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Electron impact mass spectrometry of N-(2-methylpropyl)-3-(*o*-, *m*- and *p*-R-phenyl)-2-propenamides[1]

Roberto Martinez * [1], Luis Velasco I. [2], Lino Reyes T., Rocio Pozas H., Javier A. Carballo P. and Patricia Melchor M.
1. Instituto de Quimica, 2. Facultad de Quimica, Universidad Nacional Autonoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacan 04510, México, D. F. México

Abstract. The major features of the mass spectra of eleven substituted 3-phenyl-2-propenamides of potential pharmacological interest are reported.

1. Introduction

There has been several reports on biological aspects of N-alkyl-2-propenamides and its derivatives. Some of these compounds are known to have activities such as anticonvulsant [1], insecticides [2], molluscidal [3] and other pharmacological properties [4]. One of the most important problem associated with compounds with biological properties is their potentially health hazard. Selected Ion Monitoring (SIM) offers a suitable analytical method for determination of trace amounts of pharmacological compounds [5] or their metabolites [6] in most systems. However, SIM studies requires the detection of one or more characteristic ions suitable for identification of these compounds. It is thus important to investigate the behaviour under electron impact of this kind of compounds.

As a part of our program directed towards the research of the pharmacological and mass spectral properties of such substances we report here the mass spectra of compounds **1-11**.

2. Experimental and Results

The mass spectra were measured on a Hewlett-Packard 5985 A quadrupole mass spectrometer using the direct inlet system. The spectra were recorded at an ionization chamber temperature of 190°C, an ionizing electron energy of 70eV, emission at 300μA, EM voltage 1800 V. All the compounds gave spectral data in agreement with their

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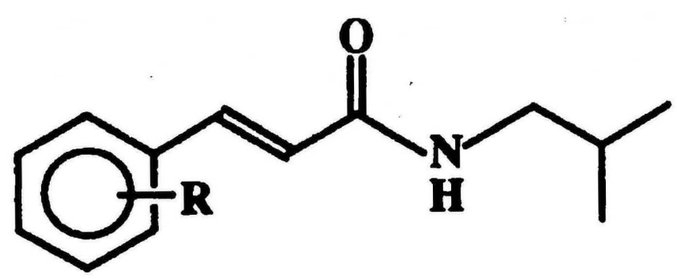
[1] Contribution no. 1175 from Instituto de Quimica, UNAM, Mexico.

structures. In the SIM experiments the gas chromatograph was equipped with an Ultra 2 (cross linked 5% PhMe Silicone) tubular capillary column (25 m x 0.32 mm ID). The conditions were: injection temperature, 230°C; column temperature program from 150° to 230°C at 10°C/min.; ion source temperature 240°C, electron impact (EI) ionization energy 70eV; accelerating voltage 3.0 kV.

The relative abundances of the principal positive ions of compounds **1-11** are shown in Table 1. The expected cleavage α- to the carbonyl group on the amide function [7] yields the ions at m/z (102 + R) and m/z (130 + R). The latter ion is the base peak in almost all the compounds analyzed. It is the presence of this species that makes the identification of 3-phenyl-2-propenamides substituted relatively easy. The elimination of 26 amu (C_2 H_2) from m/z (102 + R) ion affords an ion at m/z (76 + R). Another significant fragmentation is the β and γ cleavages to the nitrogen atom to give the ions at m/z 43 and m/z (M - 15) [8]. Likewise McLafferty rearrangement [9] yields the complementary ions of m/z (M - 57) and m/z 57.



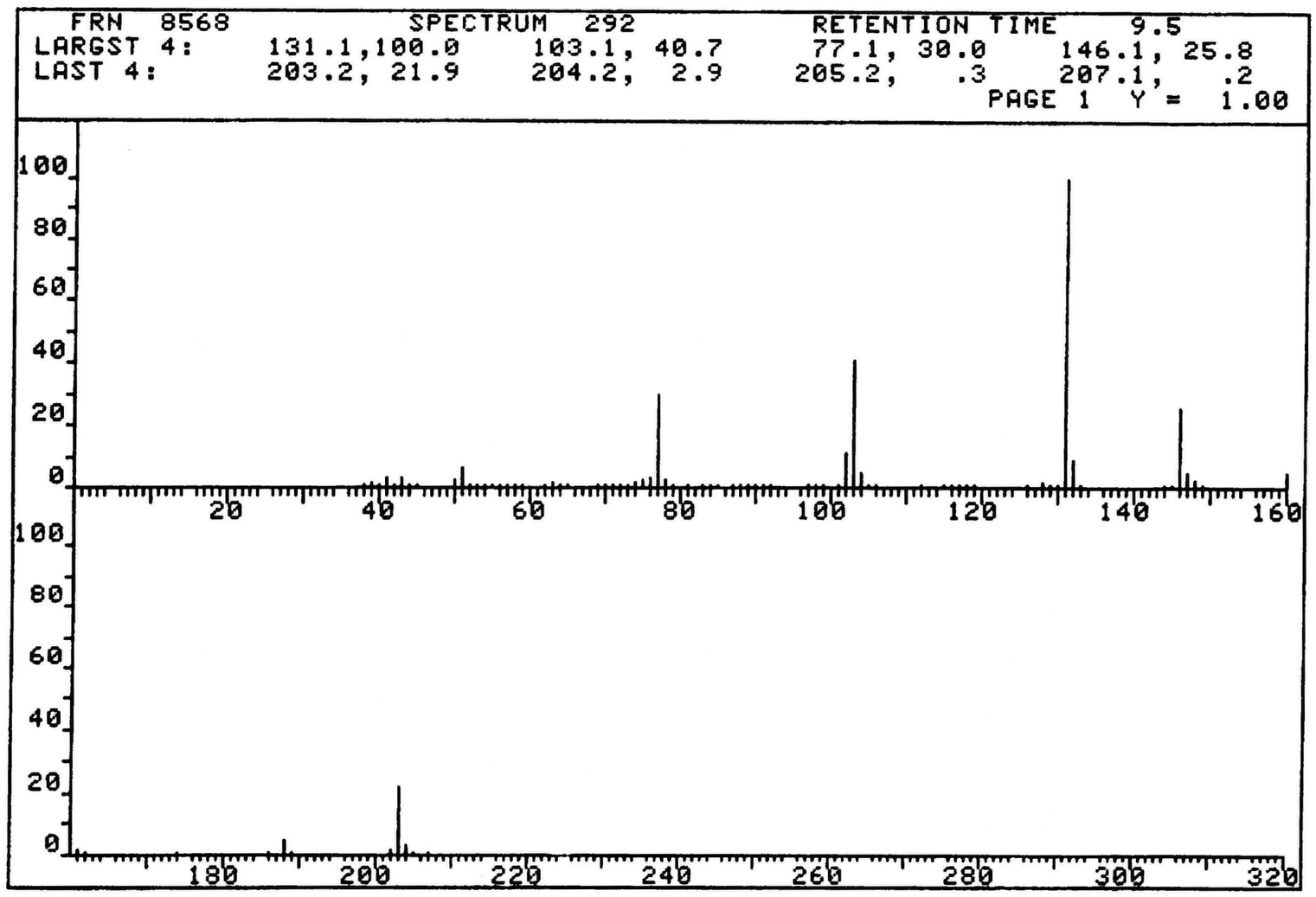
Compound	R	Name
1	H	N-(2-methylpropyl)-3-phenyl-2-propenamide
2	*o*-NO_2	N-(2-methylpropyl)-3-(2-nitrophenyl)-2-propenamide
3	*m*-NO_2	N-(2-methylpropyl)-3-(3-nitrophenyl)-2-propenamide
4	*p*-NO_2	N-(2-methylpropyl)-3-(4-nitrophenyl)-2-propenamide
5	*o*-Cl	N-(2-methylpropyl)-3-(2-chlorophenyl)-2-propenamide
6	*m*-Br	N-(2-methylpropyl)-3-(3-bromophenyl)-2-propenamide
7	*m*-F	N-(2-methylpropyl)-3-(3-fluorophenyl)-2-propenamide
8	3,5-diF	N-(2-methylpropyl)-3-(3,5-difluorophenyl)-2-propenamide
9	*p*-OMe	N-(2-methylpropyl)-3-(4-methoxyphenyl)-2-propenamide
10	3,4-diOMe	N-(2-methylpropyl)-3-(3,4-dimethoxyphenyl)-2-propenamide
11	4,5-OCH_2O	N-(2-methylpropyl)-3-[(4,5-(1,3-benzodioxolyl)]-2-propenamide

Selected-ion monitoring (SIM) experiment was used to detect N-(2-methylpropyl)-3-phenyl-2-propenamide at low concentration on ethyl acetate extracts from rat's liver [10] by monitoring m/z 131 peak.

