

# 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. They form a big number of metabolites on the leaf surface and in the leaf cells during the metabolic reactions.

In our study of <sup>14</sup>C-deltamethrin (one of the commonly used pyrethroids) we measured its free and conjugated metabolites in infusions of different kinds of tea. It is well known that a great part of metabolites is present in the form of conjugates with glucose (glucosides). After concentrating these conjugates and free metabolites with SPE we isolated fractions of free and conjugated metabolites.  $\beta$ -Glucosidase was able to break the conjugated metabolites. We quantified these aglucons and free metabolites with GC-MS/MS after methylation with diazomethan. This work shows the difference in the distribution of the metabolites in different kinds of tea.

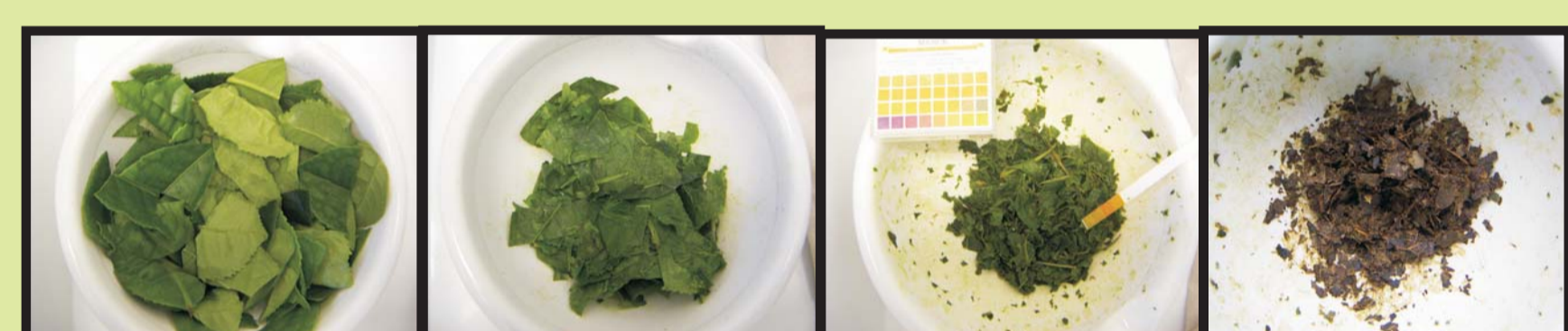
Another special point of this study was the determination of the non-extractable or bound residues (BR). After the chemical cleavage of the plant cell wall, we measured the radioactivity in each hydrolysed fraction.

## TEA PROCESSING

<sup>14</sup>C-Deltamethrin was applied to tea plants. Different kinds of tea were produced from this plant material (scheme 1).



