NWRI CONTRIBUTION 88-70

DETERMINATION AND CONFIRMATION OF SOME SYNTHETIC PYRETHROIDS AND THEIR METABOLITES IN WATER SAMPLES

by
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March 1988

MANAGEMENT PERSPECTIVE

Synthetic pyrethroids such as permethrin, cypermethrin, deltamethrin and fenvalerate are recently developed insecticides for the control of pests in farmland and vegetable crops. They have been registered in Canada for many applications since the early 1980's. Pyrethroids are being considered as a potential replacement for organochlorines, organophosphorus, and methylcarbamate insecticides since they are less persistent in the environment and less toxic to mammals than the other insecticides. However, pyrethroids are highly toxic to fish and other aquatic organisms. In order to protect the aquatic ecosystem, it is necessary to monitor the pyrethroid levels in rivers and ponds in areas where the insecticides have been applied. A method for the determination of the above-mentioned pyrethroids, and their major metabolites in water samples is presented. This work was partially funded by PESTFUND for FY 1986/87.

Dr. J. Lawrence
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Perspective gestion

Les pyréthrinoïdes synthétiques, comme la perméthrine, la cyperméthrine, la deltaméthrine et le fenvalérate, sont des insecticides récemment mis au point qui sont utilisés pour détruire les nuisibles sur les terres agricoles et sur les espèces potagères. Depuis le début des années 1980, ces produits sont enregistrés au Canada pour de nombreuses applications. On envisage d'utiliser les pyréthrinoïdes comme produits de rechange possibles des insecticides organochlorés, des insecticides organophosphorés et des insecticides à base de méthylcarbamate, car ils sont moins persistants dans l'environnement et moins toxiques pour les mammifères que les autres insecticides. Toutefois, les pyréthrinoïdes sont très toxiques pour les poissons et les autres organismes aquatiques. Pour protéger l'écosystème aquatique, il faut contrôler les concentrations de pyréthrinoïdes dans les rivières et les étangs des régions ayant fait l'objet de traitements avec ces insecticides. On présente une méthode de dosage des pyréthrinoïdes mentionnés ci-dessus et de leurs principaux métabolites dans des échantillons d'eau. Ces travaux ont été subventionnés en partie dans le cadre du PESTFUND pour l'exercice 1986-1987.

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ABSTRACT

A method for the simultaneous analysis of the pyrethroid insecticides, namely, permethrin, cypermethrin, deltamethrin, and fenvalerate and their major metabolites in water was developed. After dichloromethane extraction at pH $\leq$ 1 and cleanup on a 10% deactivated Florisil column, the parent compounds were analyzed by GC-ECD using a 12 m OV-1 column. The neutral metabolites, 3-phenoxybenzaldehyde and 3-phenoxybenzyl alcohol, were quantified by gas chromatography-mass selective detector using the selected ion monitoring technique. The acidic metabolites, 3-phenoxybenzoic acid and 3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid, were derivatized into their respective pentafluorobenzyl esters and analyzed by GC-ECD. Electron impact GC-MS data of the parent compounds and their metabolites were also acquired for the confirmation of compound identity. This procedure has been validated at sub-ppb levels using fortified distilled water samples. It has also been applied to the analysis of deltamethrin and its metabolites in water samples collected from Prince Edward Island.

Résumé

On a mis au point une méthode permettant de doser simultanément différents insecticides de type pyréthrinoïde, dont la perméthrine, la cyperméthrine, la deltaméthrine et le fenvalérate, ainsi que leurs principaux métabolites dans l'eau. Après extraction au dichlorométhane à un pH égal ou inférieur à 1, puis purification sur une colonne de Florisil désactivée à 10 %, on dose les composés d'origine par CG-DCE en utilisant une colone OV-1 de 12 m. On dose les métabolites neutres, soit le 3-phénoxybenzaldéhyde et l'alcool 3-phénoxybenzylique, en procédant par chromatographie en phase gazeuse avec un détecteur sélectif de masse et en contrôlant l'ion choisi. Dans le cas des métabolites acides, soit l'acide 3-phénoxybenzoïque et l'acide 3-(2,2-dibromovinyl)-2,2-diméthylcyclopropanecarboxylique, on forme les esters pentafluorobenzyliques correspondant que l'on dose ensuite par CG-DCE. On obtient également, dans le cas des composés d'origine et de leurs métabolites, des données CG-SM avec une source à bombardement électronique en vue de confirmer l'identité du produit. Cette méthode a été validée à des concentrations inférieures à une partie par milliard avec des échantillons fortifiées dans de l'eau distillée. Elle a également été appliquée au dosage de la deltaméthrine et de ses métabolites dans des échantillons d'eau prélevés à l'Île-du Prince-Édouard.

1.0 INTRODUCTION

In the early nineteenth century, pyrethrums, the dried flowers of chrysanthemum and daisy, were used by the Caucasian tribes to control body lice. Since then, pyrethrums were produced commercially in different parts of the world. At present, pyrethrum production is estimated at about 15,000 tons of the dried flowers per year, with half of its production coming from Kenya [1]. Several compounds including pyrethrin I and II, cinerin I and II, and jasmolin I and II [1], were isolated from pyrethrum extracts. These naturally occurring pyrethroids were all cyclopropane carboxylic acid esters with various substitutions on the side chain. Although they were very effective insecticides, the high cost of production of the natural pyrethroids as well as their instability to light and air led to the development of the stabilized synthetic pyrethroids which had similar structures and insecticidal properties as the natural analogs [2].

Among the synthetic pyrethroids developed in recent years, permethrin, cypermethrin, deltamethrin and fenvalerate received most attention because of their stability and effectiveness in field applications. These insecticides are being considered as replacements for other classes of insecticides such as organochlorines, organophosphorus, and methylcarbamates because of their high acute toxicity to insects and low toxicity to mammals. Pyrethroid insecticides are already registered in Canada for the control of pests on fruit and vegetable crops. Structures of the above synthetic pyrethroids are shown in Figure 1.

Degradation of the pyrethroids under environmental conditions has been reviewed [3]. One of the major photolytic reactions of the pyrethroids was ester cleavage to produce the dihalovinyl or p-chlorophenyl isovaleric acids. Ultimately, the 3-phenoxybenzoic acid was obtained from the alcohol or aldehyde moiety [4]. Degradation of pyrethroids in soils occurred primarily by hydrolysis and by microbial action. In general, ester cleavage, ring

hydroxylation in the 3-phenoxybenzyl moiety and hydrolysis of the cyano group occurred in soil [3]. The major degradation products are 3-phenoxybenzyl alcohol (3-PBalc), 3-phenoxybenzaldehyde (3-PBald), 3-phenoxybenzoic acid (3-PBacid), 3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA, from deltamethrin) 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropancarboxylic acid (DCCA, from permethrin and cypermethrin), CO_2, and some hydroxylated metabolites and their conjugates. The fate of permethrin and deltamethrin in model outdoor ponds has also been reported by Muir et al. [5,6]. In their studies, five degradation products were found in water, namely, cis- and trans-DCCA (for permethrin), DBCA (for deltamethrin), 3-PBalc, and 3-PBacid. Metabolism of pyrethroids in plants, insects, vertebrates, and enzyme systems has also been studied and reviewed [3,7,8].

Although they are much less toxic to mammals and do not persist in the environment, pyrethroids pose a serious hazard to the aquatic ecosystem since they are highly toxic to fish and other aquatic organisms. The toxicity and bioconcentration of pyrethroids in rainbow trout [9,10], minnows [11], and larvae [12] have been reported. In order to provide an early warning system to fish and other non-target organisms, it is necessary to monitor the residue levels of pyrethroids in rivers and ponds where the insecticides have been applied to nearby fields.

In this respect, GC-ECD and GC-MSD methods for the routine analysis of the parent pyrethroids as well as their major neutral and acidic metabolites in water samples is presented. Confirmation of compound identities by GC-MS and by chemical derivatization is also discussed.

2.0 EXPERIMENTAL

2.1 Chemicals and Materials

Reference standards: cis- and trans- Permethrin, cypermethrin (mixture of isomers) and fenvalerate (mixture of isomers) were

obtained from US-EPA. Deltamethrin (1R-cis-isomer) and DBCA (1-R-cis-isomer) were obtained form Roussel-Uclaf (Paris, France). 3-PBalc, 3-PBald, and 3-PBacid were obtained from Aldrich (Milwaukee, WI, USA).

Solvents: All solvents were distilled-in-glass grade available from Burdick and Jackson.

Reagents: Florisil, silica gel, and potassium carbonate from Fisher Scientific Co. were used.

2.2 GC-ECD Analysis

A Hewlett-Packard Model 5880A GC equipped with a Model 7671A autosampler, split/splitless injection port, Level 4 terminals, and an electron-capture detector was used. A 12 m x 0.2 mm id OV-1 fused silica capillary column was used for the analysis of parent pyrethroids. Temperature program: initial temperature, 70°C for 1.5 min, programming rate 1, 30°C/min (from 70°C to 240°C), rate 2, 2°C/min (from 240°C to 270°C), final temperature was held for 15 min. Injection port and detector temperature were 275° and 300°C, respectively. Carrier gas was helium and column head pressure was 12 psi. Makeup gas was argon/methane 95 + 5 at a flow rate of 25 mL/min.

For the analysis of the PFB esters of 3-PBacid and DBCA, the same OV-1 column and the following conditions were used: initial temperature 70°C for 0.5 min, programming rate 1, 30°C/min (from 70° to 200°C), rate 2, 5°C/min (from 200° to 280°C) and the final temperature was held for 15 min.

