Studies on Pyrethroidal Compounds Part VI. Vaporization Ratio of Pyrethroids from Burning Mosquito Coils. Yasuo Abe and Yoshio Fujita (Research Department, Pesticides Division, Sumitomo Chemical Co., Ltd., 4-2-1 Takatsukasa, Takarazuka, Hyogo 665, Japan) Received August 20, 1975. *Botyu-Kagaku*, 41, 22, 1976.

6. ピレスロイド系化合物の研究（第6報）燃焼蚊取線香からの各種ピレスロイドの揮散率

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蚊取線香からの有効成分の揮散率を測定するために，シリカゲルカラム捕集法による簡便で，しかも正確な方法を完成した．本方法を使って6種類のピレスロイドおよび7種類のそれらの異性体の揮散率を測定した．それらは（+）-*cis, trans*-tetramethrin の26.4%から（+）-*cis, trans*-phenothrin の67.8%の範囲にわたったが，大部分は50～60%の中にあった．Furamethrin と pyrethrins は蚊取線香中の含有量が低い方が揮散率が高くなった．

アレスリンの異性体（*cis, trans* および+，−）間の揮散率に差はなかった．また，線香の燃焼中に異性化が起ることはなかった．市販蚊取線香中のアレスリンは，その含有量の差にかかわらず53.2～64.7%の揮散率であった．

Pyrethrins の各6成分の揮散率を別々に測定し，jasmolin II と pyrethrin II の値が，極めて低いことを明らかにした．

Introduction

Mosquito coils can exert their insecticidal activities when toxicants are efficiently dispersed from burning coils into atmosphere. The insecticidal activities, therefore, must be based directly on toxicant content in smoke rather than that in mosquito coil. Sometimes certain mosquito coils showing higher activity than the others are found, although these coils contain the same level of toxicant. It is expected in this case that these mosquito coils might have higher vaporization ratio of toxicant (the efficiency of transfer of unchanged insecticide into smoke) than the others. An addition of some synergists for pyrethroids to mosquito coils decreases the knockdown effect of the coils[1]. In this case there might be a possibility for the synergist to suppress release of the pyrethroid from a burning mosquito coil. A simple and accurate method for determination of the vaporization ratio had been hoped to solve these problems and others.

Determing pyrethrins vaporized into smoke by volumetric or colorimetric method, Wakazono *et al.*[2] and Nagase *et al.*[3] estimated the vaporization ratios to be 4-20%. Webley analyzed an extract from silica gel trap by gaschromatography (GLC) and reported the ratios to be 30-60%[4]. Chadwick found that recovery of pyrethrins in mosquito coil smoke was 18-47% and that of (+)-*trans*-allethrin was 63%[5]. Murayama *et al.* analyzed the smoke trapped with a chilled *n*-hexane by GLC and showed recovery of allethrin was 30-36%[6].

These methods for determination of the vaporization ratio are not always satisfactory, because they required a long time and a tedious work, and gave comparatively poor reproducibility. In order to overcome these drawbacks, the authors designed an apparatus and a method. The method described below is characterized by rapidity, simplicity of procedure and high accuracy. Vaporization ratios of some pyrethroids determined by this method and some findings are reported herein.

Materials and Methods

Pyrethroids. Pyrethrins were from Dainippon Jotyugiku Co., Ltd. Twelve synthetic pyrethroids used were synthesized in our laboratory. Their purities are shown in Table 1.

Preparation of mosquito coils. Coils used in this experiment were prepared by blending pyrethroid with inert fillers. The composition of them is shown in Table 2. Burning rate, apparent density and weight of a coil were similar to commercial mosquito coils.

Collection of mosquito coil smoke. The method

Table 1. Pyrethroidal compounds.

