SURVEY OF ANTIBIOTICS RESIDUES IN HONEY ON THE SWISS MARKET

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1. INTRODUCTION
The European and American foulbrood are bacterial diseases extremely dangerous for bees, able to destroy completely and rapidly an apiary. Furthermore, these bacteria can propagate very easily to other bee-hives and presents a very high danger for honey producers. Antibiotics such as streptomycin, tetracyclines and sulfonamides are often used in bee-keeping as preventive or therapeutic treatment to protect apiary. Antibiotics such as streptomycin, tetracyclines and sulfonamides are often used in bee-keeping as preventive or therapeutic treatment to protect apiary.

Analytical methods have been developed to monitor the presence of antibiotic residues in honey. Rapid screening is performed with the Charm II test and the quantitative measurements of streptomycin, tetracycline and sulfonamide residues are done by HPLC. In case of residue levels higher than MRL a LC/MS/MS confirmation is performed.

The detailed results of a survey of around 500 honeys are presented and show a high number of positive cases, but also a lot of honeys with residue concentrations above the MRL’s and sometimes with large overtakings.

2. SWISS AND EUROPEAN LEGISLATION
The legislation varies considerably from a country to another and antibiotic therapy is authorised in some countries, but absolutely prohibited in others like in Switzerland. However, some MRL’s have been fixed in Switzerland for imported honeys. There are no MRL’s in the UE.

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Swiss MRL’s</th>
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<tbody>
<tr>
<td>Sulfonamides</td>
<td>50 µg/kg</td>
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<tr>
<td>Tetracyclines</td>
<td>20 µg/kg</td>
</tr>
<tr>
<td>Streptomycin</td>
<td>20 µg/kg</td>
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3. SCHEME OF THE ANALYTICAL PROCEDURE

Screening with Charm II Test for
Sulfonamides, Tetracyclines, Streptomycines
For sulfonamides a previous hydrolysis step is performed.

Positive samples with Charm II Test
HPLC specific analysis

Sulfonamide
Tetracycline
Streptomycin

Extraction with organic solvent
Precolumn derivatization
Acidic hydrolysis

Positive samples with residue > MRL

Confirmation with LC/MS/MS

4. REMARKS ABOUT ANALYTICAL METHODS

Sulfonamides
- 80 to 90% of sulfonamides are bound to sugars and an hydrolysis step before extraction is absolutely necessary in order to obtain good recoveries.
- Para-aminobenzoic acid (PABA), a natural substance, interferes with the Charm test screening method and creates a lot of false positives. PABA is also able to be derivatized by the fluram and become fluorescent. Furthermore, PABA interferes in the confirmation HPLC method. Generally, PABA elutes near sulfanethiazole.
- Asulam, used as a herbicide, has a chemical structure like a sulfonamide.
- Residues can be found in fields and contaminate honey. Moreover, sulfanilamide is formed by asulam degradation.
- Sometimes LC with fluorescence detection is not enough selective and LC/MS/MS confirmation is necessary.

Typical residues according to the honey origin

- No results for honey from Asia or Oceania, because only mixtures with European or American honey are sold on the Swiss market.
- In some mixture, origin is very difficult to know and only continental informations are given.
- Sometimes, the residues found are not due to an antibiotic therapy, but are the result of an illegal mixture with cheaper foreign honey

5. SURVEY OF ANTIBIOTICS RESIDUES IN COMMERCIAL HONEYS

About 501 commercial honey sampled on the Swiss market since 1998

6. CONCLUSIONS

- Analysis of antibiotic residues is difficult and classical methods with LC/fluorescence have some selectivity problems. However these methods can be used for routine purposes, but results with residues higher than MRL must be confirmed by LC/MS/MS.
- In most of countries, e.g. U.E., there is a lack in the legislation concerning antibiotic bee therapy and residues in honey. Therefore, antibiotics are often used and residues frequently found in honey. Sometimes, very high concentrations (above 1 mg/kg) are observed.

7. BIBLIOGRAPHY