC) ; Silica gel HF_{254} (Merck) was used as an adsorbent. Solvent systems for development: solvent system I, *n*-hexane : ethyl acetate 10 : 3 (v/v); solvent system II, *n*-hexane : ethyl acetate 5 : 3 (v/v); solvent system III, benzene saturated with formic acid; solvent system IV, *n*-hexane: isopropylether: dioxane 90 : 7 : 5 (v/v). Compounds were detected on the plate by UV light, iodine or 2,4-dinitrophenylhydrazin solution.

(b) Gas-liquid chromatography (GLC) ; Yanagimoto GCG-550FP (FID detector). Contents of furamethrin were determined in the way as described in the literature[10] and programmed GLC was operated as follows : Glass column ; packed with 3% silicone XE-60 on acid washed 60-80 mesh chromosorb W. Column temperatures programming ; 60-240°C at 16°C/min. Injection temperature; 230°C, detector temperature ; 240°C. Carrier gas ; nitrogen, flow rate ; 25m*l*/min.

Spectroscopy: IR were measured with a Hitachi EPI-S2 infrared spectrometer. Mass spectra were recorded with a Shimadzu LKB-9000 mass spectrometer. NMR were obtained on a Varian A-60 instrument at 60 Mcps using TMS as an internal standard.

Results and Discussion

Stability of technical furamethrin under various conditions

Stability of technical furamethrin under various storage conditions is shown in Table 1. The initial temperatures of vaporization and thermal decomposition were *ca.* 120°C and *ca.* 256°C respectively, when they were determined by differential thermal analysis.

Thermal behavior of purified furamethrin at 120-140°C

Purified furamethrin was heated at 120-140°C for 10 hr, under the condition closely similar to that of domestic electric fumigator for anti-mosquito mat. Upon heating, furamethrin turned deep brown, but neither precipitation nor turbidity occurred. It was confirmed by TLC that any volatile carbonyl compound was not trapped in 2,4-dinitrophenylhydrazine solution.

From programmed GLC and TLC, it appeared that furamethrin was stable and it produced only chrysanthemic acid (IV in Fig. 4, 4.0%) and unknown compound (0.2%) (Table 2).

Thermal behavior of technical furamethrin at 150°C

Gaschromatogram of technical furamethrin heated at 150°C for 8 hr showed a few, small peaks, and it was very similar to that of purified furamethrin stated above. But, *ca.* 0.5% pyrocin and *cis*-dihydrochrysanthemo-*δ*-lactone (V and VI in Fig.4, respectively), and 0.3% unknown compounds were detected as decomposition products in addition to (IV) (Table 2). No peak separation occurred in TLC and GLC with admixture of an authentic chrysanthemic acid. The identity of chrysanthemic acid isolated by

Table 1. Stability of furamethrin under various conditions

Storage condition				Content (%)*1				
Vessel*2	Sealed gas	Temperature (°C)	R. H. *3 (%)	initial	30days	60days	75days	90days
sealed ampoule	air	40	—	88.2	87.7 (0.6)	—	85.2 (3.4)	—
〃	〃	50	—	〃	87.4 (0.8)	—	84.0 (4.7)	—
〃	〃	60	—	〃	86.6 (1.8)	—	86.5 (1.8)	—
open ampoule	〃	40	0	〃	84.7 (4.0)	—	75.0(15.0)	—
〃	〃	〃	100	〃	85.9 (2.6)	—	82.6 (6.3)	—
sealed ampoule	〃	−5	—	82.5	82.5 (0.0)	82.0 (0.6)	—	—
〃	〃	11	—	〃	82.5 (0.0)	81.3 (1.4)	—	—
〃	〃	60	—	〃	80.8 (2.1)	79.1 (4.2)	—	—
〃	nitrogen	40	—	82.8	81.4 (1.7)	81.2 (1.9)	—	81.2(1.9)
〃	air	〃	—	〃	81.6 (1.4)	81.4 (1.7)	—	81.5(1.7)

*1 Losses (%) are indicated in parentheses.