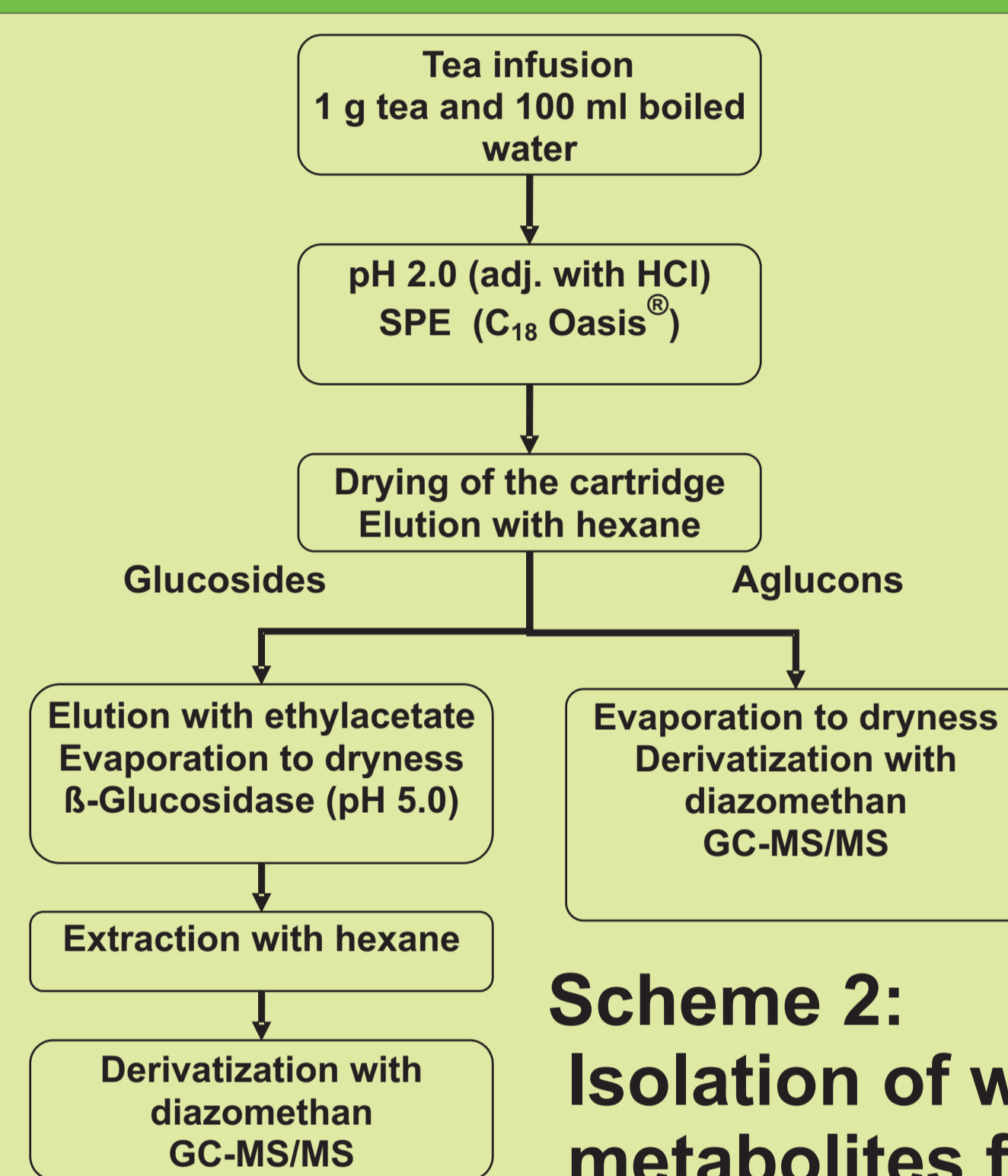
- A
- 1 Stopping fermentation (T 140°C, 1 min)
  - 2 Rolling
  - 3 Low temperature drying (50°C, 15 min)
  - 4 High temperature drying (80°C, 5 min)