2.3 GC-MSD Analysis

A Hewlett-Packard Model 5880A GC equipped with a split/splitless injection port, Model 5970B mass selective detector and data system, and a Model 7671A autosampler was used. A 30 m x 0.25 mm id SPB-5 column (Supelco Ltd.) was directly interfaced to the

electron impact (EI) ion source for maximum sensitivity. Electron energy was 70 eV. Operating temperatures were injection port 275°C, interface 280°C, column head pressure was 4 psi and carrier gas was helium. For the analysis of parent compounds, the following conditions were used: initial temperature 70° for 0.5 min, programming rate 1, 30°C/min (from 70° to 250°C), rate 2, 2°C/min (from 250° to 290°C) and the final temperature was held for 15 min. For the analysis of neutral metabolites, the following conditions were used: initial temperature, 70°C for 0.5 min, programming rate 1, 25°C/min (from 70° to 180°C), rate 2, 2°C/min (from 180° to 220°C). The PFB esters of 3-PBacid and DBCA were analyzed under the following conditions: initial temperature, 70°C for 0.5 min, programming rate 1, 30°C/min (from 70° to 220°C), rate 2, 5°C/min (from 220° to 280°C), and the final temperature was held for 15 min.

2.4 Extraction, Cleanup and Derivatization

The water sample (1 L) was acidified to pH $\leq$ 1 with 1:1 diluted H_2SO_4 and extracted for 30 min with 50 mL of dichloromethane using a magnetic stirrer. This procedure was repeated twice. The combined organic extract was then partitioned twice with 50 mL of 2% $KHCO_3$ for 2 min each. The organic layer was dried by anhydrous sodium sulfate and the solvent evaporated and replaced with iso-octane. The concentrated extract was applied to a 5 g 10% deactivated Florisil column. After the first 50 mL of hexane wash which was discarded, the parent pyrethroids and 3-PBald were eluted in 50 mL of a 1% acetone in hexane mixture. The other neutral metabolite, 3-PBalc, was eluted by 50 mL of 10% acetone in hexane. The solvents of the above two fractions were evaporated and replaced with 1.0 mL of iso-octane. The pyrethroids were then analyzed by GC-ECD and the neutral metabolites by GC-MSD.

The acidic metabolites contained in the aqueous layer in the $KHCO_3$ partitioning step was acidified to pH < 1 and re-extracted with

three 50 mL aliquots of dichloromethane. After solvent replacement with acetone, the acids were derivatized into their PFB ester according to reference [13]. After silica gel column cleanup, the esters were analyzed by GC-ECD.

3.0 RESULTS AND DISCUSSION

Due to the presence of a rigid cyclopropane ring (Figure 1), cis- and trans- isomers exist in all four synthetic pyrethroids except fenvalerate. In addition, the presence of asymmetric carbons or chiral centres in all of the above pyrethroids creates different optical isomers with R and S configurations. The isomers used in this work were: 1RS-cis- and 1RS-trans- permethrin, the cis- and trans-isomers of the 1RS, αRS-cypermethrin, mixture of 2S, αR + 2R, αS and 2S, αS + 2R, αR fenvalerate, and αS, 1R- cis- deltamethrin.

3.1 Chromatographic Analysis of Pyrethroids and Related Compounds

When a mixture of the above parent pyrethroids was chromatographed on a 12 m OV-1 fused silica capillary column, a total of nine peaks were observed. The first two were attributed to cis- and trans- permethrin, respectively. The next group of four peaks was attributed to cypermethrin and according to Cassida et al. [14,15], the first and third peaks in this group were attributed to the optical isomers of cis-cypermethrin, and the second and last to those of trans-cypermethrin. The two peaks eluting right after the cypermethrins were due to fenvalerate. Again, according to reference 15, the first fenvalerate peak was attributed to its 2S, αR and 2R, αS isomers and the second to its 2S, αS and 2R, αR isomers. The last peak in the mixture was αS, 1R-cis- deltamethrin. When the same mixture was chromatographed on a 30 m SPB-5 column, the same

order of elution was achieved for the pyrethroids and a typical chromatogram is shown in Figure 2.

Because of their high molecular weights, the parent pyrethroids chromatographed at high column temperatures. Even with a short 12 m OV-1 column, the elution temperatures of these compounds were between 260 and 270°C. Owing to the low volatility of pyrethroids, carry over of compounds (memory effects) from one sample to the next was observed when splitless injections were made. To solve this problem, it was necessary to inject a solvent blank after each sample or standard; otherwise, on-column rather than splitless injections should be made.

Although the labelled neutral metabolites 3-PBald and 3-PBalc were analyzed by liquid scintillation counting techniques [5,6], no chromatographic analytical methods have been published in the literature. Since the metabolites were not halogenated, they were insensitive to the ECD. Formation of ECD-sensitive derivatives was not pursued because of lengthy procedures since each compound would have required a specific derivatization reaction. HPLC analysis of 3-PBald and 3-PBalc was attempted in our laboratory using a 5μ reversed phase Zorbax ODS column under isocratic conditions. Separation of the two metabolites was achieved using a mobile phase made up of 15% water in acetonitrile. At a flow rate of 1 mL/min, the retention times were 3.62 and 4.55 min for 3-PBalc and 3-PBald, respectively. Although a signal to noise ratio of about 10 was achieved for a 1 ng injection of the metabolites using a variable wavelength UV detector operating at 230 nm, this technique was not applicable to the analysis of natural water samples due to interference of coextractives. A more sensitive and selective method to analyze 3-PBald and 3-PBalc was achieved by the selected ion monitoring technique using a mass selective detector. A detection limit of 0.2 ng for 3-PBalc and 0.05 ng for 3-PBald was achieved by monitoring their respective molecular ions, m/z 200 and m/z 198.

Although DCCA is a major metabolite of permethrin and cypermethrin, it was not included with the other two acidic metabolites (3-PBacid and DBCA) in the present work since reference standard of DCCA was unavailable. For the analysis of DBCA and 3-PBacid, pentaflurobenzylation was performed since the resulting derivatives were both sensitive to the ECD.

3.2 EI-GC-MS Data of Pyrethroids and Metabolites

The EI mass spectra of parent pyrethroids are given in Figures 3 to 7. As seen in these figures, the mass spectra of the isomeric species for each pyrethroid were nearly identical. The major fragment ions were: m/z 390 ($M^{+\cdot}$), 183, 163, and 127 for permethrin, m/z 415 ($M^{+\cdot}$), 209, 181, 163, and 127 for cypermethrin, m/z = 419 ($M^{+\cdot}$), 225, 181, 167, 152, and 125 for fenvalerate, and m/z 505 ($M^{+\cdot}$), 253, 208, 181, and 152 for deltamethrin. The EI mass spectra of pyrethroids were similar to those discussed elsewhere [16].

Full scan EI-GC-MS spectra of 3-PBald and 3-PBalc were also recorded and are given in Figures 8 and 9. In each case, the molecular ion was the base peak of the mass spectra. The major fragment ions included: m/z 198 ($M^{+\cdot}$), 181, 169, 141, 115, 77 and 51 for 3-PBald, and m/z 200 ($M^{+\cdot}$), 181, 153, 107, 94, 77 and 51 for 3-PBalc. The EI mass spectra of the PFB ester of 3-PBacid exhibited an intense molecular ion peak at m/a 394 (Figure 10) and the following major fragment ions: m/z 197, 189, 169, 141, 115, 77 and 51. In the case of the PFB ester of DBCA (Figure 11), the base peak was m/z 181 and the other major fragment ions were m/z 397, 279, 253, 173, 137 and 93. The molecular ion (m/z 478) was weak.

Thus, confirmation of identities of the parent pyrethroids and their metabolites can be achieved by the MSD using the scanning technique provided the level is high enough. At residue levels, confirmation of each compound can also be achieved by monitoring 2 or 3 of its characteristic ions listed above.

3.3 Confirmation of Pyrethroids by Chemical Derivatization

For those pyrethroids bearing a cyano group at the benzylic positions (i.e., cypermethrin, fenvalerate, and deltamethrin), the hydrogen on the other benzylic position is acidic and will react with PFBBr readily to yield the PFB derivatives [14]. These pentafluorobenzyl derivatives were used in the confirmation of the above three pyrethroids when a mass spectrometer was not available or used in the residue analysis since they were a few times more sensitive to the ECD than their parent compounds.

3.4 Extraction, Cleanup, Validation and Application

In order to extract the acidic metabolites together with the parent pyrethroids and the neutral metabolites, water samples were acidified to pH ≤ 1 with 1:1 diluted sulfuric acid. The presence of acid did not adversely affect the stability or recovery of the neutral compounds in the extraction steps. The neutral and acidic fractions were easily separated by partitioning with a 2% $KHCO_3$ solution. The neutral fraction was further cleaned up on a 10% deactivated Florisil column. After the first 50 mL of hexane was discarded, the parent pyrethroids and 3-PBald were quantitatively recovered in the next 50 mL of 1% acetone in hexane. The other neutral metabolite, 3-PBalc, was eluted with 50 mL of 10% acetone in hexane. The PFB esters of 3-PBacid and DBCA were cleaned by a 1 g 5% deactivated silica gel column and were eluted by 10 mL of toluene [13].

This procedure has been validated on fortified distilled and natural water samples with satisfactory recoveries (Tables 1 and 2). It has also been applied to the analysis of deltamethrin and its neutral and acidic metabolites in contaminated ground water samples collected from Prince Edward Island [17].

ACKNOWLEDGEMENTS

The authors are thankful to Drs. J. Lawrence and I. Sekerka for helpful suggestions and to Dr. J. Maguire for reference standards of deltamethrin and DBCA.