Table 1

Relative abundances (%) of principal ions in the mass spectra of N-(2-methylpropyl)-3-(*o*-, *m*- and *p*-R-phenyl)-2-propenamides.

		m/z								
Cpd No.	R	M+ 1	M^+	M- 15	M- 57	130+ R	102+ R	76+ R	5 7	4 3
1	H	25	2	8	25	100	52	30	3	6
2	*o*-NO_2	-	-	-	3	90	2	3	2	3
3	*m*-NO_2	-	1	11	4	100	2	-	4	3
4	*p*-NO_2	25	-	-	7	100	2	-	-	1
5	*o*-Cl	-	5	2	8	80	38	2	5	7
6	*m*-Br	-	1	5	12	50	12	-	4	1
7	*m*-F	25	-	8	10	100	25	3	3	3
8	3,5-diF	-	2	10	8	100	33	-	6	1
9	*p*-OMe	28	-	-	-	100	27	-	4	8
10	3,4-diOMe	-	4	-	-	100	22	-	8	2
11	4,5-OCH_2O	63	-	-	75	100	10	-	5	2



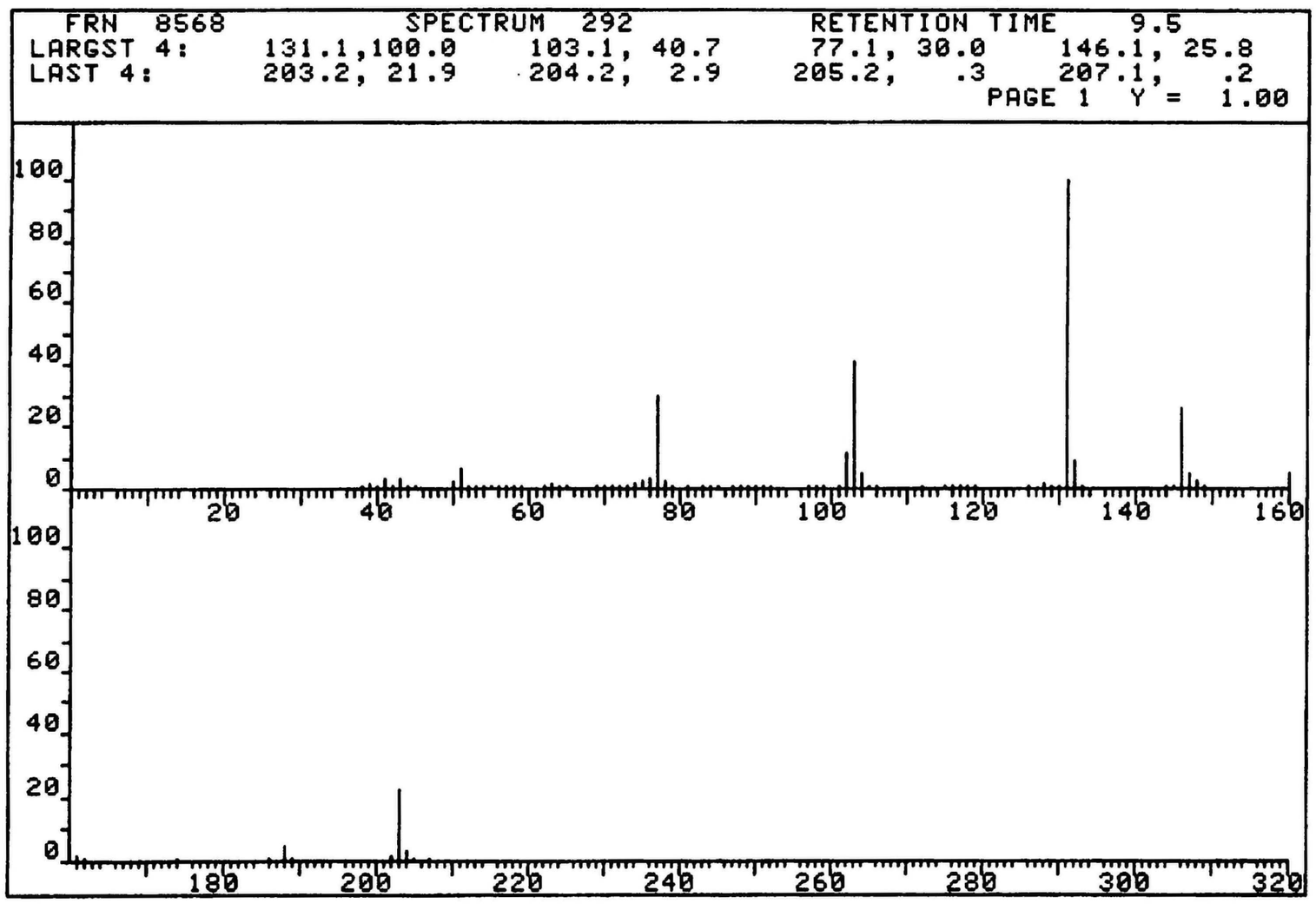
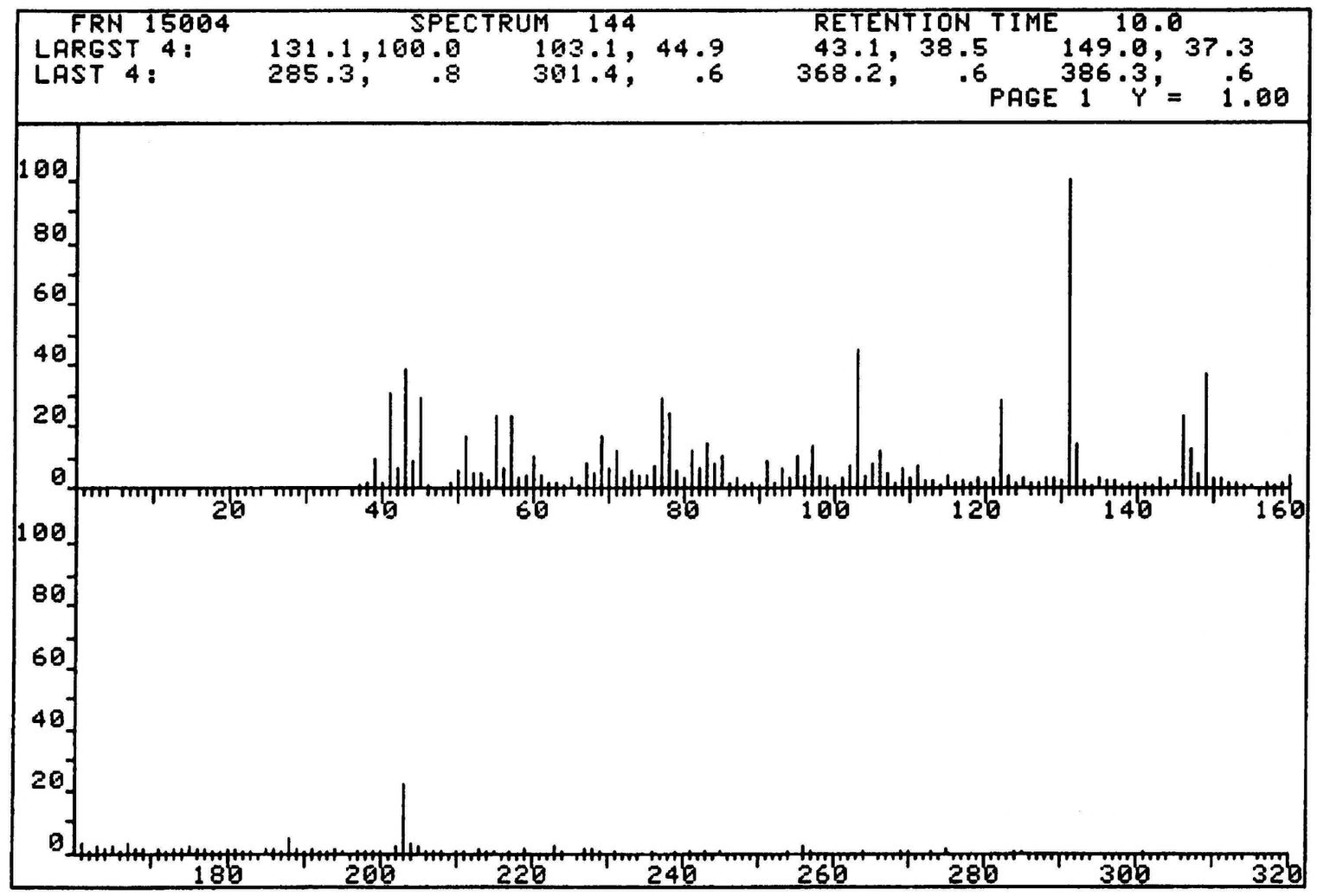


Figure 1. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide 1 at 70 eV.



