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Gas Chromatography-Mass Spectrometry of Trimethylsilyl Derivatives of Amines

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The fragmentation of twenty kinds of trimethylsilyl derivatives of amines upon electron impact is studied for the possibility of ultramicrodetermination and selective identification of amines by mass fragmentography. In addition, the selective identification of trimethylsilyl derivatives of amino acids and amines in their mass spectra is also examined. The results obtained in this study indicated that the selective identification and ultramicrodetermination of amines by mass fragmentography will be possible by monitoring the intense ion such as *m/e* 174. The *m/e* 147 ion is observed for the amines which have O-trimethylsilyl group. Both ions at *m/e* 147 and 59 are useful for the selective identification of amino acids and amines in their mass spectra. It is not always true that the ion at *m/e* 147 indicates the presence of O-trimethylsilyl group, considering from the results that this ion is observed for N-trimethylsilyl *n*-butyl esters and N-trimethylsilyl *l*-menthyl esters of amino acids.

Keywords——gas chromatography–mass spectrometry; amines; trimethylsilylation; possibility of ultramicrodetermination of amines; selective identification of amino acids and amines

In the previous paper,[2] five derivatives of five kinds of amines were investigated on the ultramicrodetermination and selective identification of amines by mass fragmentography or mass chromatography, and it was found that trimethylsilylated amines were useful for the determination of ultramicroamounts (10^{-11} g level) of amines by mass fragmentography monitoring the ion at *m/e* 174 because this derivative produced the commonly intense ion at *m/e* 174 upon fragmentation. The preceding paper[3] reported the mass spectra of fifty eight kinds of N-trimethylsilyl (TMS) amino acid TMS esters to provide the spectral basis for the further study of physiological samples. It was found that the selective identification of given amino acids was possible by monitoring the specific and intense fragment ions.

In the present paper, mass spectra of twenty kinds of amines including the previously reported five kinds of amines[2] are recorded, and each fragmentation is investigated to examine the possibility of ultramicrodetermination of amines by mass fragmentography. The present paper also deals with the selective identification of amino acids and amines in their mass spectra.

Experimental

Apparatus and Conditions——A Hitachi RMU-6MG mass spectrometer, with an 002 Datalizer using Hitac-10 computer, was used. The operation conditions for this study were the same as described previously.[4] A glass column of 1 m × 3 mm i.d. packed with 1.5% OV-101 on Diatoport S was used for this study.

Reagents and Materials——Amine salts were purchased from Tokyo Kasei Co. and Sigma Chemical Co. N,O-bis-(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane and hypovials were purchased from Pierce Chemical Co. Pyridine was used after drying over NaOH pellets.

1) Location: *1-1, Suzuki-cho, Kawasaki-ku, Kawasaki, 210, Japan.*
2) H. Iwase and A. Murai, *Chem. Pharm. Bull.* (Tokyo), **25**, 3129 (1977).
3) H. Iwase, Y. Takeuchi, and A. Murai, *Chem. Pharm. Bull.* (Tokyo), accepted.
4) H. Iwase and A. Murai, *Chem. Pharm. Bull.* (Tokyo), **25**, 285 (1977).

Preparation of 1-Amino-2-propanol and 3-Methylthiopropylamine——These amines were prepared according to the literatures[5,6] by adding tetralin and tetralin peroxide to threonine and methionine, respectively.

