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SHORT COMMUNICATION

DETERMINATION OF CYPERMETHRIN RESIDUES IN *GINGKGO BILOBA* LEAVES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT. A simple and rapid method was described for the determination of cypermethrin in *Ginkgo biloba* leaves by high performance liquid chromatography (HPLC) with UV detection. A mixture of hexane and acetone (99:1) was used to extract the samples. After the sample cleanup was carried out with a mixture of petroleum ether and ethyl acetate (9:1) cypermethrin in the sample was analyzed using a Phenomenex Luna 5 micron second-generation silica column packed with Florisil and active carbon. The recovery of cypermethrin was 81.0% and the relative standard deviation was 3.2%.

KEY WORDS: *Ginkgo biloba* leaves, Cypermethrin, HPLC

INTRODUCTION

Pyrethroids pesticides are widely used [1] and therefore, it is important to have a method available for determining pyrethroids pesticides residues. Pyrethroids pesticides residues can be determined by GC. Recently, the determination of pyrethroids by HPLC had been reported [2-9]. Lopez *et al.* [2] developed for instance a method for determination of 7 kinds of pyrethroids in vegetable with HPLC-UV. Galera *et al.* [3] determined 3 kinds of pyrethroids in soil by HPLC with HypersilC_{18} column and DAN headspace injector. An analytical method was developed to analyze 4 pesticides in vegetable using HPLC by Metwally and Osman [4]. Wei-xuan Lin *et al.* [5] analyzed pyrethroids pesticides residues in brown rice by HPLC. The analysis of pyrethroids in *Ginkgo biloba* leaves by HPLC has not been reported yet.

Cypermethrin is an important pyrethroids pesticide. It is a kind of strong pesticide and has long rudimental time. Cypermethrin is usually used to kill pest on vegetables, fruit trees and tea [10]. In this study, a mixture of hexane and acetone (99:1) was used to extract the analyte. After sample cleanup was carried out with a mixture of petroleum ether and ethyl acetate (9:1) cypermethrin in the sample was analyzed by UV detection using a Phenomenex Luna 5 micron second-generation silica column packed with Florisil and active carbon.

EXPERIMENTAL

Apparatus. Spectra-physics SP8810 HPLC, equipped with UV detector; N-1NW revolving evaporator (Tokyo Physics and Chemistry Company, Japan); high-speed homogenizer (German IKA Company); HY-4 timing multi-oscillator (JiangSu JinSheng Apparatus Factory); T500 electronic balance (ChangShu Testing Apparatus Factory); and R200D precision electronic balance (German Sartorius Company) were used.

Reagents and materials. Florisil (60-100 mesh, Shanghai, China) was activated at 650 ^{o}C for 4 h and then cooled in a desiccator. Anhydrous sodium sulfate was dried at 400 ^{o}C for 10 h. Active carbon was treated with 36.5 % hydrochloric acid.

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Cypermethrin standards were provided by Dow AgroSciences, Indianapolis (IN46268, USA). The cypermethrin standard's purity was 94.8%. The pesticide's concentration was 2.000 mg/L in hexane.

Samples treatment. 5.00 g of the chopped sample was weighed and put into a centrifugal tube, then 50.0 mL mixture of hexane and acetone (99:1) was added. The refining was extracted for 3 min. The mixture was filtrated through anhydrous sodium sulfate, and the remnant was washed with 1 mL hexane. The filter liquor was put together and dried in the evaporating dish around N_2 till it nearly dry.

9.0 g Florisil, 0.4 g active carbon and 1 cm high anhydrous sodium sulfate were packed in turn in a glass chromatographic column (30 cm x 2 cm i.d.). The concentrate was transferred to the chromatographic column pre-eluviated by 20.0 mL of the mixture of petroleum ether and ethyl acetate (9:1). Then the sample was eluted by 80.0 mL of the mixture of petroleum ether and ethyl acetate (9:1). All the eluent was collected, concentrated completely in 40 ^{o}C water bath, and then a little hexane was added, spin evaporated, and reduced to 5.0 mL with hexane. The sample was then analyzed by HPLC.

Mobile phases and columns. Chromatographic column was Phenomenex Luna 5 micron second-generation silica and 250 mm x 4.6 mm. The mobile phase (degassed ultrasonically) was a mixture of hexane and tetrahydrofuran (99:1). The detector wavelength was 254 nm and the flow rate was 1.0 mL/min. A 10.00 μL aliquot of this solution was injected into the HPLC and detected by UV according to the procedure described above.