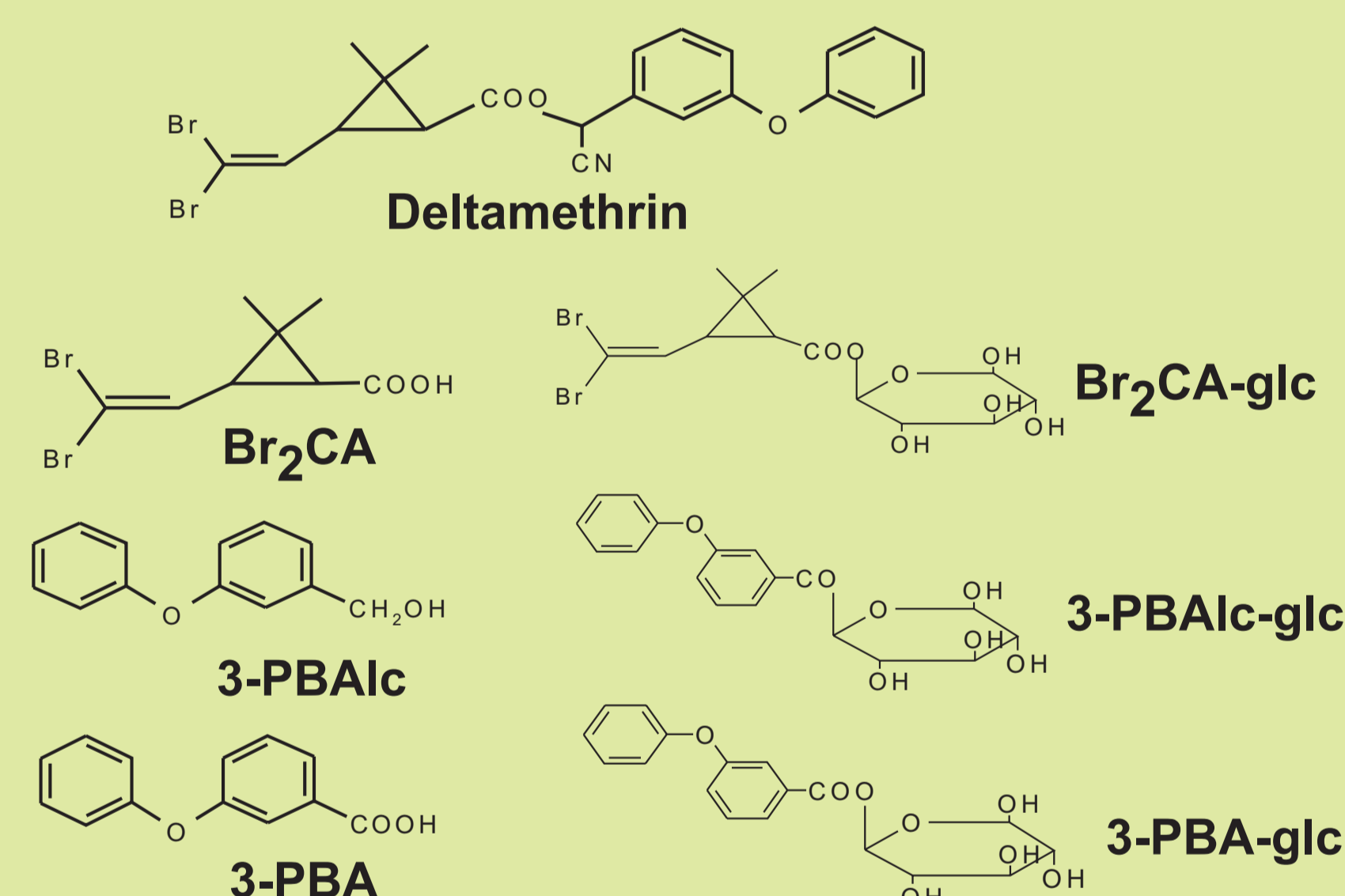
- B
- 1 Crushing
  - 2 Withering and rolling
  - 3 Fermentation at pH 4.5 (2 hours for black tea and about 1 hour for oolong tea)
  - 4 Heating and drying

Scheme 1: The steps in the processing of green (A) and black & oolong teas (B)

