TECHNICAL NOTE

J. N. Lomonte,[1] M.S.; W. T. Lowry,[2] Ph.D.; and
I. C. Stone,[2] Ph.D.

Contaminants in Illicit Amphetamine Preparations

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Samples from illicit preparations of amphetamine and methamphetamine have been analyzed by combined gas chromatography-mass spectrometry (GC/MS) to detect and identify contaminants, excipients, and by-products of manufacture. The samples were also analyzed by energy-dispersive X-ray (EDX) and by X-ray diffraction.

Among the many methods for the preparation of these materials would be the reduction of phenyl-2-propanone with simultaneous condensation of the phenyl-2-propanol produced with ammonia or methylamine to produce either amphetamine or methamphetamine, respectively. Side reactions can occur to produce polycondensation products. This paper presents some mass spectra of these contaminants and by-products found in these illicit preparations.

Experimental

The mass spectra were obtained on a Finnigan 3100D GC/MS by electron impact (EI) ionization. A Finnigan 6100 MS Data System was used for handling the data and for hard copy output. The GC column was 1.5 m by 2 mm inside diameter glass, packed with 3% OV-1 on 80/100 mesh Chromosorb WHP, and programmed from 150 to 290°C (302 to 522°F) at 20°C/min (68°F/min) with a helium gas flow of 30 ml/min.

The samples were analyzed by placing 5 mg of sample in 1 ml of methanol, allowing sugars and other insoluble diluents to settle, and injecting 1 μl of the supernatant into the GC.

A Tracor Northern EDX unit consisting of a Northern NS-880 analytical system and a Spectrace 440 sample system was used for elemental analysis. The molybdenum-filtered transmission X-ray tube was operated at 30 kV and 0.2 mA. The region from 0 to 20 keV was monitored for 100 seconds. The sample was prepared by pelletizing 0.5 g of sample with 0.5 g of pure lithium carbonate.

X-ray diffraction patterns were obtained with a General Electric XRD-5 unit equipped with a 57.3-mm Debye-Scherrer powder camera. A 2-h exposure with nickel-filtered copper radiation was obtained.

Results and Discussion

Analysis by EDX revealed the presence of a significant quantity of zinc (1 to 2 %) with minor amounts of titanium. The X-ray diffraction pattern was not identifiable as any of the zinc compounds reported in standard X-ray references. The pattern would be of value for comparison with specimens from an illicit laboratory or other preparations.

Figure 1 shows the reconstructed gas chromatogram of an illicit amphetamine preparation. As all of the compounds of interest have large mass to charge ratio (*m/e*) 91 peaks, a mass-91 limited mass chromatogram (shown in Fig. 2) makes it easier to pick out significant GC peaks.

