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# Tandem Mass Spectrometric Study of the Major Fragmentation Pathways of Some Non-ester Pyrethroid Insecticides Having Alkane, Alkene and Ether Central Linkages

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**The non-ester pyrethroid MTI-800 which has an alkane central linkage has been studied using a tandem quadrupole mass spectrometer incorporating a hexapole collision cell under positive-ion electron ionization conditions. Other structurally related insecticides, NRDC 199 and NRDC 200, which have alkene central linkages and Flufenprox which has an ether central linkage, have also been studied. Conventional mass spectrometry using the first quadrupole analyser only and tandem mass spectrometry have been used in this study. The positive-ion electron ionization mass spectrum of MTI-800 is dominated by an intense even electron ($EE^+$) 1-(4-ethoxyphenyl)-1-methylethylium ion fragment which subsequently loses ethylene from the ethoxy side chain. The influence of other isosteric or isoelectronic substitutions at the geminal dimethyl position of MTI-800 and variations at the alkane linkage is shown by additional fragmentation pathways. The relative intensities of their respective molecule ions vary from 0% to 7%. The expulsion of difluorocarbene ($:CF_2$) as a neutral species from the 1-(4-hydroxyphenyl)-2,2,2-trifluoroethylium fragment ion of Flufenprox has also been rationalized.** © **1997 by John Wiley & Sons, Ltd.**

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## INTRODUCTION

The insecticidal activity of the natural pyrethrins[1] prompted a search for synthetic analogues having improved photostability and potency combined with the capability to undergo fast biodegradation and photodegradation in the ecosphere. Work by Elliott[2] and co-workers at Rothamsted, involving the correlation of stereochemical structure and its influence on insecticidal activity, led to the discovery of many important commercial lipophilic pyrethroids which are insecticidal analogues of cyclopropanecarboxylic acid esters.

Continuing effort by various research groups worldwide, involving a sequence of isosteric and isoelectronic replacements[3,4] of the central linkages of groups originally present in pyrethrin I, which is one of the main insecticidally active components of pyrethrum, has yielded a number of new pyrethroids which have many technical advantages of experimental and commercial interest.[5–13] These new pyrethroids lack the cyclopropanecarboxylic acid ester bond, while retaining the 3-phenoxybenzyl functionality, which is important for activity. The 'non-ester-type' pyrethroids are mainly achiral, broadly insecticidal and have low mammalian toxicities, while showing markedly lower toxicities towards fish compared with pyrethroids containing the cyclopropanecarboxylic acid ester bond.

While some reports have appeared in the literature concerning the mass spectrometry of 'non-ester-type' pyrethroids,[14–17] very little effort has been devoted solely to the study of this developing class of insecticides to aid in their unambiguous detection. We have previously reported work on the positive-ion electron ionization (+EI) of the non-ester pyrethroid 'ethofenprox (MTI-500)' and its silicon-containing analogue 'SSI-116'.[18] Mass spectral data obtained from these experiments highlight the fissile nature of the central linkages of non-ester-type pyrethroids which leads to low abundance or non-existent molecule ions in their positive-ion electron ionization spectra. The principal fragmentations of both these insecticides involve homolytic cleavage and the formation of base peak ($EE^+$) carbenium ion and silicenium ion centres. Other significant fragmentations involving the expulsion of neutral species are also observed.[19] The work by McLafferty and Turecek[20] on ion dissociation mechanisms serves as a useful reference to the positive-ion electron ionization study of non-ester pyrethroid insecticides.

As a sequel to this previously reported work on non-ester pyrethroids,[19] this paper considers the electron ionization tandem mass spectrometry (+EI MS/MS) of

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other non-ester insecticide pyrethroids having alkane, alkene and ether central linkages. Tandem mass spectrometry is a powerful analytical technique which delineates connectivity relationships between precursor and product ions and is ideally suited to organic molecular structure elucidation.[21,22] The combination of low-energy collisional-activated dissociations on precursor ions and precursor ion scans of selected product ions has enabled us to investigate these insecticides. Complementary evidence affording structural and mechanistic detail was obtained from appropriate constant neutral loss scans.

Based on the experimental observations, mechanisms have been proposed to explain the major fragmentation pathways and the inherent stability of ions associated with this class of insecticides.

## EXPERIMENTAL

A VG Quattro tandem quadrupole mass spectrometer (VG Organic, Altrincham, Cheshire, UK) was used for the +EI MS and +EI MS/MS collisional-activated dissociation (CAD) experiments. Electron ionization was carried out at an electron energy of 70 eV for both sets of experiments and with a source temperature of 180 °C; the direct insertion probe was held at 80 °C. The mass spectrometer was calibrated over the mass range $m/z$ 50–500 using heptacosafluorotributylamine, $(C_4F_9)_3N$.

All MS/MS spectra were obtained using argon gas in the radiofrequency-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. All MS/MS spectra were acquired by scanning the mass range $m/z$ 50–500 at a rate of 5 s per scan. The resulting accumulated summed scan data for individual experiments were stored as averaged spectra.

Ten microgram portions of each non-ester pyrethroid as dichloromethane solutions were added to a direct insertion probe and the solvent allowed to evaporate prior to analysis.