## SPE of the Tea Infusions

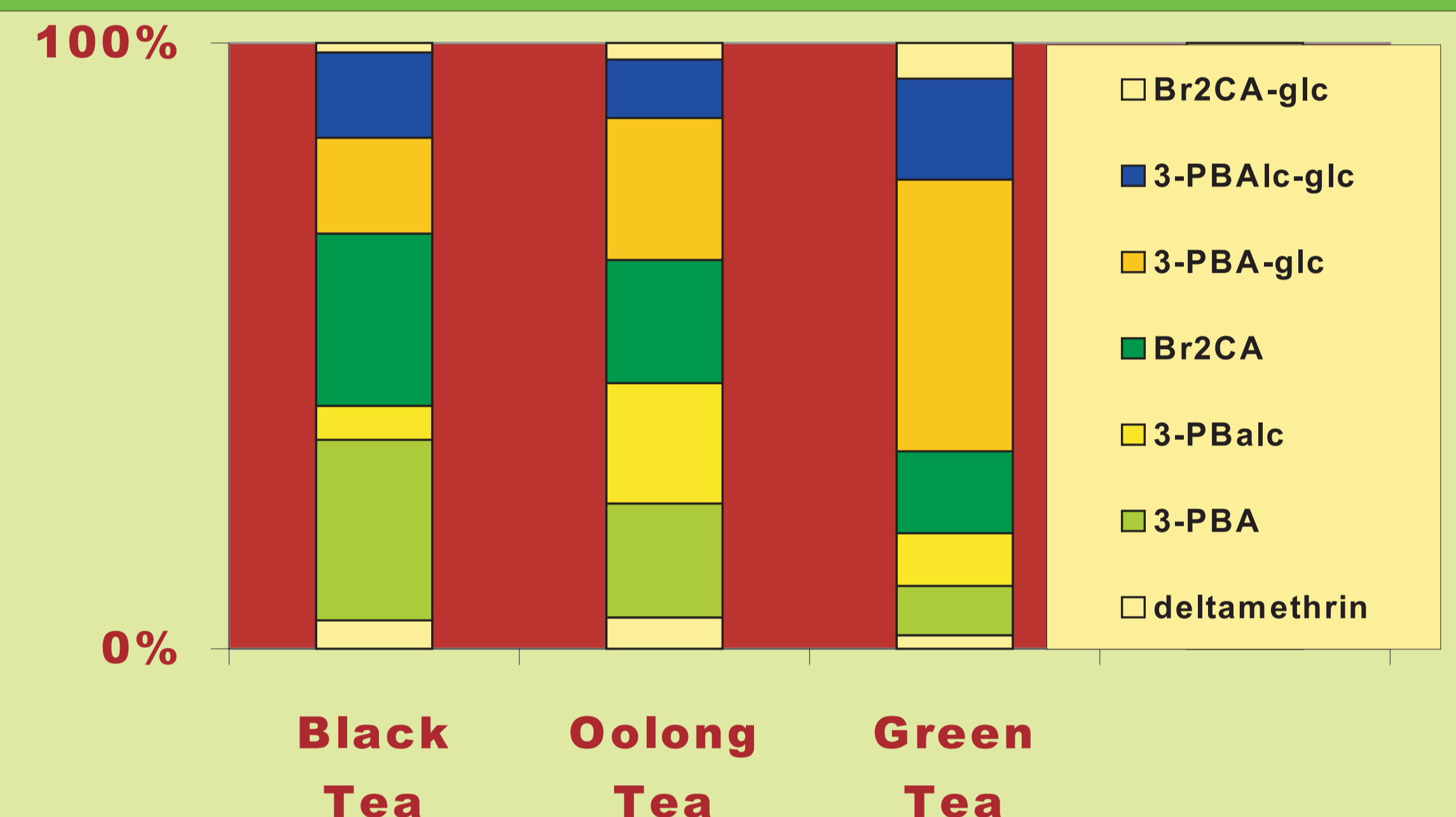


Scheme 2: Isolation of water soluble metabolites from the tea infusion



Picture 1: Chemical structures of deltamethrin