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Comparison of Electrospray Mass Spectrometry of Chrysanthemic Acid Ester Pyrethroid Insecticides with Electron Ionization and Positive-ion Ammonia Chemical Ionization Methods

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The synthetic chrysanthemic acid ester pyrethroid insecticides empenthrin and prallethrin were studied by positive-ion electrospray mass spectrometry (ES-MS) in the presence of ammonium acetate and formic acid. Ammoniated molecule base-peak ions $[M + NH_4]^+$ and significant protonated molecule ions $[M + H]^+$ were observed at low electrospray source cone voltages for both insecticides. The effect of increasing the source cone voltage (from 10 to 40 V), in particular its influence on the extent of fragmentation arising from in-source collision-induced dissociation (CID), was also investigated and found to yield interpretable spectra. The associated increase in the population of low mass fragment ions following these CID experiments makes the monitoring of class-specific ions less attractive (poor sensitivity) than the monitoring of their respective protonated and/or ammoniated molecule ions. Key fragment ions in the ES mass spectra of both insecticides were found to be identical with those obtained under positive-ion electron ionization (EI) and positive-ion (ammonia) chemical ionization (proton transfer) conditions. Additionally, a number of these key ions have been examined by both EI tandem mass spectrometry (MS/MS) and positive-ion ES-MS/MS under low-energy collision induced dissociation (CID) conditions.

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The synthetic pyrethroids are a structurally diverse class of insecticides which have been developed following continuous research efforts over the past 35 years.[1–5] This research effort was prompted by the insecticidal properties and low mammalian toxicities of the natural pyrethrins[6] and a desire to produce synthetic analogues having improved photo-stability and potency, although undergoing faster biodegradation and photodegradation than the more persistent chlorinated pesticides. Synthetic pyrethroids are applied to crops, forests, soils and animal feeds and are in household use. The resulting loss of these compounds as the intact molecules, together with their degradation products and/or metabolites, to the environment requires the detection of these compounds at the microgram and sub-microgram levels.

Electrospray ionization, which involves the desolvation of charged droplets to yield free gas-phase ions from analyte species in solution, was pioneered by Dole *et al.*[7] and, in combination with mass spectrometry,[8] has recently become attractive to the analytical chemist for its ability to ionize and detect labile, low molecular weight compounds such as sulfonylurea herbicides.[9] We have previously reported the analysis of several pyrethroids, using on-line microbore reversed-phase high-performance liquid chromatographic (HPLC) separation, coupled with positive-ion electrospray mass spectrometry (ES-MS), to generate interpretable spectra.[10] Limits of detection obtained from these experiments (in the range 12–60 pg by selected-ion monitoring) have demonstrated the capability of ES-MS to offer the analyst high sensitivity and specificity for the detection of this structurally diverse insecticide class at the trace level, compared with other ionization methods such as electron ionization (EI) or positive/negative-ion chemical ionization (CI) which singly may not offer the desired sensitivity.

We have extended our investigations, using off-line positive-ion ES-MS, to the study of the synthetic chrysanthemic acid ester pyrethroids, empenthrin and prallethrin (Scheme 1), Prallethrin is structurally similar to cinerin I, jasmolin I and pyrethrin I, which are insecticidally active components of natural pyrethrum, and also to the synthetic pyrethroid allethrin and its stereoisomer (bioallethrin). Empenthrin is an ethynylpentenyl chrysanthemate pyrethroid. The effect of increasing the ion source sampling cone voltage and its influence on the extent of fragmentation experienced by each insecticide were investigated and compared with EI and positive-ion (CI) (proton transfer using ammonia reagent gas) spectra. Selected key ions have been examined by EI and ES tandem mass spectrometry (MS/MS) under low-energy collision induced dissociation (CID) conditions.

EXPERIMENTAL

A VG Quattro tandem quadrupole mass spectrometer (up-graded to Quattro II specifications) and MassLynx data system (VG Organic, Altrincham, Cheshire, UK) were used to carry out various positive-ion ES-MS and

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ES-MS/MS experiments. All experiments were performed with the electrospray source high-voltage lens held at 0.55 kV and the electrospray probe at 4.4 kV. The source cone voltage was varied between 10 and 40 V. All ES-MS experiments were carried out with the resolution set such that the peak width at half-height of the ammoniated molecule ion (empenthrin) was 0.5 u. The mass spectrometer was calibrated over the desired mass range using polyethylene glycol.