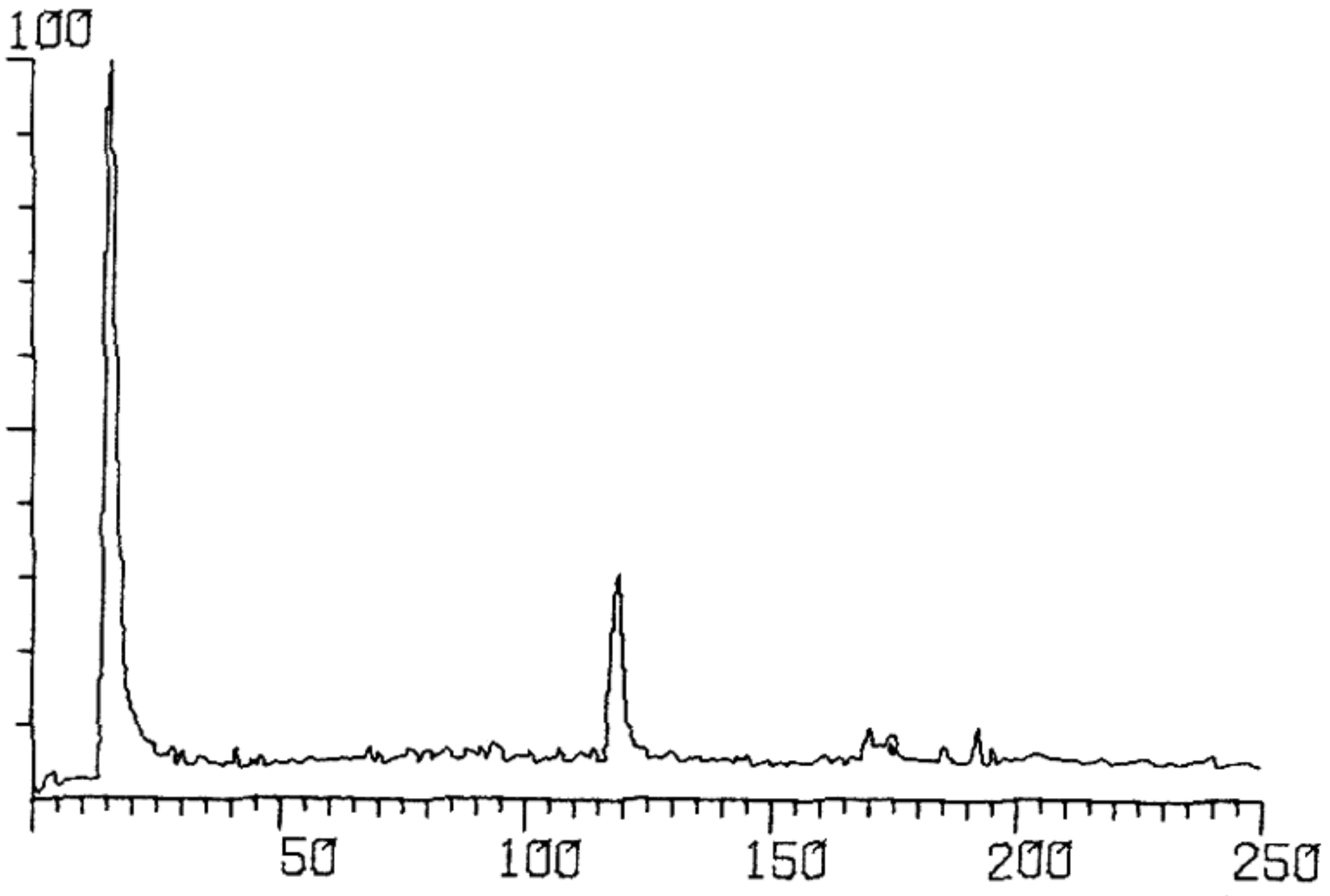

FIG. 1—*A reconstructed gas chromatogram of an illicit amphetamine preparation.*

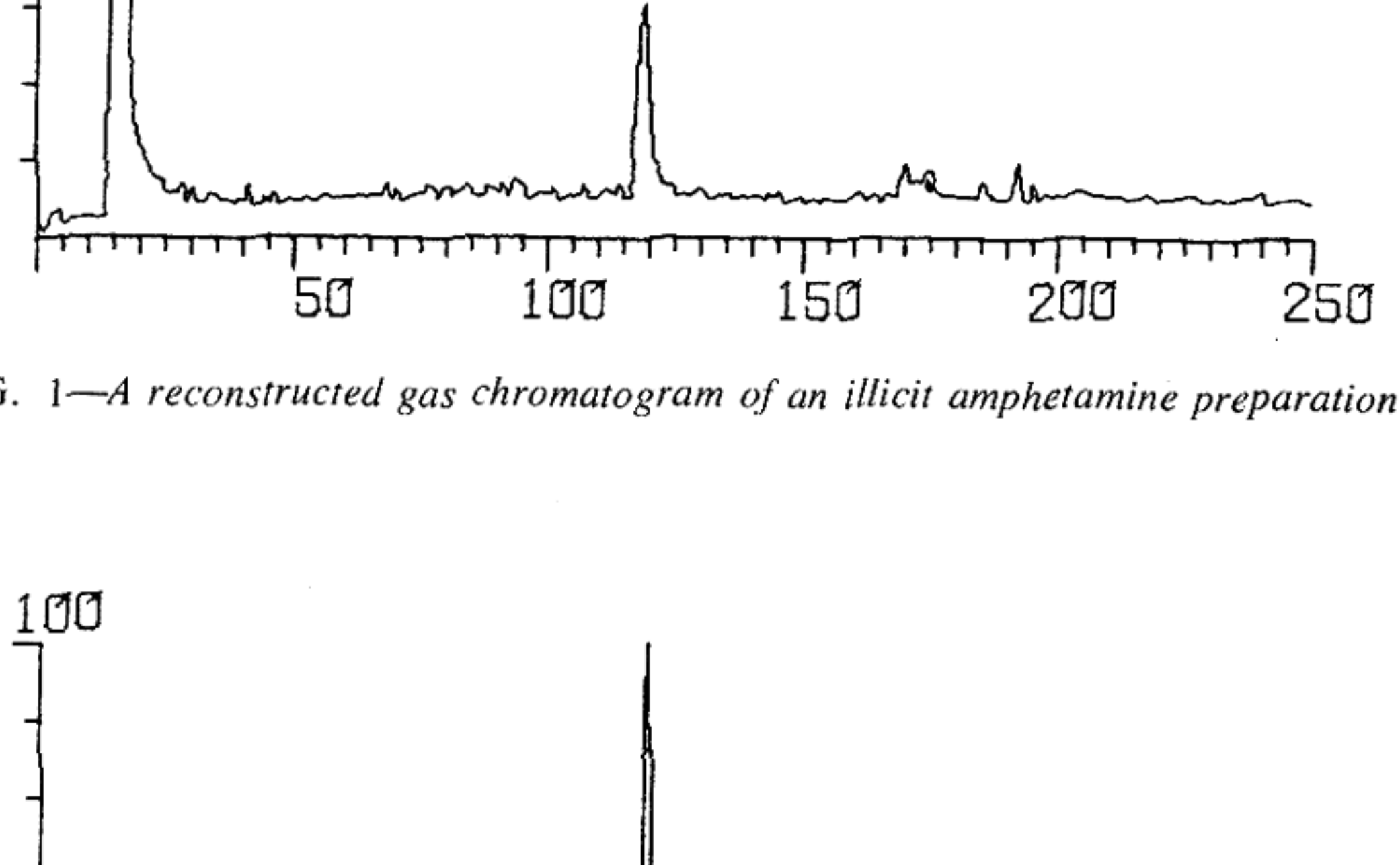

FIG. 2—*A mass-91 limited mass chromatogram of an illicit amphetamine preparation.*

Spectrum 16 (Fig. 3) shows the typical EI mass spectrum of amphetamine. Spectrum 119 (Fig. 4) shows the mass spectrum of di-(1-isopropylphenyl)-amine. This compound, MW 253, *does not give a molecular ion but does give large m/e* 44, 91, 119, and 162. The fragmentation scheme is shown in Fig. 5.

Spectrum 170 (Fig. 6) shows the mass spectrum of tri-(1-isopropylphenyl)-amine. This compound, MW 371, also does not give a molecular ion but gives large *m/e* 91, 119, and 190. The fragmentation scheme is shown in Fig. 7. There is a smaller *m/e* 44 present in the spectrum of this compound, which is formed as in the case of Spectrum 119 (Fig. 4).