Preparation of Trimethylsilylated Amines——Trimethylsilylated amines were prepared by the conventional method.[7]

TABLE I. Ten Peaks of Mass Spectra of Trimethylsilylated Amines

	$M^{+\cdot}$		$(M-15)^+$		*m/e* 174	Base peak		2nd peak		3rd peak		4th peak	
	m/e	%[a]	*m/e*	%	%	*m/e*	$\sum_{10}$%[b]	*m/e*	%	*m/e*	%	*m/e*	%
Isobutylamine	217	—	202	16.4	81.0	43	19.6	174	81.0	73	69.9	45	23.1
1-Amino-2-propanol	291	—	276	1.4	88.0	73	27.1	174	88.0	45	19.3	86	17.9
Benzylamine	251	12.7	236	84.3	15.5	91	12.2	73	85.3	336	84.3	130	57.5
β-Phenylethylamine	265	—	250	7.8	100.0	174	27.3	73	68.5	91	50.5	86	26.3
3-Methylthiopropylamine	249	7.2	234	11.9	100.0	174	20.0	73	84.5	59	36.4	86	33.4
Putrescine	376	—	361	1.5	100.0	174	34.2	73	78.2	175	17.1	59	15.3
Cadaverine	390	—	375	6.0	100.0	174	37.9	73	60.1	175	17.7	59	10.5
Tyramine	353	—	338	8.8	100.0	174	27.7	73	62.3	175	22.6	86	16.2
3-Methoxytyramine	383	—	368	4.1	100.0	174	34.9	73	82.3	175	19.2	86	13.3
Dopamine	441	—	426	3.2	100.0	174	38.4	73	77.1	175	18.6	86	8.8
Tryptamine	376	—	361	—	100.0	174	33.7	73	62.3	130	25.6	86	19.5
Serotonine	464	—	449	—	100.0	174	34.2	73	78.1	175	18.7	86	13.4
Histamine	255	—	240	6.6	—	154	27.1	73	98.9	45	19.5	102	14.6
Octopamine	369	—	354	1.8	—	73	29.9	102	93.0	267	41.2	45	15.1
Adrenaline	471	—	456	—	—	116	45.6	73	67.8	117	11.1	45	10.0
Noradrenaline	457	—	442	1.3	—	73	39.7	355	43.0	102	40.4	356	13.0
Metanephrine	413	—	398	—	—	116	45.1	73	74.1	117	10.4	45	9.7
Normetanephrine	399	—	384	1.9	—	73	36.8	102	54.4	297	48.3	45	12.2
Ephedrine	309	—	294	1.9	—	130	42.8	73	51.5	58	16.0	131	13.1
Methylephedrine	251	—	236	1.6	—	72	40.4	73	18.0	42	9.0	44	7.5

	5th peak		6th peak		7th peak		8th peak		9th peak		10th peak	
	m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
Isobutylamine	59	21.1	86	19.9	27	19.1	128	16.6	202	16.4	175	14.2
1-Amino-2-propanol	59	15.7	175	15.5	133	10.4	114	9.8	100	8.8	74	7.9
Benzylamine	162	45.5	59	38.9	45	37.5	135	30.1	100	20.9	65	19.9
β-Phenylethylamine	59	20.6	175	16.3	45	14.7	176	13.8	100	11.7	65	8.3
3-Methylthiopropylamine	45	22.4	175	19.7	61	15.7	100	14.1	234	11.9	47	10.0
Putrescine	86	9.4	214	8.7	46	7.4	172	7.1	176	6.8	74	6.6
Cadaverine	86	10.4	176	8.3	375	6.0	74	5.6	100	5.5	130	4.5
Tyramine	59	14.8	45	12.0	176	10.6	338	8.8	100	8.7	179	6.3
3-Methoxytyramine	45	12.3	59	10.8	176	7.3	179	7.0	100	6.1	74	5.5
Dopamine	45	8.2	176	7.6	74	6.5	59	5.2	179	4.9	100	4.7
Tryptamine	175	17.8	59	14.3	176	9.4	45	9.7	289	6.2	131	4.9
Serotonine	45	9.9	59	8.9	176	8.8	74	7.3	202	5.9	100	5.1
Histamine	155	13.5	59	12.1	43	11.3	74	9.3	58	8.7	240	6.6
Octopamine	103	9.9	268	9.8	74	8.1	55	6.7	147	6.3	75	5.9
Adrenaline	355	7.5	74	7.1	75	4.1	118	3.6	147	3.4	356	2.4
Noradrenaline	45	11.8	74	8.3	357	6.1	147	5.6	75	4.4	103	3.9
Metanephrine	297	8.2	74	6.2	75	4.2	118	3.2	147	2.6	298	1.8
Normetanephrine	298	10.3	74	8.8	147	5.1	75	5.1	103	4.6	299	4.2
Ephedrine	45	7.7	59	5.0	132	4.7	74	4.7	75	4.2	147	4.0
Methylephedrine	56	6.6	45	6.1	75	4.4	163	4.1	147	3.9	43	3.5