and its metabolites found in tea

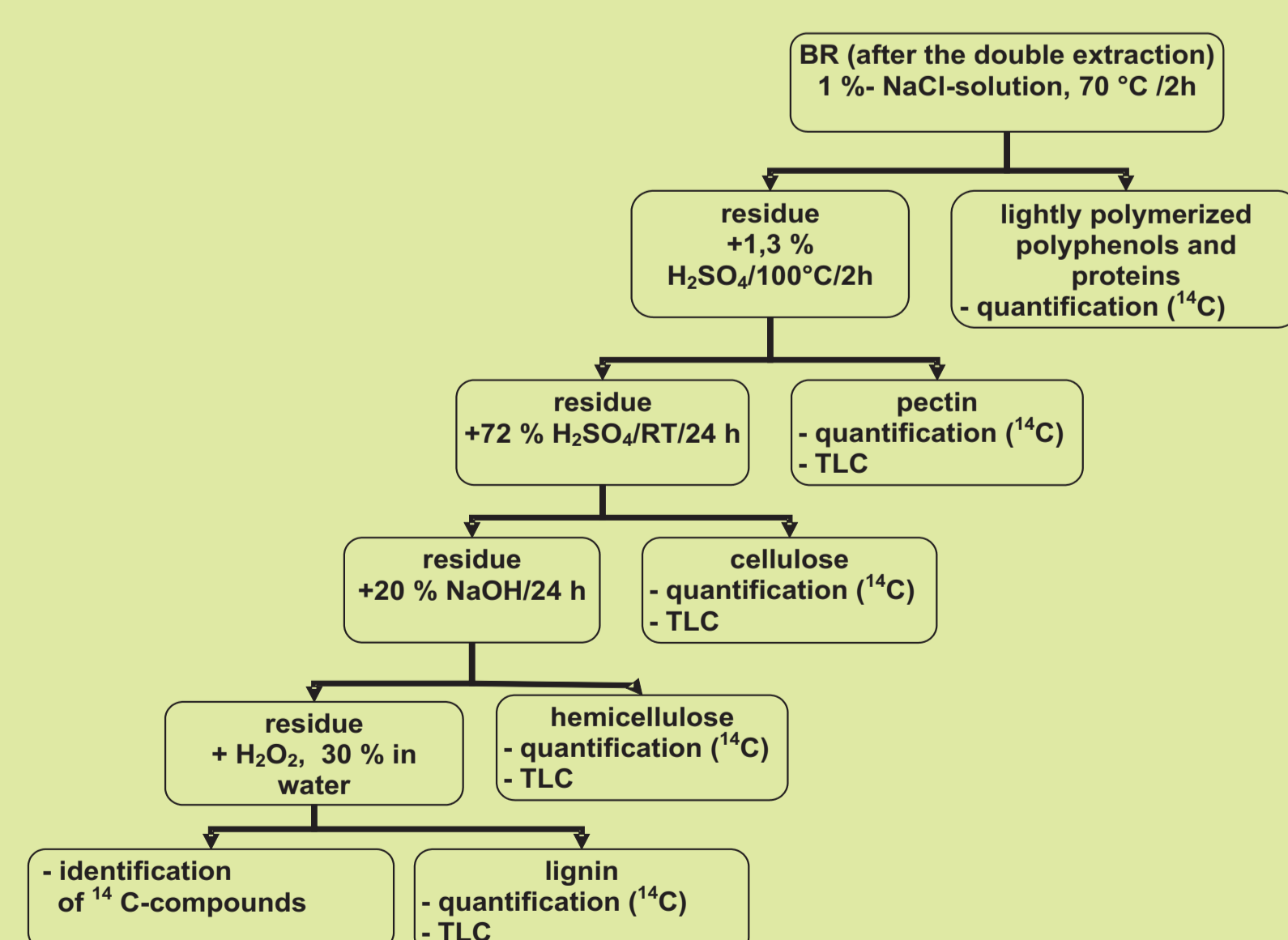
## Results



Picture 2: Distribution of deltamethrin, its free and conjugated metabolites in the tea infusions