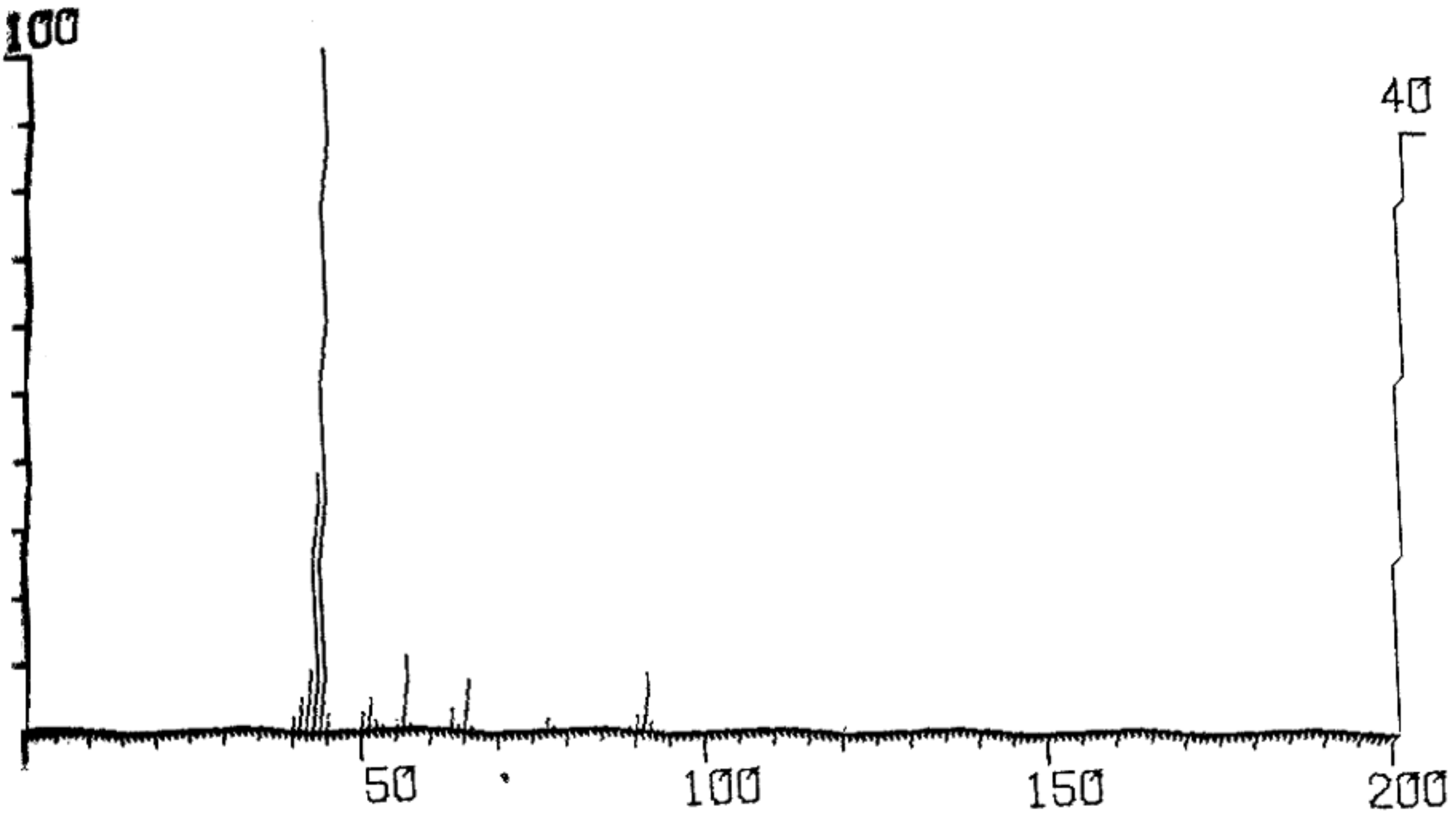

FIG. 3—*The typical electron impact mass spectrum of amphetamine.*

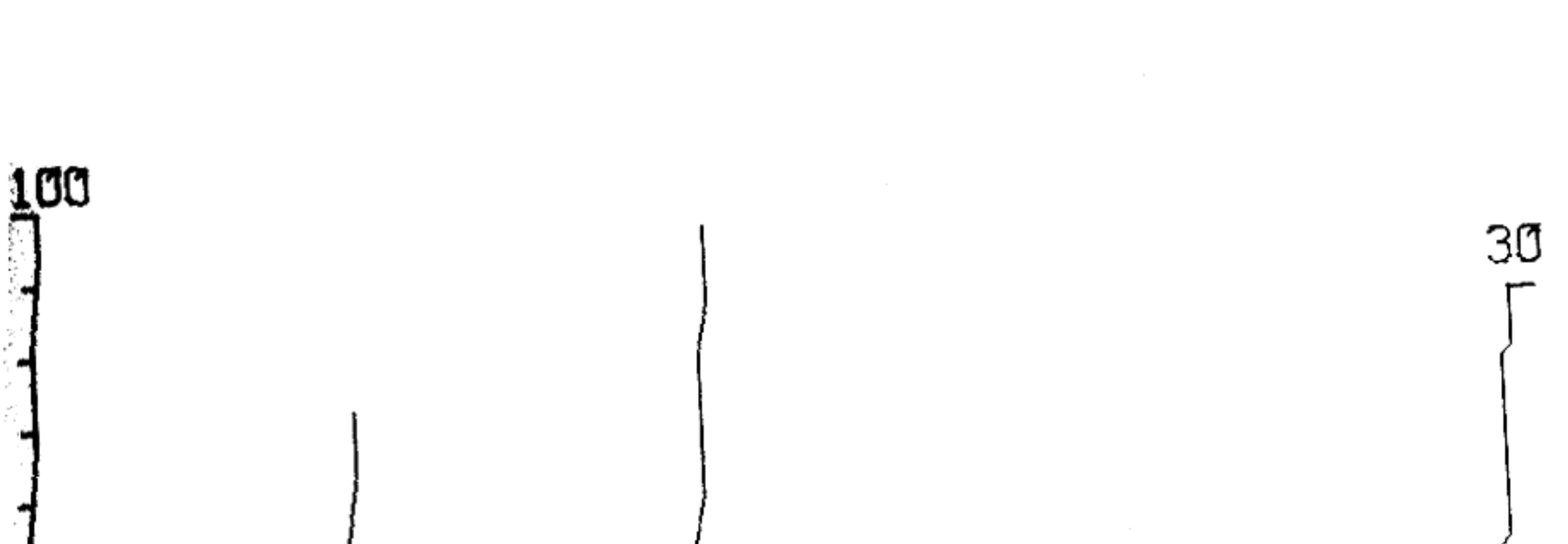

FIG. 4—*The mass spectrum of di-(1-isopropylphenyl)-amine.*

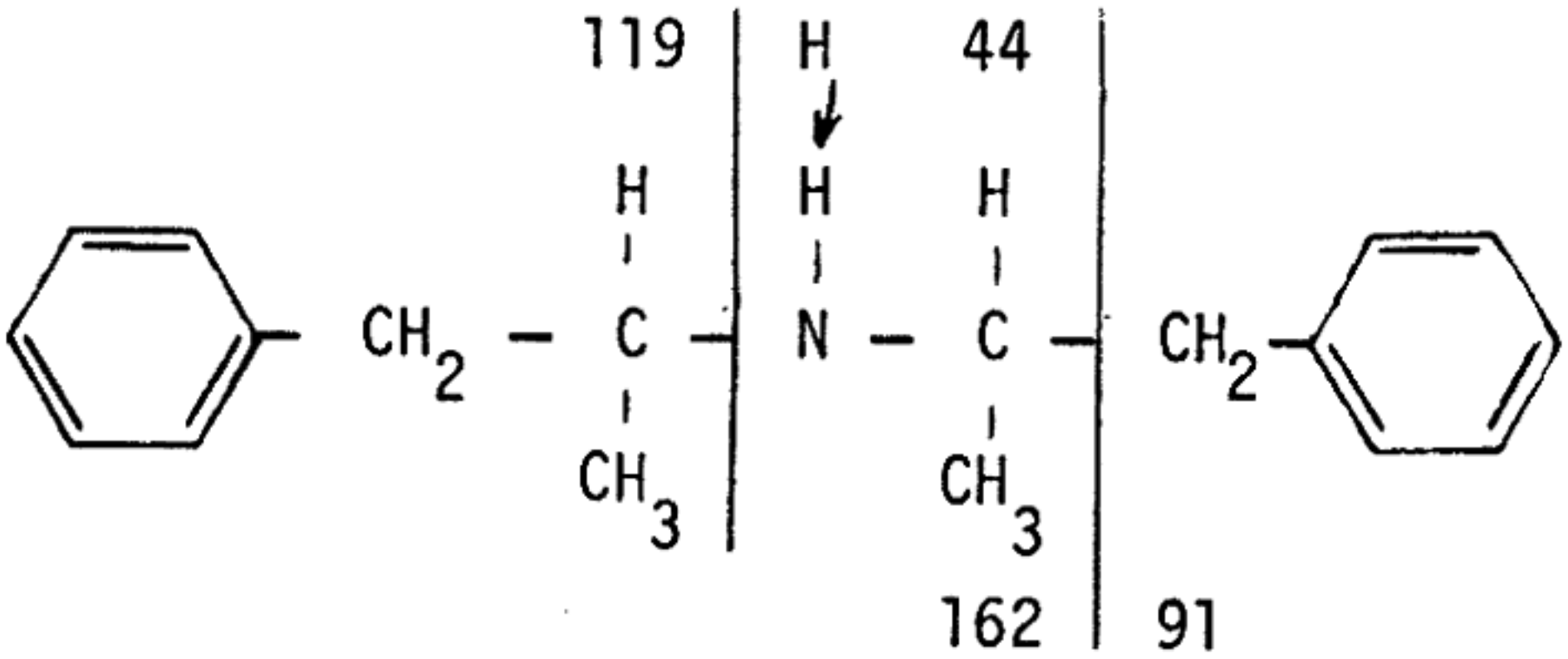

FIG. 5—*The fragmentation scheme of di-(1-isopropylphenyl)-amine.*

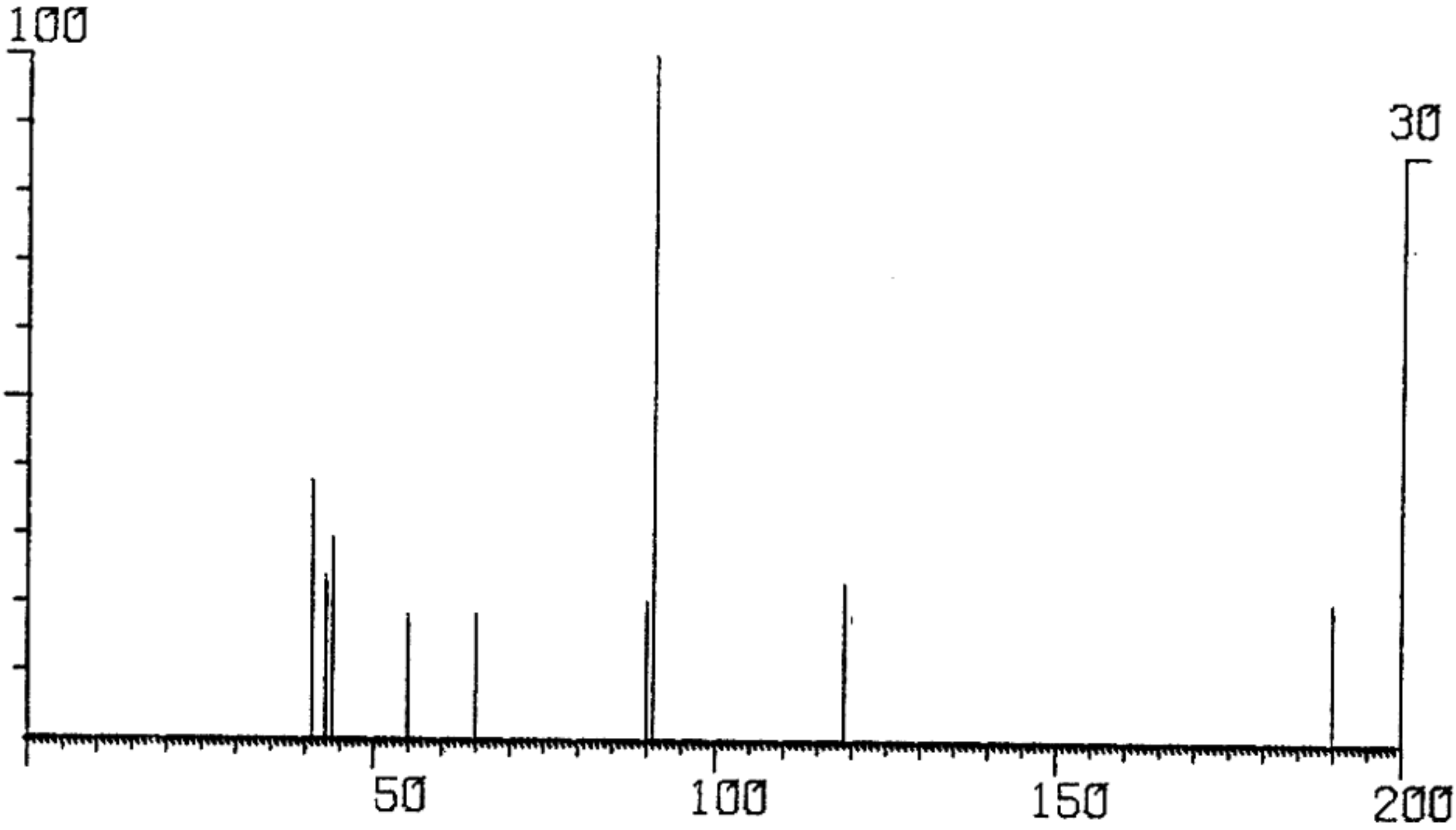

FIG. 6—*The mass spectrum of tri-(1-isopropylphenyl)-amine.*

