The occurrence of semicarbazide in the meat and shell of Bangladeshi fresh-water shrimp.

Glenn Kennedy

Head of Chemical Surveillance Branch
AFBI - Stormont
Belfast, Northern Ireland, UK
Uses of nitrofuran drugs

- Disease treatment & prevention
- Growth promotion
- Used in pigs, poultry & aquaculture
- Banned in EU 1993-1995
- No methods to detect residues
- Very unstable
- FoodBRAND - Framework 5
### FoodBRAND: new methods

<table>
<thead>
<tr>
<th>Drug</th>
<th>Bound residue</th>
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<tbody>
<tr>
<td>Furazolidone</td>
<td>AOZ</td>
</tr>
<tr>
<td>Furaltaladone</td>
<td>AMOZ</td>
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<tr>
<td>Nitrofurantoin</td>
<td>AHD</td>
</tr>
<tr>
<td>Nitrofurazone</td>
<td>SEM</td>
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</table>
Public warned over toxic prawns

By Aideen Sheehan Food Correspondent
Saturday March 16 2002

FROZEN prawns which could contain cancer-causing drugs have been withdrawn from sale and consumers warned not to eat any they may have at home.

Lyons Seafoods have withdrawn all prawns it supplies to Iceland shops throughout Ireland after tests showed many contained banned nitrofuran chemicals which can damage DNA.

Consumers who have packets of Lyons Freshwater King Prawns or Lyons Premium Quality Raw Freshwater Prawns should throw them away or return them to Iceland, Alan Reilly, of the Food Safety Authority of Ireland, said.

When the prawns were routinely tested by the Food Standards Agency in the North, 16 out of 84 samples proved positive for nitrofurans, a class of drugs used to kill micro-organisms that can damage DNA and cause cancer.
A global problem!

<table>
<thead>
<tr>
<th>Country</th>
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<tbody>
<tr>
<td>China</td>
<td>Italy</td>
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<tr>
<td>India</td>
<td>UAE</td>
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<td>Bangladesh</td>
<td>Poland</td>
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<td>Thailand</td>
<td>Indonesia</td>
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<td>Brazil</td>
<td>Venezuela</td>
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<td>Ecuador</td>
<td>Madagascar</td>
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<td>Taiwan</td>
<td>Belgium</td>
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<td>Malaysia</td>
<td>Sri Lanka</td>
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<td>Portugal</td>
<td>Argentina</td>
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<td>Greece</td>
<td>Northern Ireland</td>
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</tbody>
</table>
MRPL - Reference Point For Action
Nitrofuran metabolites 1.0 µg/ kg
Aquaculture in Bangladesh

*Penaeus monodon (Bagda)*
- Salt water cultivation
- Tiger prawn
- Extensive production

*Macrobrachium rosenbergii (Golda)*
- Freshwater cultivation
- More intensive cultivation
- Feeds: commercial & “market feed”
- Co-cultivation with rice
- 110,000 farms
- Long production chains
Penaeus spp (CN 0306 13 50) from Bangladesh

Imports increasing with time

Peak exports: Jul-Sep
Other spp (CN 0306 13 80) from Bangladesh

Imports in decline

Peak exports: Oct-Dec
The Rapid Alert System for Food and Feed (RASFF)

Annual Report 2009
Alerts: VMPs 2002 - 2009
Veterinary Medicinal Products 2009

- Nitrofurans
- Chloramphenicol
- Sulphonamides
- Tetracyclines
- Dyes
- Others
Bangladesh: Nitrofuran RASFFs
Bangladesh rejections 2008 & 2009

Almost all from Belgium
Some from United Kingdom
All recent positives - one nitrofuran
Semicarbazide

H₂N−N−H
\[\text{SEM}\]
Nitrofurans & Belgium

March 2008: started to test shell-on tails

Tissue-bound SEM residues detected

Question: A good idea or bad idea?

