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Determination of water extractable deltamethrin metabolites in different kinds of tea and non-extractable residues in tea

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INTRODUCTION

Synthetic pyrethroids are a class of widely used insecticides that have relatively low mammalian toxicities and reasonably short lifetimes in the field. Therefore, the European authority allows countries to use synthetic pyrethroids in tea crops cultivated for the European market (Anonymous, 2004; 2005). However, so far, there have been no studies of the metabolic fate of deltamethrin in tea plants. The aim of this study was to find out which metabolites of deltamethrin are present in tea infusions.

METHODS

With a metabolism study of ¹⁴C-deltamethrin we examined its major pathways in tea plants grown under greenhouse conditions. After optimizing application, the treated tea plants were grown-on for three months. Sampling took place every second week following the application. The degradation of deltamethrin in this study was prolonged by a ‘waiting period’ of 26 days, owing to greenhouse conditions. The most important process in the deltamethrin degradation is the cleavage of the ester group in the middle of the pyrethroid molecule. The most important metabolites are 3-PBA, 3Br2CA, their mono- and diglucosidic conjugates and 3-PBAld.

Another main point of this study was the investigation of the migration of water-soluble metabolites, and conjugated and free residues into the tea infusion. Different kinds of tea were produced from the treated plant materials. These teas and their infusions were analyzed for deltamethrin residues and metabolites. After the concentration of these conjugates and free metabolites with SPE, we isolated fractions of free and conjugated metabolites. Conjugated metabolites could be broken with the use of β -glucosidase. We measure amounts of these aglucons and free metabolites with GC-MS/MS after methylation with diazomethan. In this part of work we could show differences in the distribution of the metabolites in different kinds of tea.

RESULTS

Besides traces of deltamethrin, the metabolites 3-PBA, 3-PBA1c, Br2CA and their conjugates with glucose were identified in infusions of all kinds of tea. Their distribution, however, varied. In green tea infusions they were mostly present in conjugated or glucosidic form. The metabolites of black tea infusions, however, were present in their agluconic or free form. In the case of half-fermented (or oolong) tea infusions we observed a degree of conjugation with glucose of the formed metabolites between black and green teas. The degree of fermentation during tea processing is responsible for this phenomenon. These data supplied the information on the dependence of the release of deltamethrin metabolites on the degree of fermentation of the tea.

Apart from the determination of the formed extractable residues, another special aspect of this study was the determination of the bound or non-extractable residues. After the chemical cleavage of the plant cell wall, we were able to measure the radioactivity in each hydrolyzed fraction.

For this investigation five different cell wall fractions were isolated. The fractions contained lightly polymerized polyphenols and proteins, pectin, cellulose, hemicellulose and lignin. The largest part of the non-extractable radioactivity (about 30%) was found in the lignin fraction. Another part of the deltamethrin (without the radio labelling) was present, in the form of Br2CA, in the hemicellulosic fraction. After 82 days the value of non-extractable radioactivity amounted to 25% of the total applied value.

We measured the main metabolites from deltamethrin 3-PBA, 3-PBA1c and Br2CA in free form in black tea infusions and their β -glucosidic conjugates in the green tea solutions. One part of the polar metabolites from deltamethrin (12%–14%) is water soluble, and this will be extracted from the tea into the tea infusion.

The same metabolites were found in infusions of the different kinds of tea. However, their distribution varied. In green tea they were present mostly in their conjugated or glucosidic form. By contrast, the main part of black tea metabolites are aglucons in their free form. Because of the low water solubility of pyrethroids, just a small amount of deltamethrin (< 1% of the total residues) was found in both kinds of tea infusions.

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