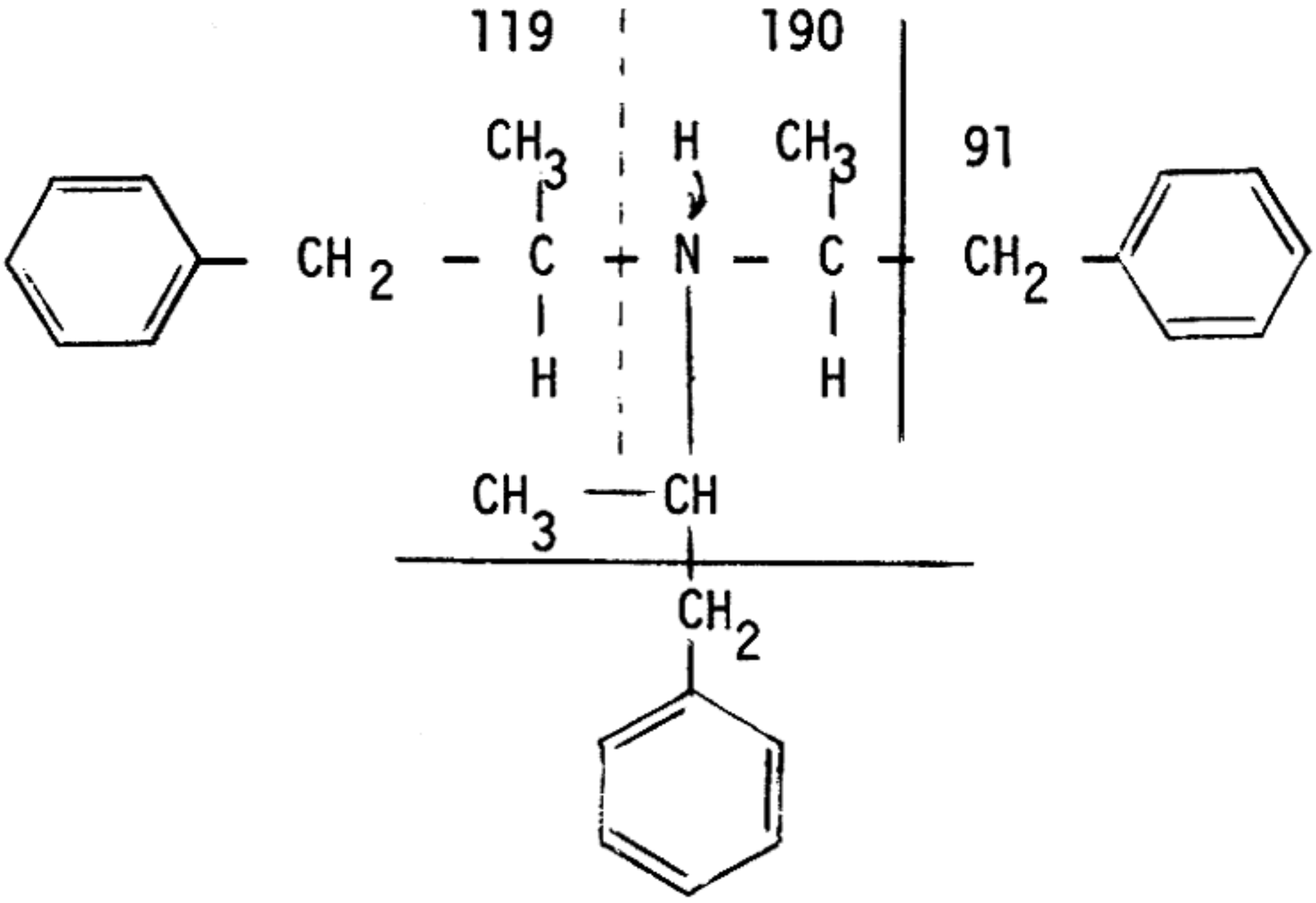

FIG. 7—*The fragmentation scheme of tri-(1-isopropylphenyl)-amine.*

The reconstructed gas chromatogram and the mass-91 limited gas chromatogram of illicit methamphetamine preparation are shown in Figs. 8 and 9, respectively.

Spectrum 20 (Fig. 10) shows the typical EI mass spectrum of methamphetamine. Spectrum 108 (Fig. 11) shows the mass spectrum of a phenyl-2-propanone derivative. This spectrum has all of the major *m/e* peaks of a phenyl-2-propanone (42, 65, 91, 119, and 134), but their relative abundances are different from the spectrum of phenyl-2-propanone itself. This GC peak may be due to a volatile zinc complex which under electron impact yields the mass spectrum of phenyl-2-propanone in an altered form.

