Korean J. Chem. Eng., **27**(1), 228-230 (2010)
DOI: 10.1007/s11814-009-0288-2

Separation of esbiothrin and D-acetylene C permethrin in electric-mosquito coils by gas chromatography

Junyu Liu and Kyung Ho Row†

Department of Chemical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Korea
(*Received 13 February 2009 • accepted 19 May 2009*)

Abstract−A simple and sensitive gas chromatography method for the simultaneous determination of esbiothrin and D-acetylene C permethrin in electric-mosquito coils using palmitic acid isopropyl as an internal standard was developed. The electric-mosquito coil samples were extracted with petroleum ether (60-90 °C) and then centrifuged at 2,000 r/min for 2.0 min. The supernatant liquids were collected into a glass bottle and 2.0 μL of it was injected into the gas chromatograph. The results showed that the means recoveries of esbiothrin and acetylene c permethrin ranged from 100.2% to 99.8%. The relative standard deviation (n=10) of allylic permethrin and acetylene C permethrin was 0.44% and 0.26%, respectively. This method is a viable alternative tool to the existing gas chromatography methods for analyzing the content of allylic permethrin and D-acetylene C permethrin in electric-mosquito coil samples.

Key words: Esbiothrin, Acetylene C Permethrin, Electric-mosquito Coils, Gas Chromatography

INTRODUCTION

Natural pyrethrins from insecticidal pyrethrum extract and synthetic pyrethroids, such as allethrin, esbiothrin, cyfluthrin, deltamethrin and acetylene C permethrin, are active ingredients in insecticidal formulations, including powders, sprays, impregnated papers, electro-evaporators and mosquito coils intended for indoor use. In developing countries, a large number of these pyrethroid formulations were extensively used as mosquito repellents in the late 20th century because of their good photostability, enhanced insecticidal activity and relatively low toxicity when compared with other organochlorine and organophosphorus insecticides [1,2]. Esbiothrin (3-Allyl-2-methyl-4-oxo-2-cyclopentenyl chrysanthemate) and acetylene C permethrin ((S)-2-Methyl-3-(2-propynyl)-4-oxocyclopent-2-enyl-(lR)-cis,trans-2,2-dimethyl-3-(2-methyl-1-propenyl) cyclopropanecarboxylate) are two improved isomeric composition of allethrin/permethrin series that were widely used in mosquito coils, electric-mosquito coils and liquid electric mosquito coils.

With people paying more and more attention to environmental protection and safety, low toxicity and no contaminated products have been desired [3-7]. Many analysis methods including liquid chromatography [8-10], second-derivative polarography [11,12] had been developed for pyrethrin determination. However, the sample preparing processes were considered complicated and time-consuming because the sample matrix is complex and many components originating from the sample may interfere with the determination. A simple, sensitive and reliable method for the quantitative determination of esbiothrin and acetylene C permethrin in insecticidal products was demanded for further investigation of their active ingredients and toxicity.

People usually use acetone as the solvent and use disbutylphalate as the internal standard. Acetone and disbutylphalate are all damaging to people's health.

In this work, esbiothrin and D-acetylene C permethrin in electric-mosquito coils were extracted with petroleum ether (60-90 °C) and then analyzed by gas chromatography (GC). By using palmitic acid isopropyl (IPP) as an internal standard and petroleum ether as extraction solvent, the recoveries of esbiothrin and acetylene c permethrin were 99.0% with relative standard deviations less than 0.44%. This method is a viable alternative tool to the existing GC methods for analyzing the content of allylic permethrin and D-acetylene C permethrin in electric-mosquito coil samples. The electric-mosquito coil is a commonly used device, which is to repel and be anti-mosquito. There are many compounds or plant extract that can be volatile on it [13].

EXPERIMENTAL

1. Materials

Esbiothrin and acetylene C permethrin were obtained from Jiansu Yangnong Chemical Co. Ltd. (≥93%) and Shanghai Quandao Co. (≥98%). Isopropyl palmitate was purchased from Kunshan Huaxin Chemical Reagent Company (GR). Petroleum ether (60-90 °C) was obtained from Tianjin North-tianyu Chemical Company (AR). Acetone was purchased from Tianjin Huadong Chemical Reagent Company (AR). All the other reagents used in the experiment were of the highest grade commercially available. Double deionized water was filtered with a 0.45 μm filter membrane before use.

2. Sample Preparation

Esbiothrin 17.35 g and acetylene C permethrin 7.58 g were put into measuring flask and then petroleum ether to 100.0 mL was added. For specimen samples, esbiothrin sample 17.42 g and acetylene C permethrin sample 7.44 g were put into measuring flaks, and then petroleum ether to 100.0 mL was added. IPP is the internal standard for both esbiothrin and acetylene C permethrin. Internal stan-

†To whom correspondence should be addressed.
E-mail: rowkho@inha.ac.kr

dard: 1.26 g IPP was dissolved in Petroleum ether to 100.0 mL.