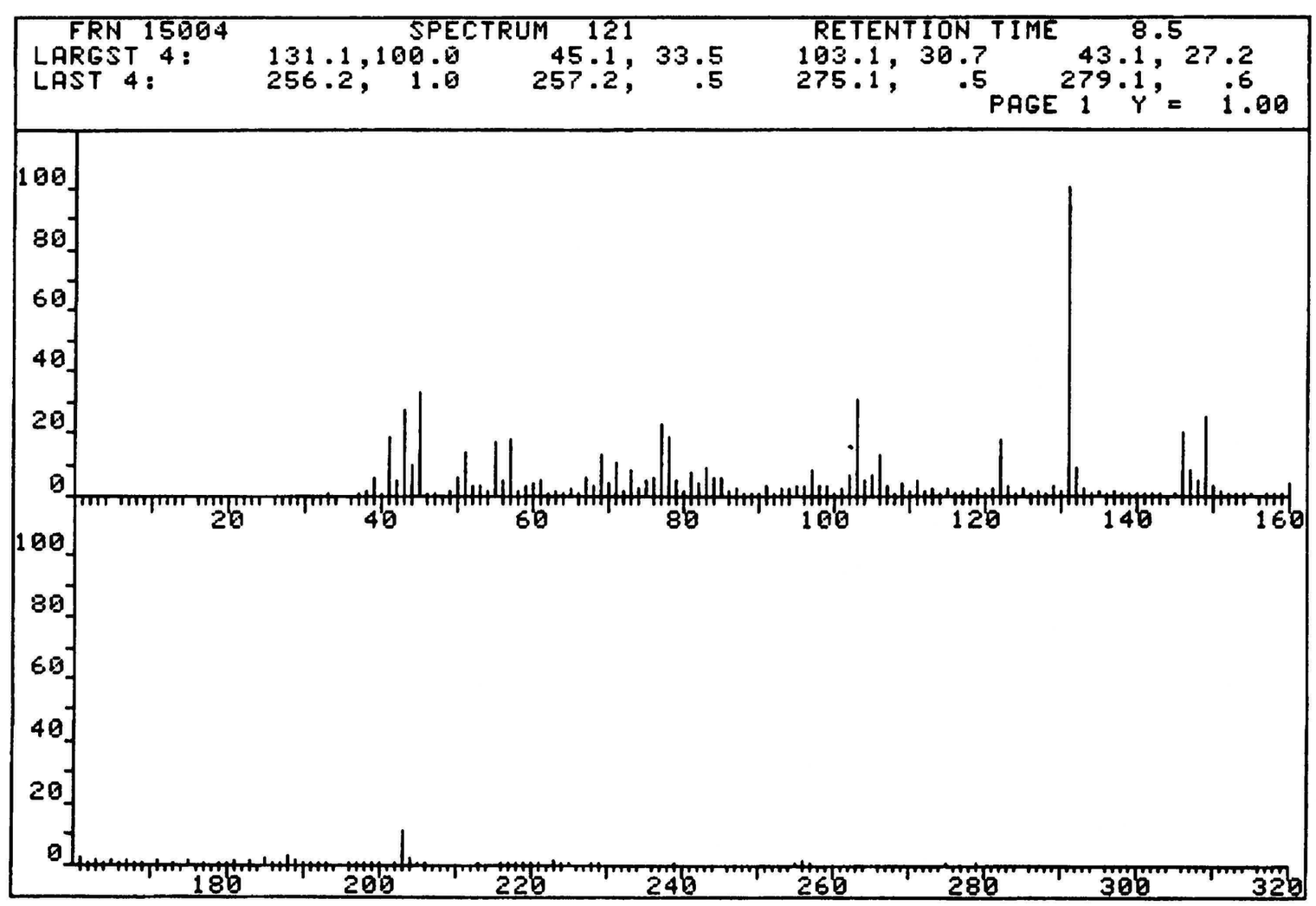
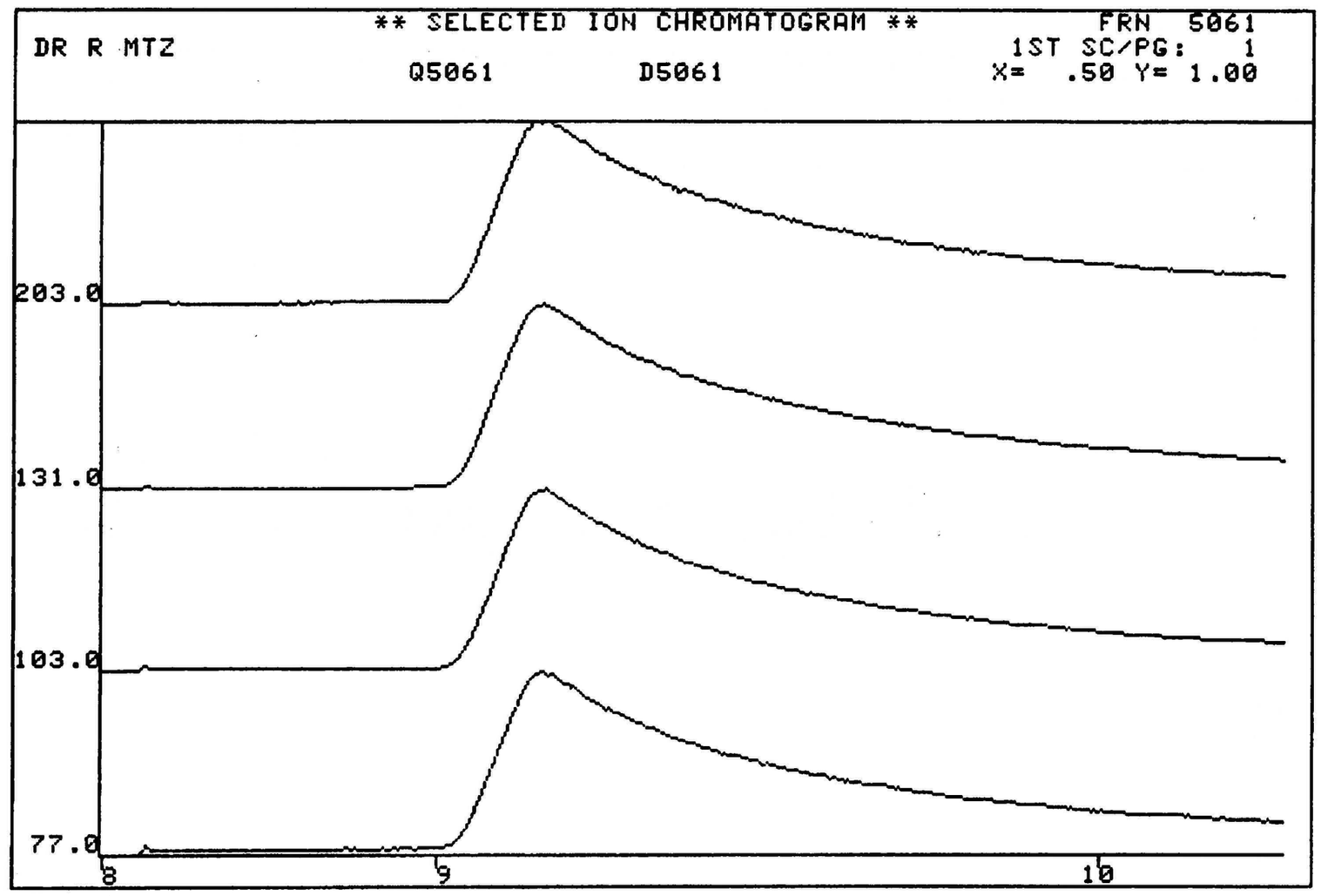


Figure 2. SIM Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide 1 from a biological sample.