a) Relative intensity (base peak=100). *b*) Percent of the total ionization over *m/e* 10.

5) T. Suyama and S. Kanao, *Yakugaku Zasshi*, **85**, 531 (1965).
6) T. Suyama and S. Kanao, *Yakugaku Zasshi*, **84**, 1012 (1964).
7) C.W. Gehrke, H. Nakamoto, and R.W. Zumwalt, *J. Chromatogr.*, **45**, 24 (1969).

Results and Discussion

Table I shows the *m/e* values and relative intensities of peaks with 1st to 10th intensities (per cent of total ionization for base peaks and pattern coefficients for the others).

Molecular Ions and (M-15) Ions

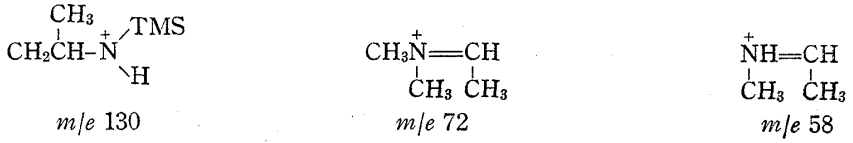
Molecular ions were observed only for benzylamine and 3-methylthiopropylamine, having the relative intensities of 12.7% and 7.2%, respectively. The sixteen kinds of amines except for tryptamine, serotonine, adrenaline and metanephrine produced the prominent ions at *m/e* (M-15), and it was strong for 3-methylthiopropylamine (11.9%), benzylamine (84.3%) and isobutylamine (16.4%). The relative intensities of the average values of the other amines were rather lower, *i.e.*, about 4%.

m/e 174 Ion

Generally, many amines having the structure of R–CH_2NH_2 exhibit the base peak at *m/e* 174. Isobutylamine, 1-amino-2-propanol and benzylamine produced the base peak at *m/e* 43, 73 and 91, respectively, and the relative intensities of the ion at *m/e* 174 from the above three amines were 81.0%, 88.0% and 15.5%, respectively. Abramson *et al.*,[8] reported that amino acids and amines having the R–CH_2NH_2 structure produced the intense ion at *m/e* 174. On the contrary, histamine, octopamine, noradrenaline and normetanephrine which have the structure of R–CH_2NH_2 did not show the ion at *m/e* 174. This fact suggests that only one TMS group was introduced into these four amines, considering from the experimental data that the ions at *m/e* (M-15), (M-102) and 102 were observed. The preceding paper[3] reported that the ion at *m/e* 174 was not observed for β-aminoisobutyric acid and the relative intensity of *m/e* 174 ion from α-methyl-ornithine was 1.2%. Accordingly, it is not always true that amino acids and amines having R–CH_2NH_2 structure gave the intense ion at *m/e* 174. The fragmentation was less abundant for amino acids than the *m/e* 174 fragment for amines. Histamine produced the base peak at *m/e* 154, and this ion was the 2nd peak for histidine.[3] Octopamine, noradrenaline and normetanephrine produced the base peak at *m/e* 73, The commonly specific ion at *m/e* 102 was observed for histamine (14.6%), octopamine (93.0%), noradrenaline (40.4%) and normetanephrine (54.4%), and the characteristic ions at *m/e* (M-102) were also detected for histamine (*m/e* 154, 100.0%), octopamine (*m/e* 267, 41.2%), noradrenaline (*m/e* 355, 43.0%) and normetanephrine (*m/e* 297, 48.3%), As previously reported,[3] β-aminoisobutyric acid produced the intense ion at *m/e* 102. Accordingly, it will be assumed that the ion at *m/e* 102 is useful for the speculation on the presence of R–CH_2NH_2 structure in which one TMS group is introduced. Adrenaline and metanephrine also exit the specific ion at *m/e* 116, corresponding to the ion at *m/e* 102. The characteristic ions at *m/e* (M-116) were also observed for adrenaline (*m/e* 355, 7.5%) and metanephrine (*m/e* 297, 8.2%).