Different sample solutions (standard solutions or specimen samples) were added into mosquito coil samples, and then sealed by aluminum film under 25 °C for 24 hours to make sure the samples were fully invaded. The obtained mosquito coil samples were cut up and mixed with 2.0 mL internal standard and 10.0 mL petroleum ether into a 15.0 mL bottle absolutely. The esbiothrin and the acetylene C Allylic were fully released into petroleum from the mosquito coil samples after one hour oscillation. Finally, the extraction solution was centrifuged for 2.0 min at 2,000 rpm and the supernatant fluid was used for further chromatographic analysis.

3. Instrument

GC analysis was performed using a Shimadzu GC-14B system equipped with an FID detector (Shimadzu, Japan). A SPH-300 and SPB-3 completely automatic air source was purchased from Beijing BCHP Analytical Technology Institute. A HS-2000 Chromatography data workstation (Yingpu Science and Technology Development Co., Ltd, Hangzhou, China) was used as a data acquisition system. 80-2 centrifugal precipitation machine was obtained from Shanghai Rongtai Biochemistry Project Limited Company. The analytical column was SE-30 Capillary column: (30 m×0.53 mm). High-purity hydrogen was used as carrier gas and programmed temperature mode was applied in this work. The temperature was programmed from 200 °C (hold 5.5 min) to 250 °C (hold 4.0 min) at 35 °C/min as the heating rate. Detection temperature was set at 265 °C.

RESULTS AND DISCUSSION

1. Determination of the Target Analytes

From the chromatogram of mosquito coil samples in Fig. 1, it can be seen that the retention time of dibutyl phthalate is 2.97 min, esbiothrin is 4.40 min and acetylene C permethrin is 4.76 min. At the same conditions, Fig. 2 shows that IPP as internal standard has similar retention time (3.83 min) with esbiothrin and acetylene C permethrin. Moreover, these three compounds can be base-line separated with other interferences. So palmitic acid isopropyl (IPP) can be used as a potential internal standard instead of the common internal standard, dibutyl phthalate, to provide more veracity for quantitative analysis.

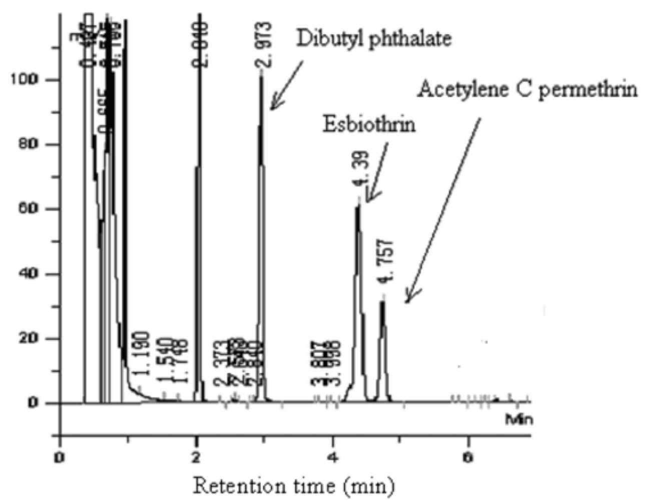

Fig. 1. Chromatogram of mosquito coils using dibutyl phthalate as internal standard materials.

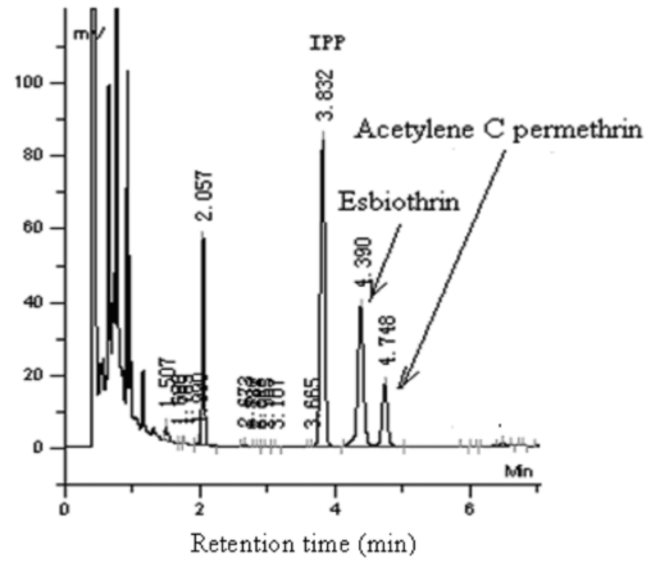

Fig. 2. Chromatogram of mosquito coils using IPP as internal standard materials.

2. Validation of the Proposed Method

Calibration curves were constructed by using the rate of peak areas of analytes with the internal standard measured at six increasing sample weights, in a range of 0. 05 to 0.20 g.