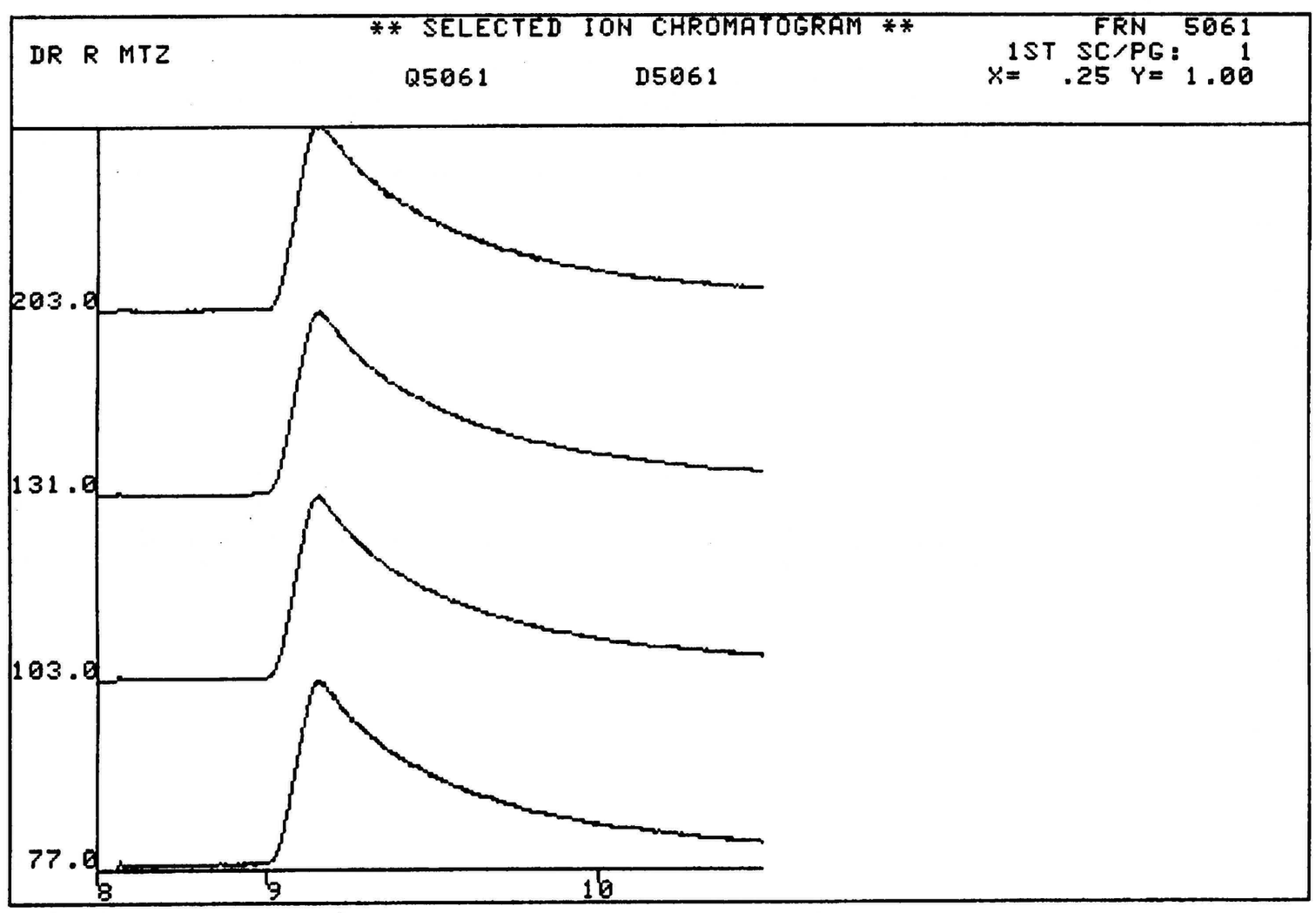


Figure 3. Selected Ion Chromatogram for compound 1 on a biological sample.

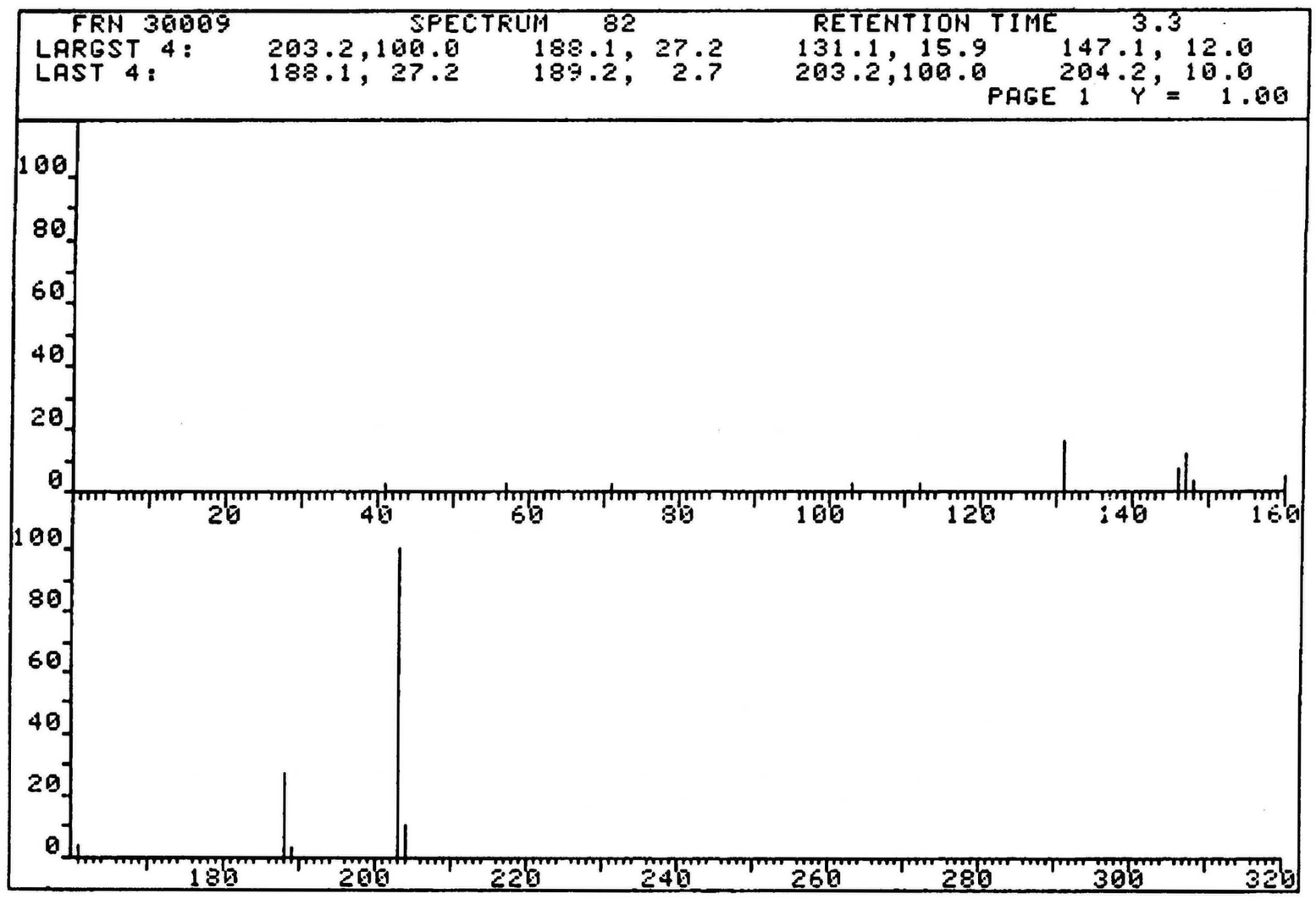
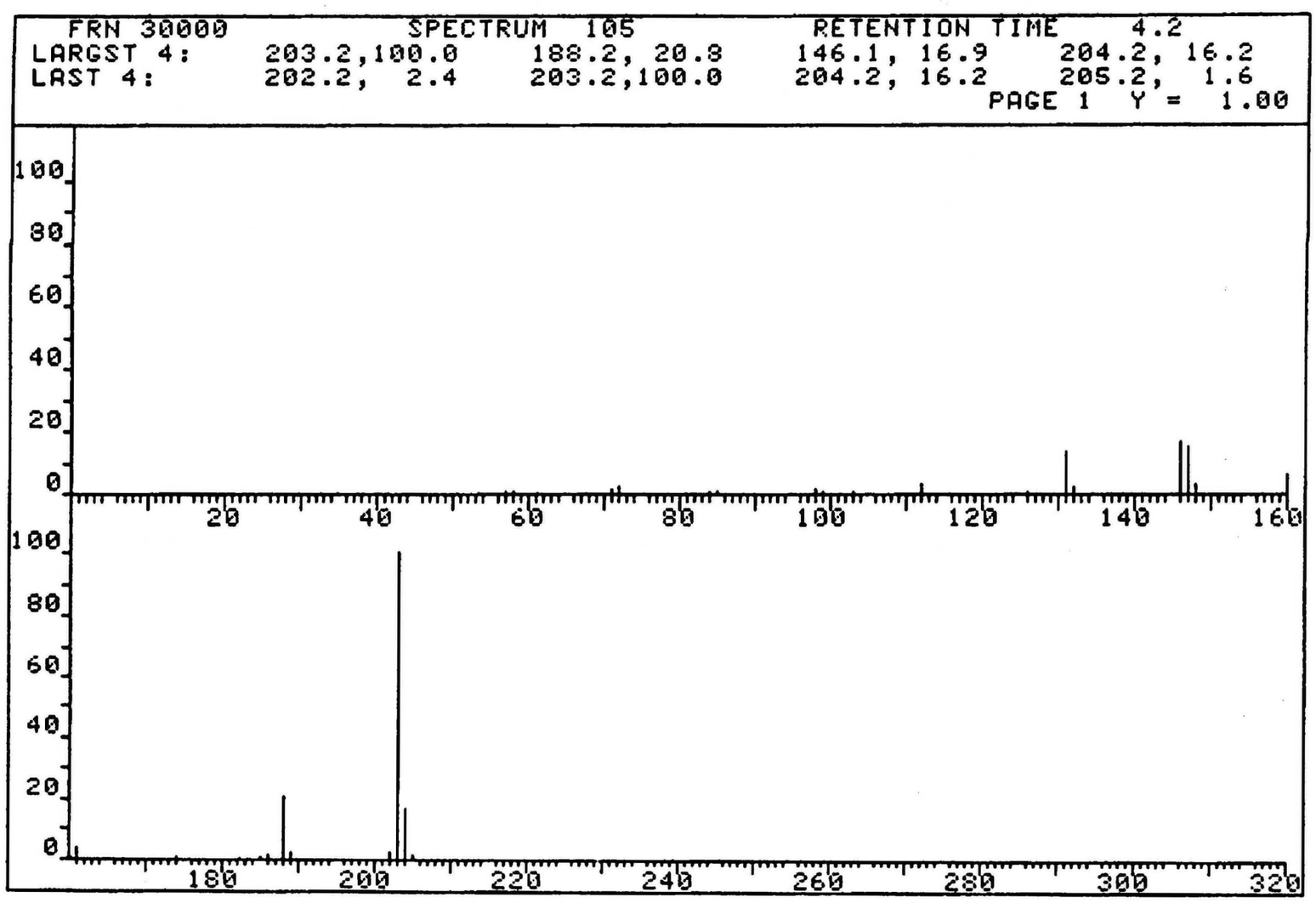


Figure 4. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide at 11 eV.