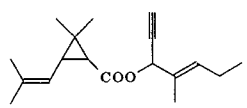
The first quadrupole analyser was used to study cone voltage induced fragmentations while CID MS/MS experiments were performed on selected ions resulting from cone voltage induced fragmentation. Individual pyrethroid standards, 25 μg mL^{-1}, in 70:30 propan-2-ol + H_2O containing 10 mM CH_3COONH_4 and 22 mM HCOOH, were infused at a rate of μL min^{-1} through the electrospray probe, via a 700 mm × 75 μm i.d. (375 μm o.d.) uncoated fused-silica capillary (Polymicro Technologies, Phoenix, AZ, USA), using a 100 μL syringe and a syringe infusion pump (Model 22; Harvard Apparatus, South Natick, MA, USA).

The positive-ion ES mass spectra of each pyrethroid, at cone voltages between 10 and 40 V, were acquired by scanning the mass range *m/z* 60–350 at a rate of 8 s per scan. The resulting accumulated summed scan data, for individual cone voltage experiments, were stored as averaged spectra. EI and positive-ion CI (ammonia) experiments were carried out using an electron energy of 70 eV with the source held at 180 °C and the direct insertion probe at 80 °C.

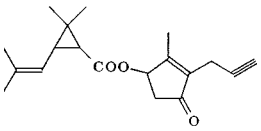
All tandem mass spectra were obtained using argon gas in the RF-only hexapole collision cell. The gas pressure was adjusted so that 50% suppression of the selected ion was obtained. The collision energy was 25 eV in the laboratory frame of reference for each experiment.

The solvents, propan-2-ol and water, were of HPLC grade (Rathburn Chemicals, Walkerburn, UK). Ammonium acetate, formic acid and chrysanthemum monocarboxylic acid were of ACS quality (Sigma–Aldrich, Poole, Dorset, UK). Individual 25 μg per mL^{-1} pyrethroid standards were freshly prepared by serial dilution of their respective stock standard solutions using 70:30 propan-2-ol + H_2O containing 10 mM CH_3COONH_4 and 22 mM HCOOH. All standards were stored in 1 mL amber-glass vials at 5 °C.

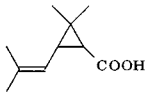
The research-grade quality pyrethroid samples used in this study were donated by Sumitomo Chemical (Osaka, Japan). Common names of each pyrethroid are used throughout this paper (see Scheme 1).



EMPENTHRIN (Vaporthrin), Cas No.96895-17-9
(E)-(RS)-1-ethynyl-2-methylpent-2-enyl (1RS)-cis-trans-2,2-dimethyl-3-(2-methylprop-1-enyl) cyclopropane carboxylate.



PRALLETHRIN (ETOC), Cas No.23031-39-9
(S)-2-Methyl-4-oxo-3-prop-2-ynylcyclopent-2-enyl (1R)-cis-trans-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane carboxylate.



CHRYSANTHEMUM MONOCARBOXYLIC ACID, Cas No.10453-89-1
2,2-dimethyl-3-(2-methylprop-1-enyl) cyclopropane carboxylic acid.

Scheme 1. Chrysanthemum monocarboxylic acid and pyrethroid structures.

RESULTS AND DISCUSSION

We studied the electrospray spectra (in the presence of ammonium acetate and formic acid) of the chrysanthemic acid ester pyrethroids empenthrin and prallethrin and compared the results with their EI and CI (ammonia) spectra.

Empenthrin (M_r = 274)

At lower cone voltages (10 V), the positive-ion electrospray spectrum of empenthrin (Fig. 1) consists predominantly of the ammoniated molecule, $[M + NH_4]^+$ (base peak, *m/z* 292) and a significant protonated molecule $[M + H]^+$ (*m/z* 275). Spectra recorded at progressively higher cone voltages show the effect of source-derived CID, which results in a diminution of the $[M + NH_4]^+$ population, with a concomitant increase in the relative abundance of the $[M + H]^+$ ion