Quantification and identification. Quantitation was carried out using calibration curves and identification was based on the retention time of pesticide.

RESULTS AND DISCUSSION

Optimization of mobile phase. The composition of the mobile phase had more effect on sample determination than the flow rate, so the composition of the mobile phase was optimized first. It turned out that the longer the analytic time, the wider the peak was and the lower the sensitivity was when the content of tetrahydrofuran was higher. However, if the content of tetrahydrofuran was lower, the isomeric compound pesticides were not separated thoroughly. The pyrethroids were separated thoroughly if the proportion of mobile phase was the mixture of hexane and tetrahydrofuran (99:1).

After the confirmation of the proportion of mobile phase, the flow rate of mobile phase was ranged from 1.0 mL/min to 1.5 mL/min. It could be seen that the peak width and the peak area did change much, so the flow rate of the mobile phase was selected as 1.0 mL/min. Good peak shape and separation results were obtained at the proportion and the flow rate above, The result is shown in Figure 1.

Regression equation. A series of pyrethroids' standard solutions was dissolved in hexane. A 10.00 μL aliquot was injected. They were analyzed by UV detector according to the proposed method. The calibration curve was obtained by plotting the peak area versus pesticides' concentration. Regression equation was $y = 120.05x - 2.889$ and the correlation coefficient was $R = 0.9991$. The concentration range of cypermethrin was 0.200-8.00 μg/mL.

Determination of sample. The method described above was carried out to determine the residue of cypermethrin in *Ginkgo biloba* leaf sample. The chromatogram of the blank *Ginkgo biloba* leaf sample and the *Ginkgo biloba* leaf sample are shown in Figure 2 and Figure 3, respectively. The recovery of cypermethrin was 81.0% and the relative standard deviation was 3.2%.

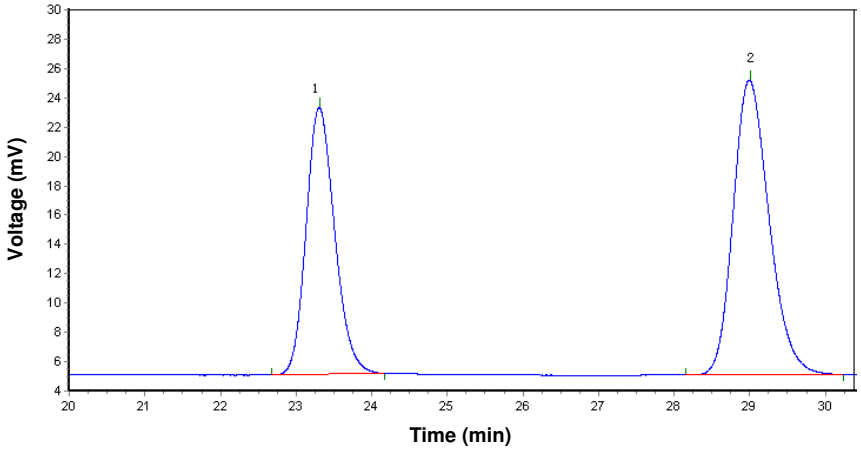

Figure 1. Chromatogram of cypermethrin standard solution. (1) 1,1-Cypermethrin and (2) 2,2-cypermethrin.

Comparison of determination of pestcide residues by GC and HPLC. GC and HPLC were compared to determine the residue of cypermethrin in *Ginkgo biloba* leaf sample. The results are shown in Table 1. The results indicate that HPLC method less sensitive than the GC method. However it can be used as an alternate to the GC method.

Table 1. Comparison of determination of pestcide residues by GC and HPLC.

Parameter	GC-ECD	GC-MS	HPLC-UV
Cleanup method	Strict	Strict	Not strict
Retention time (min)	16.828 - 17.240	19.994 - 20.277	23.307 - 29.007
Limit of detection (mg/kg)	0.002	0.05	0.1
Recovery (%)	86.8	89.1	81.0