Figure 5. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide at 12 eV.



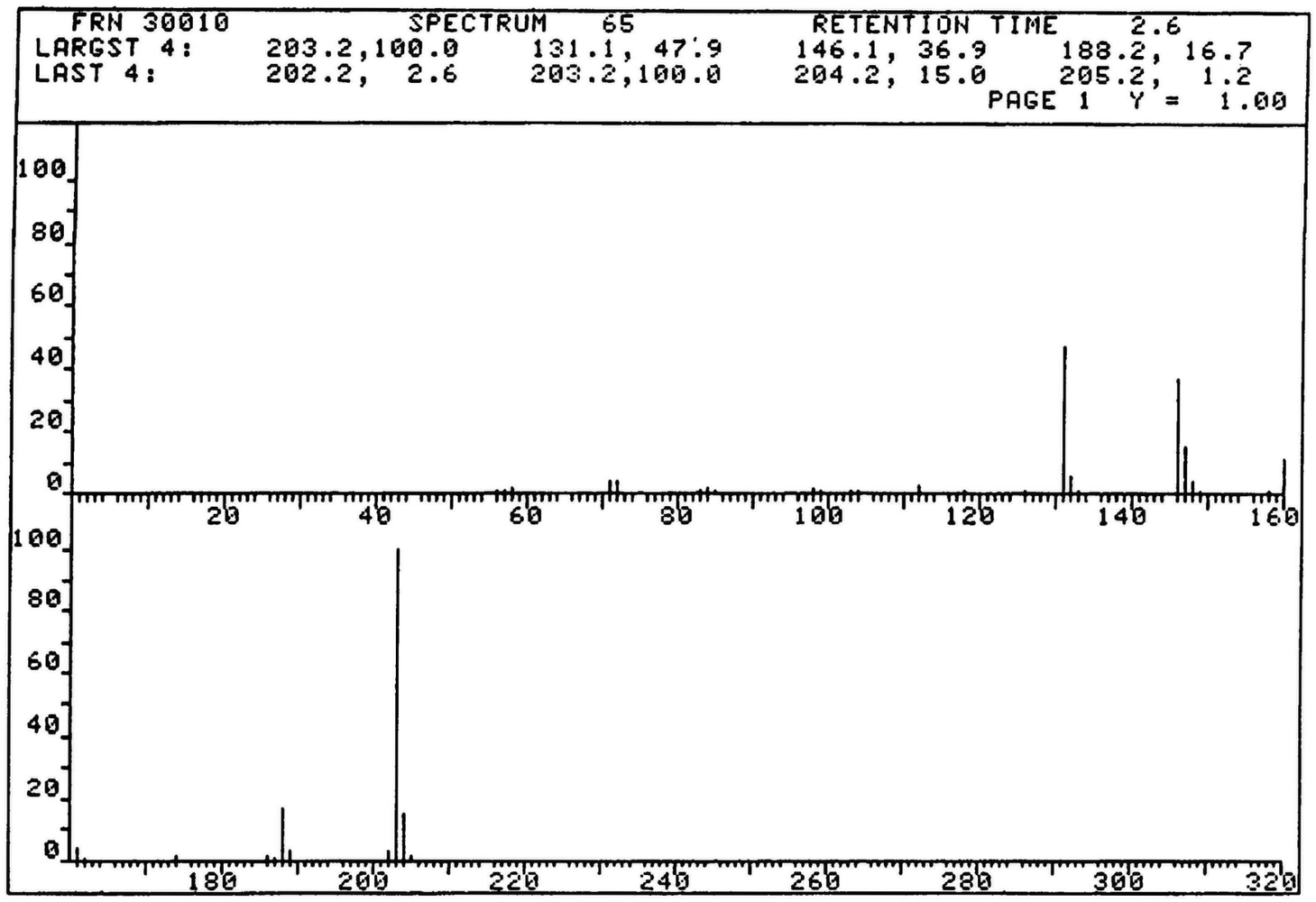
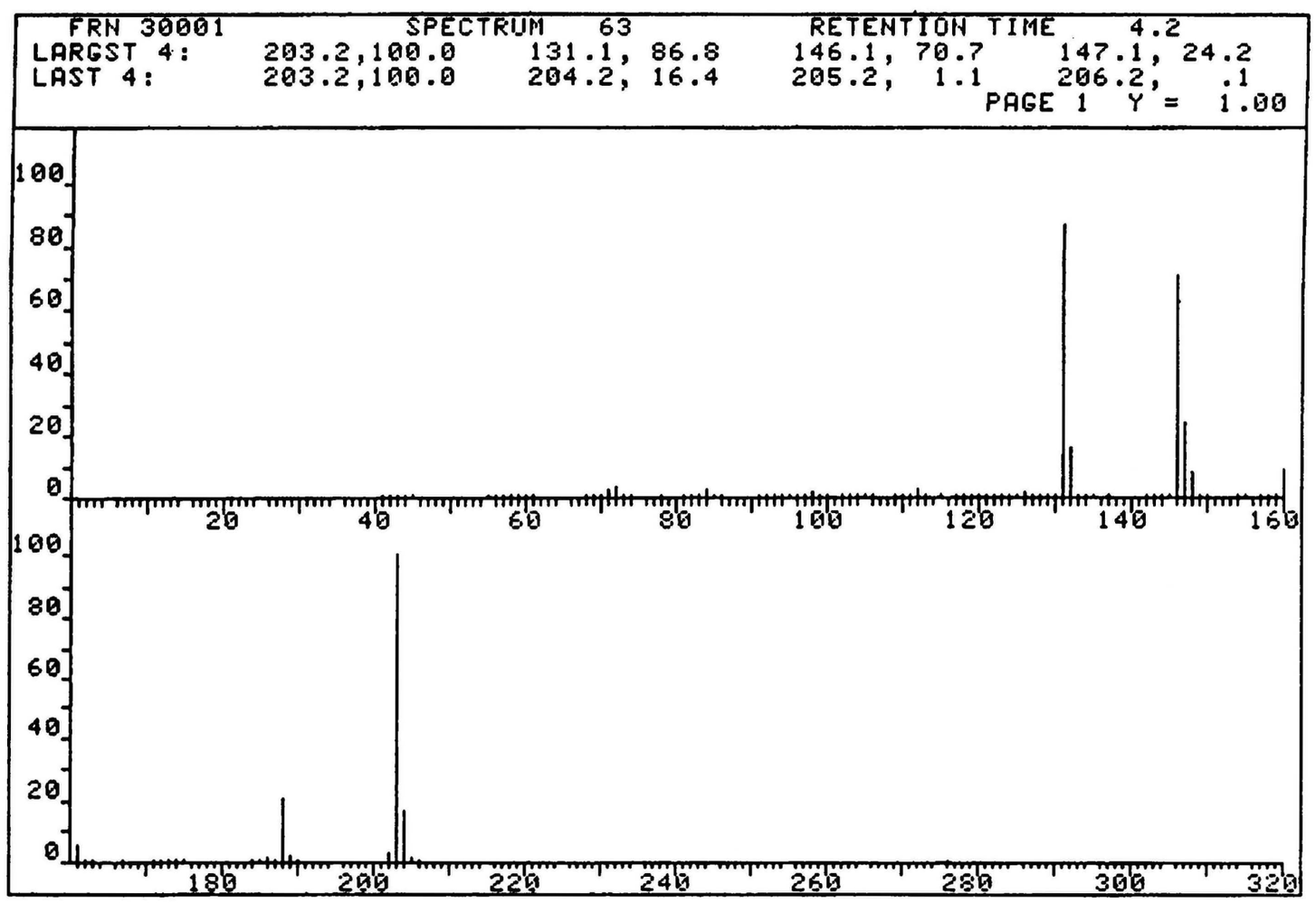


Figure 6. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 13 eV.

Figure 7. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 15 eV.