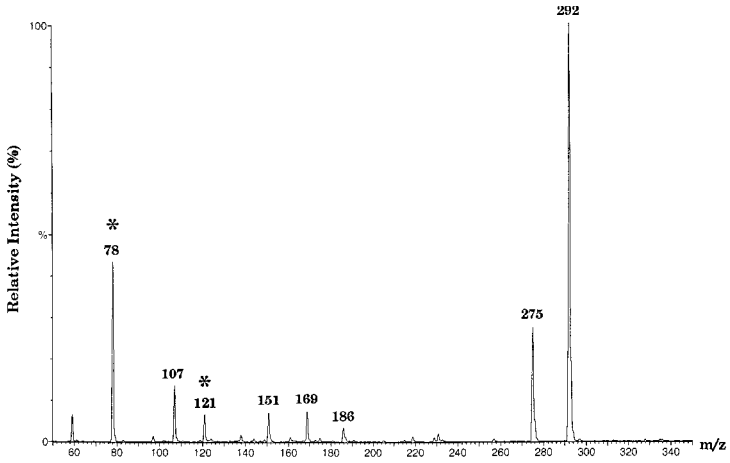


Figure 1. Positive-ion electrospray spectrum for empenthrin (cone voltage 10 V). * Solvent ions.

and of diagnostically useful fragment ions (Fig. 2). The increased relative abundance of the protonated molecule, compared with the ammoniated molecule, at higher cone voltages may result solely, or in part, from the dissociation of $[M + NH_4]^+$ to $[M + H]^+ + NH_3$. Confirmation that NH_3 can be lost directly from the $[M + NH_4]^+$ ion was provided by a constant neutral-loss scan set to monitor 17 u. An equivalent constant neutral-loss spectrum shows a similar loss of NH_3 from the ammoniated chrysanthemic acid fragment ion, *m/z* 186 (see below).

Inspection of the electrospray spectrum of empenthrin at a higher cone voltage (30 V) (Fig. 2) shows key ions at *m/z* 107 (base peak), 123, 151 and 169. An electrospray product-ion spectrum (not shown), recorded following low-energy CID of the $[M + H]^+$ ion (*m/z* 275) of empenthrin, reflects the connectivity between this ion and significant ions at *m/z* 107, 123, 151 and 169, while a further product-ion spectrum (not shown), recorded following low-energy CID of the *m/z* 169 species, indicates connectivity between this ion and significant ions at *m/z* 69, 123 and 151. The ion at *m/z* 169 is attributed to the direct formation of protonated chrysanthemic acid, $[C_{10}H_{16}O_2 + H]^+$, from the protonated molecule, following heterolytic cleavage between the chrysanthemic acid ester oxygen and the α-carbon of the ethynylpentenyl chain accompanied by hydrogen transfer (Scheme 2, pathway 1).

The product-ion spectra of both the protonated molecule (*m/z* 275) and protonated chrysanthemic acid fragment (*m/z* 169) from empenthrin indicate possible pathways for the formation of the chrysanthemyl cation, *m/z* 123, which is observed in the spectrum shown in Fig. 2. It is proposed that the chrysanthemyl cation can be formed directly from the protonated molecule following cleavage of the bond between the carbonyl carbon and cyclopropane ring (Scheme 2, pathway 2) or indirectly from protonated chrysanthemic acid (Scheme 2, pathway 3). One route to the fragment ion at *m/z* 151 (Figure 2) may involve the direct formation of the chrysanthemyl acylium ion from the protonated molecule following cleavage of the carbon–oxygen bond α to the C = O group[10] (Scheme 2, pathway 4). Another possible route to *m/z* 151 is via protonated chrysanthemic acid (Scheme 2, pathway 5). Evidence that the chrysanthemyl acylium ion (*m/z* 151) undergoes further loss, in the form of expulsion of a molecule of carbon monoxide, to form the chrysanthemyl cation (*m/z* 123) is provided by a positive-ion electrospray constant neutral-loss scan, set to monitor a loss of 28 u (Fig. 3 and Scheme 2, pathway 6).

A precursor ion spectrum (not shown) of the base peak ion, at *m/z* 107 in Fig. 2, shows that this ion can be formed directly from the protonated molecule $[M + H]^+$ or from the ammoniated species. This fragmentation has been attributed to the formation of a 1-ethynyl-2-methylpent-2-enyl cation (*m/z* 107), with the expulsion of a molecule of chrysanthemic acid (Scheme 3) as a result of heterolytic cleavage between the chrysanthemic acid ester oxygen and the α-carbon of the 1-ethynyl-2-methylpent-2-enyl ester chain. The constant neutral-loss scan in Fig. 3 also shows a significant loss of 28 u from *m/z* 107. It is proposed that this loss involves the expulsion of ethene to yield the *m/z* 79 ion, $[C_6H_7]^+$ (Scheme 3).