The catecholamine-like derivatives described above, ephedrine and methylephedrine, gave the base peaks at *m/e* 130 and 72, respectively. The former amine also produced the specific ion at *m/e* 58 (16.0%), and this ion was detected for N-TFA-L-prolyl ephedrine.[9] The stsuctuses of the ions at *m/e* 130, 72 and 58 are assumed to be as shown in Chart 1.

From the point of view stated above, it will be possible that the selective identification and ultramicrodetermination of amines by mass fragmentography monitoring the specific



m/e 130 *m/e* 72 *m/e* 58

Chart 1

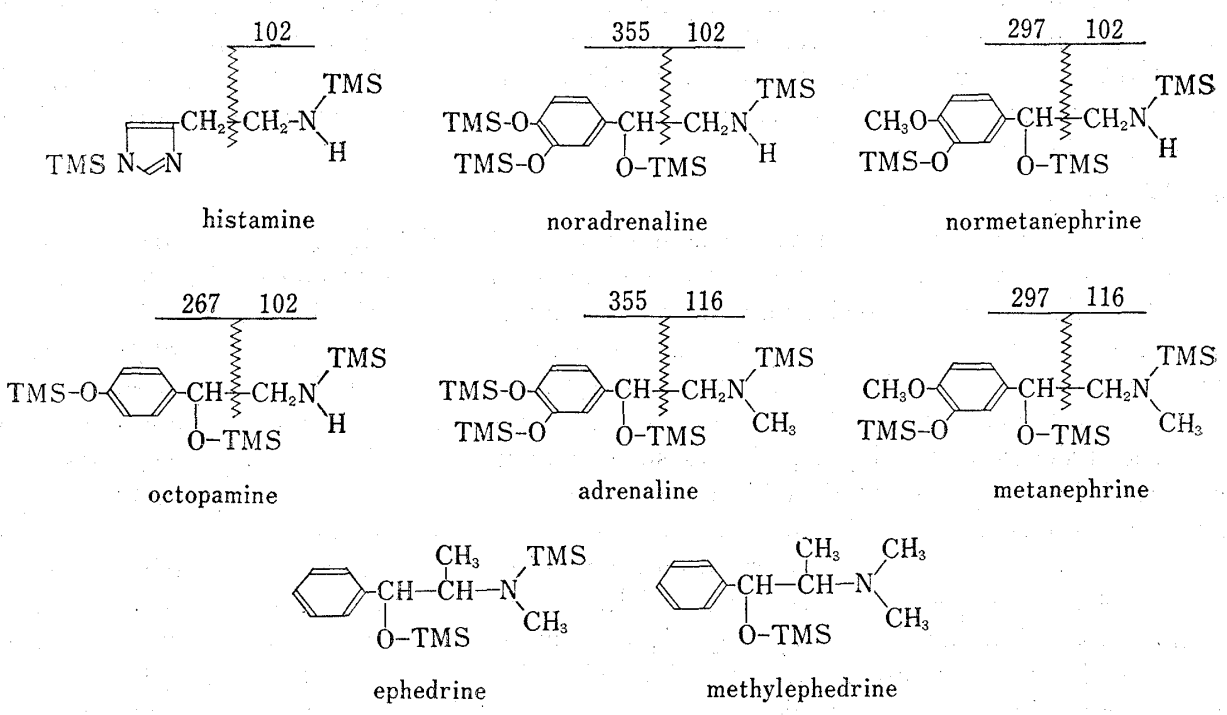
8) F.P. Abramson, M.W. McCaman, and R.E. McCaman, *Anal. Biochem.*, **51**, 482 (1974).
9) H. Iwase and A. Murai, *Chem. Pharm. Bull.* (Tokyo), **25**, 1215 (1977).