*2 2m*l*-Colorless and transparent glass ampoule. Sample scale; 200mg.

*3 Relative humidity: 0%; in a desiccator with calcium chloride.

Table 2. Percent distribution of products from heated furamethrin.

No*2 Compound	Peak area on GLC (%)*1		
	130°C (10hr)	150°C (8hr)	200°C (7hr)*3
1. Unknown		0.1	0.3
2. 〃			0.2
3. Chrysanthemic acid	4.0	4.5	63.9
4. Pyrocin, δ-Lactone*4		0.5	
5. Unknown			0.4
6. Furamethrin	95.8	94.7	34.7
7. R-CHO*5			0.2
8. R-CH=CH-CHO*5			0.2
9. Unknown	0.2	0.2	0.1

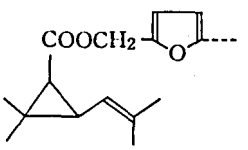
*1 Percent distributions of pyrolysis products from furamethrin as peak area on gaschromatogram.

*2 Figures are numbered in the same as the numbers in Fig. 1.

*3 EtOAC-insoluble solid (*ca.* 46%) is not included in this distribution.

*4 *cis*-Dihydrdrochrysanthemo-δ-lactone.

*5 R=chrysanthemoyloxymethylfuryl.



TLC (solvent system III) was obtained by direct comparision with an authentic specimen in IR and mp.

Compounds (V) and (VI) were eluted, under the described condition, immediately after (IV) as indicated by a sharp peak. They were not separable by GLC (3% silicone XE-60). They were however isolated by TLC on silica gel (solvent system II, R_f; (V)=0.75, (VI)=0.56). They were identified by comparing their IR with those of authentic samples. This is in accord with the result of Baba *et al.*[4] with allethrin.

Pyrolysis of furamethrin at 200°C

The purified furamethrin was heated at 200°C for 7hr, which was higher than the temperature of an electric heater for anti-mosquito mat. The resulting gummy substance consisted of oily part soluble in ethyl acetate (54%) and of insoluble dark brown solid (46%).

Gaschromatogram of the oily part showed seven peaks, in addition to furamethrin peak, for which the pyrolysis products were probably responsible (Fig. 1). The largest one (peak 3) of them comprised *ca.* 64% (Table 2). The compound was isolated by TLC (solvent system III;

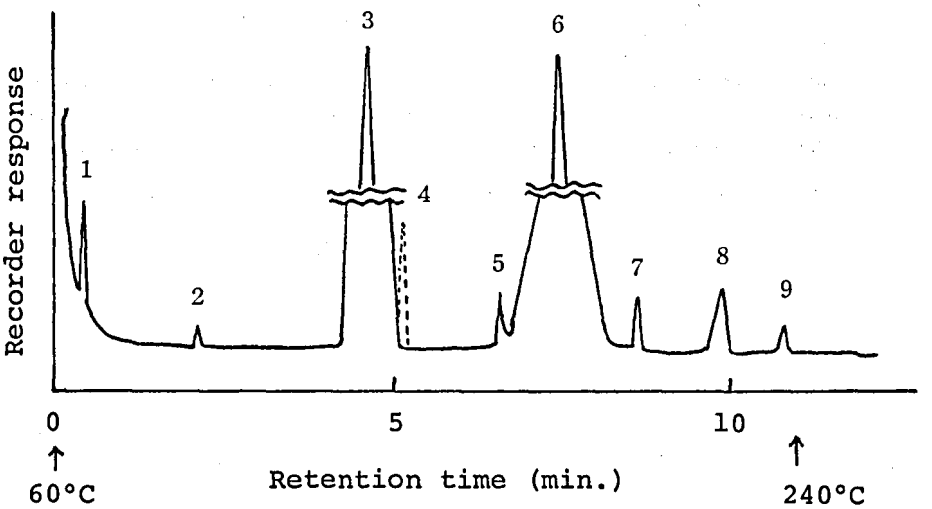


Fig. 1. Gaschromatogram of furamethrin heated at 200°C for 7 hours.

