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Research Article

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Quantitative Analysis of Cinnamaldehyde, Cinnamylalcohol and Salicylaldehyde in Commercial Biopesticides Containing Cinnamon Extract Using Gas Chromatography - Flame Ionization Detector

Sung-Jin Lim,[1†] Ji-Hye Lee,[1†] Jin-Hyo Kim,[1] Geun-Hyoung Choi,[1] Nam-Jun Cho[1] and Byung-Jun Park[1*]

[1]Chemical Safety Division, National Academy of Agricultural Science, Rural Development Administration, Jeonju 560-500, Korea

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Abstract

BACKGROUND: In an environment-friendly agriculture, plant extracts have been perceived as alternatives of synthetic pesticides. The Environment-friendly Agriculture Promotion Act of Korea has approved cinnamon extract as a matter for the production of commercial biopesticides. Thirteen commercial biopesticides containing cinnamon extract have been marketed locally. However, the analytical method for the quality control of these biopesticides containing cinnamon extract has not been studied.
METHODS AND RESULTS: Cartridge clean-up method for the determination of cinnamaldehyde, cinnamylalcohol and salicylaldehyde in biopesticides containing cinnamon extract was developed and validated by gas chromatography (GC). The clean-up method was optimized with HLB SPE cartridges for the bioactive substance in biopesticides containing cinnamon extract, and the eluate was analyzed by GC. The developed method was validated, and the LOQ and recovery rates of cinnamaldehyde, cinnamylalcohol and salicylaldehyde were 0.139, 0.067 and 0.062 mg L^{-1} and 84.2, 86.5 and 82.1%, respectively. The contents of cinnamaldehyde, cinnamylalcohol and salicylaldehyde were analyzed using the developed method in the 13 commercial biopesticides. Results showed 0.06-17.37%, <LOQ-0.01% and <LOQ, respectively.
CONCLUSION: This method would contribute to manufacturers producing biopesticides and the quality control of biopesticides containing cinnamon extract.

Key words: Biopesticide, Cinnamaldehyde, Cinnamon, Cinnamylalcohol, Salicylaldehyde

Introduction

For the past forty years, the increase of food production has been based on the increased use of synthetic pesticides for pest control (Oerke, 2006). The adverse effect of synthetic pesticides on the environment and human health encouraged the investigation of biopesticides, known to be relatively less toxic than the synthetic pesticides (Saxena, 1989; Kim and Smith, 2001; Cerejeira *et al.*, 2003; Katsumata *et al.*, 2005; Pimentel, 2005; Tripathi *et al.*, 2009).

[†]These authors contributed equally to this work.
*교신저자(Corresponding author): Byung-Jun Park
Phone : +82-63-238-3201; Fax : +82-63-238-3836;
E-mail : bjpark@korea.kr

In an environment-friendly agriculture, plant extracts have been perceived as a substitute material for synthetic pesticides, recognized as not alarming to human and animal health (Arnason *et al.*, 1989; Wink, 1993). Cinnamon is obtained from the inner bark of several species from the genus *Cinnamomum,* a native crop in Sri Lanka and tropical areas in Asia (Jakhetia *et al.*, 2010; Jayaprakasha and Rao, 2011). This has been widely used as spice and flavoring agent in foods (Aruoma *et al.*, 1989; Boelens Aroma Chemical Information Service, 2000). Its pharmacological activities such as antioxidant, antimutagenic, antiulcer, antimicrobial, antidiabetic and anti-inflammatory have been reported (Tabak *et al.*, 1999; Matan *et al.*, 2006; Mathew and Abraham, 2006; Kim *et al.*, 2006; Jayaprakasha *et al.*, 2007; Tung *et al.*, 2008). Also, cinnamaldehyde, cinnamylalcohol and salicylaldehyde, constituents of cinnamon, have been known as antifungal and insecticidal material (Wang *et al.*, 2005; Yang *et al.*, 2005; Cheng *et al.*, 2006; Cheng *et al.*, 2009).

The instrumental methods for analyzing of cinnamaldehyde, cinnamylalcohol and salicylaldehyde using liquid chromatography (LC), gas chromatography (GC)-mass spectrometry (MS) and LC-MS in food and plants has been reported (Yajima *et al.*, 1983; Friedman *et al.*, 2000; Janes and Kreft, 2008; Srivastava and Cohen, 2009; Ding *et al.*, 2011). But the content evaluation in biopesticides has not been reported yet.

Contents of the active substances in thirteen commercial biopesticides containing cinnamon extract in Korea were not also studied.