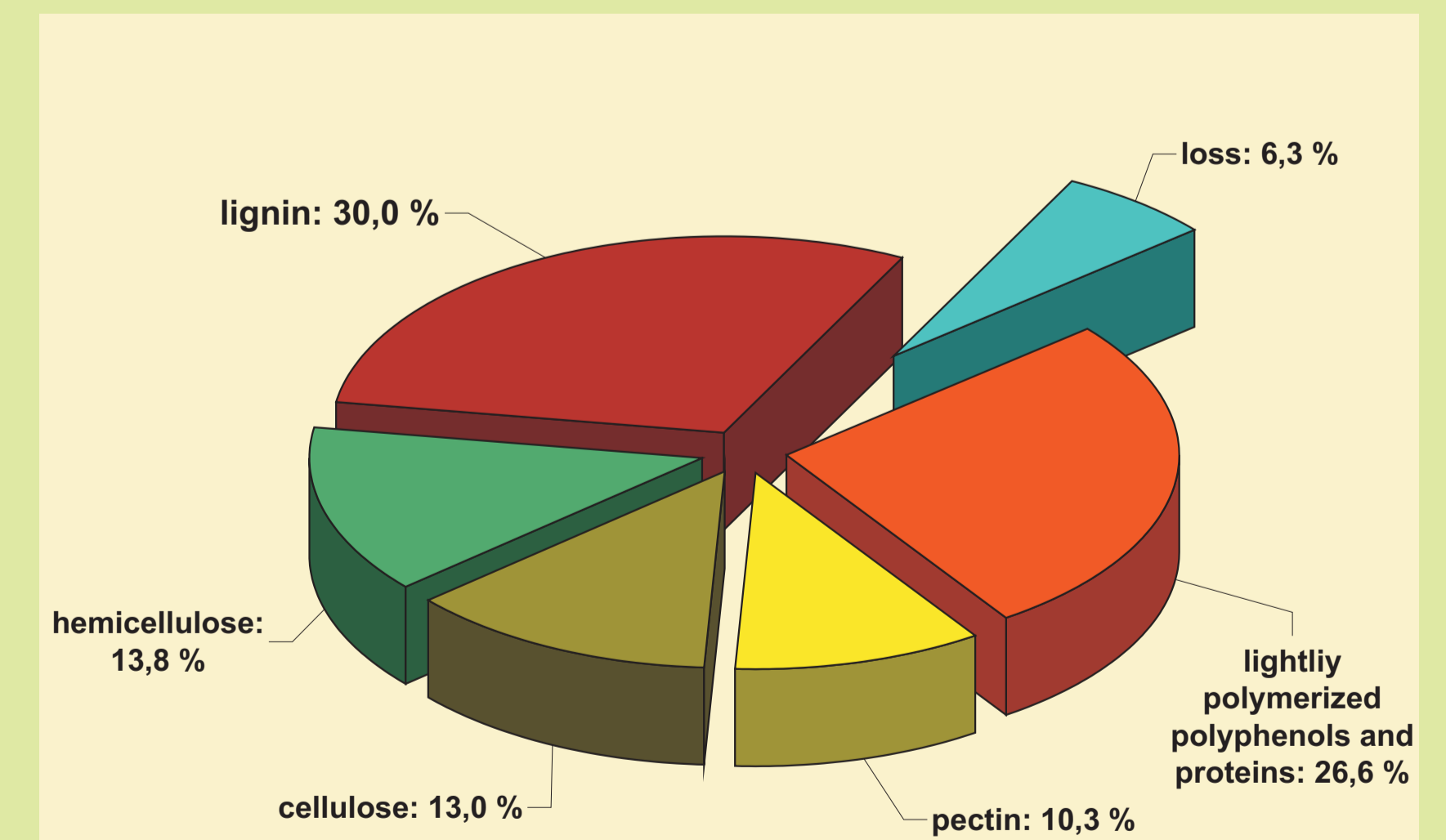
Besides of traces of deltamethrin, the metabolites 3-PBA, 3-PBAIc, Br<sub>2</sub>CA and their conjugates with glucose were identified in infusions of all kinds of tea (Pic. 1, Pic. 2). Their distribution, however, varied. In green tea infusions they were mostly present in conjugated or glucosidic form. The metabolites of black tea infusions were present in their agluconic or free form. In the case of oolong tea infusion were observed a degree of conjugation with glucose of the formed metabolites between black and green tea.

## Determination of Bound Residues



Scheme 3: Isolation of the different cell wall fractions

The scheme 3 shows the isolation of the different cell wall fractions. The fractions contained lightly polymerized polyphenols and proteins, pectin, cellulose, hemicellulose and lignin. The largest part of the non-extractable radioactivity was found in the lignin fraction (Pic. 3). Another part of the bound deltamethrin (without the radio labelling) was present in the form of Br<sub>2</sub>CA in the hemicellulose fraction. After 82 days the value of non-extractable radioactivity amounted to 25% of total applied value.



Picture 3: Distribution of the non-extracted radioactivity in cell wall fractions

## Conclusion

One part of polar metabolites from deltamethrin (12%-14%) is water soluble and is extracted into the tea infusion. The same metabolites were found in tea infusions of the different kinds of tea. In green tea they mostly were present in conjugated or in glucosidic form. Most of black tea metabolites were present in form of aglucons or in their free form. The degree of fermentation during the tea processing is responsible for this phenomenon.

The relative big part of the deltamethrin residue (25%) is not extractable and could be not determined by classical methods of extraction. However, after the tea processing or fermentation they could be free and pass over into the tea infusion.