and intense ions such as *m/e* 174 or diagnostic ions, considering from the result that about 10^{-11} g of amines were detected by mass fragmentography monitoring the ion at *m/e* 174.[2)]

The structures of histamine, catecholamines, ephedrine and methylephedrine are shown in Chart 2.

The Specific Ions Derived from TMS Group

The specific fragment ions from trimethylsilylated amines are summarized in Table II.



TMS: $-Si-(CH_3)_3$

Chart 2

Table II. Comparison of Typical Mass Spectra of Trimethylsilylated Amines

	m/e 147 %[a)]	*m/e* 103 %	*m/e* 102 %	*m/e* 100 %	*m/e* 86 %	*m/e* 75 %	*m/e* 74 %	*m/e* 73 %	*m/e* 59 %	*m/e* 45 %	*m/e* 114 %	*m/e* 128 %
Isobutylamine	—	—	—	—	19.9	—	4.3	69.9	21.1	23.1	—	16.6
1-Amino-2-propanol	14.4	—	—	8.8	17.9	—	7.9	100.0	15.7	19.3	9.8	1.9
Benzylamine	—	—	2.4	20.9	19.2	5.6	8.4	85.3	38.9	37.5	3.7	—
β-Phenylethylamine	—	—	—	11.7	26.3	—	7.2	68.5	20.6	14.7	—	—
3-Methylthiopropylamine	—	—	2.5	14.1	33.4	5.3	7.7	84.5	36.4	22.4	2.2	1.4
Putrescine	—	—	1.2	4.9	9.4	1.6	6.6	78.2	15.3	—	—	1.1
Cadaverine	—	—	1.1	5.5	10.4	2.3	5.6	60.1	10.5	4.1	1.1	—
Tyramine	—	—	1.2	8.7	16.2	3.7	8.5	62.3	14.8	12.0	—	—
3-Methoxytyramine	—	—	1.4	6.1	13.3	4.3	5.5	82.3	10.8	12.3	—	—
Dopamine	—	—	—	4.7	8.8	2.9	6.5	77.1	5.2	8.2	—	—
Tryptamine	—	4.6	—	—	19.5	1.5	—	62.3	14.3	9.7	—	—
Serotonine	—	—	1.5	5.1	13.4	2.6	7.3	78.1	8.9	19.9	—	—
Histamine	—	—	—	4.6	2.5	7.6	9.3	98.9	12.1	19.5	—	—
Octopamine	6.3	9.3	93.0	—	—	5.9	8.1	100.0	—	15.1	—	—
Adrenaline	3.4	—	—	—	—	4.1	7.1	67.8	—	10.0	—	—
Noradrenaline	5.6	3.9	40.4	—	—	4.4	8.3	100.0	—	11.8	—	—
Metanephrine	2.6	—	—	—	—	4.2	6.2	74.1	—	9.7	—	—
Normetanephrine	5.1	4.6	54.4	—	—	5.1	8.8	100.0	—	12.2	—	—
Ephedrine	4.0	—	—	1.0	—	4.2	4.7	51.5	5.0	7.7	1.3	—
Methylephedrine	3.9	3.4	2.9	—	—	4.4	1.5	18.0	—	6.1	—	—

a) Relative intensity (base peak=100).