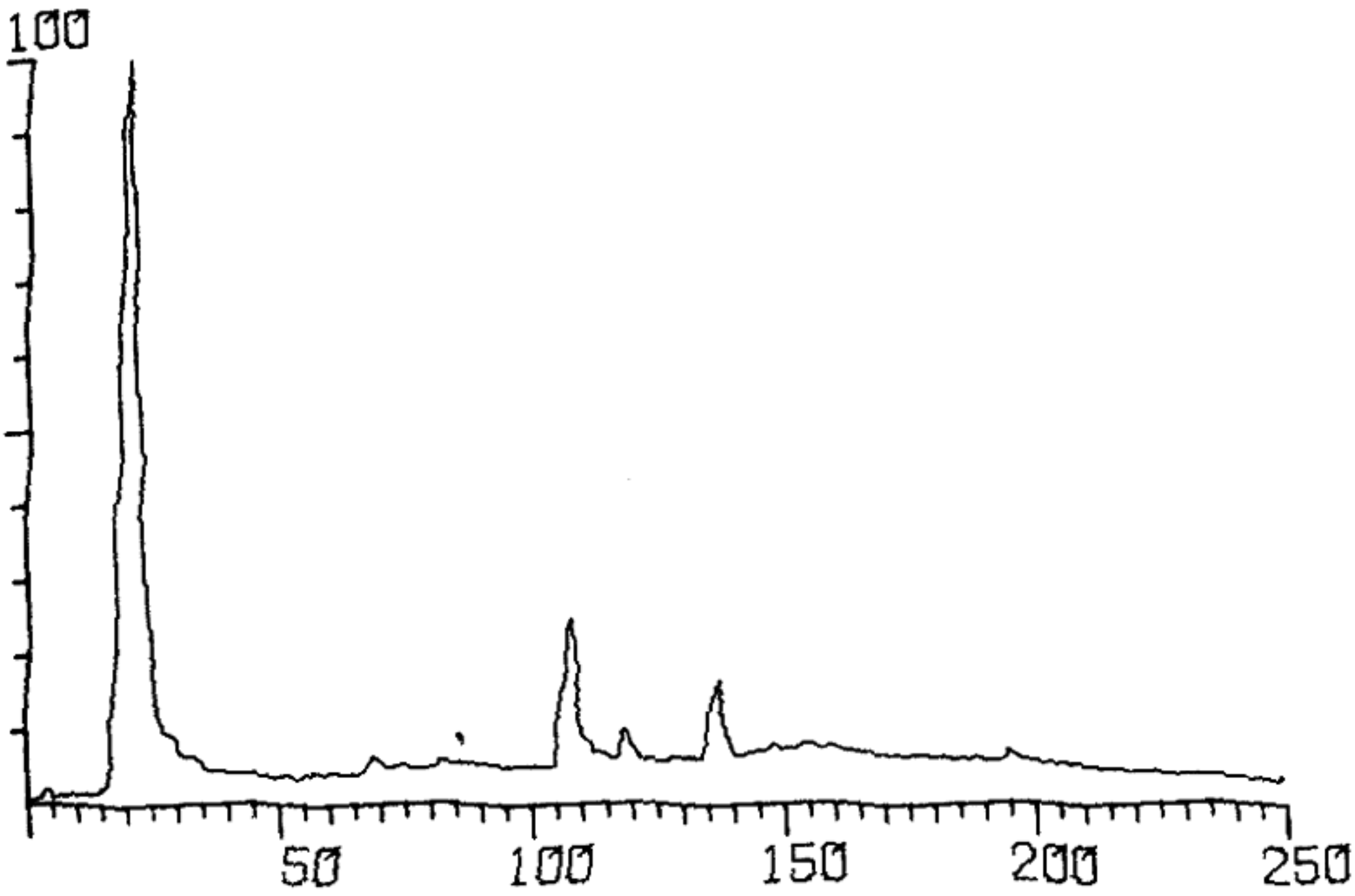

FIG. 8—*The reconstructed gas chromatogram of an illicit methamphetamine preparation.*

FIG. 9—*The mass-91 limited gas chromatogram of an illicit methamphetamine preparation.*

The GC peak at Spectrum 119 is due to di-(1-isoproplyphenyl)-amine, which has already been discussed. The presence of the di-(1-isopropylphenyl)-amine in the methamphetamine preparation is probably due to condensation splitting out methanol rather than water.