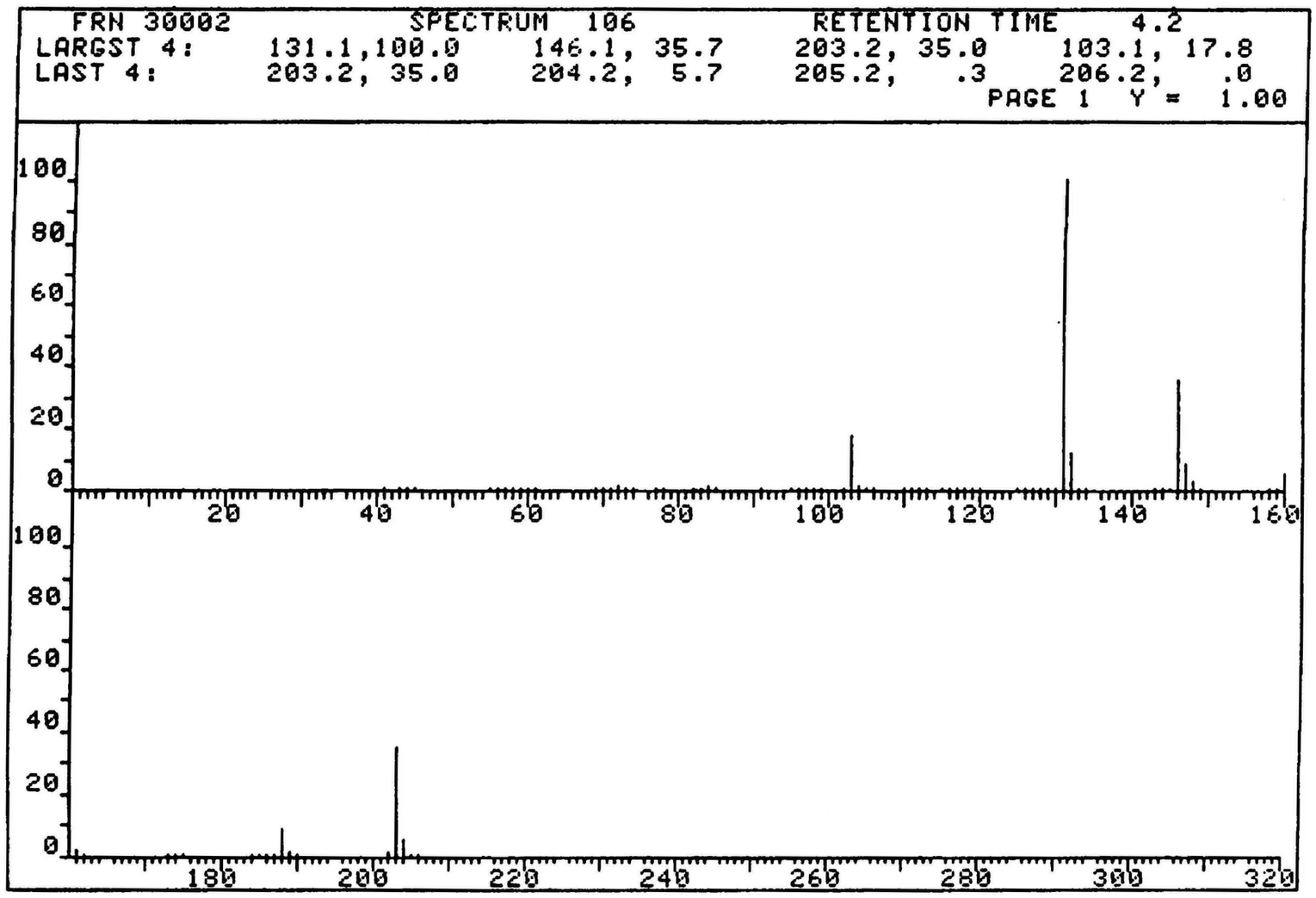
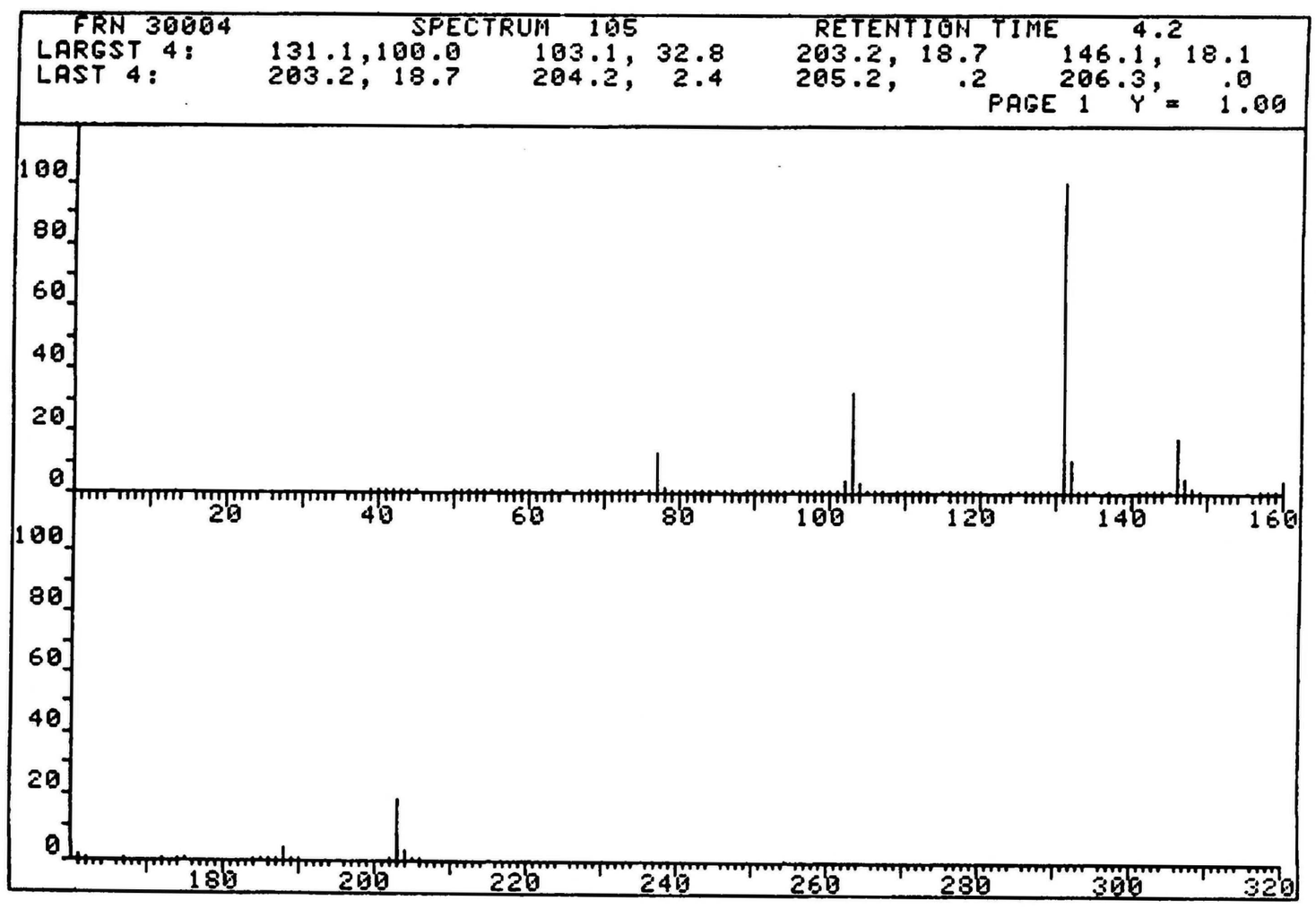


Figure 8. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 20 eV.

Figure 9. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 30 eV.