Further evidence related to the fragmentation of the acid component of empenthrin, and subsequent formation of the protonated and ammoniated chrysanthemic acids, was obtained in a parallel experiment using chrysanthemum monocarboxylic acid (Scheme 1). The electrospray spectrum of this acid (not shown), recorded in the presence of CH_3COONH_4 and HCOOH and at a sampling cone voltage of 15 V, yields the expected $[M + H]^+$ and $[M + NH_4]^+$ ions at *m/z* 169 and 186, respectively, in addition to the chrysanthemyl cation (*m/z* 123) and the chrysanthemyl acylium ion (*m/z* 151).

A positive-ion electrospray spectrum of the propan-2-ol + H_2O/CH_3COONH_4/HCOOH solvent in the absence of analyte, at a cone voltage of 15 V, yields significant ions at *m/z* 61, 78 (base peak) and 121. The ions at *m/z* 61 and 121 were assigned to the formation of protonated propan-2-ol and its protonated dimer, respectively. The base peak ion (*m/z* 78) in this spectrum arises from adduction of propan-2-ol with NH_4^+. At higher sampling cone voltages the intensities of all these ions are observed to diminish, with a corresponding increase in the population of less significant, lower intensity ions. Minor ions observed at *m/z* 391, 279 and 149 are attributed to the fragmentation of protonated bis(2-ethylhexyl)phthalate and asso-

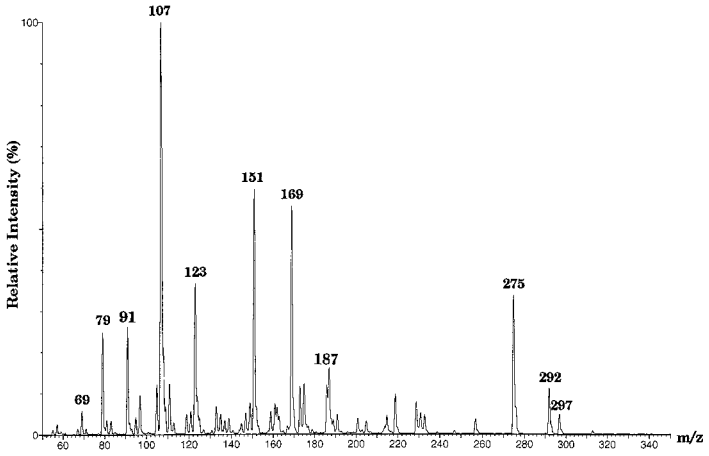


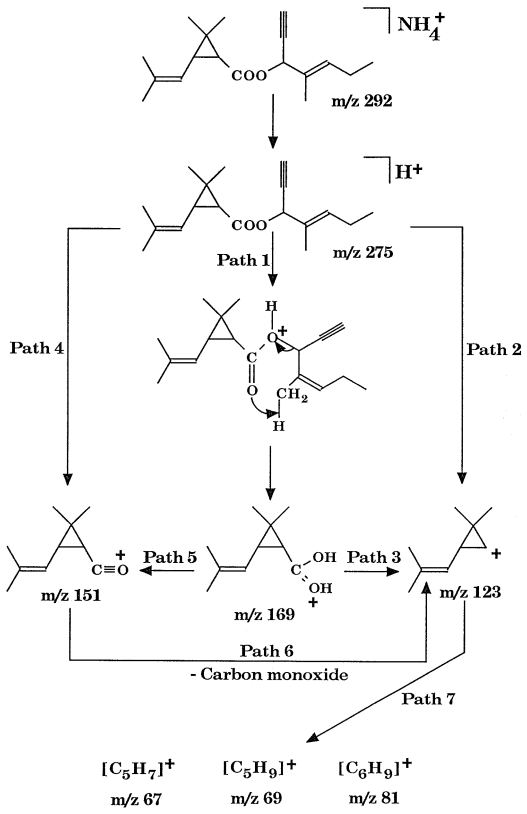
Figure 2. Positive-ion electrospray spectrum of empenthrin (cone voltage 30 V).

ciated alkyl side-chain losses to form protonated phthalic anhydride (*m/z* 149).