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TABLE 1

Percent Recovery of Pyrethroids from Replicate
Analysis of Fortified Distilled and Natural Water Samples
(Replicate = 6)

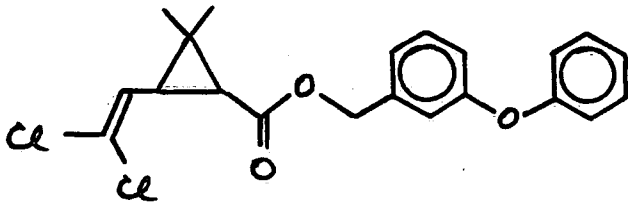
Pyrethroid	Level (µg/L)	Mean Recovery ± S.D. Distilled	L. Ontario	New Brunswick
cis-permethrin	0.50	103 + 8	100 ± 4	-
	0.05	101 ± 8	87 ± 5	99 ± 6
trans-permethrin	0.50	94 ± 7	101 ± 5	-
	0.05	97 ± 5	95 ± 8	100 ± 5
cypermethrin (total)	1.47	99 ± 6	98 ± 5	-
	0.147	96 ± 6	95 ± 4	90 ± 8
fenvalerate (total)	0.84	95 ± 6	101 ± 6	-
	0.084	97 ± 7	97 ± 5	96 ± 9
deltamethrin	0.36	94 ± 7	90 ± 3	-
	0.036	92 ± 7	91 ± 2	87 ± 9

TABLE 2

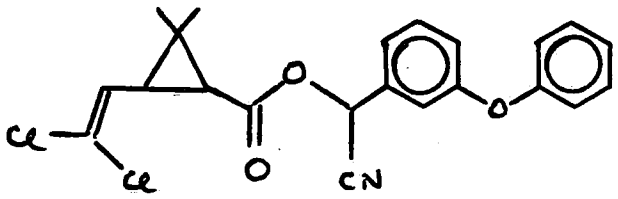
Percent Recovery of Pyrethroids Metabolites from Replicate Analysis of Fortified Distilled and Natural Water Samples

Metabolite	Level (µg/L)	Mean Recovery ± S.D.		
		Replicate	Distilled	L. Ontario
3-PBald	0.10	6	92 ± 5	90 ± 6
3-PBalc	0.10	6	85 ± 7	84 ± 8
3-PBacid	0.50	3	93 ± 5	97 ± 4
DBCA	0.66	3	99 ± 4	103 ± 7

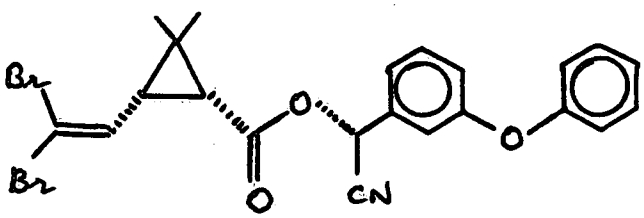
Figure 1. Structure of synthetic pyrethroids and their major metabolites.



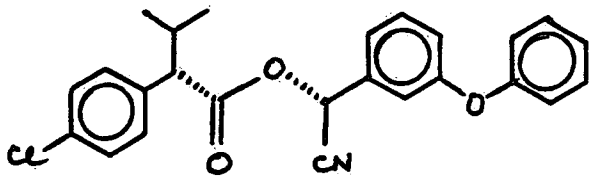
Permethrin cis- and trans-



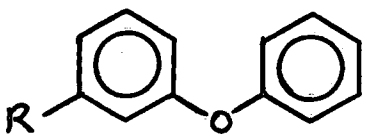
Cypermethrin cis- and trans-



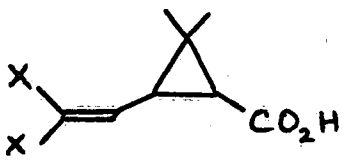
Deltamethrin αS, 1R- cis-



Fenvalerate



R = CHO for 3-PBald
R = CH_2OH for 3-PBalc
R = CO_2H for 3-PBacid



X = Br for DBCA
X = Cℓ for DCCA

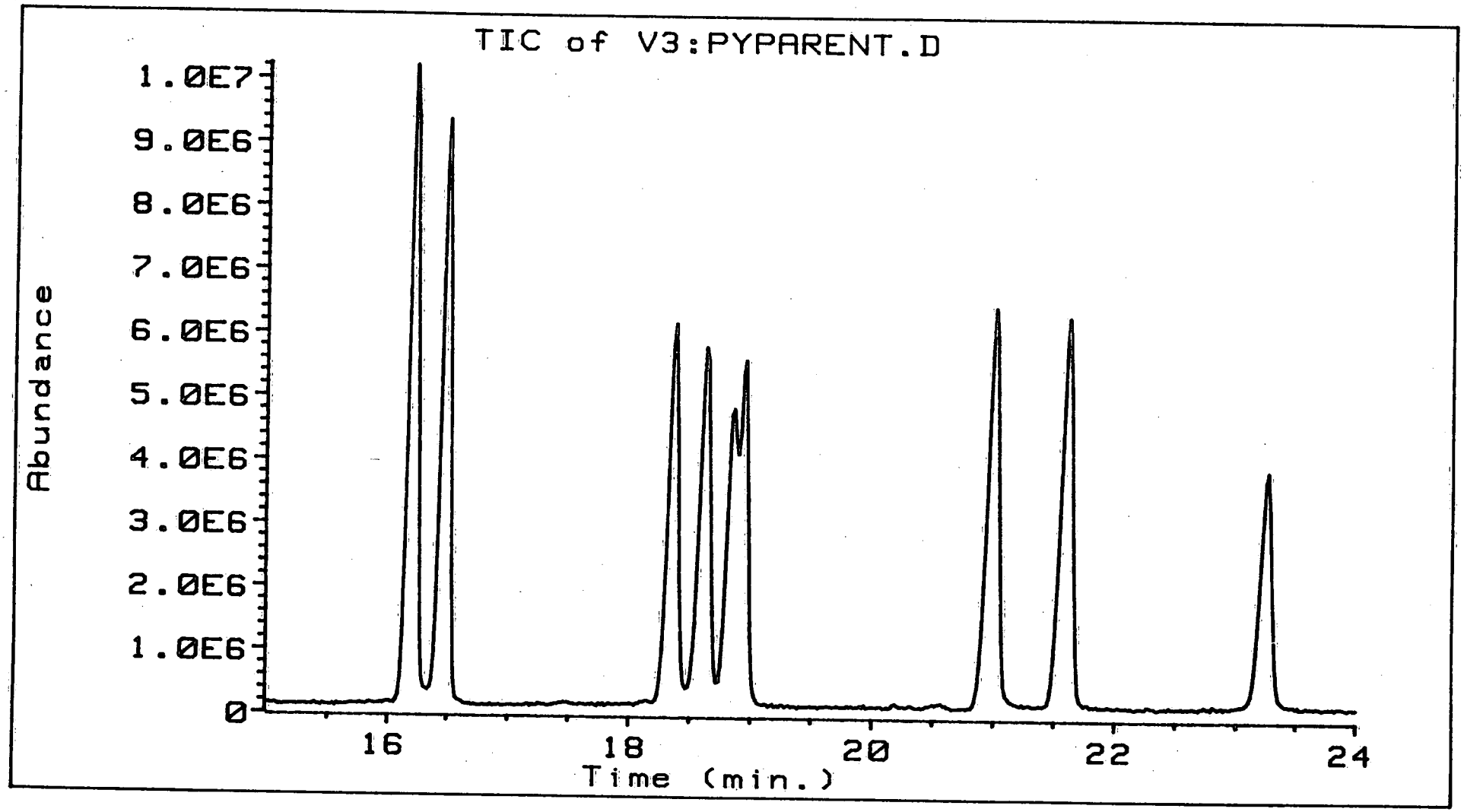


Figure 2. Total ion current chromatogram of a mixture of the four synthetic pyrethroids. See experimental for GC conditions.