Pyrethrins	19.8%	Pyrethrum extract ("Pyrethrins I" 10.4%, "Pyrethrins II" 9.4%)
(±)-*cis, trans*-Allethrin	83.5	(±)-Allethronyl (±)-*cis, trans*-chrysanthemate (Pynamin®)
(+)-*cis, trans*-Allethrin	91.9	(±)-Allethronyl (+)-*cis, trans*-chrysanthemate (Pynamin-forte®)
(+)-*trans*-Allethrin	92.8	(±)-Allethronyl (+)-*trans*-chrysanthemate
(+)-*trans*-S-Allethrin	90.0	(+)-Allethronyl (+)-*trans*-chrysanthemate
(+)-*cis, trans*-Resmethrin	91.6	5-Benzyl-3-furylmethyl (+)-*cis, trans*-chrysanthemate (Chrysron-forte®)
(±)-*cis, trans*-Tetramethrin	93.3	N-(3, 4, 5, 6-Tetrahydrophthalimido) methyl (±)-*cis, trans*-chrysanthemate (Neo-Pynamin®)
(+)-*cis, trans*-Tetramethrin	96.7	〃 (+)-*cis, trans*-chrysanthemate (Neo-Pynamin-forte®)
(+)-*trans*-Tetramethrin	95.8	〃 (+)-*trans*-chrysanthemate
(±)-*cis, trans*-Furamethrin	84.9	5-Propargyl-2-furylmethyl (±)-*cis, trans*-chrysanthemate (Pynamin-D®)
(+)-*cis, trans*-Furamethrin	88.0	〃 (+)-*cis, trans*-chrysanthemate (Pynamin-D-forte®)
(±)-*cis, trans*-Phenothrin	96.9	3-Phenoxybenzyl (±)-*cis, trans*-chrysanthemate
(+)-*cis, trans*-Phenothrin	97.7	〃 (+)-*cis, trans*-chrysanthemate

* Every ratio of *cis/trans* isomers in *cis/trans*-chrysanthemate is approximately 20/80.

Table 2. Composition of mosquito coils.

Tabu powder	30.0 wt%
Wood flour	15.0
Dye (Malachite green)	0.3
Fungistat (Sodium dehydroacetate)	0.2
Pyrethroid	0.05-1.5
Pyrethrum marc	the rest
	100.0 wt%

described by Webley was applied with a modification[4]. A piece of coil (*ca.* 7cm in length or *ca.* 1.2g in weight) was set horizontally by clipping the middle of it on a suitable stand. The stand with coil was placed to smoulder in a glass apparatus shown in Fig. 1, immediately after both sides of the coil were lit. Generated smoke was collected by gently drawing it through the silica gel column trap (Silica Gel for chromatographic use, 60-80 mesh, Kanto Chemical Co., Ltd.).

After the coil had burned, the walls of the glass apparatus and the stand were washed with acetone (200 m*l*), and adsorbates on the silica gel column were eluted with acetone. The combined acetone solution was concentrated and used for analysis.

The remaining piece of coil, if there was, was weighed and the weight of burnt coil was gained by subtracting the weight of the remainder from that of the set coil. However, the piece of coil set burned almost completely because we used a holder (stainless steel) equipped with a sharp-pointed tip as the stand.

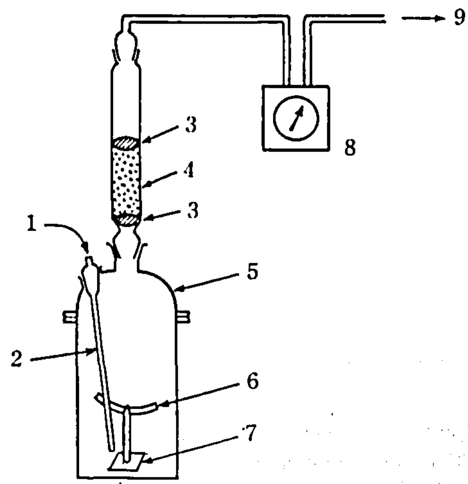

Fig. 1. Apparatus for burning coil and collecting the smoke.
1: Uptake of air 2: Glass tube for air guide 3: Cotton 4: Silica gel column (18 cm long, 2 cm I. D.) 5: Separable flask (10 cm heigh, 8 cm I. D.) 6: Mosquito coil 7: Coil holder 8: Air flow meter 9: Sucking

Analysis. The determination of pyrethroids in mosquito coil smoke was performed by GLC (FID detector). The peak areas were calculated by a half-height width method. The GLC

Table 3. GLC conditions for the determination of pyrethroids in mosquito coil smoke.