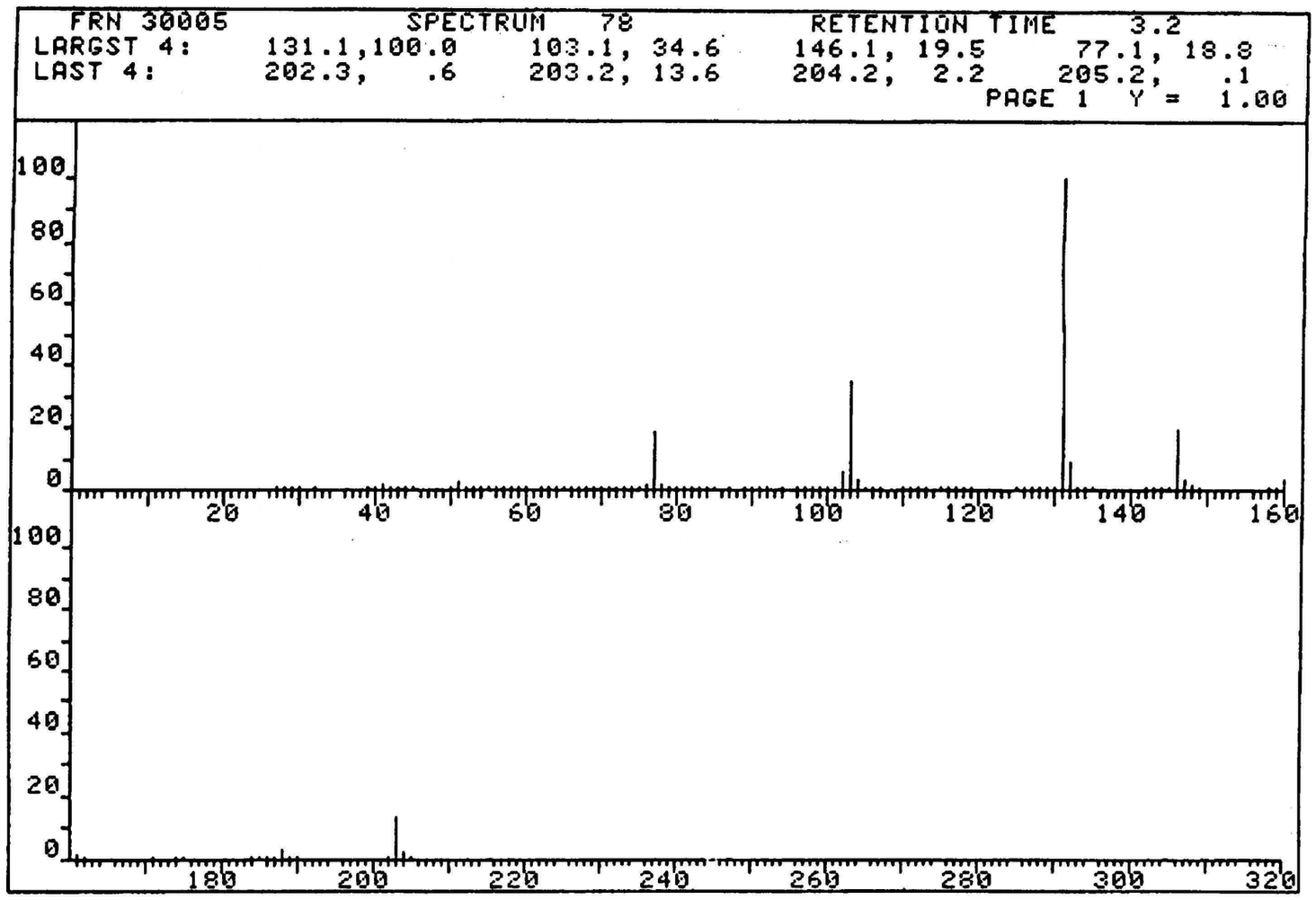
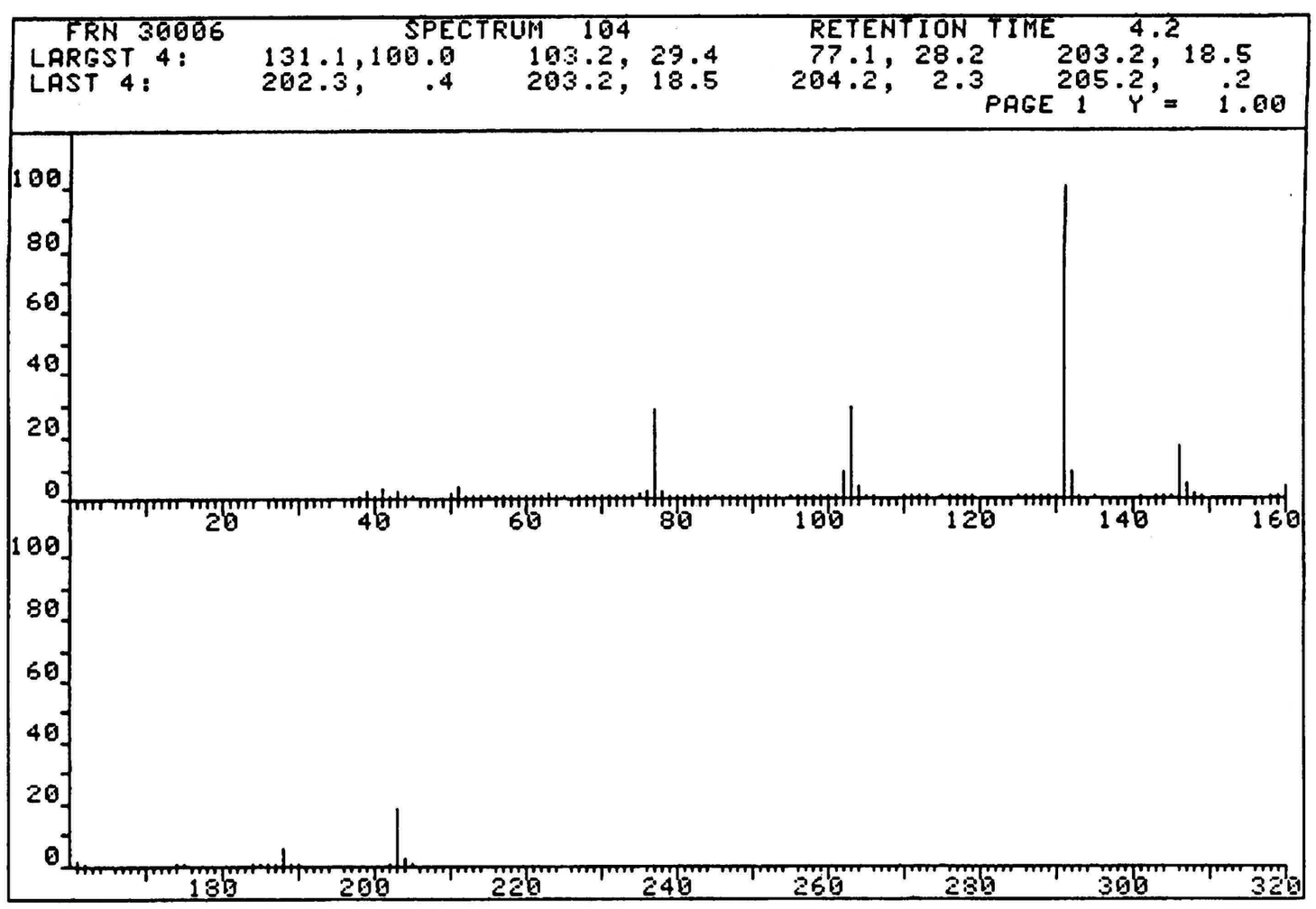


Figure 10. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 40 eV.

Figure 11. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 50 eV.