All samples used in this study were of research grade quality. Common names or research codes of the pyrethroids have been used throughout this paper; refer to Scheme 1. MTI-800, NRDC 199 and NRDC 200 were supplied by IACR-Rothamsted, Harpenden, Herts, UK and Flufenprox (ICI A5682) by Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire, UK.

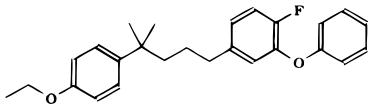
## RESULTS AND DISCUSSION

The positive-ion electron ionization mass spectra (+EI) of MTI-800, NRDC 200, NRDC 199 and Flufenprox are shown in Figs 1–4, respectively.

### MTI-800 [Relative molar mass (RMM) = 392]

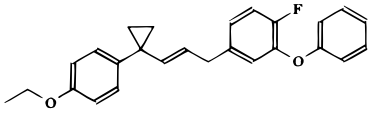
The +EI spectrum of MTI-800, having a ×5 magnification above $m/z$ 190 (Fig. 1), shows a very weak molecule ion (<2% relative abundance). The base peak is at $m/z$ 163 and other significant ions occur at $m/z$ 181 and 201 (<6% and <3% relative abundance) are also observed.

The major fragmentation of MTI-800 can be attributed to homolytic cleavage between the benzylic carbon



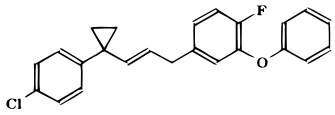

MTI-800, Cas No. 89764-44-3

1-(3-phenoxy-4-fluorophenyl)-4-(4-ethoxyphenyl)-4-methylpentane



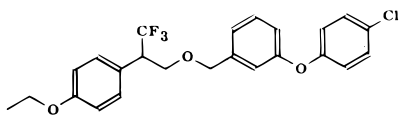

NRDC 200, Cas No. 100846-04-6

1-(4-ethoxyphenyl)-1-[(E)-(3-phenoxy-4-fluorophenyl)prop-1-enyl]cyclopropane




NRDC 199, Cas No. 100846-02-4

1-(4-chlorophenyl)-1-[(E)-(3-phenoxy-4-fluorophenyl)prop-1-enyl]cyclopropane




FLUFENPROX, Cas No. 107713-58-6

1-(4-chlorophenoxy)-3-[[2-(4-ethoxyphenyl)-3,3,3-trifluoropropoxy]methyl]-benzene

**Scheme 1.** Non-ester-type pyrethroid structures.

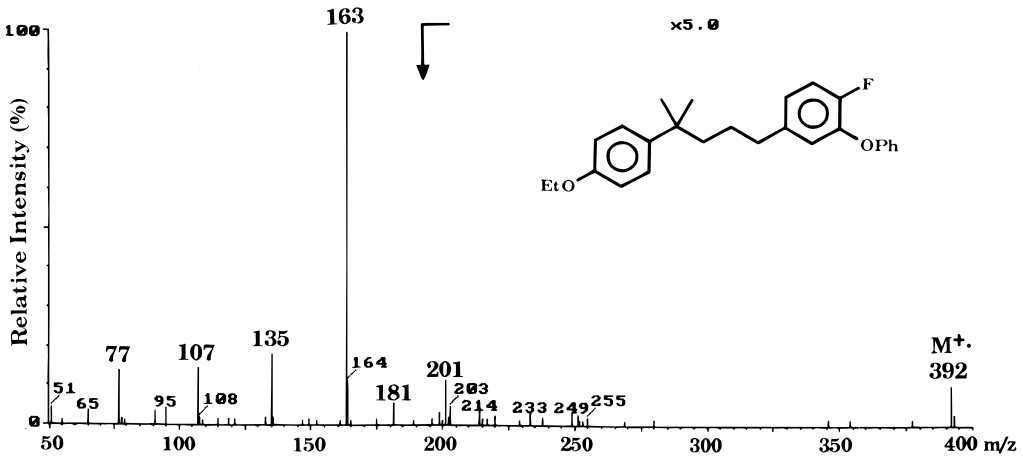
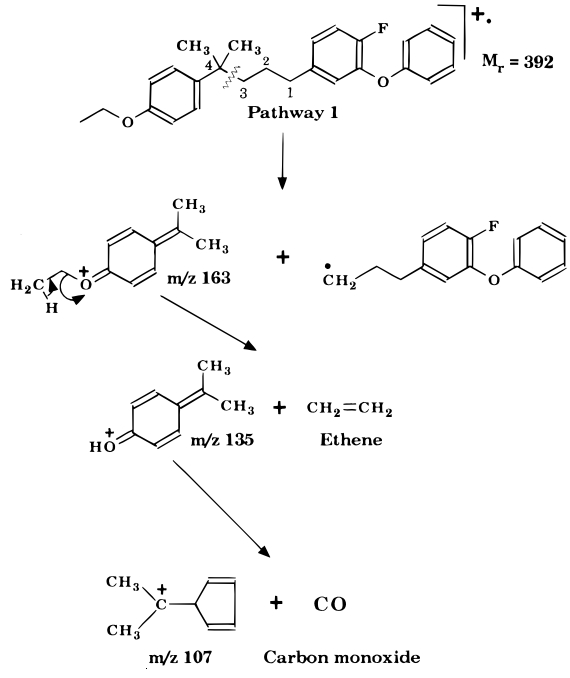