The electron ionization spectrum of empenthrin (Fig. 4) shows a dominant base peak ion at *m/z* 123 and a molecular ion of very low relative abundance (< 0.5%), which reflects the fissile nature of the bond between the chrysanthemic acid ester oxygen and α-carbon of the alcohol portion of the insecticide. The fragment ions at *m/z* 79, 91, 107, 123 (base peak) and 151 in this spectrum are also observed in the corresponding electrospray spectra of empenthrin whereas the *m/z* 168 ion (Fig. 4), which has been attributed to the formation of chrysanthemic acid following homolytic cleavage and hydrogen transfer, appears in the electrospray spectrum as the protonated species.

Additional evidence that the major fragmentations of empenthrin are associated with the carbonyl function is given by an electron ionization product-ion spectrum of the molecular ion at *m/z* 274 (Fig. 5) which yields key fragment ions at *m/z* 107, 123, 151 and 168. The spectra of empenthrin obtained under electrospray and electron ionization conditions contain a number of common fragment ions, which provides evidence that these species have similar internal energies.

The positive-ion ammonia CI spectrum of empenthrin (not shown) yields a base peak ion at *m/z* 107 together with the predicted $[M + H]^+$ and $[M + NH_4]^+$ species and other significant ions which are identical with fragment ions observed in its electrospray spectrum.



Scheme 2. Proposed major fragmentation pathways of empenthrin following positive-ion electrospray ionization.

Prallethrin (M_r = 300)

The positive-ion electrospray spectrum of prallethrin, recorded at a lower cone voltage, (Fig. 6) demonstrates similar behaviour to empenthrin, yielding predominantly the $[M + NH_4]^+$ ion base peak at *m/z* 318) and a significant $[M + H]^+$ ion at *m/z* 301. The electrospray spectra of prallethrin also show the same trends in fragment ion production at progressively higher cone voltages as were found for empenthrin, with a diminution of the $[M + NH_4]^+$ population, and a corresponding increase in the abundance of the $[M + H]^+$ ion and of diagnostically useful fragment ions at *m/z* 123, 133, 151 and 169. All of these ions, with the exception of the *m/z* 133 species, are associated with the acid component of prallethrin and are observed to undergo similar fragmentations to those associated with the acid portion of empenthrin. The *m/z* 133 ion is attributed to the formation of a 2-methyl-4-oxo-3-prop-2-ynylcyclopent-2-enyl cation, by expulsion of a molecule of chrysanthemic acid directly from the protonated molecule, $[M + H]^+$, following heterolytic cleavage between the chrysanthemic acid ester oxygen and the cyclopentenyl ring (Scheme 4).

A precursor-ion scan (not shown) of the *m/z* 133 ion of prallethrin shows connectivity between this ion and the $[M + H]^+$ ion and provides confirmatory evidence

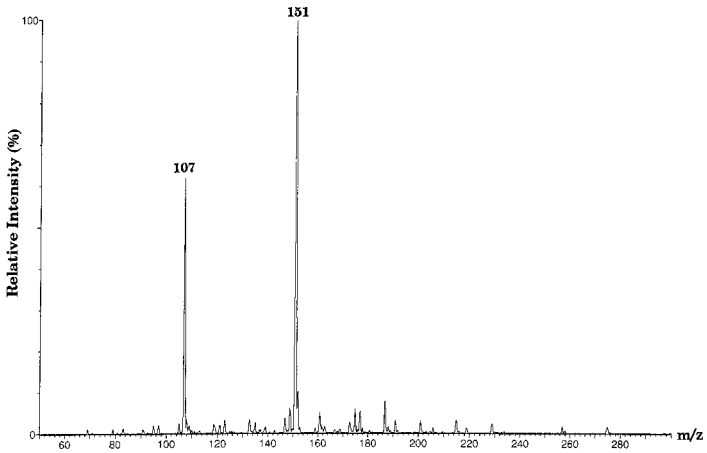
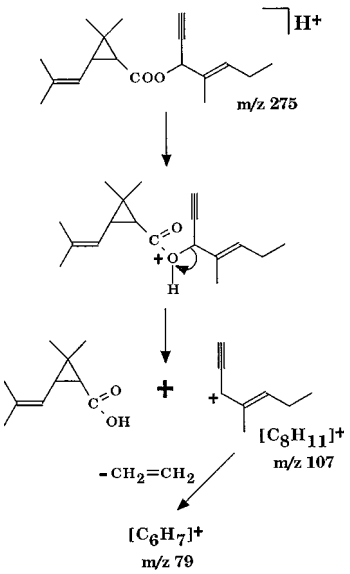


Figure 3. Empenthrin, positive-ion electrospray constant neutral-loss scan of 28 u.