Either: naturally occurring in shells

   a bad idea

Or: Nitrofurazone (metabolite) binds to chitin

   a good idea
Nitrofurazone and semicarbazide

The purpose of this short paper is to review the current status of semicarbazide (SEM) as a putative metabolite of nitrofurazone and to comment on the possibilities that SEM may have a source unrelated to the deliberate or inadvertent administration of nitrofurazone.

1) Is SEM a metabolite of nitrofurazone?

Four independent lines of evidence support the contention that SEM is a metabolite of nitrofurazone, in exactly the same way that AOZ is a metabolite of furazolidone.
5) Choice of method/sample

Based on current information, the only likely source of possible false positive results involving SEM originates from the alleged occasional presence of SEM in materials used in product coatings. This may cause concern if total residues are determined in the whole product, as opposed to tissue-bound residues in the meat part of the product. We are therefore firmly of the opinion that the most appropriate method to use is detection of bound residues (as opposed to total residues) in poultry/prawn meat (rather than in the finished product). In our view, this will minimise the risks of false positive results and will remove any criticism that the methods are being applied to sample matrices for which they have not been appropriately validated.
NOTE ON ANALYSIS OF NITROFURANS RESIDUE
SEMI-CARBAZIDE CONFIRMATION
Sanders P

1 - When testing composite food, only analyze the part of the product which is of animal origin, for example only the meat part of breaded products.

2- The detection of total (free+ bound) residues of metabolites of nitrofurans can be maintained at the screening level.

3- In case of a non compliant sample for total SEM, a sample must be reanalyzed for the bound residues of SEM only. To this end, free SEM should be extracted/washed out prior to this confirmation test.
Field study - Bangladesh

Field work - BSFF, Dhaka
Analytical work - AFBI Belfast
Wild-caught shrimp - different locations
Snail meat
Feedingstuffs
Shrimps previously tested at FI QC
<table>
<thead>
<tr>
<th>Location &amp; Date</th>
<th>Nitrofuran parents (µg/kg)</th>
<th>SEM (µg/kg)</th>
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<tbody>
<tr>
<td>Bagherhat 12/08/09</td>
<td>&lt;CCα</td>
<td>N.D.</td>
</tr>
<tr>
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<td>34.3</td>
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## Sampling

### Wild catch shrimp

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<tr>
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<td>Hobigong</td>
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**Around**
Effect of sampling point

No significant differences
Some “fliers”
SEM occurs naturally?
SEM in shells

No significant differences SEM occurs naturally.
Comparison – meat & shell

SEM in shell ~ 100 times higher than meat
Field study - Conclusions

SEM occurs naturally in Golda shell

Testing of tail & shell together: inadvisable

Can high levels in shell “contaminate” meat?
SEM in "cored" samples

P < 0.02

SEM (µg/kg)

Sample (n=12)

Inner meat

Outer meat
The diagram illustrates the SEM (µg/kg) levels for different parts of the shell. The soft shell has the highest SEM levels, followed by the outer meat, while the inner meat has the lowest levels.
Shrimp epidermis

New cuticle synthesised in epidermal layer
Old shell shed to allow for growth
SEM appears to be surface associated
What happens to the epidermis?
Associated with shell or meat?
Meat

Epidermal layer

Shell
What could be happening?

Chemical composition of chitin
Unusual amino acids from algae
“Secondary metabolites” from other organisms
Gigartinine
Similar to SEM
Does release SEM
When analysed for nitrofurans
Secondary metabolites

Trying to source this compound
Findings in other widely farmed species

Tissue-bound SEM in shells of:

*Penaeus monodon*
  Black Tiger prawn
  18.2 ± 5.3 µg/ kg (n=5)

*Litopenaeus vannamei*
  Pacific white prawn
  6.2 ± 2.8 µg/ kg (n=5)
Next step?

SEM occurs naturally in shrimp shells.
Epidermal SEM can contaminate meat
Is the presence of SEM a risk to health?
Is the use of nitrofurazone a risk to health?
Is there an alternative?
Analyse sample “core” for “bound” residues?
Is the MRPL/ RPA reasonable?
Thank you for listening...