**Figure 1.** Positive-ion electron ionization spectrum of MTI-800, having a ×5 magnification above *m/z* 190.

of the 4-ethoxyphenyl group and the adjacent methylene group (C3) of the 4-methylpentane chain. This results in the formation of the even electron ($EE^+$) 1-(4-ethoxyphenyl)-1-methylethylium base peak ion[23] at *m/z* 163 (Scheme 2, pathway 1). A product ion spectrum of the molecule ion of MTI-800, *m/z* 392 (not shown), indicates a significant direct fragmentation pathway to this carbenium ion centre at *m/z* 163. A product ion spectrum *m/z* 163 (Table 1) shows connectivity between this ion and the *m/z* 135 and 107 fragment ions. It is proposed that the *m/z* 135 ion $[C_9H_{11}O]^+$ is formed by loss of ethene from the ethoxy group. The *m/z* 135 ion then undergoes a loss of CO to yield the *m/z* 107 fragment ion $[C_8H_{11}]^+$ (Scheme 2, pathway 1). Supportive evidence for these losses is provided by a constant neutral loss scan of 28 Da (not shown).




**Scheme 2.** Fragmentation pathway 1 of MTI-800 following positive-ion electron ionization.

Ethene may also be lost from other sites on the *m/z* 163 carbenium ion centre, but these losses are less likely. As an example, NRDC 199 (see later), which has a similar structure to MTI-800, with a 4-chlorophenyl functionality instead of a 4-ethoxyphenyl functionality, shows no corresponding loss of 28 Da (ethene) from its (chlorophenyl)cyclopent-2-ene carbenium ion centre at *m/z* 177.

Homolytic benzylic cleavage between the phenoxy-fluorobenzyl carbon and adjacent methylene group of the 4-methylpentane chain of the molecule ion results in the formation of a 3-phenoxy-4-fluorobenzylium ion at *m/z* 201. A product ion scan of this ion (not shown) shows connectivity between *m/z* 201 and the *m/z* 181 fragment ion through loss of a molecule of hydrogen fluoride from *m/z* 201. This can be followed by a Wagner–Meerwein-type rearrangement (ring expansion) to yield a tropylium benzofuran-type ion[23] (Scheme 3, pathway 2). Supportive evidence that a molecule of HF has been lost from the *m/z* 201 fragment ion is provided by a constant neutral loss scan of 20 Da (Table 2). The low abundance of the *m/z* 201 and 181 ions in the +EI spectrum of MTI-800 (Fig. 1) suggests that the formation of the 3-phenoxy-4-fluorobenzylium ion and subsequent loss of a molecule of HF to yield the tropylium benzofuran-type ion are only minor fragmentation pathways.

**Table 1. +EI product ions following low-energy CAD of selected precursor ions**

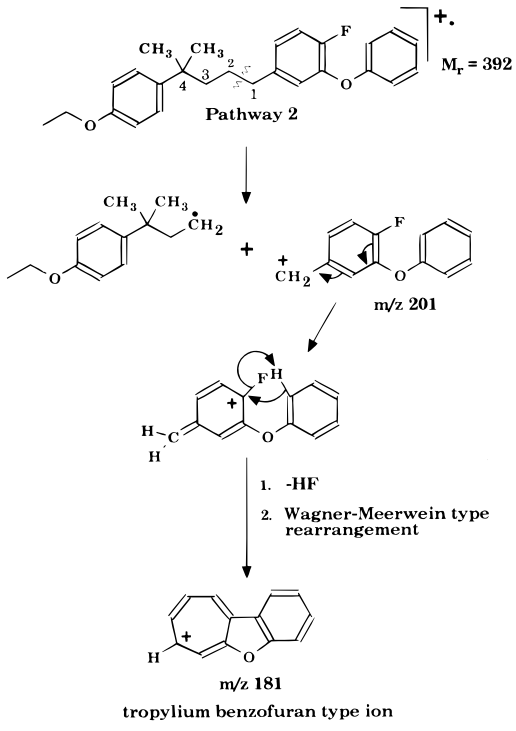
| Pyrethroid | Precursor ion *m/z* | RA (%) | Product ions *m/z* |
|---|---|---|---|
| MTI-800 | 163 | 100 | 135 (8), 107 (<3) |
| NRDC 200 | 388 [$M^{+\cdot}$] | 100 | 359 (12, 187 (48) |

Bracket value = percentage relative abundance (RA).

**Table 2. +EI precursor ions giving rise to the following neutral losses**

| Pyrethroid | Neutral loss (Da) | Precursor ion *m/z* |
|---|---|---|
| MTI-800 | 20 | 201 (100) |
| Flufenprox | 50 | 175 (100) |

Bracket value = percentage relative abundance (RA).




**Scheme 3.** Fragmentation pathway 2 of MTI-800 following positive-ion electron ionization.

Inspection of the spectra of the insecticides NRDC 200 (Fig. 2) and NRDC 199 (Fig. 3), which have the same 4-fluoro-3-phenoxy-benzyl functionality as MTI-800, indicates that they undergo vinylic cleavage of their propenyl chains, from their respective molecule ions, to form 3-phenoxy-4-fluorobenzylium ions at *m/z* 201. These *m/z* 201 ions are complementary to the base peaks at *m/z* 187 and 177, respectively, but are of low relative abundance (1.4% for NRDC 200 and 2.6% for NRDC 199).