TABLE III. Comparison of Typical Mass Spectra of N–TMS Amino Acid Trimethylsilyl Esters

	m/e 147 %[a)]	*m/e* 103 %	*m/e* 102 %	*m/e* 100 %	*m/e* 86 %	*m/e* 75 %	*m/e* 74 %	*m/e* 73 %	*m/e* 59 %	*m/e* 45 %	*m/e* 114 %	*m/e* 128 %
Gly	16.0	1.2	—	8.0	12.0	7.6	9.0	100.0	19.1	28.5	—	—
Sar	18.0	—	1.3	1.3	3.7	9.5	8.0	92.9	14.8	23.7	—	—
Ala	13.9	2.9	1.5	5.8	3.9	11.4	8.4	87.8	14.5	27.5	—	1.1
β-Ala	23.2	—	—	12.8	14.8	18.4	8.6	100.0	18.2	28.0	—	—
α-Aba	12.0	1.5	—	5.2	1.8	11.7	8.6	89.2	13.7	25.7	2.1	—
β-Aba	16.4	—	3.5	22.9	1.8	25.1	11.5	100.0	19.9	30.0	3.3	—
β-Aiba	13.6	9.3	100.0	1.7	3.4	13.5	9.0	67.8	10.0	16.9	1.4	—
γ-Aba	28.3	—	—	9.7	15.3	30.6	9.2	100.0	16.2	21.7	2.2	—
Nva	10.3	1.4	1.1	4.6	1.0	10.4	8.2	86.4	12.2	21.8	3.0	1.6
Val	12.4	1.7	—	7.4	1.3	13.0	10.6	100.0	13.1	25.6	4.2	2.3
Nle	7.3	1.5	1.5	4.1	1.4	7.2	7.9	72.4	10.2	15.4	2.1	1.4
Leu	8.4	1.2	4.2	4.2	1.0	7.3	7.1	73.0	11.1	17.1	—	2.4
Ile	10.1	—	1.3	6.1	1.5	8.9	8.5	90.0	9.0	20.6	1.4	2.5
tert-Leu	9.3	—	—	10.4	—	11.0	7.4	100.0	7.3	20.5	—	2.6
α-Cap	6.6	1.0	1.5	4.6	1.2	7.6	6.2	63.2	8.5	11.8	5.2	2.6
Ser	11.7	2.4	—	13.0	—	8.3	7.9	100.0	6.4	20.2	1.7	—
Thr	8.8	—	1.8	4.6	—	9.2	8.6	100.0	5.8	19.0	1.9	3.2
Pro	7.0	—	—	1.7	—	7.9	6.7	75.4	8.1	20.4	—	—
Pip	4.8	—	—	1.5	1.2	8.9	7.6	75.4	11.5	23.8	—	—
Hypro	6.9	—	—	—	1.2	13.2	7.8	100.0	6.6	19.1	—	—
Pga	14.5	—	—	2.3	2.4	20.9	10.5	100.0	10.0	32.0	—	—
Tca	7.9	—	—	1.0	3.0	11.3	8.6	100.0	9.6	24.4	—	—
AMCHA	5.1	10.2	39.0	—	1.7	14.7	5.9	47.8	7.9	7.8	—	—
Ana	3.9	—	—	—	—	14.1	8.4	100.0	4.9	27.6	—	—
Asp	11.8	1.7	—	18.6	—	15.6	11.5	100.0	6.3	18.1	—	—
Glu	15.6	—	—	5.8	1.0	24.2	11.6	100.0	7.6	20.3	2.1	18.8
Adi	15.2	—	—	10.5	—	28.1	14.8	100.0	7.2	19.6	—	19.5
Asn	9.0	—	—	7.1	—	19.9	10.3	100.0	4.5	15.8	2.0	—
Gln	13.2	—	—	2.7	—	28.6	11.7	100.0	4.6	17.6	—	6.2
Met	10.4	1.4	—	6.1	—	19.9	11.5	100.0	12.5	31.5	2.7	28.9
Eth	9.3	1.2	—	9.0	1.1	56.1	9.0	100.0	12.4	30.6	3.6	34.5
Met(O)	11.0	7.1	1.7	5.6	—	35.1	17.7	89.1	6.2	25.4	—	71.7
Met(O_2)	8.3	—	—	3.4	1.0	19.5	6.3	69.2	5.8	12.6	3.0	100.0
CySH	42.5	4.2	4.0	73.8	3.5	38.3	41.1	99.0	33.9	86.1	4.3	—
Cys	16.5	2.0	1.4	16.4	—	11.4	9.0	100.0	5.4	12.6	1.5	—
Pen	21.4	—	—	5.0	—	9.4	8.4	100.0	6.4	17.7	—	3.8
Pg	8.4	2.3	—	—	—	11.3	11.0	100.0	11.5	32.2	—	—
Phe	12.2	2.8	—	12.5	—	10.3	9.1	100.0	5.3	22.5	—	—
Tyr	7.8	1.1	—	9.5	—	10.0	9.4	100.0	3.3	16.6	—	—
DOPA	5.4	—	—	5.7	—	7.3	8.4	100.0	2.0	14.5	—	—
Trp	3.0	—	—	1.8	—	7.9	8.1	100.0	2.0	18.2	—	—
5H-Trp	—	—	—	7.9	—	9.3	8.9	100.0	2·0	14.3	—	—
Kyn	11.0	1.6	—	5.4	—	24.7	12.2	100.0	4.6	18.2	—	—
His	3.8	—	—	4.6	—	7.6	9.4	100.0	4.3	21.2	—	—
Orn	10.7	1.7	5.9	7.0	7.9	7.6	10.8	100.0	9.2	10.3	2.8	5.6
Lys	11.8	—	3.0	9.9	7.9	7.8	9.7	100.0	10.4	10.3	—	17.8
MeAla	9.7	1.1	—	8.6	—	12.3	9.2	93.9	8.5	24.9	6.4	—
MeAba	10.5	—	—	1.9	—	11.8	8.4	85.9	8.1	20.3	6.4	3.0
MeVal	9.6	—	—	2.2	1.8	11.2	9.1	100.0	8.0	21.1	12.9	1.9
MeLeu	9.4	—	—	9.1	—	9.3	8.6	75.3	7.6	18.2	9.1	—
MeIle	9.1	—	—	3.2	—	11.2	10.1	100.0	7.8	21.5	14.0	2.1
MeGlu	11.6	1.0	—	—	—	21.9	11.2	100.0	4.9	19.9	5.8	—
MeMet	10.0	—	—	1.3	—	17.3	12.3	100.0	8.7	30.4	10.1	—
MeTyr	8.0	1.0	—	1.2	—	12.5	9.3	100.0	2.9	14.0	17.1	—
MeDOPA	9.2	—	—	1.0	—	9.4	11.4	100.0	2.6	17.6	20.9	—
MeTrp	4.3	—	—	—	—	7.7	8.5	100.0	2.5	16.9	10.8	—