Peak assignment:

1, 2, 5, 9; unknown
3; Chrysanthemic acid (IV)
4; Pyrocin (V) and *cis*-Dihydrochrysanthemo-δ-lactone (VI)
6; Furamethrin (I)
7; 5-Formyl-2-furylmethyl chrysanthemate (II)
8; 5-(2′-Formylethenyl)-2-furylmethyl chrysanthemate (III)

R_f 0.48), and identified as *d, l-trans*-chrysanthemic acid by mixed mp test, elementary analysis, IR, and NMR (Tab. 3). Found: C, 71.88; H, 9.66 %. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. Other workers[4,15,8] also detected (IV) as a pyrolysis prpduct from allethrin and tetramethrin.

Peak 6-compound was identified as furamethrin by mixed GLC, IR and MS (Tab. 3). Peak 7- and 8-compounds assumed a brown color on TLC by spraying 2,4-dinitrophenylhydrazine solution. They were separated by TLC (solvent system I; R_f, peak 7=0.40, peak 8=0.35). IR of peak 7-compound (Tab. 3) suggested that it was an α, β-unsaturated aldehyde (1683cm^{-1}) with an ester linkage (1729cm^{-1}). NMR of that component (Tab. 3, Fig. 2) showed 2 protons of furan (δ 6.55, 7.14) and 12 protons for 4 methyl groups, which were *gem*-dimethyl (δ 1.14, 3H; 1.25, 3H) and isopropenyl (δ 1.70, 6H) groups.

Pattern of peaks in high magnetic field was very similar to that of chrysanthemate. These results suggested that it was a chrysanthemate with a furan ring. Moreover, by consideration of elementary analysis and MS, m/e 276 (M^+) (Tab. 3), it is concluded that the peak 7-compound is 5-formyl-2-furylmethyl chrysanthemate (II). Found: C, 70.70; H, 7.54%. All of them were in fair agreement with those of an authentic specimen.

IR (Fig. 3) of peak 8-compound (Tab. 3) was characteristic of an α, β-γ, δ-unsaturated aldehyde (1677, 1634, 1582cm^{-1}) with an ester linkage (1730cm^{-1}). NMR of the compound (Table 3) showed a furan ring (δ 6.48, 6.69), an isopropenyl (δ 1.70, 6H) and dimethyl (δ 1.14, 3H; 1.25, 3H) groups. α, β-γ, δ-Unsaturated aldehyde protons (δ 7.15, 1H; 6.52, 1H; 9.58, 1H) were supported also by IR. These facts suggested that it was a chrysanthemate containing a furan ring. MS, m/e 302 (M^+), and elementary analysis indicated a molecular formula, $C_{18}H_{22}O_4$. Found: C, 70.48; H, 7.60%. Considering these results, it is supposed that the compound is 5-(2′-formylethenyl)-2-furylmethyl

Table 3. Spectroscopic data for the compounds isolated from the furamethrin heated at 200°C.