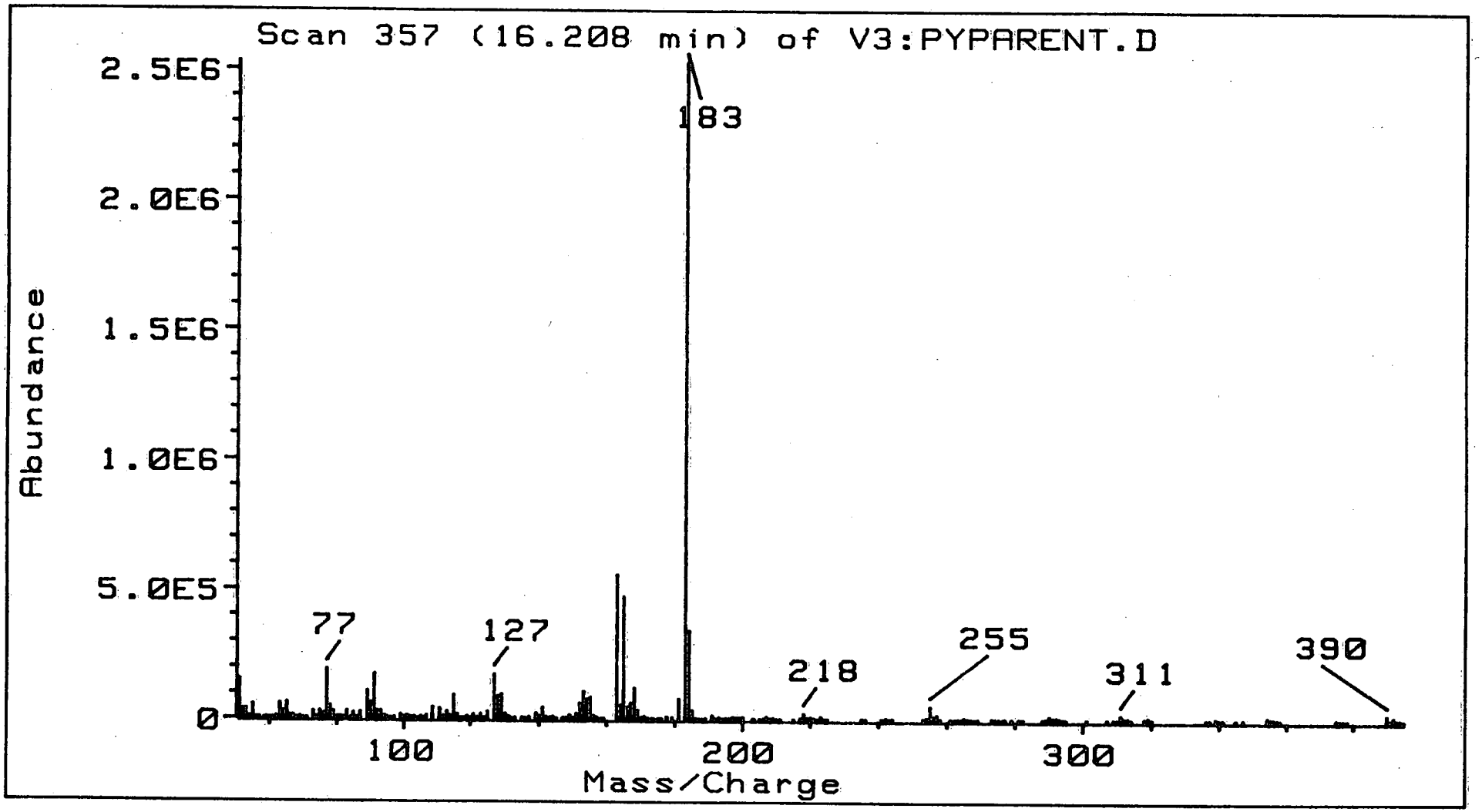


Figure 3. Mass spectrum of cis-permethrin.

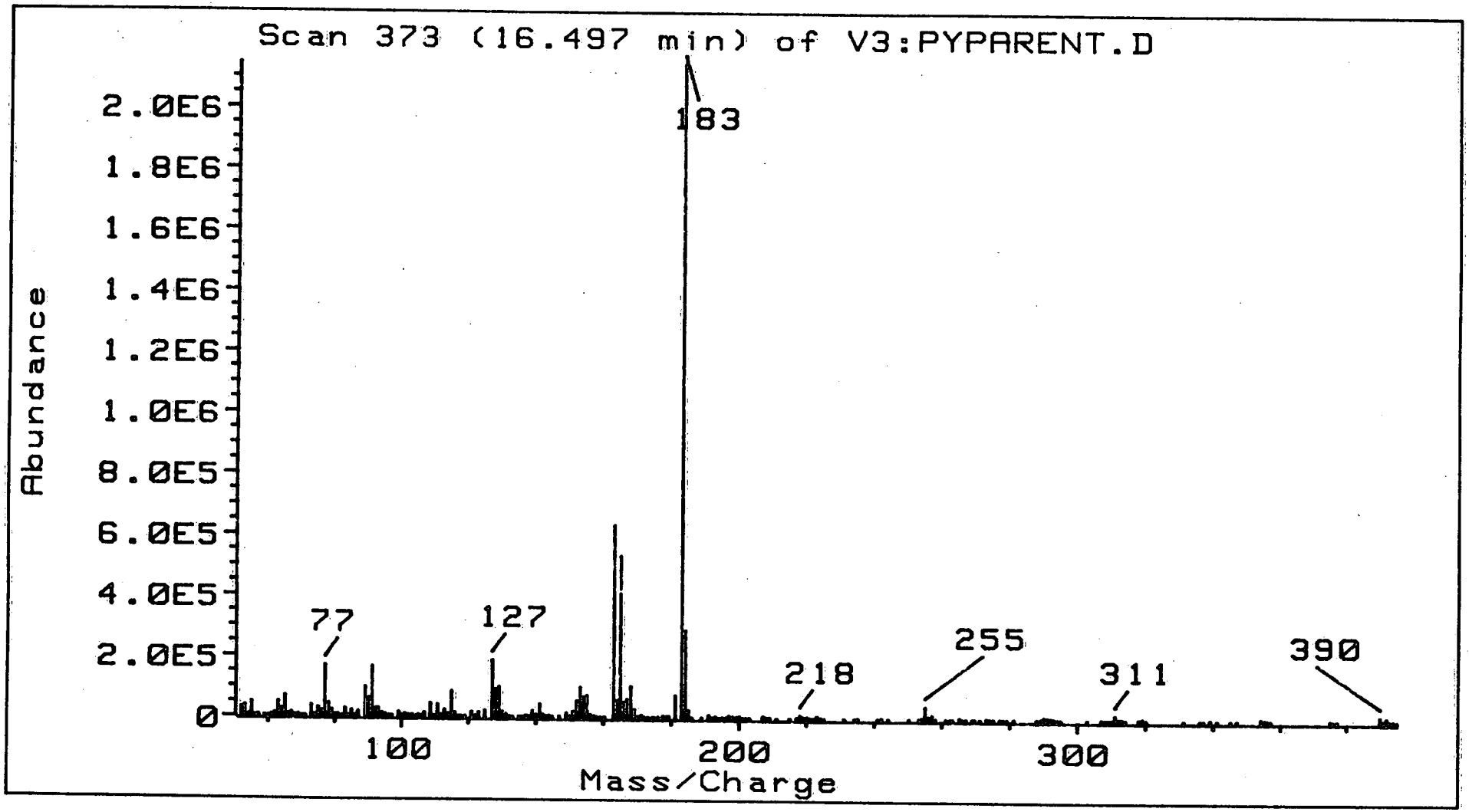


Figure 4. Mass spectrum of trans-permethrin.

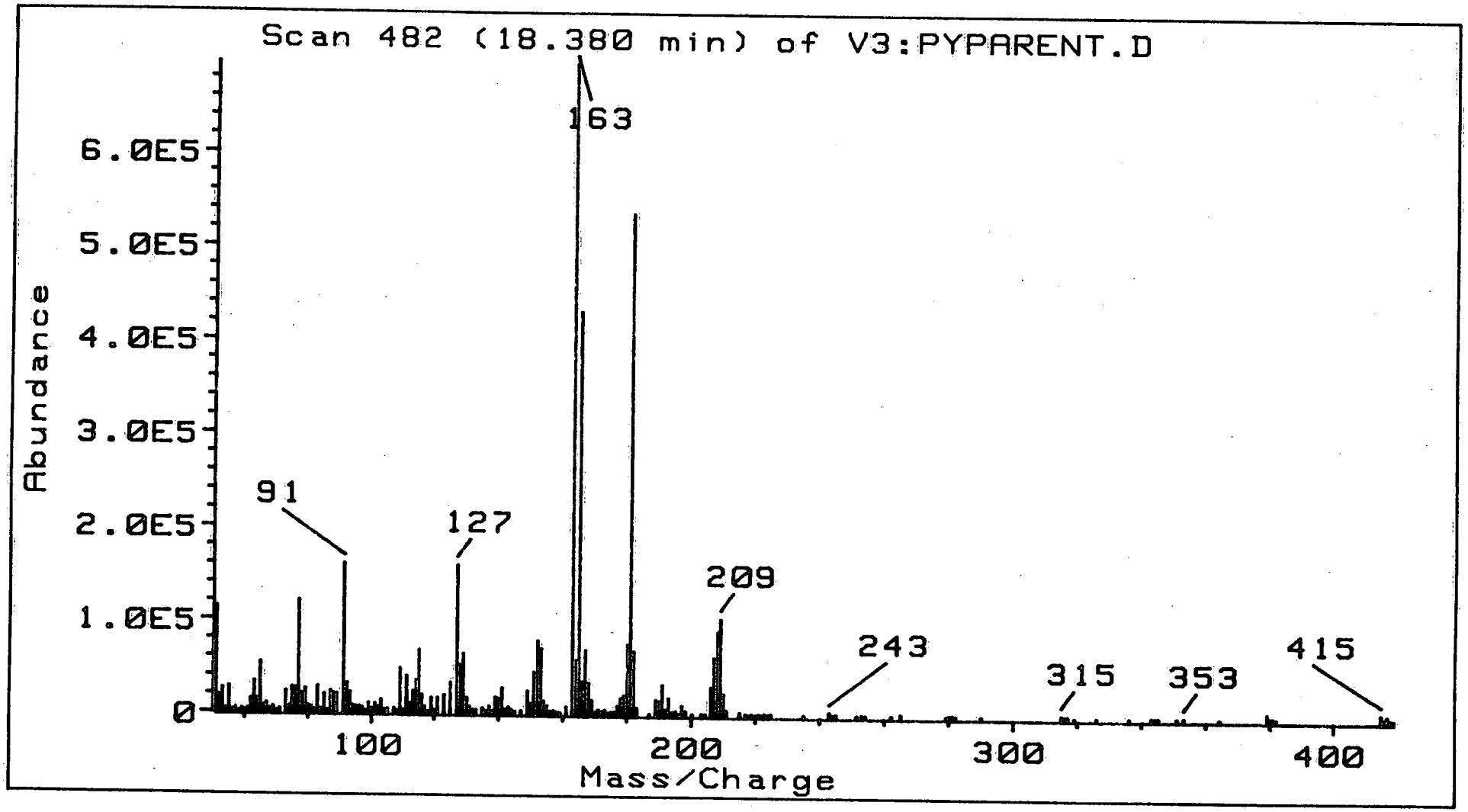


Figure 5a. Mass spectra of cypermethrin isomers.