Recently, the limonoids analysis method for the quality control of commercial biopesticides was reported by Lee *et al.* (2013). This method used the hydrophilic lipophilic balance (HLB) solid phase extraction (SPE) cartridge for clean-up and ultra-performance liquid chromatography (UPLC) for the determination of insecticidal limonoids in biopesticides containing neem extract. Lim *et al.* (2014) reported that insecticidal matrine substances in commercial biopesticides containing *Sophora flavescens* extract could be quantified by clean-up method using ENVI-Carb SPE cartridge.

This study was aimed to define the marker compound of cinnamon based on the crop protection effect and to develop the clean-up method and GC conditions for the determination of cinnamaldehyde, cinnamylalcohol and salicylaldehyde in biopesticides containing cinnamon extract. The study also conducted to investigate the contents of cinnamaldehyde, cinnamylalcohol and salicylaldehyde in commercial biopesticides.

Materials and Methods

Chemicals and reagents

Cinnamaldehyde (99% purity), cinnamylalcohol (97% purity) and salicylaldehyde (98% purity) were purchased from Sigma-Aldrich, Saint Louis, USA. The high pressure liquid chromatography (HPLC) grade acetone was obtained from Tedia, Ohio, USA. The ENVI-Carb solid phase extraction (SPE) cartridge (500 mg, 6 mL), HLB SPE cartridge (60 mg, 3 mL) and Florisil SPE cartridge (1000 mg, 6 mL) were purchased from Supelco, Philadelphia, Waters, Milford, and Applied Separations, Pennsylvania, USA, respectively. Thirteen (11, liquid type and 2, solid type) commercial biopesticides containing cinnamon extract were purchased from eight local companies in Korea.

Selection of marker compounds in biopesticides

Three constituents in the cinnamon extract were selected as marker compounds in the biopesticides: cinnamaldehyde, cinnamylalcohol and salicylaldehyde. GC with flame ionization detector (FID) was used for content analysis.

Method for marker compounds analysis

The marker compounds in biopesticides containing cinnamon extract were analyzed using the ENVI-Carb and HLB SPE cartridges. One mL of diluted biopesticide (100 times) with distilled water (DW) was placed in the ENVI-Carb SPE cartridge and eluted with 12 mL of hexane (3 mL×4). The organic phase was concentrated using an evaporator (Rotavapor R-124) purchased from Büchi, Flawil, Switzerland. Dried residue was then re-dissolved in 2 mL same solvent for GC analysis. The clean up using a HLB SPE cartridge was performed with the modified method of Lee *et al.* (2013). One mL of diluted biopesticide (20 times) with DW was loaded on the HLB SPE cartridge which was activated with 2 mL of acetone and 1 mL of DW, and eluted with 6 mL (2 mL×3) of acetone after washing with 2 mL of distilled water. Eluate was evaporated and re-dissolved in 5 mL of acetone for the analysis.

Gas chromatography analysis

GC conditions for analyzing cinnamaldehyde, cinnamylalcohol and salicylaldehyde, were: system, Agilent 6890 series with FID (Agilent, Santa Clara, USA); column, RTX-5 (30 m × 0.25 mm × 0.25 mm, RESTEK, Pennsylvania, USA); carrier gas, He (99.999%, 6 mL min^{-1}); injector temperature, 230℃; oven temperature, initial 70℃ (2 min hold), 3℃ min^{-1}, 93℃, 30℃ min^{-1}, 130℃, 3.5℃ min^{-1}, 140℃, 40℃ min^{-1}, 300℃; detector temperature, 300℃; and injection volume, 1 μl.

Method validation

Sample preparation and analytical methods were validated in terms of linearity, limits of quantitation (LOQ), confirmatory and precision. The linearity of the calibration curves was evaluated by standard solution at concentrations 0.05, 0.1, 0.5, 1, 5 and 10 mg L^{-1}, respectively, with five replications. The LOQ for cinnamaldehyde, cinnamylalcohol and salicylaldehyde were the concentration that produced a signal-to-noise ratio of 10. Confirmatory test was done based on the recovery assay results of samples spiked with all analytes at 6 mg L^{-1}, with three replications. Recoveries were calculated by comparing the extracted amounts to the spiked with calibration curves of the cinnamaldehyde, cinnamylalcohol and salicylaldehyde, respectively. The intermediate precision, expressed as relative standard deviation (RSD, %), was determined through the replicates data (five replications) for three days at different levels.

