Chapter 5: Mass spectrometry

5.1 We can suggest first that the peak at *m/z* 60 is the molecular ion (giving a molecular weight or relative molar mass of 60). The M+1 peak, which will typically reflect the occurrence of those molecules with one ^{13}C atom in the molecule, has an intensity of ca. 2% of that of the peak at *m/z* 60-suggesting that the molecule under investigation contains two carbon atom (each carbon atom will have a 1.1% chance of being ^{13}C rather than ^{12}C).

Clues to the molecular structure include the occurrence of peaks at *m/z* 45 (M-15, probably from loss of a methyl group) and 43 (M-17, which suggests loss of a hydroxyl group; OH has a mass of 17). This suggests a structure CH_3CO_2H (formula $C_2H_4O_2$) with fragmentation from the molecular ion $[CH_3CO_2H]^+$ to give CH_3CO^+ (*m/z* 43) and $^+C(O)OH$ (*m/z* 45), both of which have the positive charge stabilized by delocalization onto the oxygen, via its lone pair (cf. $^+CH_2OH$, page 110, section 5.5). Note that the proposed formula $C_2H_4O_2$ has the correct molecular weight.

5.2 (a) 1,1-Dibromoethane has the molecular structure CH_3CHBr_2 and formula $C_2H_4Br_2$. Remember that carbon and hydrogen have relative molar masses of 12 and 1 respectively and that bromine has two isotopes (^{79}Br and ^{81}Br) of more or less equal abundance. Thus the molecular peaks (and their weights) will be $C_2H_4{}^{79}Br_2$ (*m/z* 186), $C_2H_4{}^{79}Br^{81}Br$ *m/z* 188) and $C_2H_4{}^{81}Br_2$ (*m/z* 190) giving three peaks of *m/z* values 186, 188, and 190, with relative intensities 1:2:1 (the combination of ^{79}Br and ^{81}Br can be achieved in two ways.)

(b) Dichloromethane has the structure and formula CH_2Cl_2. Remember that each chlorine atom may be the isotope ^{35}Cl or ^{37}Cl, the former being three times more abundant that the latter. Thus the molecule will be much more likely to contain two ^{35}Cl isotopes than one ^{35}Cl isotope and one ^{37}Cl isotope, and the molecule containing two ^{37}Cl isotopes will be comparatively scarce in abundance. There will be three peaks at *m/z* values 84, 86, and 88, in the approximate ratios 9:6:1 (you are encouraged to work out why these ratios are appropriate).

5.3 You should note the molecular formula $C_9H_{10}O_2$ which corresponds to the molecular ion peak present at *m/z* 150. Two particularly characteristic features of the mass spectrum are the ions at *m/z* 91 and 43, which might well be characteristic of the benzyl group ($C_6H_5CH_2^+$) and the acetyl CH_3CO^+ group respectively (check that the proton NMR spectrum, information in Exercise 4.4, page 101 supports this). If this were to be the case, that would leave one carbon atom and one oxygen atom to be accounted for (and we might note the strong evidence for a carbonyl group in the infra-red spectrum, with $v = 1750\ cm^{-1}$: see Exercise 2.13, page 127).

The peak at *m/z* 108 in the mass spectrum corresponds to the loss of mass 43; the fact that an even fragment is lost strongly suggests than an elimination of a molecule (e.g. via a rearrangement) has occurred, rather than simple fragmentation.

This behaviour would be expected for the structure benzyl acetate $C_6H_5CH_2OC(O)CH_3$; check that in particular the proton NMR shifts, and lack of splittings are consistent with this, and note that the rearrangement gives a positive ion for $C_6H_5CH_2OH^+$ via loss of $O{=}C{=}CH_2$ (*cf*. the behaviour of diethyl ether, shown on page 113).

5.4 Let's start by identifying the peak at *m/z* 902 as being the (protonated) molecular ion of the nonapeptide and noting that the ion at *m/z* 884 has lost 18 mass units (i.e. loss of water from the protonated molecule). This is typical of the 'start' of *b*-type fragmentation process (loss of water to leave a fragment RCO^+); the peak at *m/z* 884 is thus represented as *b*(1-9). The peak at 902 we can call *y*(1-9), being the complete nonapeptide.