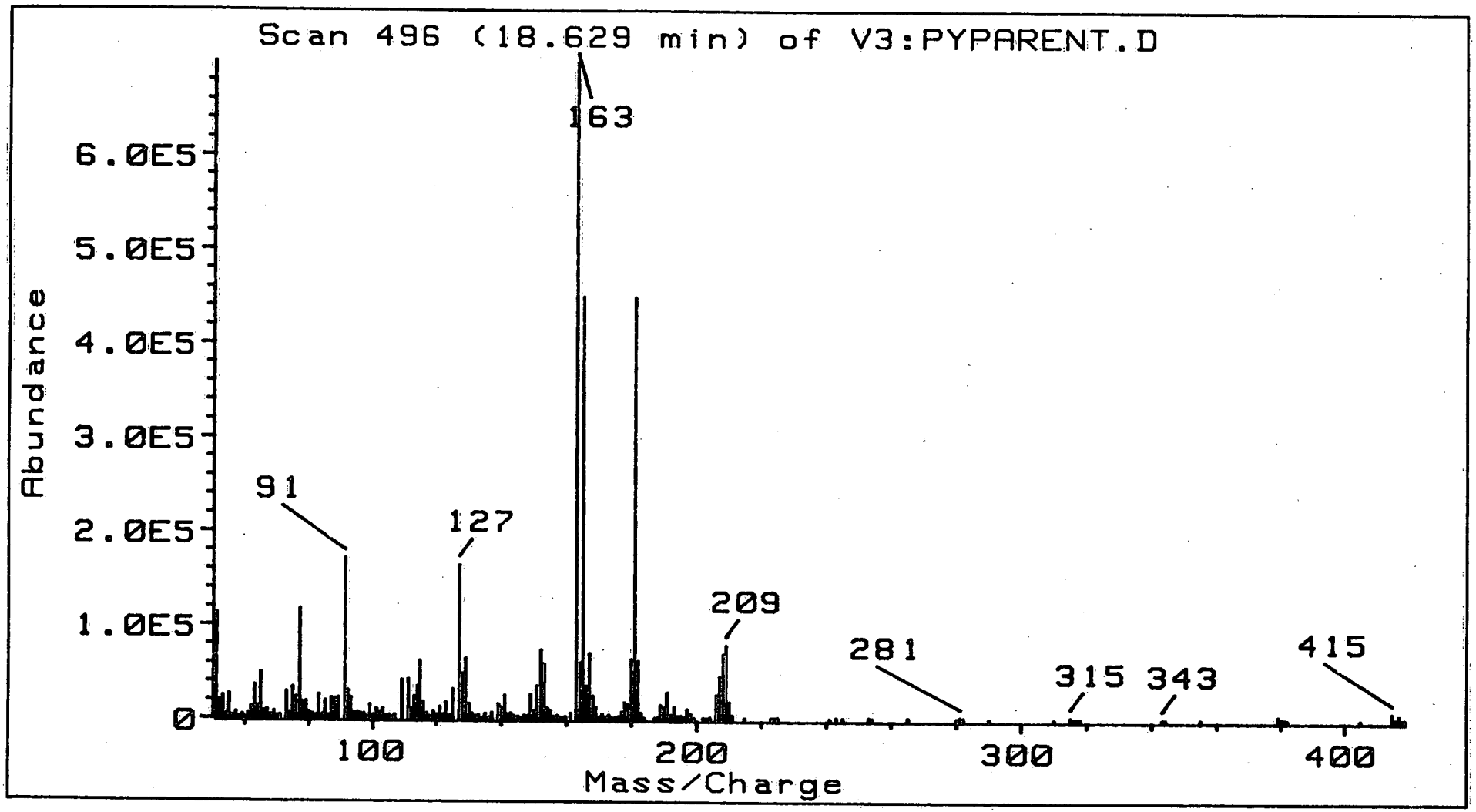


Figure 5b, Mass spectra of cypermethrin isomers.

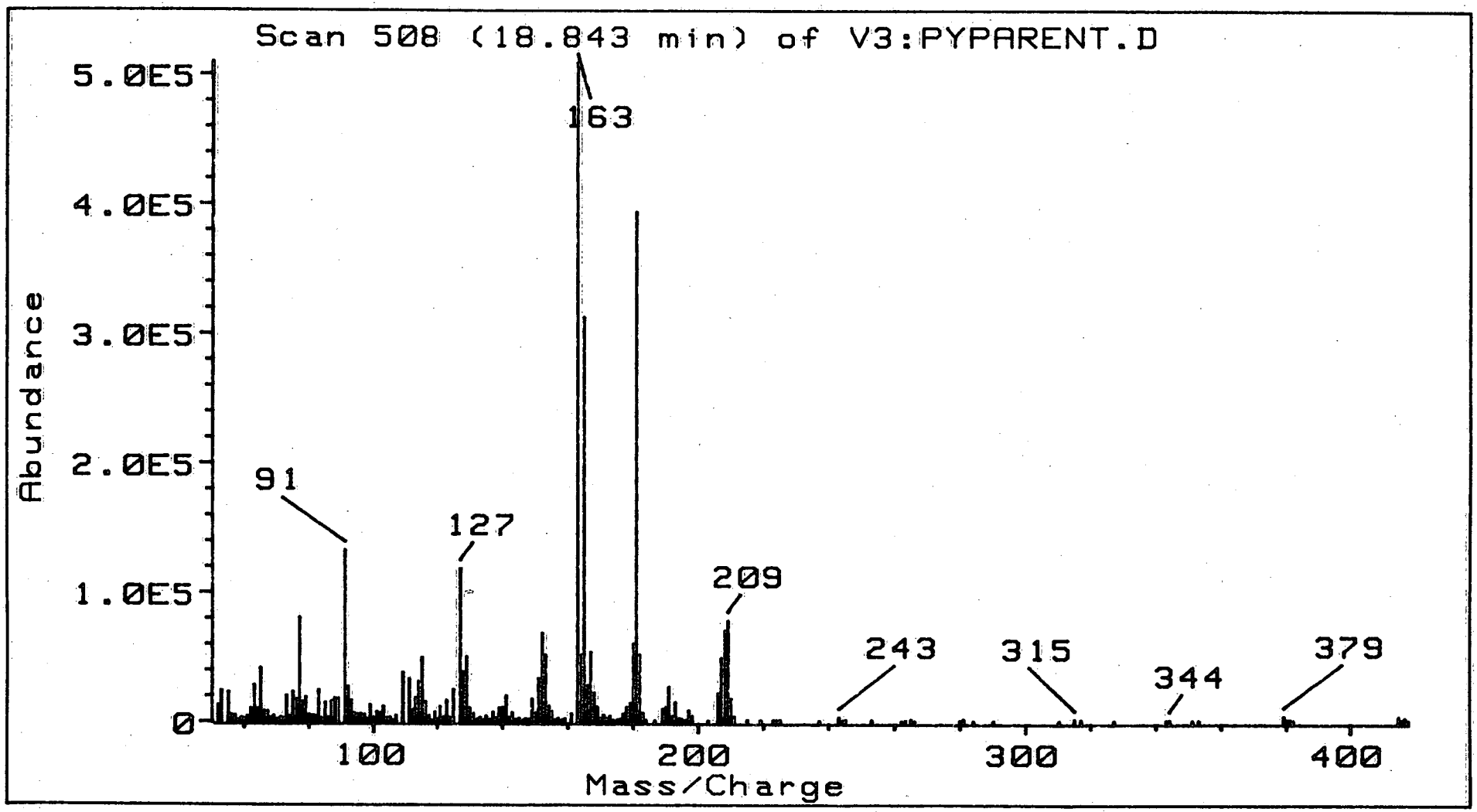


Figure 5c. Mass spectra of cypermethrin isomers.