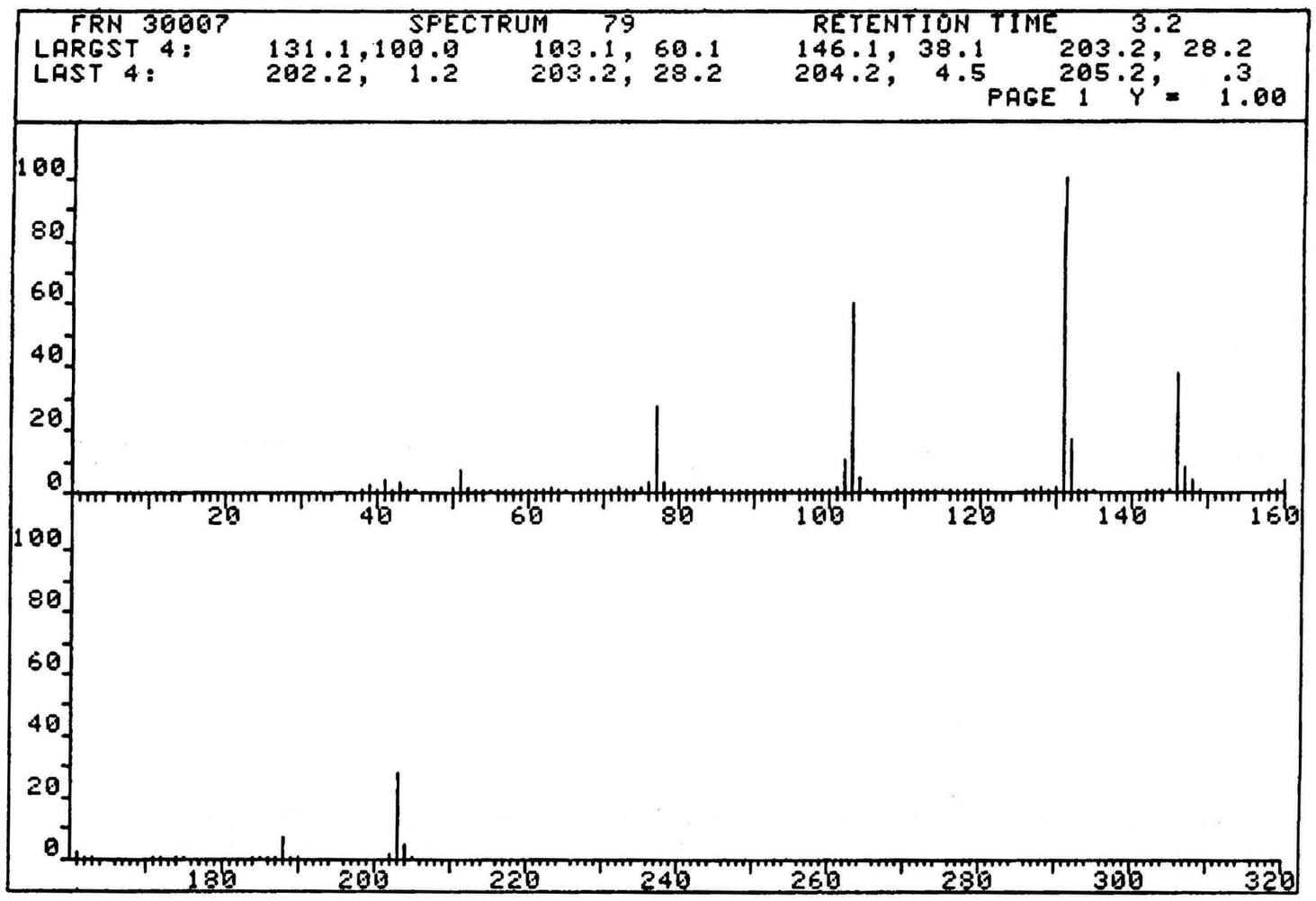
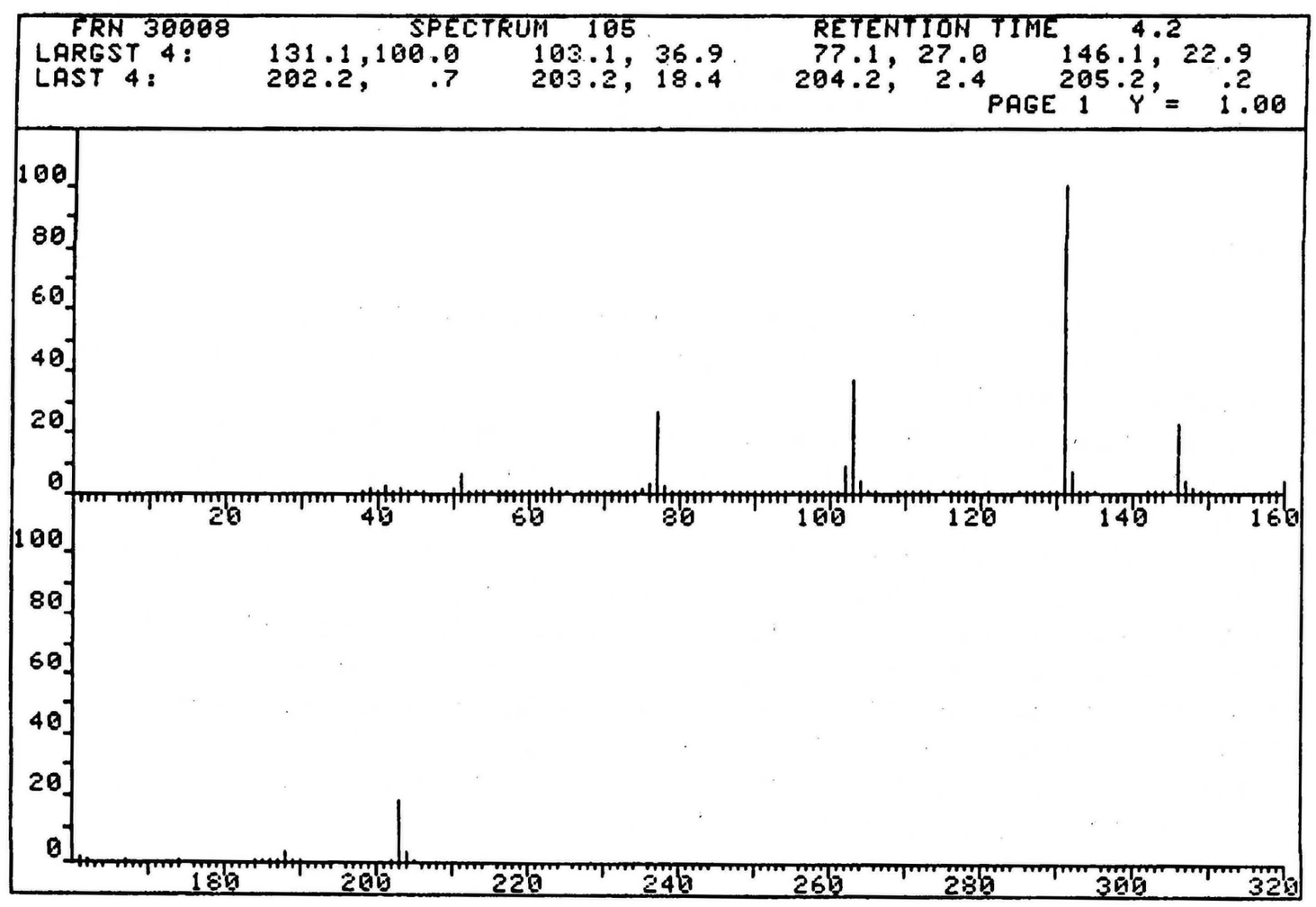


Figure 12. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 60 eV.

Figure 13. EI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** at 70 eV.



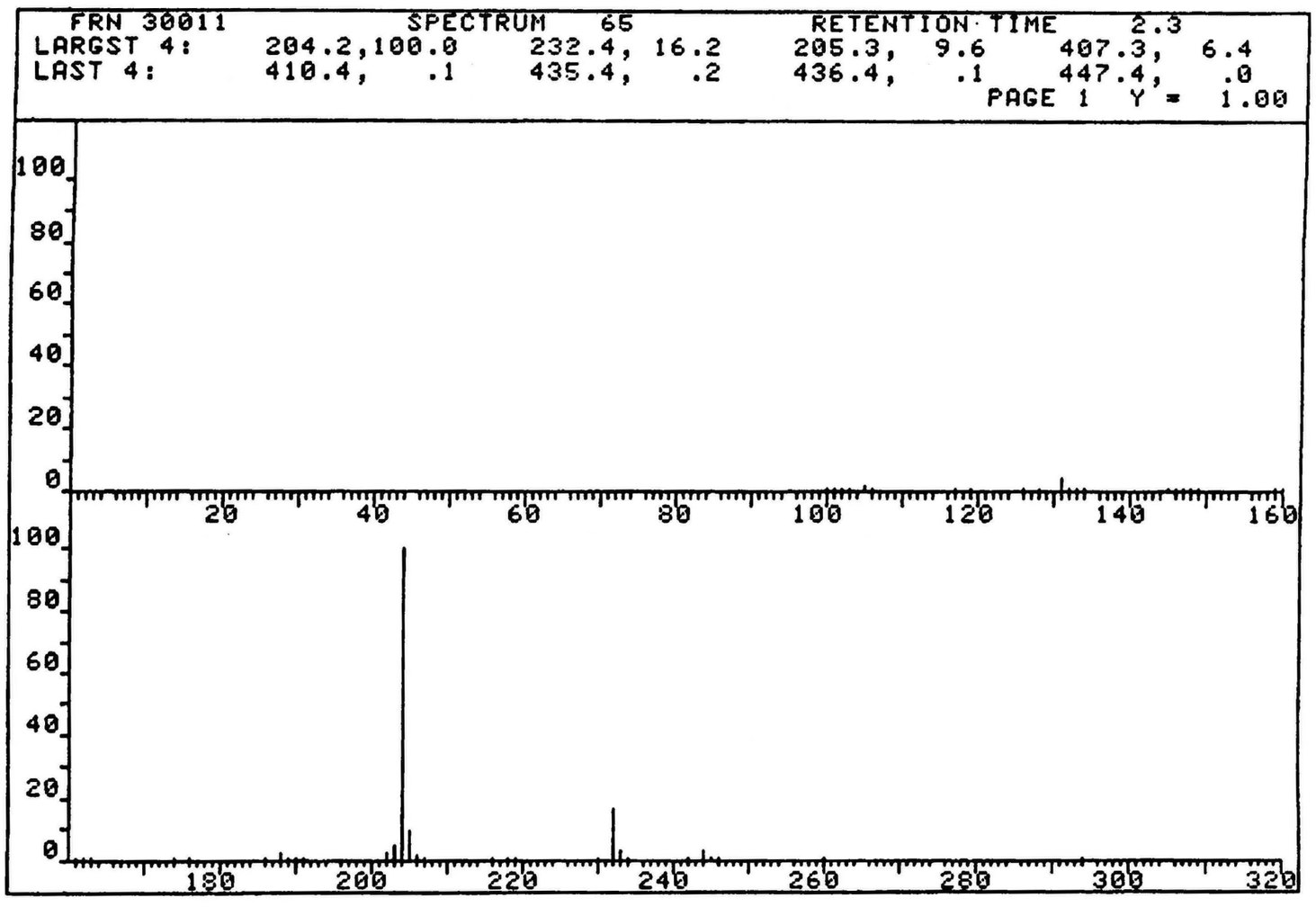


Figure 14. CI Mass Spectra of N-(2-methylpropyl)-3-phenyl-2-propenamide **1** using methane as ionizing agent.

3. Conclusion

Compounds **1-11** gave characteristic positive ions with high intensities under electron impact. These positive ions have diagnostic values and may be of importance for selected ion monitoring assay of biological samples.

4. References

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[2] I. Kubo, J. A. Kocke, T. Matsumoto, and T. Kamikawa, *ACS Symp. Ser.* (Pestic. Synth. Ration. Approaches) **255** (1984) 163.
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