As in the case of MTI-800, loss of HF from these carbenium ion centres (*m/z* 201) is observed (not shown). The low abundance of the *m/z* 201 and 181 ions in the +EI spectrum of NRDC 200 (Fig. 2) and NRDC 199 (Fig. 3) again suggests that the formation of the 3-phenoxy-4-fluorobenzylium ion and subsequent loss of a molecule of HF to yield the tropylium benzofuran-type ion is only a minor fragmentation pathway for both insecticides. These minor fragmentation pathways contrast with the behaviour of the cyclopropanecarboxylic ester pyrethroids,[24] where there is a significant fragmentation pathway involving homolytic cleavage of the equivalent benzylphenoxy–oxygen bond to yield the phenoxytropylium ion at *m/z* 183.

## NRDC 200 (RMM = 388)

In contrast with MTI-800, NRDC 200 has no geminal methyl groups and differs by having an alkene central linkage. The +EI spectrum of NRDC 200 (Fig. 2) is dominated by an intense ion at *m/z* 187, while the molecule ion at *m/z* 388 has a relative abundance of <1%. Other significant fragment ions occur at *m/z* 77, 131, 159 and 181.

A product ion scan of the molecule ion of NRDC 200, *m/z* 388 (Table 1), indicates connectivity between this species and ions at *m/z* 187 and 359. The major fragmentation pathway is associated with the *m/z* 187 ion and can be attributed to homolytic cleavage between the (4-ethoxyphenyl)cyclopentene–benzylic bond following a vinylcyclopropene–cyclopentene rearrangement[25] of the molecule ion. This results in the formation of the even electron ($EE^+$) 1-(4-ethoxyphenyl)-cyclopent-2-ene carbenium ion at *m/z* 187 (Scheme 4).

A product ion spectrum (not shown) of the 1-(4-ethoxyphenyl)cyclopent-2-ene carbenium ion, *m/z* 187, of NRDC 200 shows connectivity between this ion and the *m/z* 159 and 131 fragment ions. It is proposed that the 1-(4-hydroxyphenyl)cyclopent-2-ene carbenium ion (enol tautomer) $[C_{11}H_{11}O]^+$, *m/z* 159, is formed by loss of ethene from the ethoxy group of the *m/z* 187 species in a similar manner to MTI-800. The *m/z* 159 ion then expels a molecule of carbon monoxide to yield a 1-(cyclopent-2,3-diene)cyclopent-2-enyl-type cation at *m/z* 131, $[C_{10}H_{11}]^+$ (Scheme 4). A precursor ion scan (not shown) of *m/z* 159 also shows connectivity between this ion and *m/z* 187. Supportive evidence that ethene and carbon monoxide have been expelled from the *m/z* 187 and 159 ions, respectively, is provided by a constant neutral loss scan of 28 Da.

The ion at *m/z* 359 in the product ion spectrum of the molecule ion of NRDC 200 (Table 1) is formed by loss of an ethyl radical from the ethoxy group of the molecule ion.

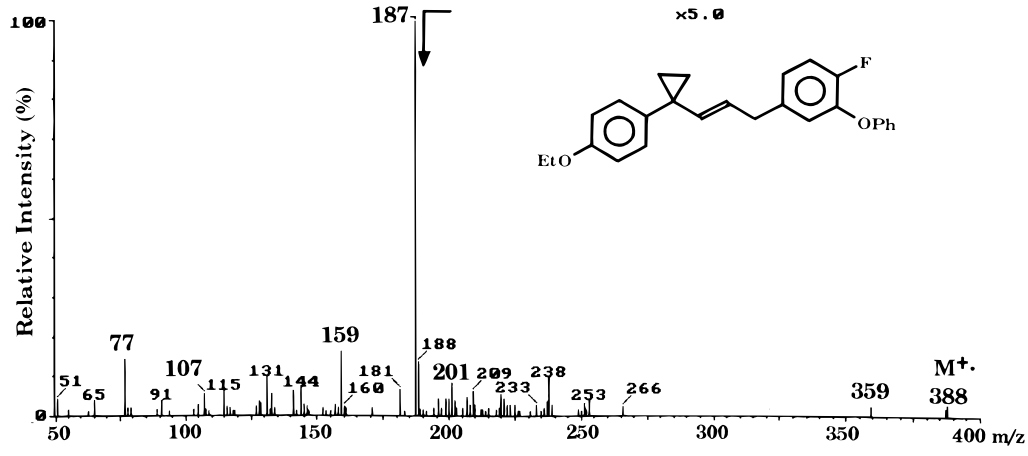
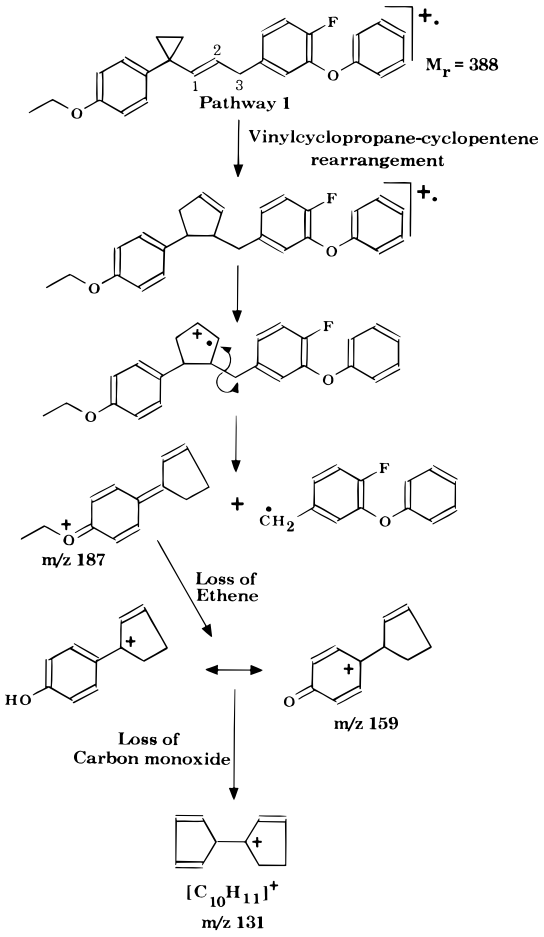