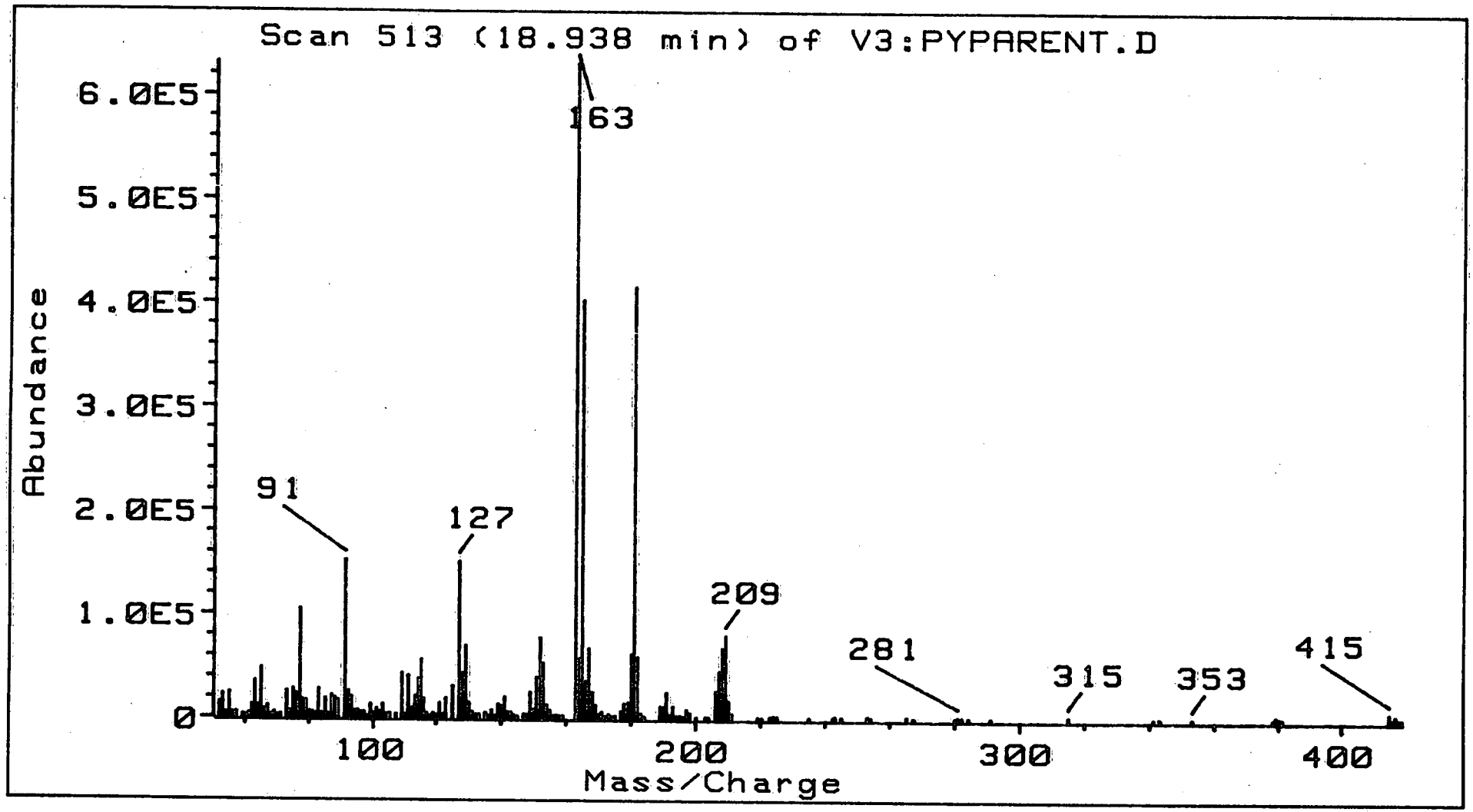


Figure 5d. Mass spectra of cypermethrin isomers.

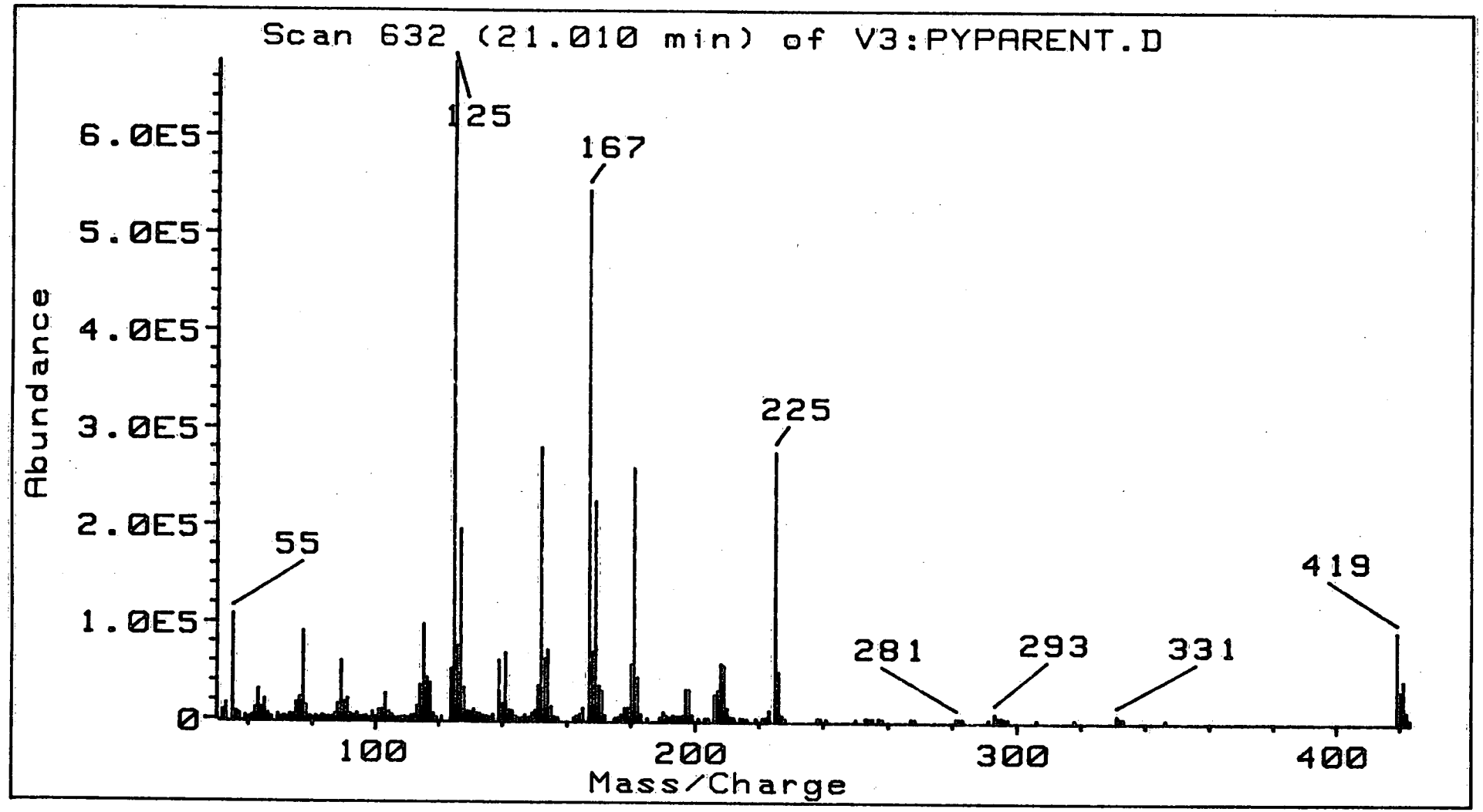


Figure 6a. Mass spectra of fenvalerate isomers.

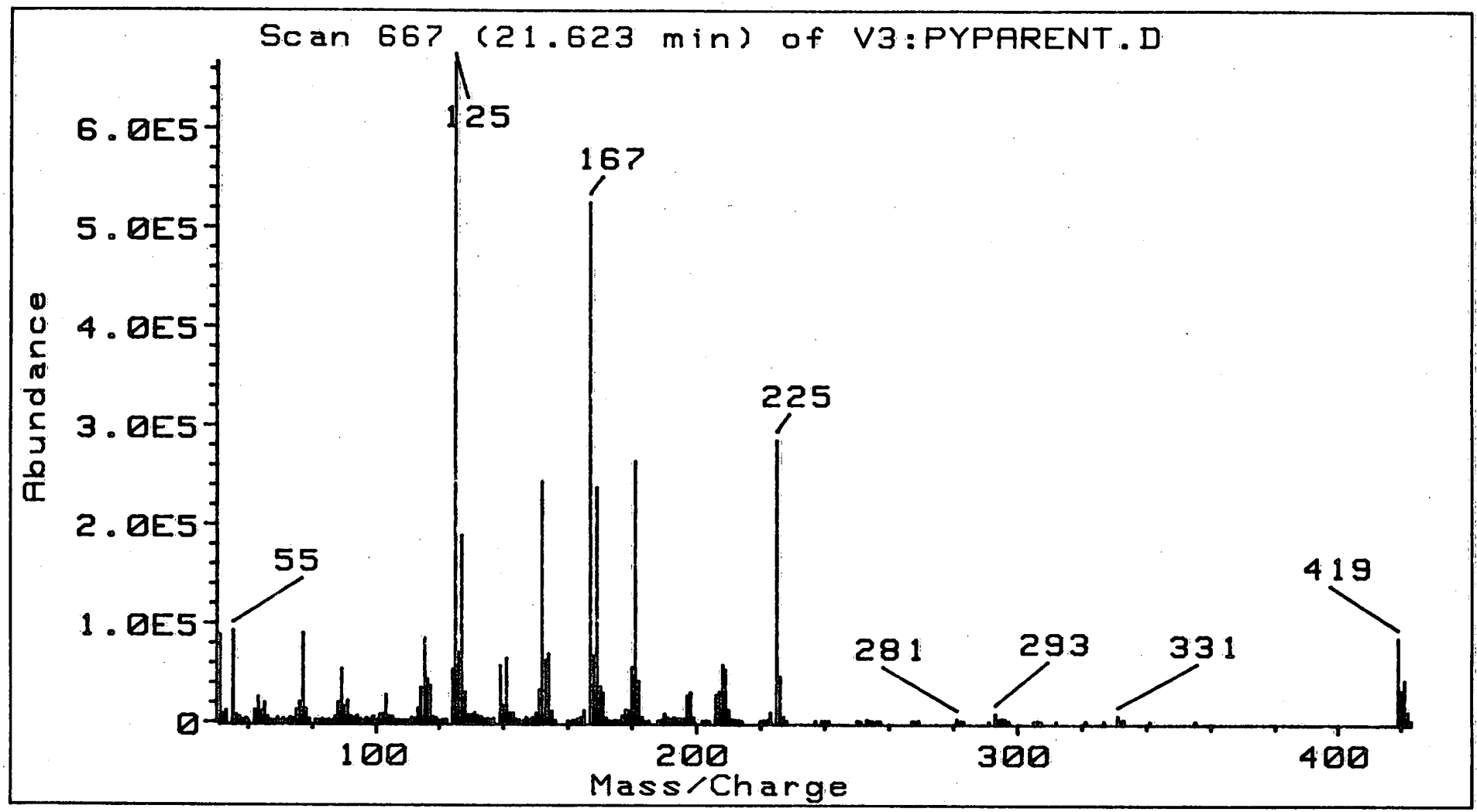


Figure 6b. Mass spectra of fenvalerate isomers.