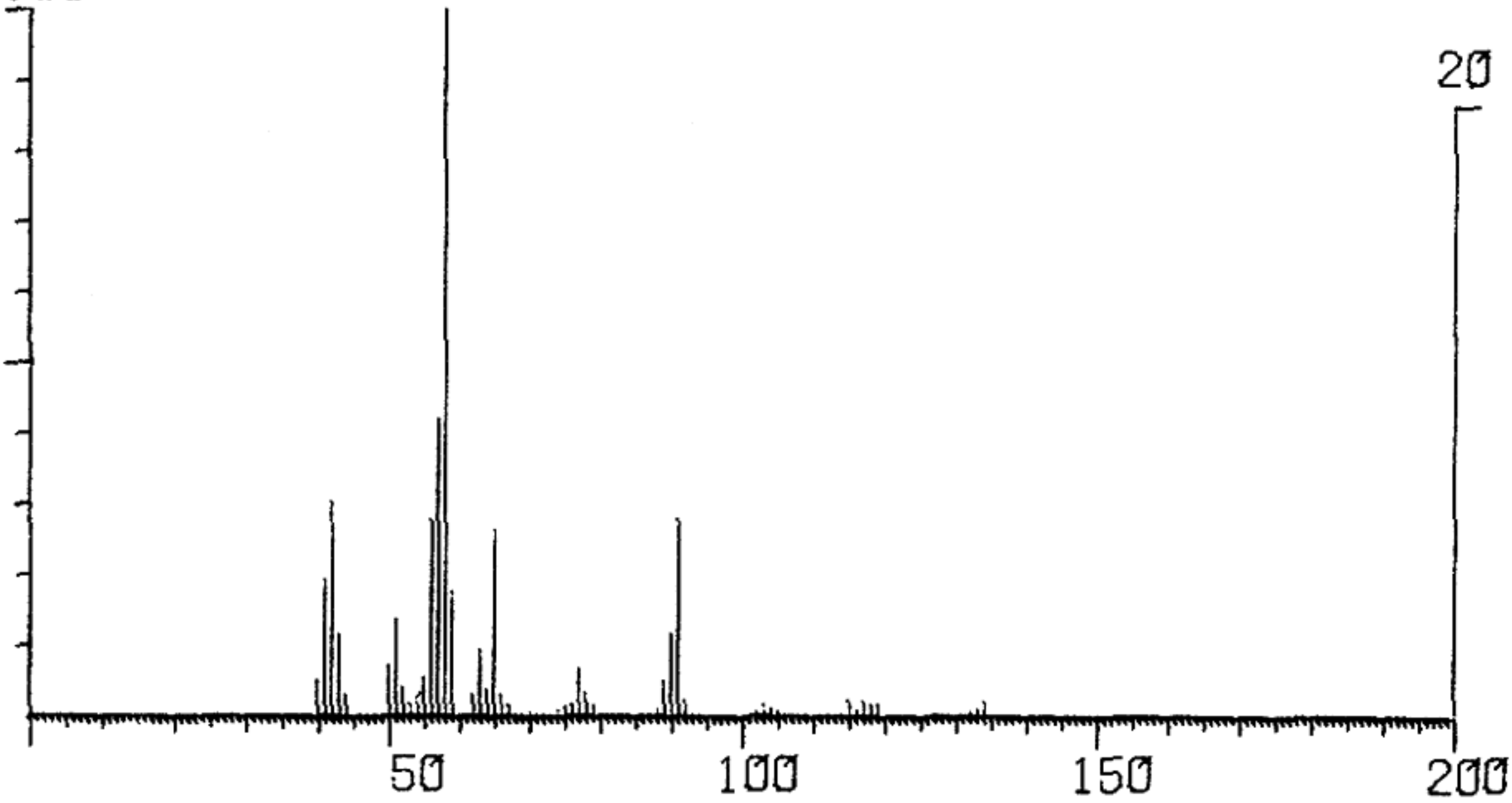

FIG. 10—*The typical electron impact mass spectrum of methamphetamine.*

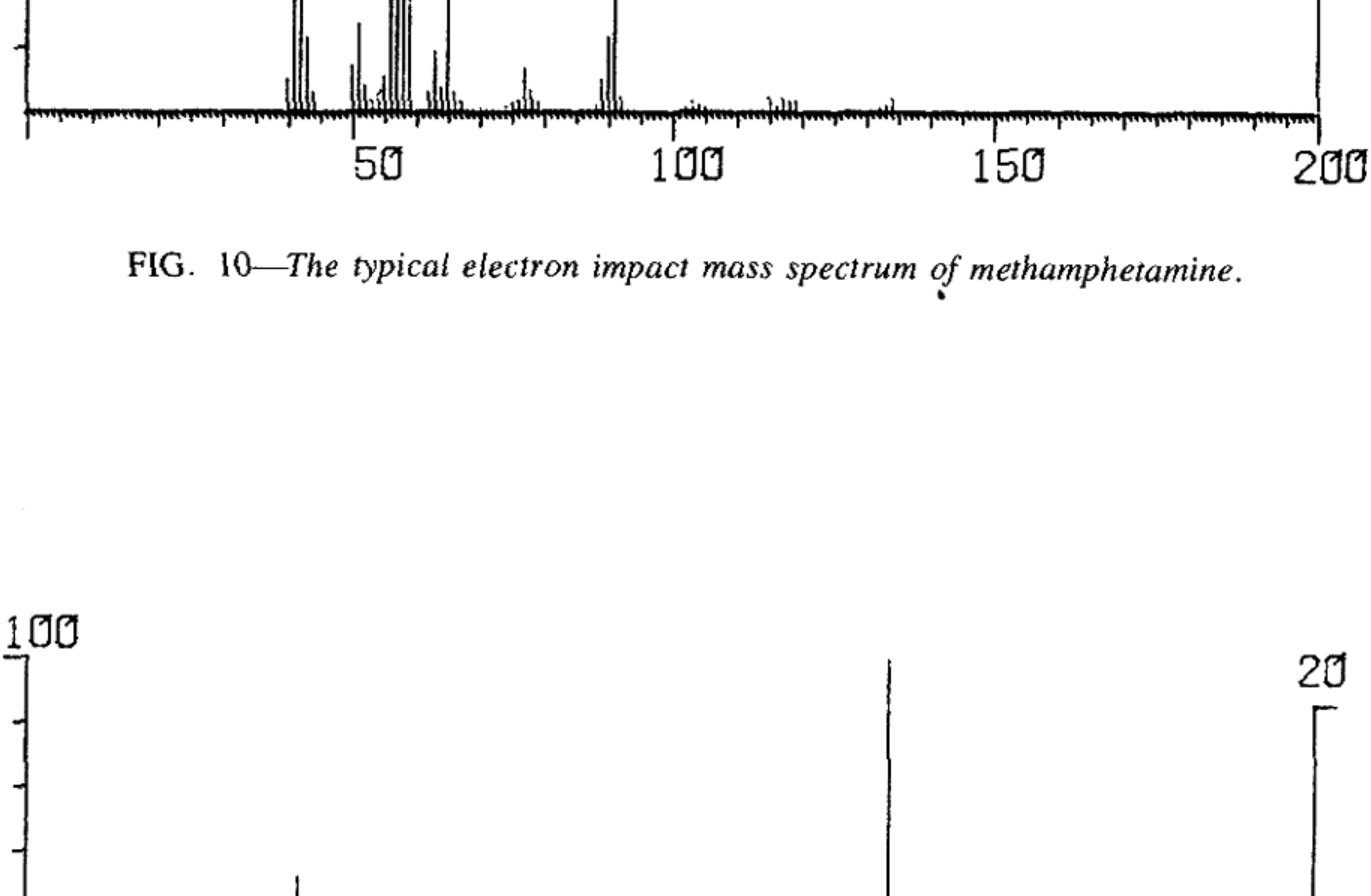

FIG. 11—*The mass spectrum of a phenyl-2-propanone derivative.*

Spectrum 137 (Fig. 12) shows the mass spectrum of di-(1-isopropylphenyl)-methylamine. This compound, MW 267, does not give a molecular ion but does give large *m/e* 58, 91, 119, and 176. The fragmentation scheme is shown in Fig. 13. Di-(1-isopropylphenyl)-methylamine has been found in illicit methamphetamine samples [*1*].

Efforts to make these polycondensation products from commercially pure amphetamine sulfate and hydrochloride by thermal degradation and by acid/base hydrolysis failed to produce detectable quantities. Therefore it appears these polycondensation products are unique for noncommercially prepared materials.

Conclusions

The illicit origin of amphetamine-type drugs can generally be determined by the detection of contaminants and by-products present in the samples. The multidisciplinary analytical approach yields data of potential value for comparative examinations. For example, illicit laboratory specimens or other amphetamine samples can be compared by means of X-ray spectra, even though the absolute identification of the organometallic compounds is not possible.