Scheme 3. Formation of a 1-ethynyl-2-methylpent-2-enyl cation and subsequent loss of a molecule of ethylene following positive-ion electrospray ionization of prallethrin.

for fragmentation, via *m/z* 301, to form the cyclopentenyl cation (Scheme 4). A positive-ion electrospray constant neutral-loss scan, recording a loss of 28 u (not shown), shows that the two significant ions to lose 28 u are *m/z* 151 and 133. The *m/z* 151 (chrysanthemyl acylium) ion loses carbon monoxide to form the chrysanthemyl cation, *m/z* 123. It is proposed that the *m/z* 133 ion also loses a molecule of carbon monoxide to yield the *m/z* 105 ion, $[C_8H_9]^+$ (Scheme 4).

The appearance of significant ions (< 10% relative abundance) in the electrospray spectra of empenthrin at *m/z* 297 and prallethrin at *m/z* 323, as the source cone voltage is increased, is attributed to the formation of sodiated adducts, $[M + Na]^+$. The ubiquitous nature of sodium makes it difficult to eliminate from analytical procedures. The increase in the relative abundance of the $[M + Na]^+$ ion, at higher cone voltages, may be attributed to a greater stability of this species relative to the $[M + H]^+$ and $[M + NH_4]^+$ ions.

The positive-ion (ammonia) chemical ionization spectrum of prallethrin (not shown) yields the predicted $[M + H]^+$ and $[M + NH_4]^+$ (base peak) species as well as other significant ions which are also observed in its electrospray spectrum. In contrast to empenthrin, however, prallethrin does not yield a significant

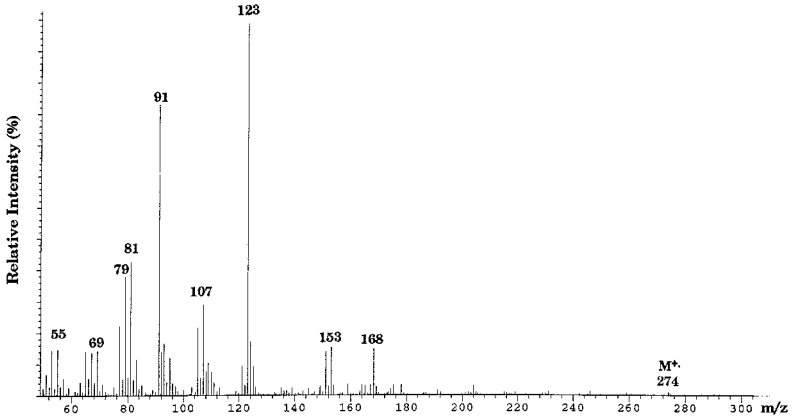


Figure 4. Electron ionization spectrum of empenthrin.

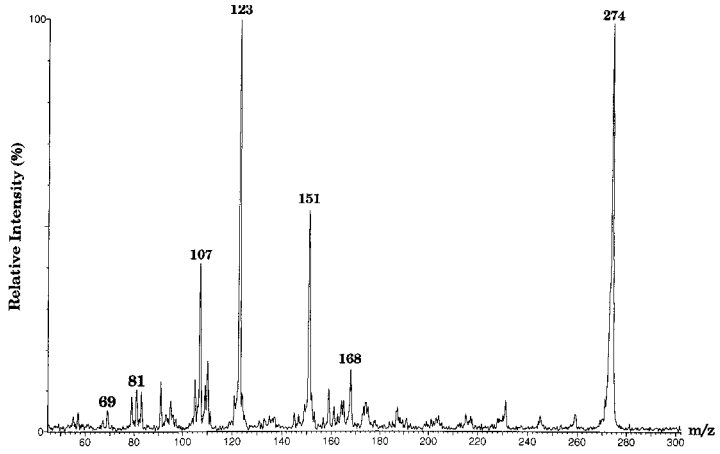
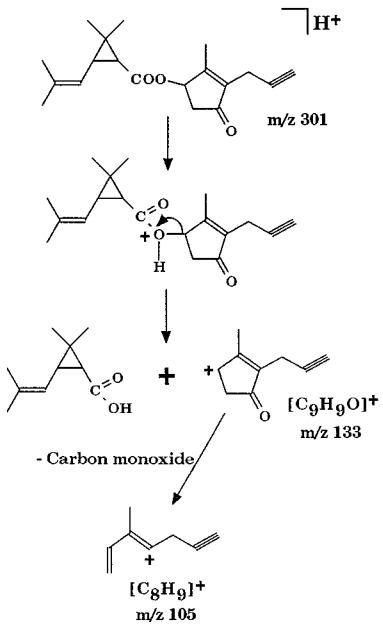