Conditions	Pyrethrins	Allethrins	Resmethrins
Column	Glass (1.0m × 3mm⌀)	Stainless steel*2	Stainless steel*2
Liquid phase*1	2% XE-60	5% DC-200+10% QF-1	2% XE-60
Column temperature	180°C	195°C	180°C
Injection temperature	230°C	230°C	220°C
Internal standard (IS)	Dicyclohexyl phthalate	Di-*n*-hexyl sebacate	Phenothrin
Retention time (min) Pyrethroid	3-6	4.5	5.3
Retention time (min) IS	11.0	7.5	8.5
Instrument*3	(a)	(b)	(b)

Conditions	Tetramethrins	Furamethrins	Phenothrins
Column	Stainless steel*2	Glass (0.75m × 3mm⌀)	Stainless steel*2
Liquid phase*1	5% DC-200+10% QF-1	15% DC HV Grease	5% SE-30
Column temperature	210°C	180°C	200°C
Injection temperature	240°C	210°C	220°C
Internal standard (IS)	Benzyl butyl phthalate	Allethrin	Resmethrin
Retention time (min) Pyrethroid	7.5	6.5	12.0
Retention time (min) IS	4.7	11.5	8.0
Instrument*3	(b)	(b)	(b)

*1; Each liquid phase was coated on acid-washed and silanized Chromosorb W (60-80 mesh).
*2; Stainless steel column (1.5m × 3mm⌀).
*3; (a) Shimadzu GC-5A (FID detector). Gas flow rate; carrier (nitrogen) 40ml/min, hydrogen 40ml/min and air 0.9 liter/min.
(b) Yanagimoto GCG-550F (FID detector). Gas flow rate; carrier (nitrogen) 25ml/min, hydrogen 30ml/min and air 0.9 liter/min.

operating conditions are shown in Table 3. It was preliminarily confirmed that in these conditions each pyrethroid and internal standard were not interfered with peaks originating from inert fillers of coils.

Ratios of *cis/trans* isomers were determined by GLC using a column (2.5m×3mm⌀) packed with 2% DC QF-1 on acid-washed and silanized Chromosorb W (60-80 mesh)[7].

Vaporization ratio (V.R.). Vaporization ratio of pyrethroid from a burning mosquito coil was calculated according to the following equation.

$$\mathrm{V.R.}\ (\%) = \frac{\text{Pyrethroid in the smoke}}{\text{Pyrethroid in the coil}} \times 100$$

Results and Discussion

Silica gel in the column trap

Twelve grams of silica gel were packed into a glass column (Fig. 1). After collecting smoke from a mosquito coil containing (±)-*cis, trans*-allethrin (0.60%), the silica gel was divided into equal 3 parts. Allethrin in the each part was determined (Table 4). Most of collected allethrin (*ca.* 90%) distributed itself in a lower part of the silica gel column. There was a little (1.0%) in a middle part and 9.7% on the glass wall of the separable flask and coil holder. No allethrin was detected in a higher part of the column, indicating that 8g of silica gel were enough to collect allethrin in smoke.

Table 4. Distribution of (±)-*cis, trans*-allethrin collected from mosquito coil smoke.

Place (silica gel)	Allethrin determined
Higher part (4g)	0.00mg (0.0%)
Middle part (4g)	0.04 (1.0%)
Lower part (4g)	3.52 (89.3%)
Others*	0.38 (9.7%)
Total	3.94mg (100.0%)

* The glass wall of a separable flask and the surface of a coil holder.