Then look at the remainder of the peaks (starting at the highest) and try to find matches in the mass differences which correspond to residual masses of specific amino acids (see Table 5.1, page 124). For example, for the *y*-series, *m/z* 831 can be seen as 902-71, which corresponds to "loss" of alanine from the parent (see Figure 5.19); the peak at 734 (i.e. loss of 97) suggests proline as the next amino acid.

The *b*-series can be worked out, starting from *m/z* 884, and noting, first, the next peak (at 737) indicating a difference which corresponds to phenylalanine, then down to 638 (difference of 99, which corresponds to valine).

For each subsequent peak, you should be able to work out, with reference to Table 5.1, page 124 that the two series of fragment differences, and hence the order of acids is as follows;

b-type	*y-type*
884 phenylalanine (147) 737 valine (99) 638 aspartic acid (115) 523 glycine (57) 466 proline (97) 369	902 alanine (71) 831 proline (97) 734 leucine/isoleucine (113) 621 serine (87) 534 proline (97) 437

This gives the nonapetide's sequence as;

ala-pro-leu (or ileu)-ser-pro-gly-asp-val-phe

amino terminus carboxyl terminus

Note: the hamologen in the sequence of the two peptides (nana- and hexa-peptide), suggesting that the hexapeptide is formed from the nanapeptide in the fermentation process.

5.5 The molecule X is propionaldehyde (propanal), CH_3CH_2CHO. Note first that the molecule simply contains C, H, and O (no other heteroatom) and then look for clues for functional groups from the Tables in Chapters 2-5.

For example, the infra-red absorption at 1720 cm^{-1} strongly suggests the presence of a carbonyl group (C=O) which is also indicated by the ^{13}C NMR absorption at 204 δ: the UV

spectrum is also consistent with this. The ^{1}H NMR has three major peaks, with integration in the ratio 3 : 2 : 1, suggestive of CH_3 and CH_2 groups (the triplet and quartet patterns indicate that there are adjacent to each other, identifying the presence of an ethyl group) and the remaining proton appears to be in the CH=O group (identified from the characteristic δ value of 9.80: there is also a small splitting from the adjacent CH_2). This gives the structure CH_3CH_2CHO (and formula C_3H_6O) – check that this corresponds to the C, H, O analysis to the occurrence of three carbons in the ^{13}C NMR spectrum, and to the appearance of the 'heaviest' ion (m/z 58, attributed to the molecular ion of C_3H_6O).
The mass spectrum helps confirm this, with peaks at 57 ($CH_3CH_2CO^+$) and in the range 27 – 29, from the ethyl group ($CH_3CH_2^+$ and ^+CHO both have m/z 29).

5.6 A good starting point is to note that the molecule Y contains just C and H, and if we assume that the 'heaviest' mass spectrum peak (106) is the molecule ion, then we have a formula C_8H_{10}.

The ^{1}H NMR spectrum contains three types of hydrogen (in the ratio of 5 : 2 : 3) – suggesting an aromatic ring (δ 7.1) and an ethyl group (the peaks of intensity 2 and 3 are linked to each other, giving the quartet and triplet splittings we expect for this structure. C_6H_5 – and – CH_2CH_3, joined directly (as ethyl benzene) give us the correct formula and molecular weight.

Further support for this structure comes from the appearance of the π – π* bands in the UV absorption (cf. information for benzene in Table 3.1, page 60) and the aromatic and aliphatic C-H structures in the IR (3050, 2950 cm^{-1} respectively) (note the lack of C=O on this occasion), and the peaks with characteristic m/z values of 77 ($C_6H_5^+$) and, importantly, the most abundant ion 91, the base peak $C_6H_5 – CH_2^+$, which has a particularly stable structure.

Note also the evidence from the ^{13}C NMR that there are six distinctly different carbon-atom environments in the molecule (4 in the arene region, 2 alkyl).