Do you eat asparagus, and if so do you notice a particular unpleasant smell in your urine some time afterwards? If so you are not alone – between $\frac{1}{3}$ and $\frac{1}{5}$ of the population notice this smell. It seems probable that sulfur-containing amino acids such as methionine are broken down in the body to other sulfur-based compounds. These, like many sulfur-containing compounds, have an unpleasant smell. (Hydrogen sulfide, $\text{H}_2\text{S}$, is the compound that causes the smell of bad eggs.)

The reason that not everyone can smell ‘asparagus-pee’ is the subject of debate. Scientists remain divided on why people have different urinary responses to eating asparagus. One camp thinks only about half of the population have a gene enabling them to break down the sulfur-containing amino acids in asparagus into their smellier components. Others think that everyone digests asparagus the same way, but less than half of us have a gene that enables us to smell the specific compounds formed in the digestion of asparagus.

Questions

1. The amino acid methionine has the formula

   ![Methionine structure](asparaguspee.png)

   Perhaps surprisingly the amino acid asparagine contains no sulfur. Find out the names and formulae of the two other naturally-occurring amino acids that contain sulfur.

2. This question is about ‘asparagus-pee’.

   It has long been known that after eating asparagus, many people can detect an odd odour in their urine. (Whether or not a person can actually smell it is apparently genetic.)
In the 19th century it was thought that the compound responsible for the smell in so-called ‘asparagus-pee’ was methanethiol, CH₃SH.

In a more recent study, no methanethiol was detected in the vapour from asparagus-pee but two other sulfur-containing compounds, A and B, were identified by mass spectrometry. The M⁺ ion for compound A is at \( m/e = 102 \); for compound B, \( m/e = 150 \).

For comparative purposes, compounds A and B were also prepared in the laboratory from propenoic acid by the following routes.

\[
\begin{align*}
\text{Compound A} & \rightarrow \text{by-product} \\
\text{Compound B} & \rightarrow \text{by-product}
\end{align*}
\]

Compound A reacts with HBr to give Y and with Br₂ to give two isomers, Z₁ and Z₂.

Y is not optically active and has two peaks for its M⁺ ion at \( m/e = 182 \) and 184 (1:1 ratio).

Z₁ and Z₂ are enantiomers (optical isomers) and their M⁺ ions have \( m/e = 260, 262, \) and 264 (ratio 1:2:1).

(a) State the role of the reagent ‘DCC’:
   \( i \) catalyst; \( ii \) hydrating agent; \( iii \) dehydrating agent; \( iv \) hydrogenating agent or \( v \) dehydrogenating agent.

(b) Suggest structures for compounds A, B, W, X, Y, Z₁, and Z₂.

(c) Both A and B may be hydrolysed in water, releasing methanethiol (hence the earlier suspicion of this compound).

Write balanced equations for the hydrolysis reactions of both A and B.

[Naturally occurring bromine is a 1:1 mixture of \(^{79}\text{Br} \) and \(^{81}\text{Br} \) ]