**Figure 2.** Positive-ion electron ionization spectrum of NRDC 200, having a ×5 magnification above *m/z* 190.




**Scheme 4.** Fragmentation pathway 1 of NRDC 200 following positive-ion electron ionization.

## NRDC 199 (RMM = 378)

The insecticide NRDC 199 is an analogue of NRDC 200 having a 4-chlorophenyl functionality instead of a 4-ethoxyphenyl functionality. The +EI spectrum of NRDC 199 (Fig. 3) shows a base peak at *m/z* 177 ($^{35}$Cl) and an associated ion at *m/z* 179 ($^{37}$Cl). The molecule ion at *m/z* 378 has a relative abundance of <2%, as has the fragment ion at *m/z* 343 formed by loss of a chlorine radical from the molecule ion. Other significant fragment ions occur in the +EI spectrum at *m/z* 77, 115, 141, 142 and 181 (Fig. 3).

The major fragmentation pathway of NRDC 199 is associated with the formation of the base peak fragment ion, *m/z* 177, from the molecule ion, which is attributed to rearrangement of the vinylcyclopropane group to a cyclopentene followed by homolytic cleavage between the (4-chlorophenyl)cyclopentenyl group and the adjacent phenoxyfluorobenzyl carbon (C3). This results in the formation of the even electron ($EE^+$) 1-(4-chlorophenyl)cyclopent-2-ene carbenium ion (Scheme 5, pathway 1). A precursor ion scan (not shown) of the *m/z* 177 ion shows direct connectivity between this species and the molecule ion.

Product ion spectra (not shown) of the *m/z* 177 ion $[C_{11}H_{10}Cl]^+$ and its associated $^{37}$Cl isotope (*m/z* 179) show connectivity between these species and ions at *m/z* 141 and 142. The *m/z* 141 and 142 ions are formed through losses of a molecule of hydrogen chloride and a chlorine radical from *m/z* 177/179, $[C_{11}H_{10}Cl]^+$, to form a substituted benzyne-type ion $[C_{11}H_9]^+$ (Scheme 5, pathway 3) and a $[C_{11}H_{10}]^{\cdot+}$ ion (Scheme 5, pathway 2) respectively. Confirmation of the loss of a chlorine radical from *m/z* 177/179 is provided by a precusor ion scan (not shown) of *m/z* 142, while supportive evidence that a molecule of hydrogen chloride has been expelled from the *m/z* 177 and 179 ions is provided by constant neutral loss scans (not shown) of 36 and 38 Da, respectively. Inspection of the +EI spectrum (Fig. 3) shows that these expulsions of hydrogen chloride and a chlorine radical to form *m/z* 141 and 142 ions, respectively, are significant fragmentation processess.

The 36 Da neutral loss spectrum yields significant precursor ions at *m/z* 151 and 125, showing losses of hydrogen chloride from these species. Additionally, a 38 Da neutral loss spectrum shows the presence of significant precursor ions at *m/z* 153 and 127, which confirms similar losses of HCl from the corresponding $^{37}$Cl-containing ions. It is proposed that the *m/z* 151 ion $[C_9H_8{}^{35}Cl]^+$ and the *m/z* 153 ion $[C_9H_8{}^{37}Cl]^+$ are formed by elimination of an ethyne molecule from the chlorophenylcyclopropyl ethylium ion (*m/z* 177/179) and that the *m/z* 151 and 153 ions subsequently lose hydrogen chloride to form a substituted benzyne-type ion *m/z* 115, $[C_9H_7]^+$ (Scheme 5, pathway 4).

