A Simple HPLC-UVD Method for Detecting Etofenprox in Green Tea Using Sample Hydration

Sung-Woo Kim1, A. M. Abd El-Aty2*, Young-Jun Lee1, Su Myeong Hong3, Young Mi Seo4, Jae-Han Shim1*

1Natural Products Chemistry Laboratory, Chonnam National University, Gwangju, Republic of Korea
2Department of Pharmacology, Faculty of Veterinary Medicine, Cairo University, Egypt
3Department of Agri-food Safety, National Academy Science, Rural Development Administration, Suwon, Republic of Korea
4Department of Nursing, Wonkwang Health Science University, Iksan, Republic of Korea

Abstract

To establish the maximum residue limit (MRL) of etofenprox in green tea, this study was carried out to estimate the residue levels using high performance liquid chromatography-UV detection. The samples were hydrated and extracted with acetonitrile and cleanup was conducted using NH₂-solid phase extraction cartridges. The separation was achieved on a Germini® C₁₈ column with the mobile phase consisting of acetonitrile: distilled water (85:15, v/v) at a flow rate of 1.0 mL/min. The linearity in the concentration range of 0.02 to 2.0 ppm was excellent with a determination coefficient (R²) of 1.000. Recovery at two fortification levels (0.2 and 1.0 ppm) ranged from 89.9 to 94.6% with a relative standard deviation < 5%. The present method provides sufficient sensitivity as reflected by the values of limit of detection (LOD) and limit of quantification (LOQ). The LOD and LOQ were 0.006 and 0.02 ppm, respectively. The method developed here was successfully applied to analyze field incurred samples. This proposed method was effective and could be used for routine analysis of etofenprox in various tea samples at very low concentrations.

Keywords: Etofenprox, Green tea, residue analysis; High performance liquid chromatography, NH₂-cartridge

Introduction

Etofenprox (2-(4-ethoxyphenyl)-2-methylpropyl-3-phenoxybenzyl ether), a synthetic ethoxy pyrethroid insecticide, has been used to control insects, including leafhoppers, bugs, whitefly, aphids, and plant hoppers on paddy rice, fruit, vegetables, and tea.

Tea is the most commonly consumed drink in the world after water.

Green tea is very rich in polyphenolic compounds such as epicatechin, catechins, epicatechin-3-gallate, and epigallocatechin-3-gallate (EGCG), which are the major polyphenols in the plant.

Etofenprox in Green Tea Using Sample Hydration

Objective

The aim of this study was to detect the concentrations of etofenprox in green tea using a simple, economical, sensitive, and accurate HPLC method.

Materials and Methods

Sample
- Green tea
- Standard etofenprox
- Acetone, acetonitrile (McCN), n-hexane, anhydrous sodium sulfate (Na₂SO₄), and sodium chloride (NaCl)

Extraction method

Sample (5 g)

Add water (30 mL), MeCN (100 mL)
Shaking and filtration
Separation with n-hexane (100, 50 mL)
Evaporation

Clean-up (NH₂ cartridge)

Loading with n-hexane (6 mL)
Washing with n-hexane (6 mL)
Eluting 6% of EtOAc in n-hexane
Evaporation
Dissolved in 5 mL acetone

HPLC-UVD analysis

Instrumental conditions

Model Shimadzu liquid chromatography system
Column A Germini®NL-C₁₈ column (4.6 × 250 mm, 5.0 µm, Phenomenex, Torrance, CA, USA)
Isocratic condition Acetonitrile: water (85:15, v/v)
Flow rate 1.0 mL
UV wavelength 225 nm
Injection Volume 20 µL
Retention time 12.5 min

Results

Table 1. Analytical conditions of HPLC-UVD for etofenprox in dried green tea.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>R²</th>
<th>LOD</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etofenprox</td>
<td>1.0</td>
<td>0.006</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 2. Determination coefficient (R²), limit of detection (LOD, ppm), and limit of quantification (LOQ, ppm) of etofenprox in green tea.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Sample</th>
<th>Fortified concentration (ppm)</th>
<th>Recovery (%)</th>
<th>Mean ± RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etofenprox</td>
<td>Green tea</td>
<td>0.2</td>
<td>91.3</td>
<td>89.4</td>
</tr>
<tr>
<td></td>
<td>Green tea</td>
<td>1.0</td>
<td>94.6</td>
<td>93.4</td>
</tr>
</tbody>
</table>

Table 3. Recovery of etofenprox in green tea

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Day after treatments</th>
<th>Residual levels (ppm)</th>
<th>Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 time</td>
<td>1</td>
<td>2.94</td>
<td>2.93 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.02</td>
<td>2.97 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.76</td>
<td>3.77 ± 0.05</td>
</tr>
<tr>
<td>2 times</td>
<td>1</td>
<td>3.60</td>
<td>3.62 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.70</td>
<td>3.64 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.03</td>
<td>8.02 ± 0.08</td>
</tr>
</tbody>
</table>

Table 4. Residual levels of etofenprox in green tea at different time intervals following application

Fig. 2. Chromatograms of etofenprox analyzed by HPLC-UVD.
(a) Standard etofenprox at 2.0 ppm, (b) untreated green tea sample, (c) fortified green tea sample at 1.0 ppm, and (d) field incurred sample.

Conclusions

The recoveries were obtained in the range of 89.9% and 95.9%.
- The recovery is satisfactory, suggesting that the extraction conditions are good and have no effect on the eluted analyte.
- Obviously, the matrix components as well as the NH₂-SPE cartridge used for the clean-up procedure did not affect the recovery yield of etofenprox from green tea.
- Etofenprox residues on green tea sample ranged from 2.97 to 3.77 and 3.64 to 8.02 ppm, for the one and two time applications, respectively.

Homepage: http://altair.chonnam.ac.kr/~jhshim
E-mail: jhshim@jnu.ac.kr