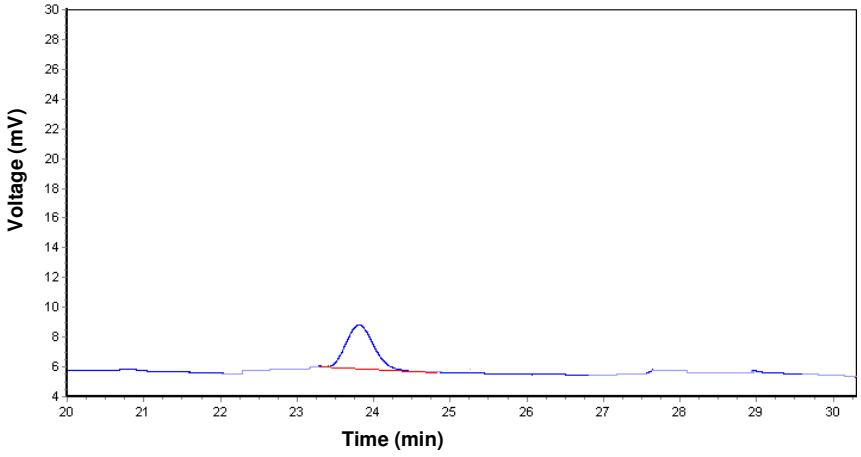

Figure 2. Chromatogram of the blank *Ginkgo biloba* leaf sample.

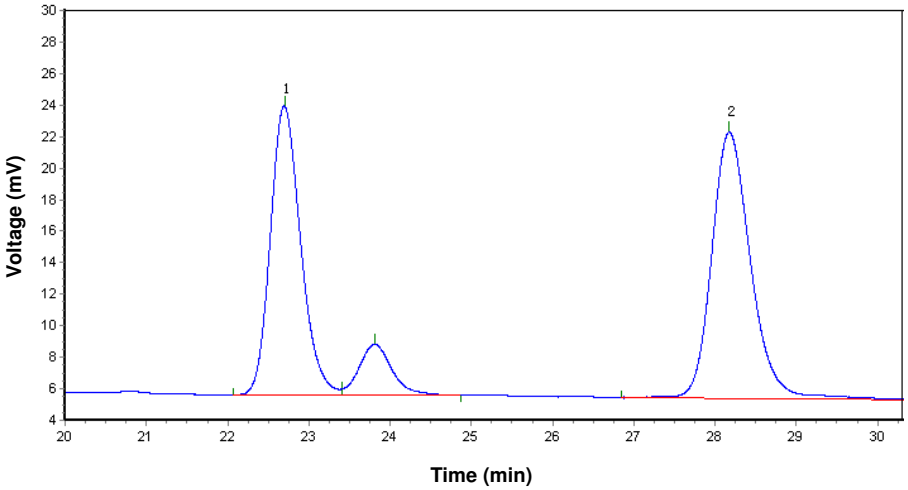

Figure 3. Chromatogram of *Ginkgo biloba* leaf sample. (1) 1,1-Cypermethrin and (2) 2,2-cypermethrin.

CONCLUSION

An efficient method for the analysis of pyrethroids residues in *Ginkgo biloba* leaves by HPLC with UV detector using Phenomenex Luna 5 micron second-generation silica column was developed. The method was simple to determine the residue of pyrethroids with HPLC. The procedure described above may be helpful in formulating the residual standard of determining pyrethroids with HPLC in some departments or countries.

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REFERENCES

1. Chen, Z.M.; Wan, Y.H. *J. Chromatogr. A* **1996**, 754, 367.
2. Lopez, T.L.; Garcia, M.D.G.; Vidal, J.L.M. *Anal. Chim. Acta* **2001**, 447, 101.
3. Galera, M.; Vidal, J.L.M. *J. Chromatogr. A* **1996**, 727, 39.
4. Metwally, M.E.S.; Osman, M.S. *Food. Chem.* **1997**, 59, 283.
5. Lin, W.; Li, J.; Wang, M. *Chinese J. Health Laboratory Technology* **2001**, 11, 31.
6. Wang, I.H.; Subramanian, V.; Moorman, R. *J. Chromatogr. A* **1997**, 766, 277.
7. Frenich, A.G.; Galera, M.M.; Vidal, J.L.M. *J. Chromatogr. A* **1996**, 727, 27.
8. Chun, Y.; Li, L. Gong, Z. *J. Xiamen University (Natural Science)* **2003**, 42, 78.
9. Zhang, Y.; Peng, L.; Zhou, H. *J. Qiqihar University* **2002**, 18, 40.
10. Liu, Q.; Zhu, G. *New Edition Using Manual of Pesticide* (in Chinese), Science and Technology Press of Shanghai: Shanghai; **2000**.