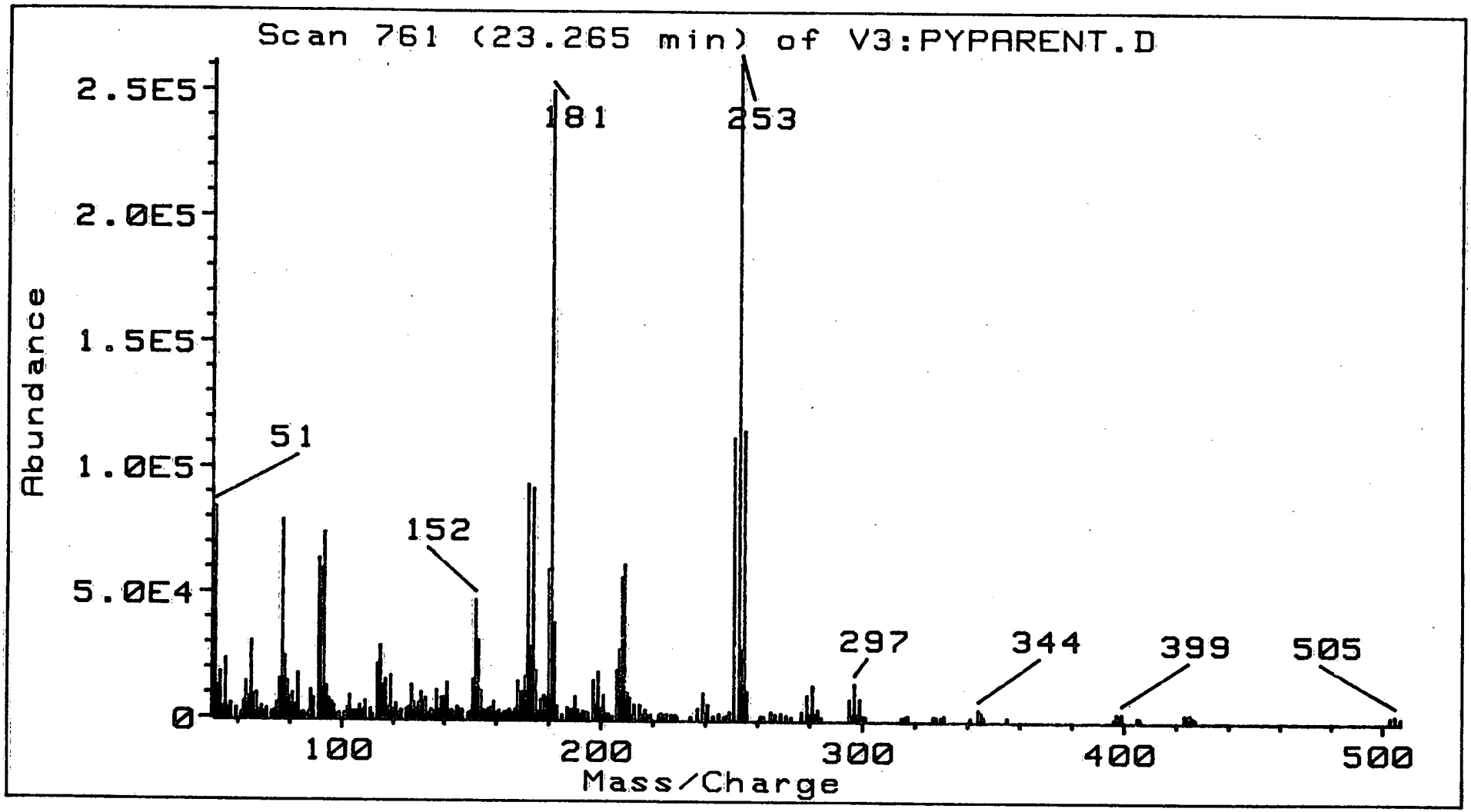


Figure 7. Mass spectrum of deltamethrin.

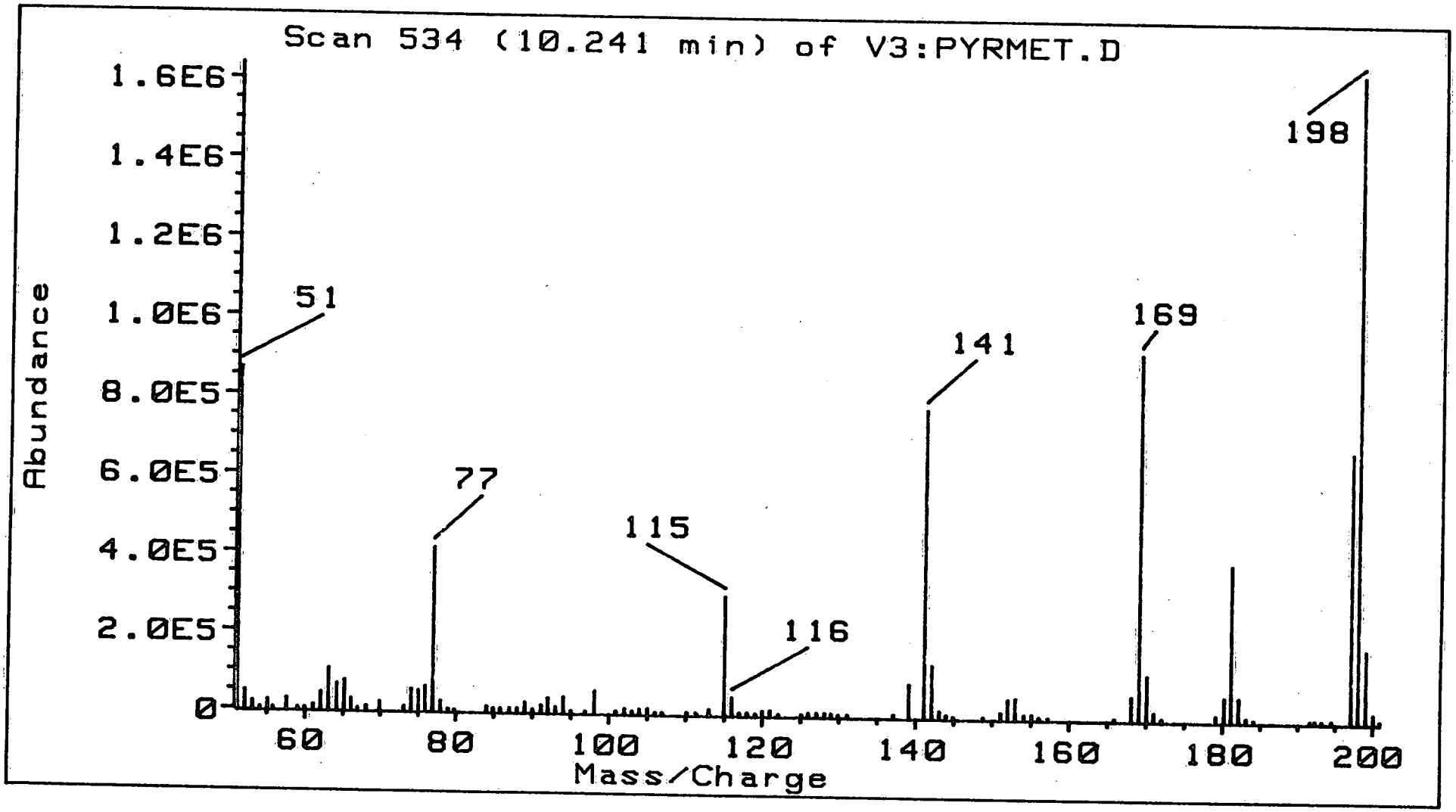


Figure 8. Mass spectrum of 3-PBald.