	m/e 147 %	*m/e* 103 %	*m/e* 102 %	*m/e* 100 %	*m/e* 86 %	*m/e* 75 %	*m/e* 74 %	*m/e* 73 %	*m/e* 59 %	*m/e* 45 %	*m/e* 114 %	*m/e* 128 %
Me-5H-Trp	5.1	—	—	—	—	5.9	7.6	100.0	1.1	12.1	10.6	—
MeOrn	8.2	1.8	9.6	3.5	—	7.8	15.8	100.0	8.7	17.2	6.9	3.2

a) Relative intensity (base peak=100).

Abbreviations; Sar, sarcosine; Aba, amino-*n*-butyric acid; Aiba, amino-iso-butyric acid; Nva, norvaline,; Nle, norleucine; Cap, amino-*n*-caprylic acid; Pip, pipecolic acid; Pga, pyroglutamic acid; Tca, 4-thiazolidinecarboxylic acid; AMCHA, *trans*-4-(Aminomethyl)-cyclohexane carboxylic acid; Ana, anthranilic acid; Adi, α-aminoadipic acid; Eth, ethionine; Met (O), methionine sulfoxide; Met (O_2), methionine sulfone; Pen, penicillamine; Pg, phenylglycine; 5H-Trp, 5-hydroxy-tryptophan; Kyn, kynurenine; Me-α-methyl.