	IR spectrum (ν_{max}cm^{-1}, NaCl cell)
Peak 3	(Nujol) 1690 (-COOH), 1241, 1108, 850.
Peak 6	(Liquid film) 3300 (≡C-H), 1724 (-COO-), 1559, 1188, 1150, 1108, 849, 788.
Peak 7	(Liquid film) 1729 (-COO-), 1683 (C=C-CHO), 1635 (C=C).
Peak 8	(Liquid film) 1730 (-COO-), 1677 (C=C-C=C-CHO), 1634, 1582 (conjugated diene).
	NMR spectrum ($\delta^{CCl_4}_{TMS}$, 60Mc)
Peak 3	1.16 (3H, s, CH_3-), 1.30 (3H, s, CH_3-), 1.71 (6H, s, $\begin{matrix}CH_3\\CH_3\end{matrix}$>C=), 2.02 (1H, dd, J=7.8, 4.8, H-C), 4.89 (1H, dm, J=7.8, H-C=), 12.08 (1H, b, -COOH).
Peak 7	1.14 (3H, s, CH_3-), 1.25 (3H, s, CH_3-), 1.70 (6H, d, J=1.0, $\begin{matrix}CH_3\\CH_3\end{matrix}$>C=), 2.08 (1H, dd, J=5.4, 10.1, H-C), 4.93 (1H, dm, J=10.1, H-C=), 6.55 (1H, d, J=3.5, H-C=), 7.14 (1H, d, J=3.5, H-C=), 9.61 (1H, s, -CHO).
Peak 8	1.14 (3H, s, CH_3-), 1.25 (3H, s, CH_3-), 1.70 (6H, d, J=1.0, $\begin{matrix}CH_3\\CH_3\end{matrix}$>C=), 4.87 (1H, dm, J=9.0, H-C=), 5.04 (2H, s, O-CH_2-C=), 6.48 (1H, d, J=3.0, H-C=), 6.52 (1H, dd, J=7.2, 16, =CH-CO), 6.69 (1H, d, J=3.0, H-C=), 7.15 (1H, d, J=16, -CH=), 9.58 (1H, d, J=7.2, -CHO).
	Mass spectrum (m/e)
Peak 6	285 (M^+-1), 168, 139 (base peak), 123, 119, 81.
Peak 7	276 (M^+), 167, 123 (base peak), 109, 81.
Peak 8	302 (M^+), 135 (base peak), 136, 123, 107, 81.

* Peak numbers are shown in Figure 1.

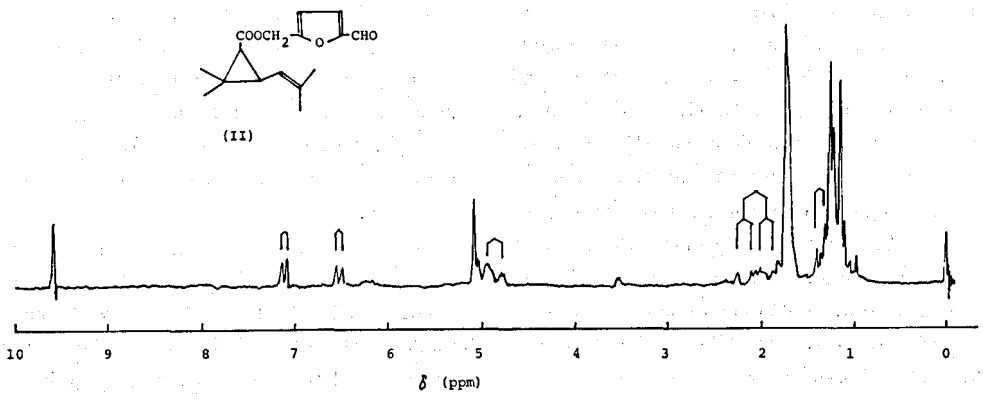


Fig. 2. NMR Spectrum of a product from furamethrin heated, 60 Mc in CCl_4(TMS).