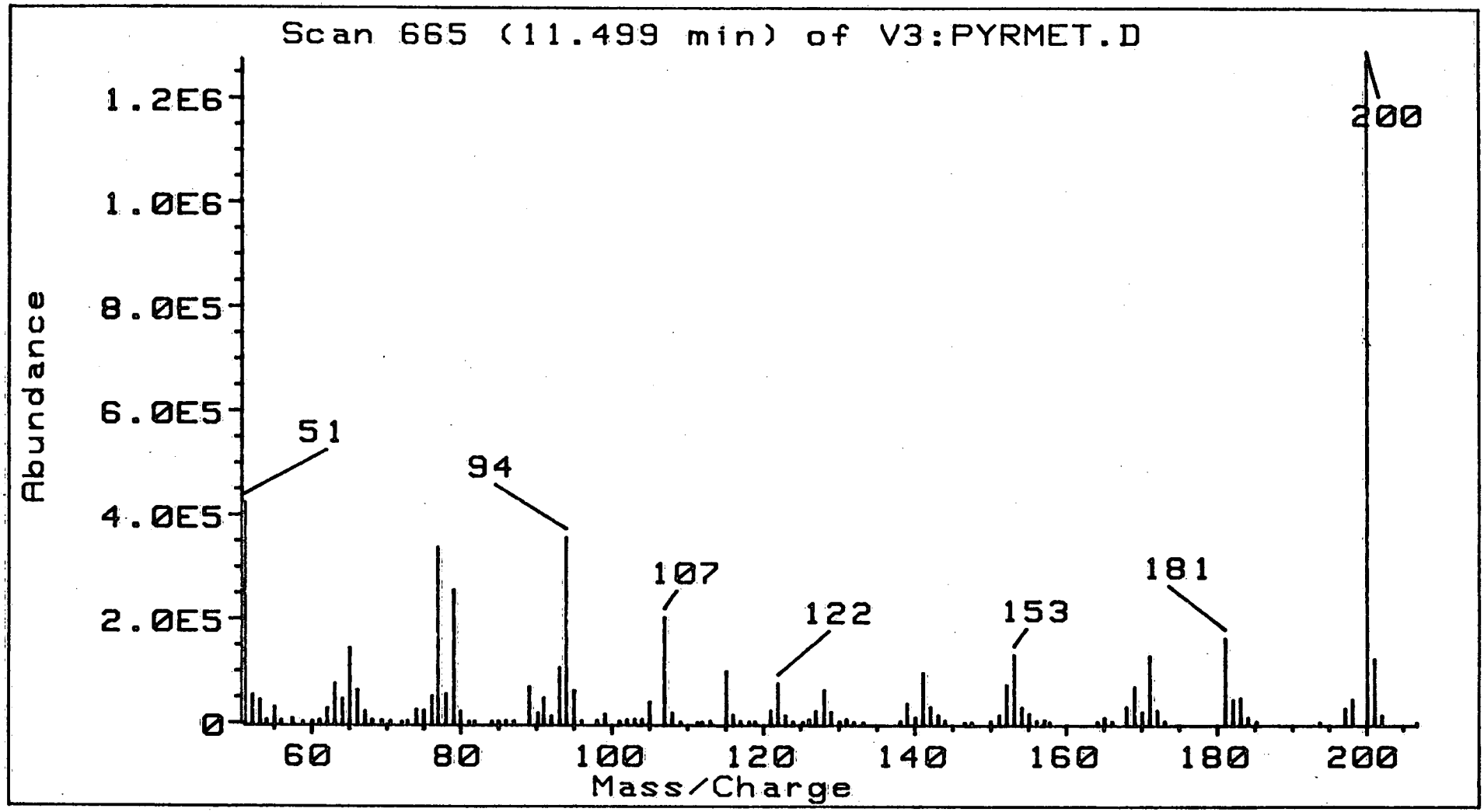


Figure 9. Mass spectrum of 3-PBalc.

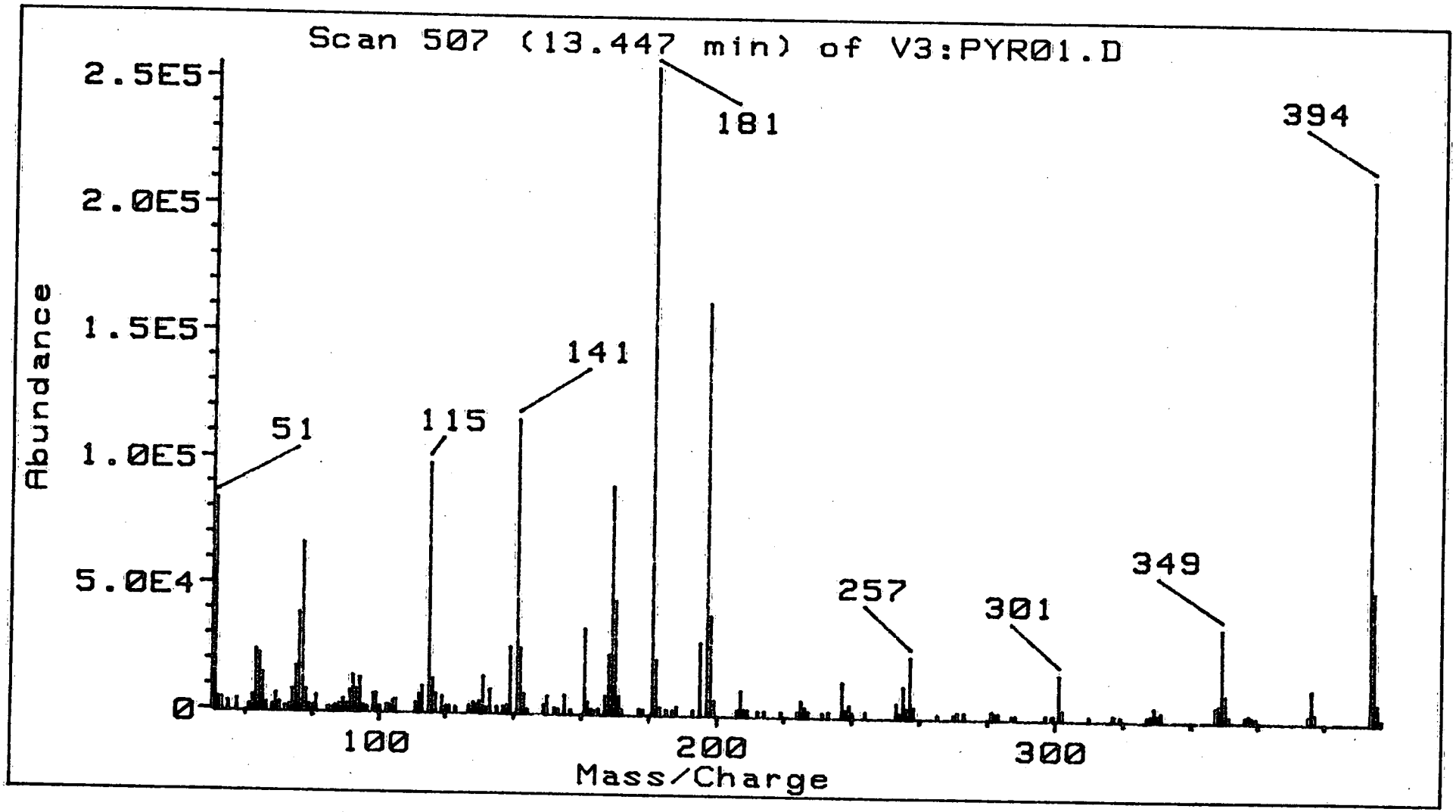


Figure 10. Mass spectrum of the PFB ester of 3-PBacid.

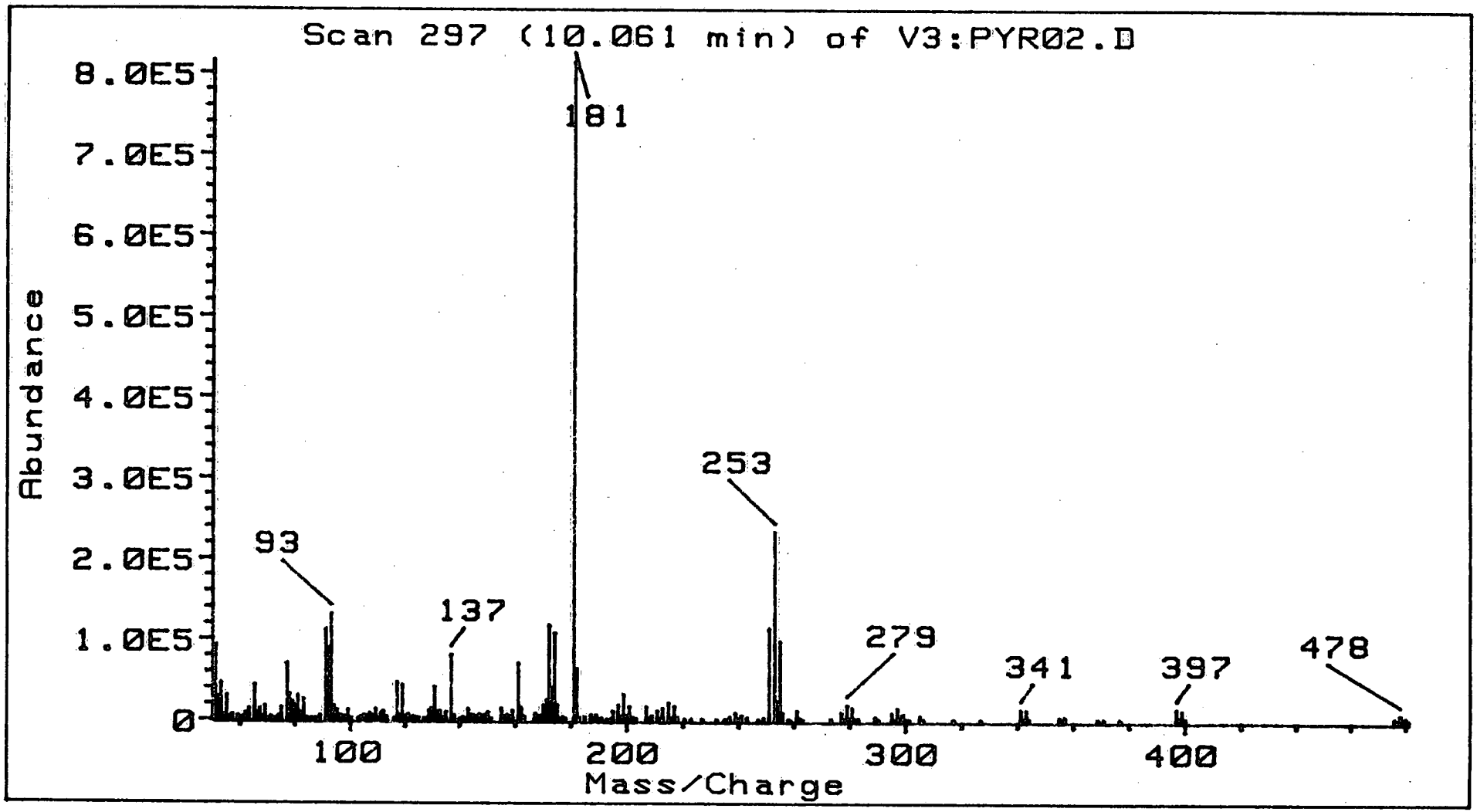


Figure 11. Mass spectrum of the PFB ester of DBCA.