An examination was made on the fragmentation features of the trimethylsilylated amines which have hydroxy benzyl group or have not. As can be seen in Table II, the former amines (hydroxy benzyl group) produce the specific ion at *m/e* 147 and do not exhibit the ion at *m/e* 86. Ephedrine produces the ions at *m/e* 100 (1.0%) and 59 (5.0%). However, the former six amines do not produce these ions. In contrast, the *m/e* 147 ionwas not observed for the latter amines except for 1-amino-2-propanol (CH_3–$\underset{\underset{OH}{|}}{CH}$–$CH_2$–$NH_2$). However, the ions at *m/e* 86 and 59 were observed for all the latter amines, different from the former amines. The ion at *m/e* 100 was detected for the amines except for isobutylamine and tryptamine. Considering from the experimental results, it seems to be reasonable to assume that the amines, having the structure of hydroxy benzyl group or hydroxy propyl group, produce the ion at *m/e* 147. Bergström *et al.*[10] and Horning *et al.*[11] reported that the abundant siloxanium ion at *m/e* 147 ($(CH_3)_2Si{=}\overset{+}{O}{-}Si(CH_3)_3$) indicated the presence of O–TMS group in the molecules. On the other hand, the amines which have not the above structures, produce the ions at *m/e* 86 and 59, and do not produce the *m/e* 147 ion. It is concluded that the above fragment ions play the important role for the detremination of structures of amines, although the relative intensities were not so intense.

A comparison was then made on the specific ions for amino acids and amines.

N–TMS amino acid TMS esters[3] produce the specific ions such as *m/e* 147, 86, 75, 73 and 59. The specific ions derived from N–TMS amino acid TMS esters are summarized in Table III. The ion at *m/e* 147 was observed for fiftyseven kinds of amino acids except for 5-hydroxy-tryptophan, having the relative intensities of the average value of 11.2%, and it was especially strong for cysteine (42.5%). N–TMS amino acid TMS esters produced the both diagnostic ions at *m/e* 147 and 59 in their mass spectra. These fragment ions were not observed for eighteen kinds of trimethylsilylated amines except for 1-amino-2-propanol and ephedrine. Accordingly, it may be supposed with some exceptions that the fragment ions at *m/e* 147 and 59 are useful for the selective identification of N–TMS amino acid TMS esters and trimethylsilylated amines in their mass spectra. The fragment is less abundant for amines that the *m/e* 147, 75, 74 and 73 fragment ions for amino acids. There was no notable difference in the fragmentation between the TMS derivatives of amines and amino acids.

An examination was also made on the specific ion at *m/e* 147 from N–TMS *n*-butyl esters[3] and N–TMS *l*-menthyl esters[3] of six amino acids (alanine, valine, leucine, proline, aspartic acid and glutamic acid). As described above, the ion at *m/e* 147 indicates the presence of O–TMS group in the molecule. However, the *m/e* 147 ion was observed for N–TMS *n*-butyl esters of alanine (5.3%), valine (7.5%), leucine (1.2%), aspartic acid (1.3%) and glutamic acid (1.5%), and N–TMS *l*-menthyl esters of valine (3.0%), aspartic acid (1.4%) and glutamic acid (5.3%). Therefore, it is not always true that the *m/e* 147 ion indicates the presence of O–TMS group in the molecule.

10) K. Bergström, J. Gurtler, and R. Blomstrand, *Anal. Biochem.*, **34**, 74 (1970); K. Bergström and J. Gurtler, *Acta Chemica Scandinavica*, **25**, 175 (1971).

11) M.G. Horning, E.A. Boucher, A.M. Moss, and E.C. Horning, *Anal. Lett.*, **1**, 713 (1968).