Results and Discussion

Marker compound selection

Three substances, namely, cinnamaldehyde, cinnamylalcohol and salicylaldehyde were selected as marker compounds of cinnamon for their characteristics of crop protection. Commercial biopesticides generally contains a surfactant as additive. FID has also been used for the component analysis in matrix containing surfactant (Tacx and German, 1989; Fendlnger *et al.*, 1992; Yan *et al.*, 2012). Thus, FID was used for analyzing the three marker compounds. Findings showed that cinnamaldehyde, cinnamylalcohol and salicylaldehyde showed good sensitivities and retention times of 11.06, 11.55 and 5.03 min, respectively (Fig. 1).

Method of biopesticides analysis

In cleaning the biopesticides containing cinnamon extract, ENVI-Carb and HLB SPE cartridges were used. Usefulness of these cartridges for analyzing the marker compounds in biopesticides was reported by Lee *et al.* (2013) and Lim *et al.* (2014). Results showed that the recovery rates of three tested substances in liquid and solid-type biopesticides were lower than 50% during the clean-up method using an ENVI-Carb SPE cartridge. This method was used for the clean-up of matrine and oxymatrine in commercial biopesticides containing *Sophora flavescens* (Lim *et al.*, 2014).

The HLB SPE cartridge was used for the clean-up of marker compounds such as azadirachtin A, azadiracchtin B, deacetylsalannin and salannin in commercial biopesticides containing neem extract (Lee *et al.*, 2013). Using this method, the recovery rates of cinnamaldehyde, cinnamylalcohol and salicylaldehyde

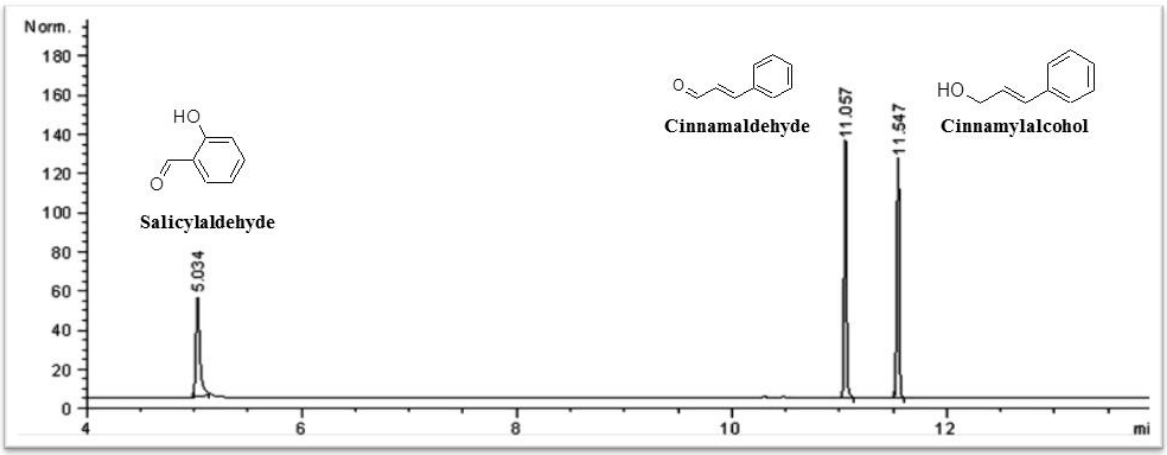

Fig. 1. Chromatogram and structure of cinnamaldehyde, cinnamylalcohol and salicylaldehyde.

in liquid and solid-type biopesticides were 82.1-86.5 and 77.1-89.3%, respectively (Table 1). From these results, HLB SPE cartridge was selected for clean-up method which showed the good recovery rates of cinnamaldehyde, cinnamylalcohol and salicylaldehyde. Hence, these results indicated that the HLB SPE clean-up method was accepted for cinnamaldehyde, cinnamylalcohol and salicylaldehyde analysis in biopesticides containing cinnamon extract (Fig. 2).