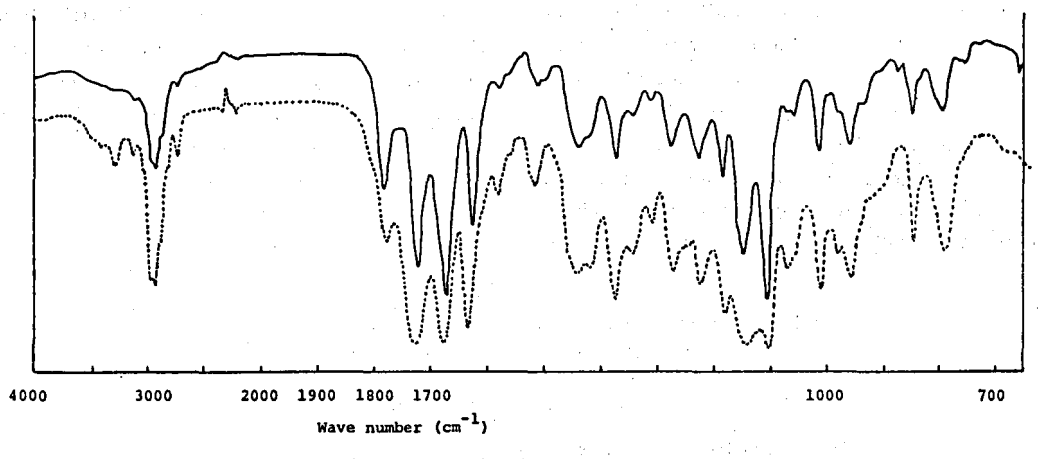


Fig. 3. IR Spectra of a product (peak 8) obtained from heated furamethrin.
——; authentic sample
·····; thermal decomposition product from furamethrin

chrysanthemate (III). This conclusion was confirmed by comparision with an authentic sample. As for a configuration of the formylethenyl group, the formyl is likely oriented *trans* relative to the furan ring because of the large coupling constant ($J = 16$cps) for vicinal protons of the double bond.[12]

Compounds (V) and (VI), which occurred as pyrolysis products from the technical furamethrin, were not detected on TLC and GLC. An alcoholic moiety of furamethrin (propargylfurylmethylalcohol) and its derivatives (propargylfurfural, furfurylalcohol, furfural) were not observed on GLC. 5-Propadienylfurylmethyl chrysanthemate (hereafter referred to as PDC), which might be readily formed by isomerization of propargyl group of furamethrin,[11,16] was not found on GLC and TLC (solvent system IV).

A *cis/trans* ratio of the technical furamethrin used was 20/80, while that of the purified furamethrin was 5/95.[10] This indicates that *cis*-furamethrin was eliminated through recrystallization. It was already reported that at 300-400°C, even *trans*-chrysanthemic acid was isomerized into lactones ((V) and (VI)), but *cis*-chrysanthemic acid was converted into lactones at 150°C or so.[4,13,14] This may account for the absence of (V) and (VI) in the pyrolysis products of purified furamethrin.

The ethyl acetate-insoluble solid (VII) did not melt over 300°C. Elementary analysis: C, 78.66; H, 6.84%. IR (KBr) showed an isopropenyl

cyclopropane (843, 1105 cm^{-1}), a furan ring (1600, 770cm^{-1}) and an ester linkage (1147, 1185, 1727 cm^{-1}). The spectrum was almost similar to those of furamethrin or PDC. But acetylene and propadienyl absorption (1942cm^{-1}) were lacking. From these results, it seems likely that the compound is a polymer of chrysanthemate, resulting from an alteration of a propargyl side chain in an alcoholic portion of furamethrin.

Proposed pathways for pyrolysis of furamethrin

A small amount of (II)), (III), and (IV) were detected by gaschromatography of pyrolysis products from PDC at 200°C for 1 hr, while PDC was not detected in pyrolysis products from furamethrin (I). The compounds (II) and (III) in the products from PDC were identified by mixed TLC with authentic samples. By heating at 200°C for 7 hr, (III) disappeared nearly completely and (IV) increased. This showed that (III) decomposed further, owing to its instability.

The formation of (II) and (III), and ready isomerization of propargyl to propadienyl group suggest the forming pathways of these compounds as shown in Fig. 4. After a hydrogen radical would be abstracted from propargyl group of furamethrin by oxygen, an allenyl radical (VIII) would form by radical rearrangement. The propargyl and allenyl radicals in radical equilibrium might be subjected to air oxidation, producing (II) and (III) respectively. Compound (IV) would arise from pyrolysis of (I) and the resulting (IV) would give (V) and (VI). It can be assumed that (IV) would be formed by radical decomposition of (I), because the hydrolysis of (I) should afford propargylfuryl methylalconol, but neither propargylfurylmethylalcohol nor its derivatives was detected. It may be due to radical polymerization of furan ring that alcohol moiety or its cleaved fragments were not found.

IR of AcOEt-insoluble solid (VII) was very similar to that of PDC, and the elementary analysis data of the former compared well with those of the latter. Thus, the pyrolysis proceeds mainly through allenyl radical path. It seems presumable that major portion of the (VII) may be produced by polymerization of the allenyl radicals.