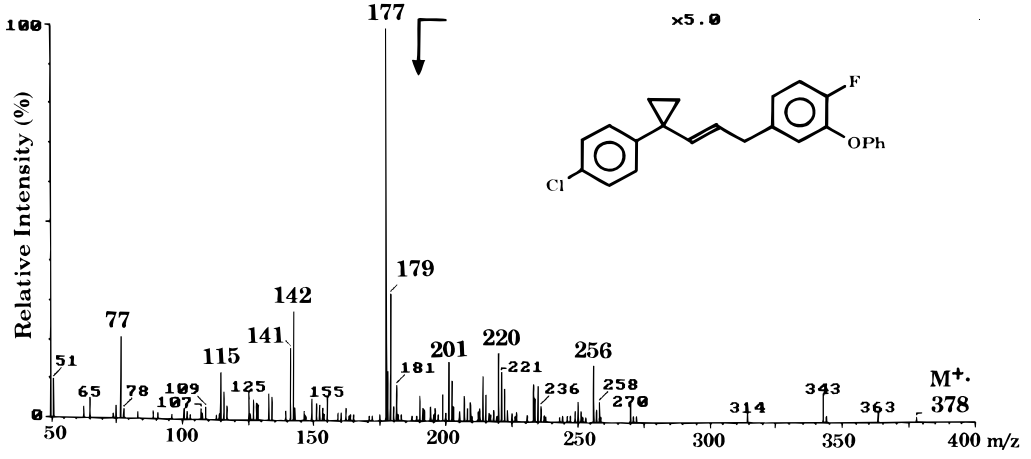
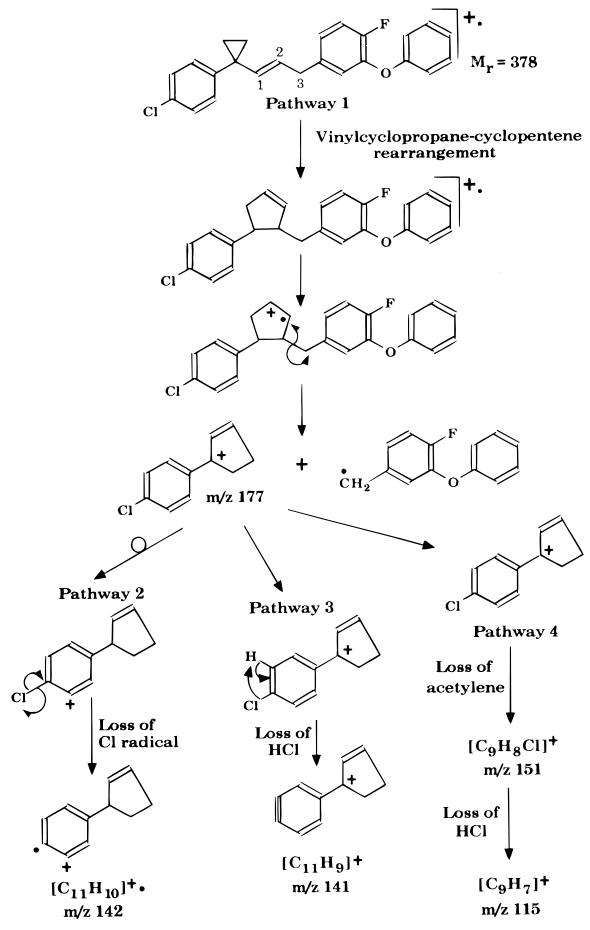



**Figure 3.** Positive-ion electron ionization spectrum of NRDC 199, having a ×5 magnification above *m/z* 190.




**Scheme 5.** Fragmentation pathways of NRDC 199 following positive-ion electron ionization.

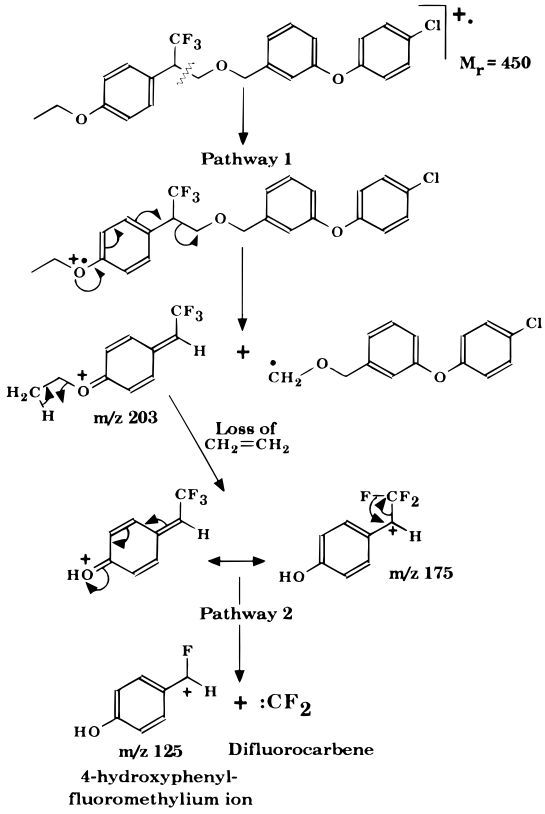
## Flufenprox (RMM = 450)

Flufenprox, which has an ether central linkage, is essentially an analogue of the non-ester pyrethroid MTI-500 (Ethofenprox)[18] in which the geminal methyl groups of MTI-500 have been substituted by a hydrogen atom and a trifluoromethyl group and the benzene ring of the phenoxy group is chlorinated to form a 4-chlorophenoxy substituent (Scheme 1).