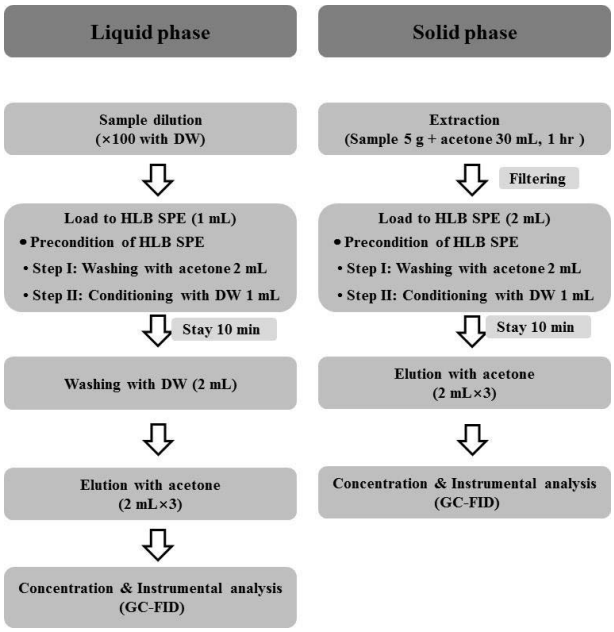

Fig. 2. Flow charts for cinnamaldehyde, cinnamylalcohol and salicylaldehyde analysis in the liquid and solid phase biopesticides.

Method validation

The calibration curves of three substances were prepared form a concentration of 0.05-10 mg L^{-1} by its peak area, respectively. The coefficient of correlation of all calibration curves was 0.9999. The LOQs of cinnamaldehyde, cinnamylalcohol and salicylaldehyde were 0.062, 0.139 and 0.067 mg L^{-1}, respectively (Table 1). Confirmation of the analytical method was carried out in terms of recovery rates of the spiked sample having no cinnamon extract. Recovery rates of cinnamaldehyde, cinnamylalcohol and salicylaldehyde in liquid and solid-type biopesticides obtained 82.1-86.5 and 77.1-89.3% by the established method, respectively (Table 1). The inter- and intra-day precision methods were measured by recovery rates of cinnamaldehyde, cinnamylalcohol and salicylaldehyde for three days. The method was found effective since RSD percentages ranged from 1.9-5.9% and below 15, the normal percent value (Table 1). These results showed that the analytical method including clean-up procedure was suitable for determination of marker compounds contents in biopesticides containing cinnamon extract.

Marker levels in commercial biopesticides

Marker levels of commercial biopesticides containing cinnamon extract were determined with the developed method. The developed method for cinnamaldehyde, cinnamylalcohol and salicylaldehyde analysis was also applied to commercial biopesticides containing cinnamon extract. Figure 3 presents the representative chromatogram of the cinnamaldehyde, cinnamylalcohol and salicylaldehyde contents in biopesticide samples.

Cinnamaldehyde, cinnamylalcohol and salicylaldehyde in all samples were detected at 0.06-17.37%, <LOQ-0.01% and <LOQ, respectively (Table 2). The antibacterial activity of cinnamon and its main inhibitory component, the cinnamaldehyde, were reported by Ouattara *et al.* (1997) and Jayatilaka *et al.* (1995). The effectiveness of cinnamaldehyde against molds and yeasts was also reported by López-Malo *et al.* (2002). Nguefack *et al.* (2001) also reported that cinnamon oil at 1000 mg L^{-1} concentration completely inhibited the growth of *Aspergillus flavus*. Ten of the

Table 1. Validation parameters

Compounds	Linearity (r^2)	LOQ (mg L^{-1})	Recovery rate[a] (%)		RSD (%)			
					Inter-day		Intra-day	
			Liquid product	Solid product	Liquid product	Solid product	Liquid product	Solid product
Cinnamaldehyde	0.9999	0.139	84.2±1.2	89.3±3.3	2.4	3.3	3.1	4.7
Cinnamylalcohol	0.9999	0.067	86.5±1.2	88.5±3.4	2.3	3.4	1.9	5.0
Salicylaldehyde	0.9999	0.062	82.1±1.0	77.1±5.1	2.0	5.1	3.6	5.9

[a]The data represent the mean values ±SD of three replicates.