Thermal stability of furamethrin in practical use

(a) Anti-mosquito mat; The purified furamethrin (60mg) was impregnated in pressed fiber mat (35×22×3mm, 850mg). The anti-mosquito mat was heated on an electric heater at 120-135°C for 2 hr. Generated vapor was introduced into methylene chloride traps chilled with ice and salt.

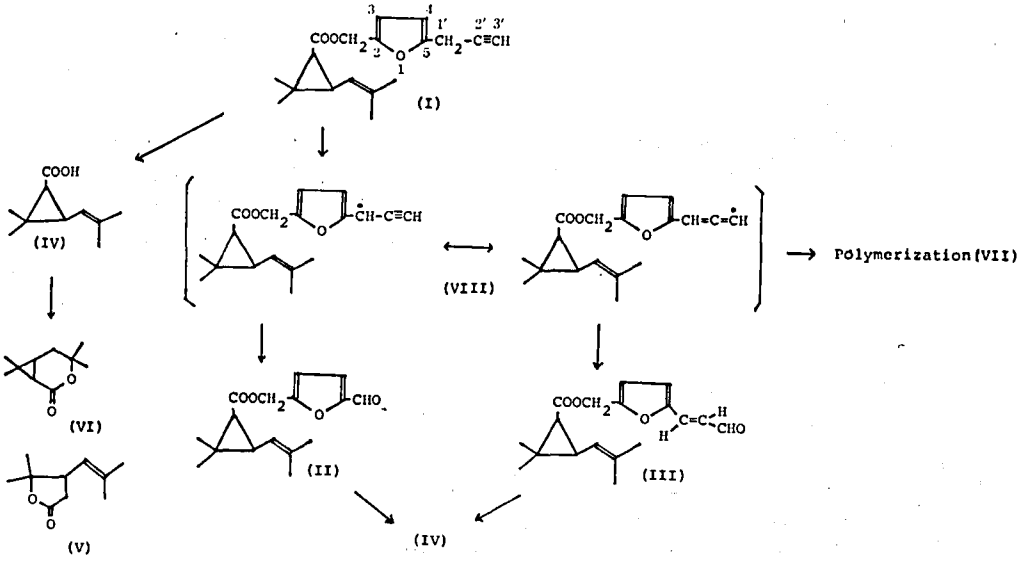


Fig. 4. Proposed pathways for thermal decomposition of furamethrin.

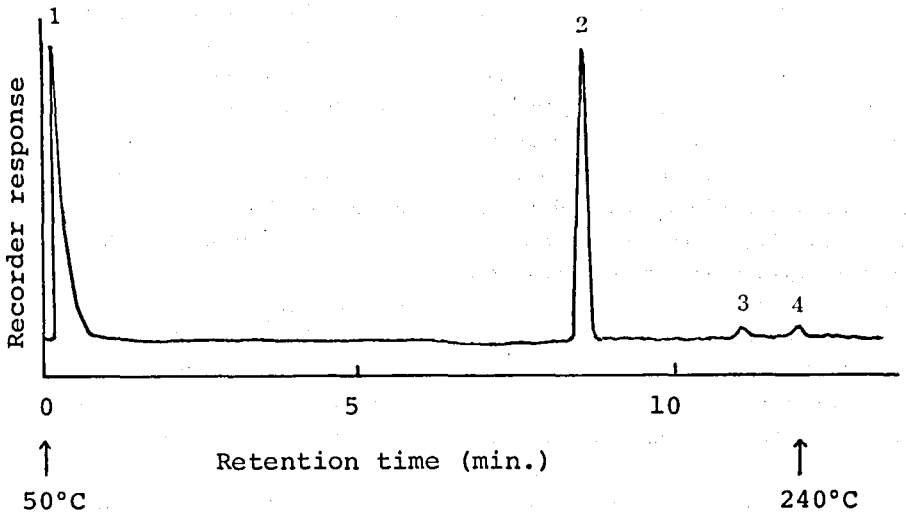


Fig. 5. Gaschromatogram of extract from heated anti-mosquito mat, using programmed temperatures.
Peak assignment: 1; Solvent (acetone), 2; Furamethrin (I),
3; 5-Formyl-2-furylmethyl chrysanthemate (II),
4; 5-(2′-Formylethenyl)-2-furylmethyl chrysanthemate (III).