Figure 5. Electron ionization product-ion spectrum following low-energy CID of the molecular ion of empenthrin (*m/z* 274).

chrysanthemyl acylium fragment ion at *m/z* 151 under CI conditions. The electron ionization spectrum of prallethrin (Fig. 7) also shows the absence of a chrysanthemyl acylium ion (*m/z* 151), compared with spectra obtained under electrospray conditions.

The electron ionization spectrum of prallethrin (Fig. 7) shows the predicted chrysanthemyl cation base peak (*m/z* 123) and a molecular ion $[M]^{+\cdot}$ of low relative abundance (< 4%). The ions at *m/z* 133 and 134 are equivalent to those reported by Crombie *et al.*[11] for the natural pyrethrin esters. These ions arise from heterolytic cleavage between the chrysanthemic acid ester oxygen and the cyclopentenyl ring to form the cyclopentenyl cation species, *m/z* 133 $[C_9H_9O]^+$ and 134 $[C_9H_{10}O]^{+\cdot}$. It is noticeable that there is no significant ion at *m/z* 134 in the electrospray spectrum of prallethrin, suggesting that formation of this odd-electron species is not a favoured fragmentation route.



Scheme 4. Formation of a cyclopentenyl cation from heterolytic cleavage between the chrysanthemic acid ester oxygen and the cyclopentenyl ring of prallethrin following positive-ion electrospray ionization.

The fragment ion observed at *m/z* 153 in the electron ionization spectra of both insecticides (Figs 4 and 7) is attributed to the loss of a methyl radical from the chrysanthemic acid fragment ion, $[C_{10}H_{16}O_2]^{+\cdot}$. Additional evidence of this loss is provided by an electron ionization product-ion spectrum of prallethrin (not shown), following low-energy CID of the *m/z* 168 ion, $[C_{10}H_{16}O_2]^{+\cdot}$, which shows connectivity between this ion and the *m/z* 153 ion.

An electron ionization product-ion spectrum, recorded following low-energy CID of the chrysanthemyl cation (*m/z* 123) from prallethrin indicates connectivity between this ion and significant ions at *m/z* 67, 69 and 81. It is proposed that the ion at *m/z* 69 $[C_5H_9]^+$ is formed by elimination of a molecule of but-1,3-diene from the chrysanthemyl cation $[C_9H_{15}]^+$. The ions at *m/z* 68 $[C_5H_7]^+$ and 81 $[C_6H_9]^+$ are consistent with the elimination of molecules of butene and propene, respectively, from the chrysanthemyl cation. The elimination of butene and propene under electron ionization conditions is in good agreement with the findings of Pattenden *et al.*,[12] who proposed these losses while studying the mass spectra of the constituents of natural pyrethrum. These low-mass fragment ions are also observed in the electron ionization spectrum of empenthrin (Fig. 4) and in the electrospray spectra of both prallethrin and empenthrin (Scheme 2, pathway 7) at higher sampling cone voltages.

Under electron ionization conditions, the chrysanthemyl cation (*m/z* 123) is common to a family of chrysanthemic acid ester insecticides. It appears, almost invariably as the base peak, in the spectra of the natural pyrethrins (cinerin I, jasmolin I, pyrethrin I) and of the synthetic pyrethroids (allethrin, cyphenothrin, prothrin, phenothrin and resmethrin) and represents an excellent class-specific ion for monitoring purposes. While electrospray mass spectrometry of chrysanthemic acid ester pyrethroids yields interpretable spectra at higher cone voltages, the increase in the population of low-mass fragment ions, as the source cone voltage is increased, makes the monitoring of class-specific ions less attractive (poor sensitivity) in electrospray mass spectrometry than the monitoring of the respective protonated and/or ammoniated molecules.