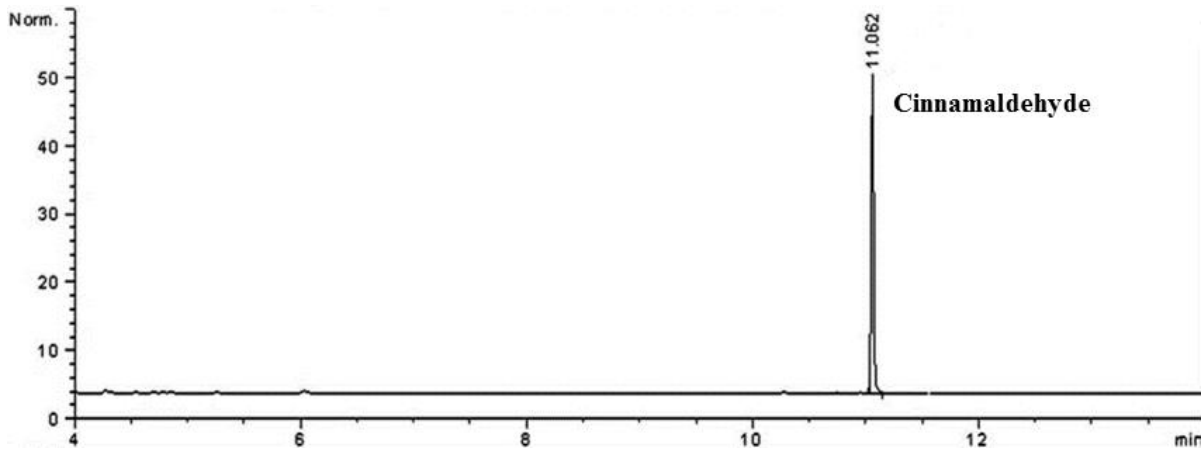

Fig. 3. Representative chromatogram of cinnamaldehyde, cinnamylalcohol and salicylaldehyde in biopesticide samples.

Table 2. Cinnamaldehyde, cinnamylalcohol and salicylaldehyde contents of cinnamon extract using developed method in commercial biopesticides

Samples		Cinnamaldehyde (%)	Cinnamylalcohol (%)	Salilcylaldehyde (%)	Total (%)
Liquid product	1	0.07	< LOQ	< LOQ	0.07
	2	3.40	< LOQ	< LOQ	3.40
	3	0.09	0.01	< LOQ	0.10
	4	0.60	< LOQ	< LOQ	0.60
	5	3.26	< LOQ	< LOQ	3.26
	6	0.86	< LOQ	< LOQ	0.86
	7	1.33	< LOQ	< LOQ	1.33
	8	10.21	< LOQ	< LOQ	10.21
	9	17.37	< LOQ	< LOQ	17.37
	10	1.87	< LOQ	< LOQ	1.87
	11	0.06	< LOQ	< LOQ	0.06
Solid product	1	5.54	< LOQ	< LOQ	5.54
	2	0.11	< LOQ	< LOQ	0.11

thirteen commercial biopesticide samples containing more than 1000 mg L^{-1} cinnamaldehyde, were found effective for crop protection. Its proportion was noted to be 77% (Table 2).

The concentration of bioactive substances in commercial biopesticides, which were generally scattered for crop protection after 100-1000 times dilution with water, was lower at more than 100 times. Therefore, the bioactive substance contents in the studied commercial biopesticide samples were expected to be lower than 1000 mg L^{-1} for antimicrobial activity.

Conclusion

Cinnamaldehyde, cinnamylalcohol and salicylaldehyde, the characteristic constituents of cinnamon for crop protection, were selected as marker compounds. HLB SPE cartridge clean-up method for the determination of three marker compounds in biopesticides containing cinnamon extract was developed and validated by GC -FID.

Results showed that cinnamaldehyde, cinnamylalcohol and salicylaldehyde showed good sensitivities in GC-FID and retention time was 11.06, 11.55 and 5.03 min, respectively. Recovery rates of the three marker compounds in liquid and solid-type biopesticides were lower than 50% with the clean-up method using an ENVI-Carb SPE cartridge. Using the HLB SPE cartridge method, the recovery rates of marker compounds in liquid and solid-type biopesticides were 82.1-86.5 and 77.1-89.3%, respectively.

The inter- and intra-day precision was measured by comparing the recovery rates of cinnamaldehyde, cinnamylalcohol and salicylaldehyde for three days. And RSD ranged from 1.9 to 5.9% to be acceptable value for analytical criteria. These results showed that the experimental method including clean-up and instrumental analysis were suitable for analyzing the

cinnamaldehyde, cinnamylalcohol and salicylaldehyde contents in biopesticides containing cinnamon extract.

Cinnamaldehyde, cinnamylalcohol and salicylaldehyde contents in commercial biopesticide samples were detected at 0.06-17.37%, <LOQ-0.01% and <LOQ, respectively. Ten of the thirteen commercial biopesticide samples containing more than 1000 mg L^{-1} cinnamaldehyde would be effective for crop protection. Its proportion was noted to be 77%.

The initial findings on the analysis of cinnamaldehyde, cinnamylalcohol and salicylaldehyde in biopesticides have been proven to contribute in the manufacture and quality control of biopesticides for crop protection.

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