Programmed GLC of the trapped solution showed a single peak and it was identical with that of purified furamethrin. It could be considered that volatile decomposition product was scarcely generated under the conditions employed for commercial anti-mosquito mat. This is also supported by tracer techniques using ^{14}C-labeled furamethrin.[17]

Gaschromatogram (Fig. 5) of the extract (residue in mat) from the heated anti-mosquito mat did not show the presence of any compound to be eluted prior to (I). Two peaks were found at higher column temperature than that of (I). They were identified as (II) and (III) by mixed GLC with authentic samples. These pyrolysis compounds were not detected in the trapped solution. It is safely considered that most of the pyrolysis compounds would reside in the heated mat because of their low vapor pressures (Table 4). It appears that vapor from anti-mosquito mat consists of (I) alone.

(b) Mosquito coil ; Smoke from mosquito coils containing technical furamethrin at 0.5 wt% was trapped in the same way as mentioned above. The solution in the traps was concentrated and injected into GLC (Fig. 6).

Many peaks were observed in GLC (A), but when compared with (B) of mosquito coil without furamethrin, two peaks (t_R; (I) =17.5min, BHT =10.5min) were distinguished. Many other peaks were apparently attributable to vegetable components of mosquito coil base. This is in accord

Table 4. Vapor pressures of some furylmethyl chrysanthemates and BHT*.

Compound	Vapor pressure (mm Hg, 135°C)
BHT	3.77
Furamethrin (I)	1.69
5-Formyl-2-furylmethyl chrysanthemate (II)	0.62
5-(2′-Formylethenyl)-2-furylmethyl chrysanthemate (III)	0.20

* Determined by gaschromatography according to the manner reported by Jensen *et al.*[18]