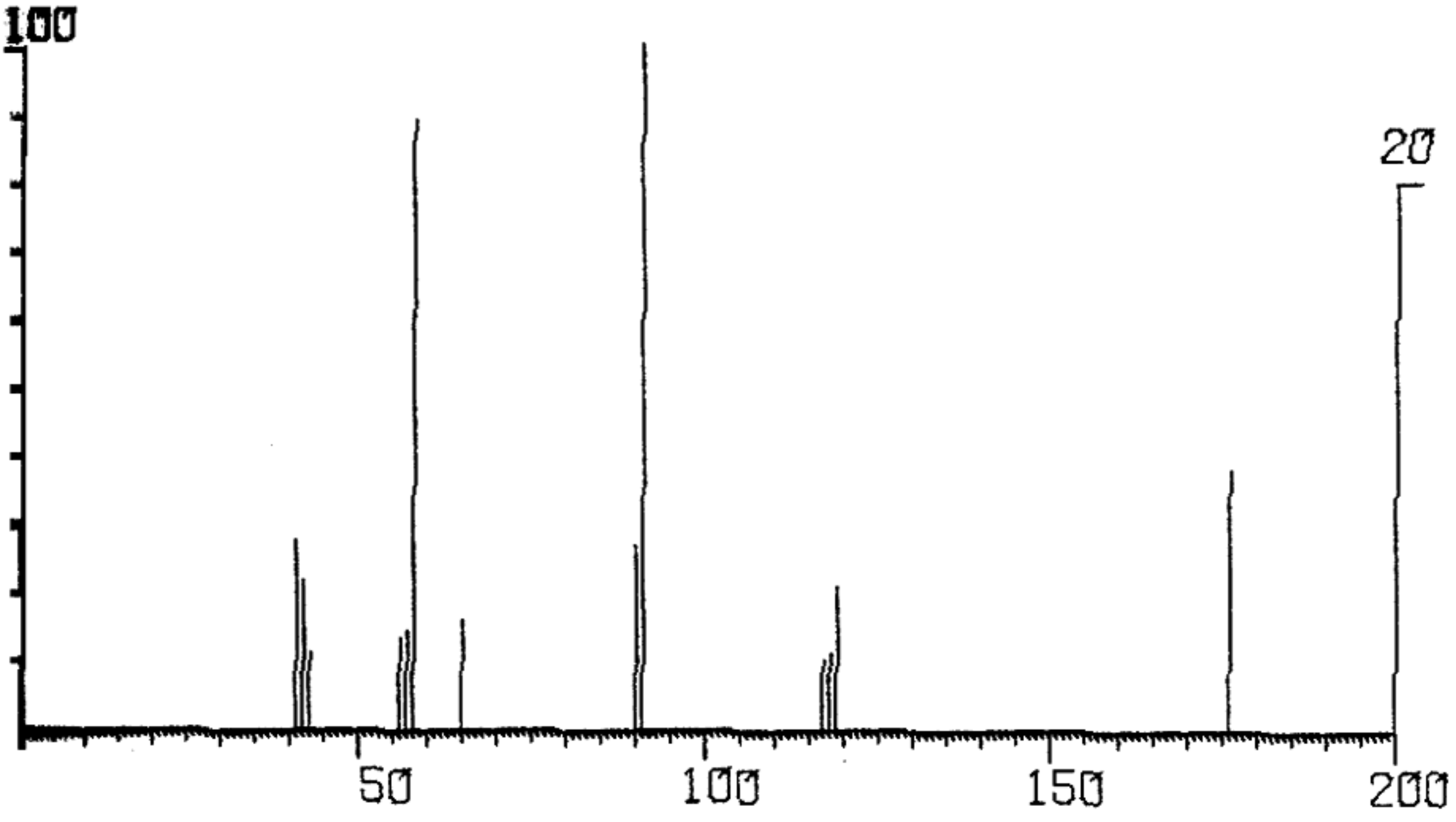

FIG. 12—*The mass spectrum of di-(1-isopropylphenyl)-methylamine.*

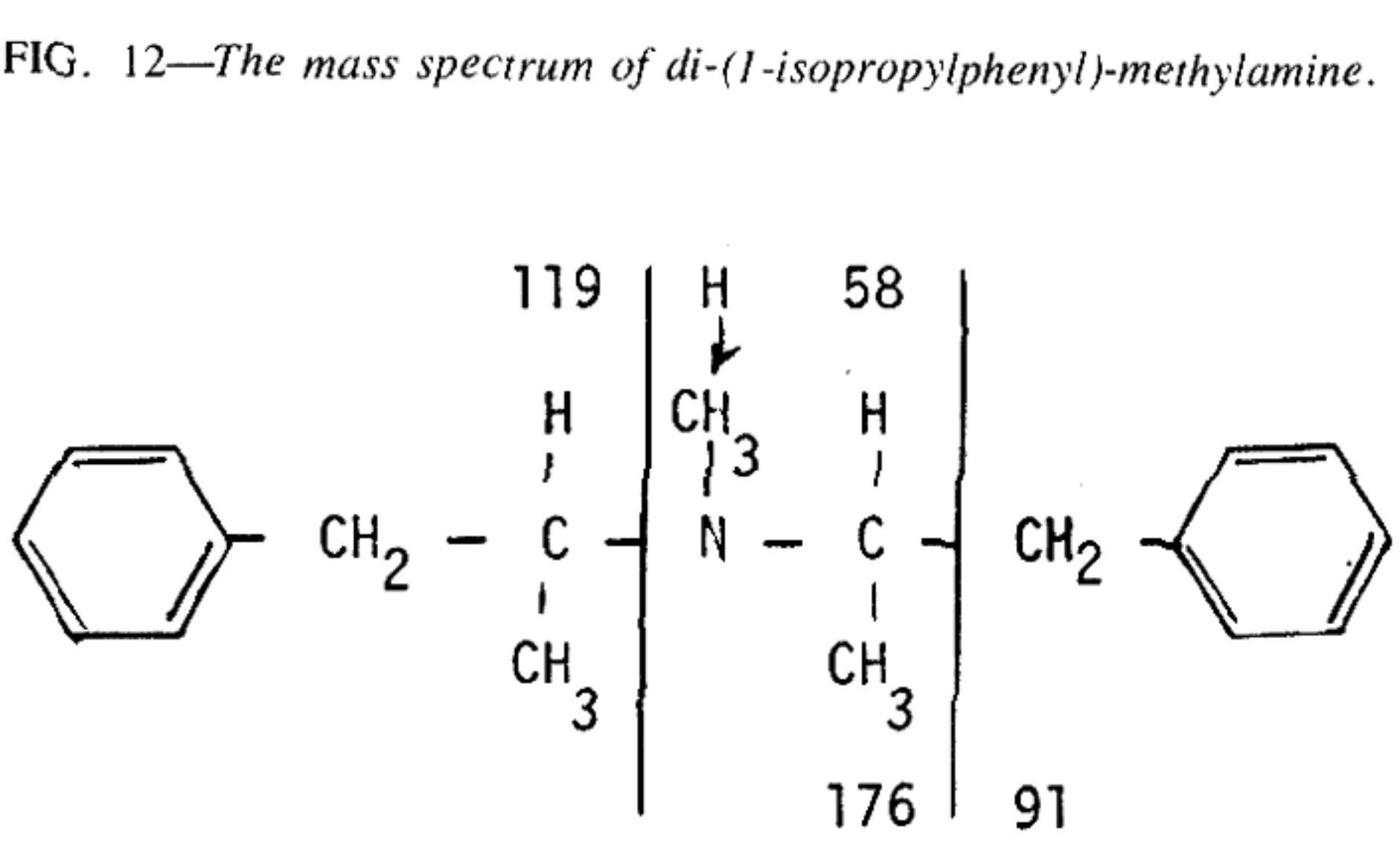

FIG. 13—*The fragmentation scheme of di-(1-isopropylphenyl)-methylamine.*

Nothing is known of the pharmacological and toxicological properties of these by-products, although some similarity to benzphetamine is probable.

Summary

Samples from illicit preparations of amphetamine and methamphetamine were investigated by combined gas chromatography-mass spectrometry (GC/MS) to detect and identify contaminants, excipients, and by-products from manufacture. In addition, these samples were subjected to energy-dispersive X-ray (EDX), and it was determined that the preparations of these compounds were made in the present of zinc, probably as a reductant. In addition to identifying polycondensation products from these preparations, the illicit origin of amphetamine-type drugs can generally be determined by the detection of contaminants and by-products present in submitted samples. Thus, a multidisciplinary analytical approach yields data of potential value for comparative examinations and possibly for legal purposes.

References

[1] Bailey, K., Boulanger, J. G., LeGault, D., and Taillefer, S. L., "Identification and Synthesis of Di-(1-Phenylisopropyl)-Methylamine, an Impurity in Illicit Methamphetamine," *Journal of Pharmaceutical Sciences*, Vol. 63, No. 10, Oct. 1974, pp. 1575–1578.