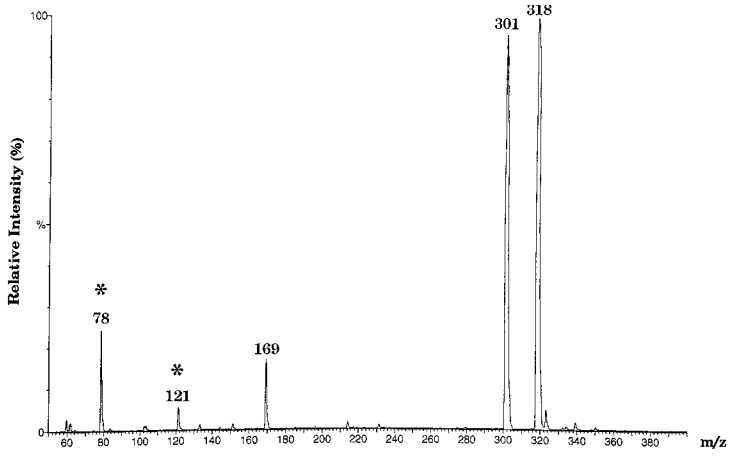


Figure 6. Positive-ion electrospray spectrum of prallethrin (cone voltage 15 V).
* Solvent ions.

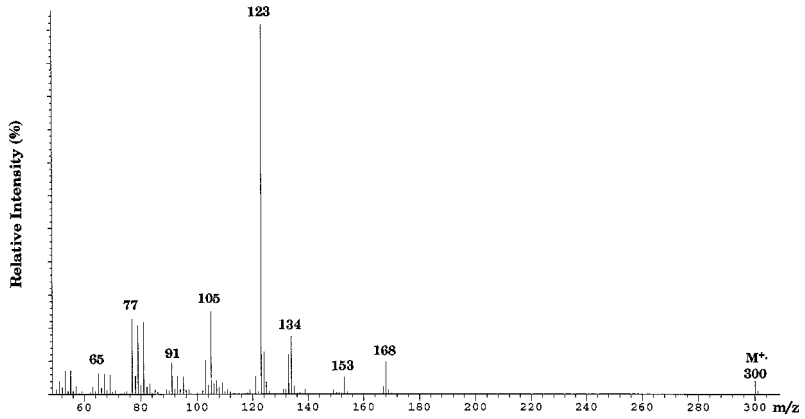


Figure 7. Electron ionization spectrum of prallethrin.

CONCLUSION

The positive-ion electrospray spectra of the chrysanthemic acid ester pyrethroids empenthrin and prallethrin under low sampling cone voltage settings yield predominantly ammoniated molecule ions, and significant protonated molecule ions, thus showing that fragmentation via thermal degradation is not a major process. This contrasts with their positive-ion electron ionization spectra, which show significant fragmentation associated with the fissile nature of the bond between the chrysanthemic acid ester oxygen and α-carbon/ring of the alcohol component of the molecule and, as a result, yield molecular ions of low abundance.

The positive-ion (ammonia) CI spectra of prallethrin and empenthrin contain the predicted ammoniated and protonated molecules as well as other significant ions which are also observed in their electrospray spectra as the sampling cone voltage is increased. In contrast to empenthrin, however, prallethrin does not yield a significant chrysanthemyl acylium fragment ion under either electron or chemical ionization conditions.

This study has demonstrated the capability of positive-ion electrospray mass spectrometry to generate interpretable fragmentation spectra of chrysanthemic acid ester pyrethroid insecticides by source derived collision-induced dissociations, and to yield diagnostically useful fragment ions that are identical with fragment ions observed in either their electron ionization and/or positive-ion (ammonia) CI spectra. Whereas electrospray mass spectrometry of chrysanthemic acid ester pyrethroids yields interpretable spectra at higher cone voltages, the associated increase in the population of low-mass fragment ions as the source sampling cone voltage is increased makes the monitoring of class-specific ions less attractive (poor sensitivity) than the monitoring of their respective protonated and/or ammoniated molecules.

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