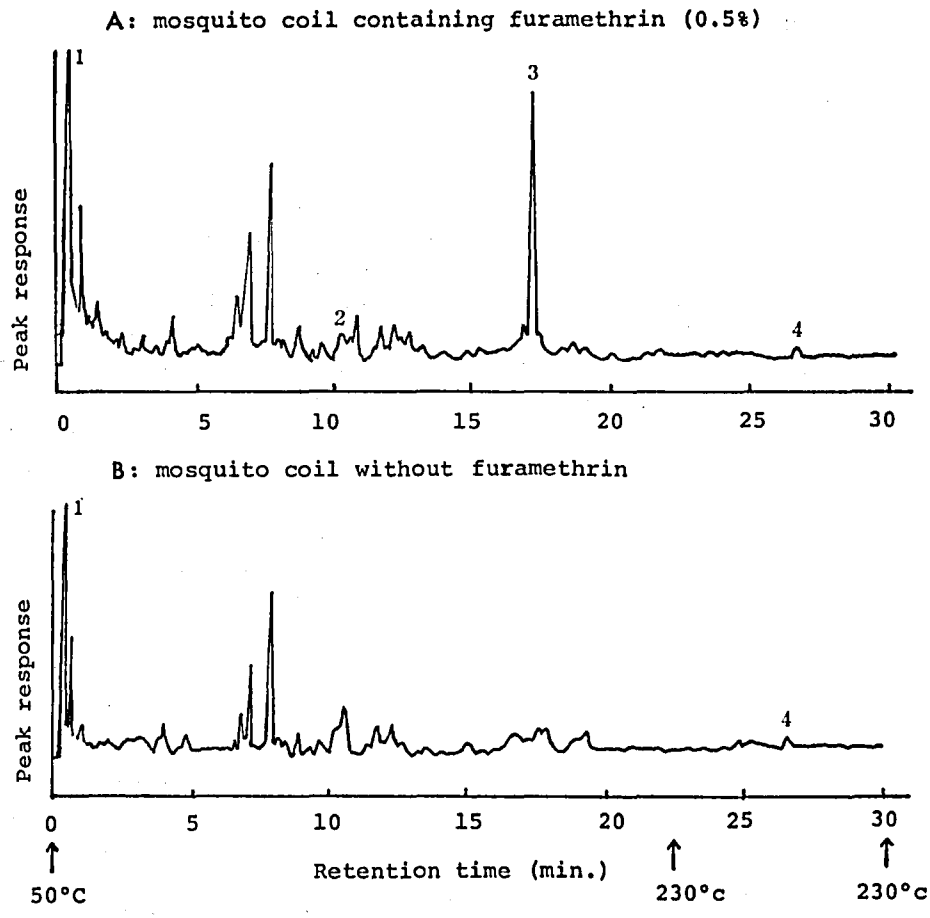


Fig. 6. Gaschromatograms of smoke from furamethrin mosquito coil, using programmed temperatures.

Peak assignment: 1; Solvent
2; B.H.T.
3; Furamethrin
4; Malachite green (Dye)

with the result reported by Nakanishi *et al.*[5] on the proparthrin coil, which is a closely similar chemical to (I).

Summary

Thermal behavior of furamethrin was investigated by heating in atmosphere at temperature ranging over 120-200°C. Chrysanthemic acid, pyrocin, *cis*-dihydrochrysanthemo-δ-lactone and two unsaturated aldehydes were identified as pyrolysis products from furamethrin. The way of formation thereof is proposed. No pyrolysis product of furamethrin was found in the vapor from an electric fumigator and the smoke of burned mosquito coil containing furamethrin in practical use.

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Studies on the Increment of the Efficacy of Insecticides (Part XII). On the Effects of Combining two Pyrethroids. Akifumi HAYASHI (Laboratory of Applied Entomology, Taisho Pharmaceutical Co., Ltd., Department of Medical Zoology, Tokyo Medical and Dental University) Received November 7, 1973. *Botyu-Kagaku*, 39, 10, 1974. (with English Summary 12)

2. 殺虫剤の効力増進に関する基礎的研究（第12報）2種ピレスロイドの混用効果について

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Phthalthrin と proparthrin を混合して用いることは実用的価値のあることが明らかになった．混合割合は proparthrin: phthalthrin; 80 : 20, 60 : 40 が効果的である．

最近，pyrethroid の開発が盛んで，resmethrin, prothrin, proparthrin, phthalthrin などが登場している．しかし，従来の pyrethrins に比較して phthalthrin を除き，いずれもノックダウン効果が劣る．このことは家庭用殺虫剤の空間噴霧剤として使用する場合，きわめて不利である．この欠点を補うとともに新しい合成 pyrethroid の特徴をいかすため混合剤の検討が必要である．本実験では速効性を持つ phthalthrin と致死力の強い proparthrin の混用効果について検討を行ない知見を得たので報告する．

本文に入るに際し，種々御指導を賜った名古屋大学名誉教授弥富喜三博士，東京医科歯科大学加納六郎教授，実験に協力された田中哲雄氏に御礼申し上げる．

実験材料および方法

供試薬剤：実験に用いた殺虫剤は proparthrin（吉富製薬株式会社製造）と phthalthrin の2種類で，いずれも工業用原体である．

供試昆虫：実験に用いたイエバエ *Musca domestica vicina* Macqu.，高槻系は当研究室で累代飼育中の羽化後4日目から5日目の成虫である．チャバネゴキブリ *Blattella germanica* L. も当研究室で累代飼育中の成虫である．

実験方法：実験は局所施用法，0.5m³箱型法およびDS型法の3方法で実施した．

局所施用法は供試薬剤をアセトンで所定濃度に稀釈し，微量注射器でイエバエの胸部背板に0.5μlあて処理し，24時間後の致死率を観察した．0.5m³箱型法は