Recovery of allethrin from silica gel column

Elution of applied pyrethroids from silica gel would be almost same when they are eluted with acetone (R_f on silica gel TLC developed with acetone: 0.58-0.63). Recovery of (±)-*cis, trans*-allethrin from silica gel column, therefore, as a representative of pyrethroids, was determined. As shown in Fig. 2, recovery of allethrin reached 98.5% by 2 times'elution (each time; 20m*l* of acetone). Almost 100% was recovered by 3 times'elution. Thus in the following experiment,

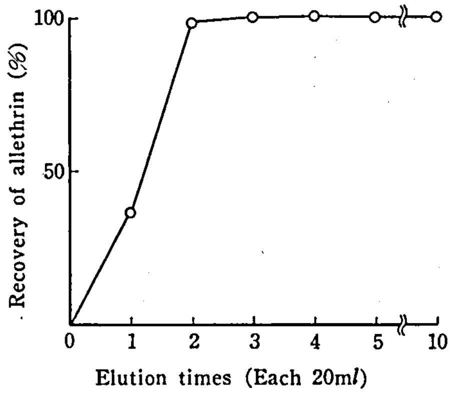

Fig. 2. Relation of recovery of (±)-*cis, trans*-allethrin to elution times with each 20 m*l* of acetone.

elution was made 4 times with each 20m*l* of acetone to recover them completely.

Air flow rate

Relation of air flow rate to burning rate of a mosquito coil in the apparatus used in this experiment is shown in Table 5. One mosquito coil (*ca.* 78cm in length; *ca.* 13g in weight) usually continues burning for a period of 7-7.5 hr in a

Table 5. Relation of air flow to burning rate of a mosquito coil in the apparatus.

Air flow rate (liter/min)	Burning rate* (mg/sec)
2.0-2.2	0.413
2.3-2.5	0.484
2.6-2.8	0.500
3.0-3.2	0.509

* Measurements were repeated 8 times.

usual room, therefore, the burning rate for the room condition can be estimated at 0.481-0.516 mg/sec. In this experiment, the air flow rate was set to 2.5-2.7 liter/min in order to keep burning in the same condition as in a usual room.

Reproducibility of determination

Vaporization ratios of 2 mosquito coils were determined to check reproducibility to this silica gel-trap method (Table 6). Coefficients of variation for a series of 5 determinations were 2.44-2.54 without being influenced by different content of allethrin.

Table 6. Reproducibility of determination of vaporization ratio from burning mosquito coils.

Content of allethrin* in mosquito coil		0.30%	0.50%
		Vaporization ratio (%)	
Exp. No.	1	58.2	57.0
	2	58.4	60.3
	3	61.8	58.8
	4	60.6	60.8
	5	58.1	57.8
Average		59.4	58.9
Standard deviation		1.51	1.44
Coeff. of variation		2.54	2.44

* (±)-*cis, trans*-Allethrin.

Losses of smoke were negligibly small because of a mosquito coil burning in a closed apparatus, therefore, a very high reproducibility was gained, compared with that of Webley's[4]. The extract from silica gel trap, even without pre-treatment for purification, gave satisfactory result by GLC (FID detector). This method is more convenient and of higher accuracy than Webley's method.

Vaporization ratios of various pyrethroids

Vaporization ratios of 6 kinds of pyrethroids and 7 kinds of their isomers from burning mosquito coils were determined (Table 7). They ranged from 26.4% of (+)-*cis, trans*-tetramethrin to 67.8% of (+)-*cis, trans*-phenothrin. Most of the ratios were in 50 to 60%. The vaporization ratios of 2 phenothrin isomers got over 60%, and those of pyrethrins and 3 tetramethrin isomers were below 50%.

Tetramethrin isomers showed the lowest vaporization ratio (*ca.* 30%), which was equal to nearly half the vaporization ratios of allethrin

Table 7. Vaporization ratios of various pyrethroids from burning mosquito coils.

Pyrethroid \ Content in coil (%)	Vaporization ratio (%) 0.05	0.15	0.30	0.60	1.50
Pyrethrins	—	54.2	39.7	35.6	31.2
(±)-*cis, trans*-Allethrin	57.6	58.9	58.0	57.5	57.3
(+)-*cis, trans*-Allethrin	57.8	58.8	60.3	61.0	—
(+)-*trans*-Allethrin	57.3	60.7	59.3	57.8	—
(+)-*trans*-S-Allethrin	—	60.8	60.7	61.2	—
(+)-*cis, trans*-Resmethrin	62.7	57.1	55.9	56.4	54.1
(±)-*cis, trans*-Tetramethrin	33.9	29.3	27.2	30.5	29.0
(+)-*cis, trans*-Tetramethrin	—	26.4	27.8	30.1	29.3
(+)-*trans*-Tetramethrin	34.1	35.1	33.1	33.5	33.6
(±)-*cis, trans*-Furamethrin	—	53.5	49.6	48.8	48.2
(+)-*cis, trans*-Furamethrin	58.9	54.5	47.2	45.2	45.6
(±)-*cis, trans*-Phenothrin	67.0	63.0	63.8	64.8	64.9
(+)-*cis, trans*-Phenothrin	67.8	65.0	63.0	67.5	65.9