$A_{standard}/W_{standard}/=A_{sample}W_{sample}$ Here, W_{sample} is the weight of the sample, A_{sample} is the area of the sample; $W_{standard}$ is the weight of the sample, $A_{standard}$ is the area of the sample.

At the optimum chromatography conditions, different weight standard samples were added to the mosquito coils and pretreated according to the previous description for chromatographic determination. The regression equations were

$y=7.5006\times(r^2=0.9999)$

x is from 0.05 g to 0.2 g, x is the weight of the samples.
for esbiothrin, and

$y=3.2078\times(r^2=0.9999)$.

x is from 0.05 g to 0.2 g, x is the weight of the samples.
for acetylene C permethrin, respectively.

3. Precision and Recoveries

To make sure of the subject in the detection limit, this experiment took the added recovery method. Mosquito coil tablets (added 140 mg standard samples) were measured 10 times in parallel to find the relative standard deviation was 0.4% for esbiothrin and 0.3% for acetylene C permethrin. The mean recoveries of esbiothrin and acetylene C permethrin in the electric-mosquito coil samples were evaluated by spiking seven different levels of standard analytes to the controlled samples, and the results are shown in Table 1 and Table 2. The results show that the mean recovery for esbiothrin was 100.2% with SRD 1.3%, and the mean recovery of acetylene C permethrin was 99.8% with SRD 1.5%. So the method is reliable and can be used for the determination of esbiothrin and acetylene C permethrin in mosquito coil products.

Table 1. The recoveries of esbiothrin in mosquito coils tablets

No.	Quantity of sample (mg)	Quantity of measure (mg)	Quantity of added (mg)	Recovery (%)	Averrage (%)	RSD (%)
B1	4.35	8.62	4.27	100.1	100.2	1.3
B2	7.01	14.35	7.23	101.6		
B3	8.39	17.27	8.69	102.2		
B4	12.02	23.96	11.97	99.8		
B5	15.36	30.41	14.98	100.5		
B6	19.02	35.66	16.92	98.3		
B7	0.0	24.66	24.47	99.2		

Table 2. The recoveries of acetylene C permethrin in mosquito coils tablets

No.	Quantity of sample (mg)	Quantity of measure (mg)	Quantity of added (mg)	Recovery (%)	Average (%)	RSD (%)
B1	1.86	3.65	1.83	97.9	99.8	1.5
B2	3.00	6.13	3.09	101.1		
B3	3.59	7.37	3.72	101.7		
B4	5.12	10.22	5.12	99.6		
B5	6.57	13.02	6.41	100.5		
B6	8.14	15.24	7.24	97.8		
B7	0.00	10.45	10.47	99.8		

CONCLUSIONS

Esbiothrin and D-acetylene C permethrin in electric-mosquito coils were extracted with petroleum ether (60-90 °C) and then analyzed by gas chromatography. The results show this method is suitable for analyses of the chemical compounds in the electric-mosquito coils. It will be a great help to the researcher in the related anti-mosquito area.

ACKNOWLEDGMENTS

This research was supported by Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (2009-0072787).

REFERENCES

1. A. Ramesh and M. Balasubramanian, *Analyst*, **123**, 1799 (1999).
2. T. G. Floore, C. B. Rathburn, A. H. Boike, J. S. Coughlin and M. J. Greer, *J. Am. Mosq. Control Assoc.*, **8**, 58 (1992).
3. M. Narendra, N. C. Bhatracharyulu, P. Padmavathi and N. C. Varadacharyulu, *Chemosphere*, **67**, 1065 (2007).
4. Y. Matoba, A. Inoue and Y. Takimoto, *J. Pesticide Sci.*, **29**, 313 (2004).
5. F. A. Abdel-Mohdy, M. G. Fouda, M. F. Rehan and A. S. Aly, *Carbohydr. Polym.*, **73**, 92 (2008).
6. F. W. Mosha, R. J. Njau and J. Alfred, *Med. Veter. Entomolo.*, **6**, 44 (1992).
7. A. Ramesh and A. Vijayalakshmi, *J. Environ. Monitoring*, **3**, 191 (2001).
8. C.H. Lentza-Rizos, E. J. Avramides and E. Visi, *J. Chromatogr. A*, **921**, 297 (2001).
9. Y. C. Ling and I. P. Huang, *J. Chromatogr. A*, **695**, 75 (1995).
10. Z. Du, X. Zhu and R. Xiang, *Chem. Res. Appl.*, **9**, 429 (1997).
11. Q. Wu and K. Liu, *Chin. J. Ana. Chem.*, **21**, 1095 (1993).
12. Q. Wu and K. Liu, *Ana. Lab.*, **12**, 7 (1993).
13. U. Sakulku, O. Nuchuchua, N. Uawongyart, S. Puttipipatkhachorn, A. Soottitantawat and U. Ruktanonchai *Int. J. Phytorem.*, **105-111**, 372 (2009).