The +EI spectrum of Flufenprox (Fig. 4) shows a molecule ion at *m/z* 450 ($^{35}$Cl) of 5.5% relative abundance and an associated $^{37}$Cl ion at *m/z* 452. The base peak ion in the spectrum is at *m/z* 203 and other significant ions occur at *m/z* 77, 89, 107, 125, 175, 181 and 217/219.

A precursor ion scan (not shown) of the *m/z* 203 ion of Flufenprox shows connectivity between this ion and the molecule ion *m/z* 450/452. This spectrum provides evidence that one fragmentation route is directly from the molecule ion to *m/z* 203. It is proposed that the *m/z* 203 ion arises from homolytic cleavage between the α-carbon of the trifluoromethyl group and the adjacent methylene group of the ether chain to form an even electron ($EE^+$) 1-(4-ethoxyphenyl)-2,2,2-trifluoroethylium ion (Scheme 6, pathway 1).

A product ion spectrum of the molecule ion, *m/z* 450, (not shown) indicates connectivity between this ion and




**Scheme 6.** Fragmentation pathways 1 and 2 of Flufenprox following positive-ion electron ionization.

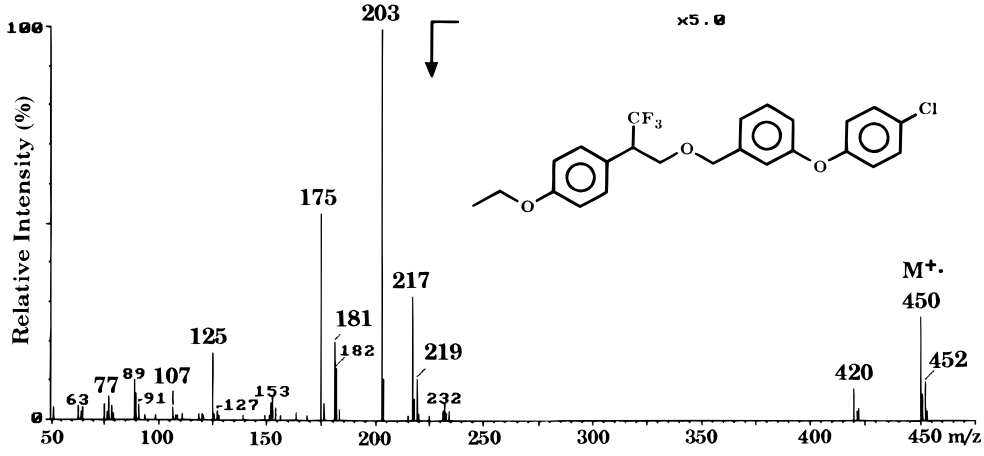



**Figure 4.** Positive-ion electron ionization spectrum of Flufenprox, having a ×5 magnification above *m/z* 225.

ions at *m/z* 175, 203, 217 and 420. A product ion spectrum of *m/z* 452 shows connectivity between this ion and ions at *m/z* 175, 203, 219 and 422. The *m/z* 219 and 422 ions in this spectrum correspond to the $^{37}Cl$ isotopes of *m/z* 217 and 420, respectively.

A product ion spectrum of the *m/z* 203 ion shows connectivity between this ion and the ions at *m/z* 125 and 175. It is again proposed that the *m/z* 175 ion is formed by loss of ethene from the ethoxy group to yield a 1-(4-hydroxyphenyl)-2,2,2-trifluoroethylium fragment ion $[C_8H_6F_3O]^+$ (Scheme 6, pathway 1). Supportive evidence for ethene loss from the *m/z* 203 ion is provided by a constant neutral loss scan of 28 Da (not shown).

A product ion scan of the *m/z* 175 ion shows connectivity between this ion and the *m/z* 125 species and supportive evidence of this loss from the *m/z* 175 ion $[C_8H_6F_3O]^+$ is provided by a 50 Da neutral loss spectrum (Table 2). We propose that *m/z* 125 is the 4-hydroxyphenyl-fluoromethylium ion $[C_7H_6FO]^+$ and that it is formed by direct expulsion of difluorocarbene ($:CF_2$) from *m/z* 175 (Scheme 6, pathway 2).

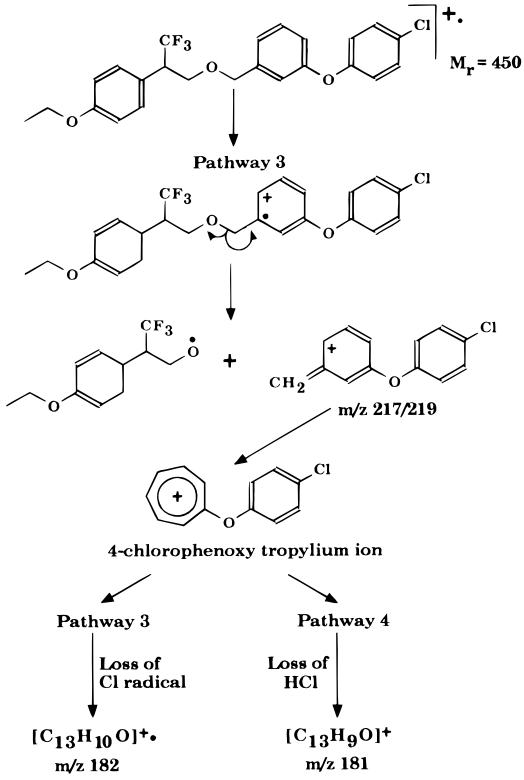
Carbenes are extremely reactive species which are commonly formed synthetically by concerted elimination or via carbanion, radical or carbocation intermediates.[26] While evidence of the existence of free carbenes is rare, the gas phase unimolecular generation of dihalocarbenes by mass spectrometric methods[27] is not uncommon and provides indirect support for their existence. As an example, the mass spectra of short-chain ($<C_4$) fluoroalkanes, fluoroalkenes and analogues of these compounds containing either chloro or both chloro and bromo substituents show the expulsion exclusively of difluorocarbene ($:CF_2$) from even electron ($EE^+$) fragment ions following loss of a halogen radical from the molecule ion. The preferential loss of difluorocarbene from mixed haloalkanes and haloalkenes reflects the greater stability of difluorocarbenes compared with their chloro- and bromo-containing counterparts.