isomers. This is probably one of the reasons that tetramethrins do not show any satisfactory effect in a mosquito coil although they have excellent knockdown effect in aerosol or solution formulations. Vaporization ratio was not necessarily proportional to stability of the compound to heat. Tetramethrins are more stable to heat than allethrins, but they showed lower vaporization ratios. It is likely that stability to heat and vapor pressure at initial vaporizing temperature of a compound are complicatedly concerned with vaporization ratio of the compound.

The low vaporization ratio of pyrethrins would be mainly attributable to the lability of pyrethrin I and pyrethrin II to heat[4,5]. The higher vaporization ratio of allethrin isomers should be a reason of their (practical) usefulness for a mosquito coil.

Vaporization ratios were almost the same one another among 4 allethrin isomers, between 2 furamethrin isomers and between 2 phenothrin isomers. (+)-*trans*-Tetramethrin had a little higher vaporization ratio than other 2 tetramethrins. Possibly geometrical and optical isomerism might not affect so largely the vaporization ratios of them.

As to relationship between vaporization ratio and content of a pyrethroid in a mosquito coil, the vaporization ratios of 4 allethrins, 3 tetramethrins and 2 phenothrins were nearly constant, regardless of the different content. The vaporization ratio of resmethrin increased with the decrease of content. This tendency was, however, not so prominent. This inverse relationship between vaporization ratios and contents was also found in 2 furamethrins and remarkably in pyrethrins. There was found a possibility that vaporization ratio of pyrethrins might be nearly equal to that of allethrins at a low content of them. This fact may relate to stability of these compounds to heat because pyrethrins (and also furamethrin) are comparatively unstable to heat. It is believed that pyrethroids appear to be volatilized in the partly carbonized zone (*ca.* 2mm long) behind the burning tip[8]. It takes *ca.* 1.7 min for 2 mm long mosquito coil to burn. Two mm long mosquito coil contains 0.2 mg and 0.05 mg of pyrethroid in 0.60% and 0.15% pyrethroid coils, respectively. Low vaporization ratio in high content of pyrethroid may presumably arise from that the time (*ca.* 1.7 min) is not enough for volatilization of 0.2 mg. of the pyrethroid.

Murayama *et al.* reported that vaporization ratio of (±)-*cis, trans*-allethrin was 28-34% and reached maximum at 0.708% of content in a mosquito coil[6]. They led the smoke into chilled *n*-hexane traps and determined by GLC. We got about 20% higher vaporization ratio than they did, and we could not find the optimum content. It is considered that this discrepancy probably resulted from difference of collection method of smoke and composition of mosquito coil.

Tetramethrins are not so much effective against mosquitoes and houseflies in a mosquito coil as they are in aerosol and solution formulations. In this way, it has been said that there is fairly large difference between effectiveness of an insecticide in a mosquito coil and that in a solution. We would be likely able to discuss on fairly high correlation between them by introduction of vaporization ratios. This point is presently under work.

The *cis/trans* ratio of allethrin in mosquito coil smoke

The *cis/trans* ratios of 4 kinds of allethrin in mosquito coil and in mosquito coil smoke were determined by GLC (Table 8). The results indicate that *cis/trans* ratios of allethrin in mosquito coil smoke are little different from those in mosquito coil. This result means that vaporization ratio is almost the same between *cis*- and *trans*-allethrin, and between (+)- and (−)-allethrin, and that isomerization of allethrin does not occur by heating during burning of mosquito coils. This was also confirmed by spectroscopic analysis (IR, NMR) of allethrin isolated from smoke of a mosquito coil containing (+)-*cis*-allethrin.

