LECTURE 2

REMOVAL OF OFF-FLAVOURS IN SOME AUSTRALIAN CRUSTACEA BY IONISING RADIATION

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BY IONISING RADIATION

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Australia is a major producer of crustacean foods, both for local consumption and export. However, the development of an export industry based on the deep sea royal red prawn, *haliporoides sibogae* and the shallow water shovel nosed lobster or balmain bug, *Ibacus peronii* has been hampered by the sweet garlic off-flavour often encountered in both these species.

Analysis of headspace volatiles from homogenates of these creatures by combined gas chromatography-mass spectroscopy, g.c.-m.s. accompanied by sniffing of the effluent from a g.c. column showed that the garlic off-flavour composition was complex.

The royal red prawn contained two chemically distinct molecules responsible for the garlic off-flavour. One was the extremely volatile arsenic containing trimethylarsine \((\text{CH}_3)_3\text{As}\) and the other the sulphur based bis-(methylthio)methane, \(\text{CH}_3\text{SCH}_2\text{SCH}_3\). These compounds were routinely found in concentrations of \(0.04 \mu\text{g kg}^{-1}\) and \(3.0 \mu\text{g kg}^{-1}\) respective.

The balmain bug also contained both bis-(methylthio)methane and trimethylarsine, however, these were found in vastly different concentrations compared to the royal red prawn. Trimethylarsine was estimated to be present at only \(0.002 \mu\text{g kg}^{-1}\), whereas bis-(methylthio)methane was present at much higher concentrations ranging from 20 to 100 \(\mu\text{g kg}^{-1}\), and so is the predominant cause of the garlic off-flavour in the balmain bug.

Live balmain bugs showed no sign of the garlic off-flavour, however after death, some adult males developed this, and the concentration increased exponentially with time at ambient temperatures. Bis-(methylthio)methane would appear to be an indicator of spoilage in some adult male balmain bugs.
However, in the case of the royal red prawn the garlic flavour apparent immediately on landing the catch, was found in both sexes, and its concentration did not increase with time at ambient temperatures.

This species of prawn is trawled for in depths of 250-300 fathoms where water temperatures lie between 5 and 10°C. As this species is thin shelled and fragile, breakage of the shell and some damage to the flesh is incurred during trawling, which usually takes place over 2 hrs, and by the time the catch is landed, 99% of it is dead. Biochemical reactions leading to formation of off-flavours may therefore occur long before the catch is landed, and so it is difficult to assess if this is a spoilage problem.

So far it has been difficult to build up an export market for both of these species. The royal red prawn is present in vast quantities off the continental shelf, and as yet is not efficiently fished for. An attempt to build up an export market with France was in part unsuccessful because of the offensive garlic off-flavour. The Japanese were interested in importing balmain bug tails, however, the presence of the garlic off-flavour prevented the establishment of an export industry.

Recently a method for removing this noxious odour was developed which involved γ-irradiation of the affected crustacea using a cobalt-60 source. Irradiation as a method of food processing and/or extending shelf life of a variety of foods has been known for many years, and is now gaining acceptance as a viable adjunct to more traditional food treatments. However, this is the first documented case of γ-irradiation improving the flavour of the final product.

Eight freshly caught male balmain bugs were snap frozen in liquid nitrogen, and then cut in half longitudinally. At this stage it was observed that four of the crustacea had an offensive garlic-like odour. While still frozen, each crustacean was subjected to γ-irradiation, one half of each was given a dose of 25 kGy and the other a dose of 5 kGy.
At the end of the treatment, the halves treated with the higher dose showed no sign of the off-odour, while those at the lower dose still had a slight odour which did not increase in intensity after storage at room temperature for 24 hrs. Under normal circumstances the garlic like odour would have increased rapidly with time on thawing. From these experiments it would appear that a high dose of γ-irradiation completely removes the existing off-odour, and also prevents its further formation. At the lower doses the off-odour is not completely removed and again no further increase in its concentration is apparent.

An aqueous solution of bis-(methylthio)-methane, the compound mainly responsible for the garlic like odour in balmain bugs was irradiated with a dose of 25 kGy. Examination of this solution after treatment showed that it was odourless and that bis-(methylthio)-methane had been destroyed.

A further trial irradiation was carried out on royal red prawns contaminated with the garlic like off-flavour. Samples were irradiated at much lower doses than the balmain bugs, the doses given were 0.5 and 1.0 kGy. Irradiation removed all traces of the off-flavour, but in those irradiated at the higher dose a slight burnt flavour was noticeable.

Examination of the irradiated aqueous solution of bis-(methylthio)-methane showed that sulphonic acid was present. Presumably the other expected product would be methanol. However, it is extremely difficult to detect small quantities of methanol in an aqueous environment.

It is of interest to note that in both the irradiated crustacea and the irradiated aqueous solution of bis-(methylthio)-methane no methane thiol, CH₃SH or hydrogen sulphide, H₂S were detected. These could be expected radiolysis products of bis-(methylthio)-methane if the environment was sufficiently reducing.
The other component responsible for the garlic off-flavour, especially in the royal red prawn is trimethylarsine. No irradiation work on this compound has been carried out to date for two reasons. Firstly, trimethylarsine is extremely toxic, in fact trialkylated arsines represent the most toxic form of arsenic because of their pronounced lipid solubility. Secondly, not only is it extremely volatile, but it oxidises very rapidly and so presents handling problems. Both of these factors make it impossible to conduct taste panel work on trimethylarsine.

Further work is to be carried out to establish the correct doses required for the removal of the off-flavour without production of further undesirable flavours in both species of crustacea examined.

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