As discussed earlier, the product ion spectra of the molecule ions of Flufenprox, *m/z* 450 ($^{35}Cl$) and *m/z* 452 ($^{37}Cl$), show connectivity between these ions and ions at *m/z* 217 and 219, respectively. It is proposed that formation of the *m/z* 217/219 ions is through homolytic cleavage of the benzylphenoxy–oxygen bond in the molecule ion to form a 4-chlorophenoxytropylium ion (Scheme 7, pathway 3).

Product ion spectra (not shown) of the *m/z* 217 and 219 ions indicate that these ions expel a chlorine radical homolytically from the chlorophenoxy tropylium ion to form the ($OE^{\cdot+}$) *m/z* 182 ion $[C_{13}H_{10}O]^{\cdot+}$ (Scheme 7, pathway 3). Additionally, neutral loss scans of 36 and 38 Da show loss of hydrogen chloride from the *m/z* 217 and 219 ions (Scheme 7, pathway 4).

The +EI product ion spectra of the molecule ions *m/z* 450 ($^{35}Cl$) and *m/z* 452 ($^{37}Cl$) of Flufenprox also show connectivity between these precursor ions and ions at *m/z* 420 and 422, respectively (see earlier). The formation of the *m/z* 420 and 422 species is attributed to the loss of formaldehyde (30 Da) from the molecule ion. A neutral loss scan of 30 Da (not shown) also supports this loss from the molecule ion.

Inspection of the spectra of other 4-ethoxyphenyl-containing non-ester pyrethroids having alkane and/or alkene central linkages shows no evidence for such losses of formaldehyde from their molecule ions. This suggests that the loss of formaldehyde from the molecule ion of Flufenprox involves the ether central linkage via a rearrangement involving the cleavage of two bonds.




**Scheme 7.** Fragmentation pathways 3 and 4 of Flufenprox following positive-ion electron ionization.

## CONCLUSION

The fissile nature of the bonds forming the central linkages of these non-ester-type pyrethroids, when examined under electron ionization mass spectrometric conditions, leads to spectra showing weak or non-existent molecule ions.

The major fragmentation pathway of the non-ester pyrethroids is associated with the formation of base peak carbenium ion centres following homolytic cleavage of their respective central alkane, alkene or ether linkages. The inherent stability associated with these carbenium ion centres should make these species attractive candidates for selected ion monitoring in order to provide lower limits of detection in environmental analysis.

With the exception of NRDC 199, these carbenium ion centres undergo a significant common loss involving the expulsion of ethene from the aromatic ethoxy groups. The carbenium ion centre of NRDC 199, which has a 4-chlorophenyl functionality instead of a 4-ethoxyphenyl functionality, shows losses of both hydrogen chloride and a chlorine radical.

The mass spectra of MTI-800, NRDC 199, and NRDC 200 also show another homolytic benzylic cleavage involving the phenoxyfluorobenzyl carbon and adjacent methylene group of the central linkage to form

a phenoxyfluorobenzylium ion at $m/z$ 201. These $m/z$ 201 ions fragment further via a Wagner–Meerwein-type rearrangement to yield a tropylium benzofuran-type ion at $m/z$ 181 by expulsion of a molecule of hydrogen fluoride. The mass spectrum of Flufenprox also shows an equivalent homolytic cleavage of the benzylphenoxy–oxygen bond of the molecule ion to form a $^{35}$Cl chlorophenoxy tropylium ion ($m/z$ 217) and its corresponding $^{37}$Cl isotope ($m/z$ 219). This chlorophenoxy tropylium ion ($m/z$ 217/219) undergoes further losses involving the expulsion of hydrogen chloride and a chlorine radical.

The multifunctional nature of non-ester-type pyrethroid insecticides is reflected in their spectra, which show many other fragmentation pathways, especially involving the expulsion of neutral species. Perhaps most significant among these fragmentations is the expulsion of difluorocarbene from the $m/z$ 175 ion centre of Flufenprox. Carbenes are extremely reactive species which are commonly formed synthetically by concerted elimination or via carbanion, radical or carbocation intermediates. While evidence of the existence of free carbenes is rare, the gas phase unimolecular generation of dihalocarbenes by mass spectrometric methods is not uncommon and provides indirect support for their existence.

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