Vaporization ratios of allethrin from commercial mosquito coils

Vaporization ratios were determined with 7 blands of mosquito coils available from market in Japan. Allethrin contents in these mosquito coils were determined in our laboratory (Table 9).

Table 9. Vaporization ratios of (±)-*cis, trans*-allethrin from commercial mosquito coils.

Mosquito coil*1	Content of allethrin in mosquito coil (%)	Vaporization ratio (%)
A	0.58	58.4
B	0.57	61.9
C	0.47	64.7
D	0.40	53.2
E	0.32	56.7
F	0.27	53.5
G	0.19	59.5

*1; Every mosquito coil was obtained commercially in market.

All of them contained (±)-*cis, trans*-allethrin at 0.19-0.58%, showing remarkable difference between maximum and minimum.

Vaporization ratios of allethrin were in the range of 53.2 to 64.7%. There was not so much difference among them. Average of them were 58.3%. This is almost the same as vaporization ratio of allethrin from mosquito coils prepared for the tests (Table 7). The data are *ca.* 20% higher than those reported about commercial mosquito coils by Murayama *et al*[6]. This discrepancy would be probably, as described previously, attributable to difference of collection method of smoke.

Vaporization ratio of 6 components of natural pyrethrins

The method of Webley was applied with a modification[4]. Purified "pyrethrins I" (a mixture of cinerin I, jasmolin I and pyrethrin I, purity

Table 8. The *cis/trans* ratios of various allethrins in mosquito coils and mosquito coil smoke.

Allethrin*1	*trans*-Isomer (%)*2 In mosquito coil	*trans*-Isomer (%)*2 In mosquito coil smoke
(±)-*cis, trans*-Allethrin	79.1	80.4
(+)-*cis, trans*-Allethrin	82.9	80.6
(+)-*trans*-Allethrin	99.4	99.2
(+)-*trans*-S-Allethrin	99.8	98.8

*1; Determination was performed in mosquito coils containing each 0.15, 0.30 and 0.60% of allethrin.

*2; *trans*-Allethrin in a *cis/trans* mixture.
Average of 3 replicates.

87.6%) and "pyrethrins II" (a mixture of cinerin II, jasmolin II and pyrethrin II, purity 90.6%) were used for the test[9]. Two mosquito coils containing 0.30% of "pyrethrins I" and of "pyrethrins II" respectively were burned in the apparatus separately. Each component of pyrethrins in the smoke and in the extract from the corresponding mosquito coil was compared quantitatively on the GLC. Peak areas were calculated by weighing paper traces.

As shown in Table 10, vaporization ratios of 3 esters of chrysanthemic acid were higher than those of the corresponding esters of pyrethric acid. This might be the reason why "pyrethrins II" showed lower effectiveness than "pyrethrins I"

Table 10. Vaporization ratio of 6 components of natural pyrethrins.

Component	Vaporization ratio (%)	Reported* (%)	
		(1)	(2)
Cinerin I	55.6	47	64
Jasmolin I	63.0	—	65
Pyrethrin I	30.4	34	40
Cinerin II	41.4	45	53
Jasmolin II	17.1	—	45
Pyrethrin II	15.1	18	20
Mean	37.1	36	48

*; (1) P. R. Chadwick; *Mosquito News*, 30, 162 (1970).
(2) D. J. Webley; *Pyrethrum Post*, 9, 4 (1968).

in mosquito coil although "pyrethrins II" gave quick knockdown effect in oil spray[9]. Values of pyrethrin I and II showed less than half values of jasmolin I and cinerin II, respectively. The low vaporization ratio of pyrethrin I and II would probably result from easy decomposition of them by heat[10]. Pyrethrin I and II are major components and the largest insecticidal principles of pyrethrins[10,11]. It is therefore considered that their low vaporization ratios would limit their usefulness in mosquito coils.

The value of jasmolin II was much smaller than that reported by Webley[4]. He used a mosquito coil, in which the content of pyrethrins was not definite because the coil was prepared by dipping a piece of blank coil into a pyrethrins solution (a mixture of 6 components). And jasmolin I and II were not completely separated from cinerin I and II, respectively on his GLC, because of unsuitable GLC conditions. These would cause this disagreement.

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