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INFRARED AND MASS SPECTRA OF α -AMINO ACID AMIDES

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During the course of study for free amino acids composition of ladino clover seeds, three α -amino acid amides —L-tyrosine-amide, L-leucineamide and L-phenylalanineamide— were isolated from the basic amino acid fraction.¹⁾ In IR spectrum (KBr) of L-tyrosineamide hydrochloride, carbonyl stretching vibration (amide I) was observed at uncommonly high wave number (1705 cm^{-1}). IR spectra of leucineamide hydrochloride and phenylalanineamide hydrochloride could not be determined at that time because the amount of the isolated compounds was very small. All of three amides did not give M^+ ion, but gave $M^+ + 1$ ion in mass spectra. Little attention has been drawn on these unexpected matters. Therefore, this study was attempted to ascertain whether these two features are common for α -amino acid amides. These spectra data, if established, will be available for identification of this kind of compounds.

The following amino acid amide hydrochlorides were prepared from corresponding L-amino acid with conventional manners²⁾ and their purity was confirmed by paper chromatography, NMR spectrum and elemental analysis; leucineamide hydrochloride, aspartic acid diamide hydrochloride, phenylalanineamide hydrochloride, valineamide hydrochloride, alanineamide hydrochloride, methionineamide hydrochloride and α -aminoisobutyric acid amide hydrochloride. O-Methyltyrosineamide hydrochloride was prepared as follows; N-Acetyl-L-tyrosine was treated with dimethylsulfate, hydrolyzed with hydrochloric acid and O-methyltyrosine thus obtained was used for amide preparation. Anal. Found: C, 52.33; H, 6.55; N, 11.97. Calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2 \cdot \text{HCl}$: C, 52.06; H, 6.51; N, 12.15. mp. 207.9°C (d). $[\alpha]_{\text{D}}^{13} = +19.4$ (c=2 in water). NMR ($\delta_{\text{DSS}}^{\text{p,20}}$); 3.18 (2H, d, J=7 Hz), 3.86 (3 H, s), 4.26 (1 H, t, J=7 Hz), 7.02 and 7.29 (both 2 H, d, J=9 Hz).

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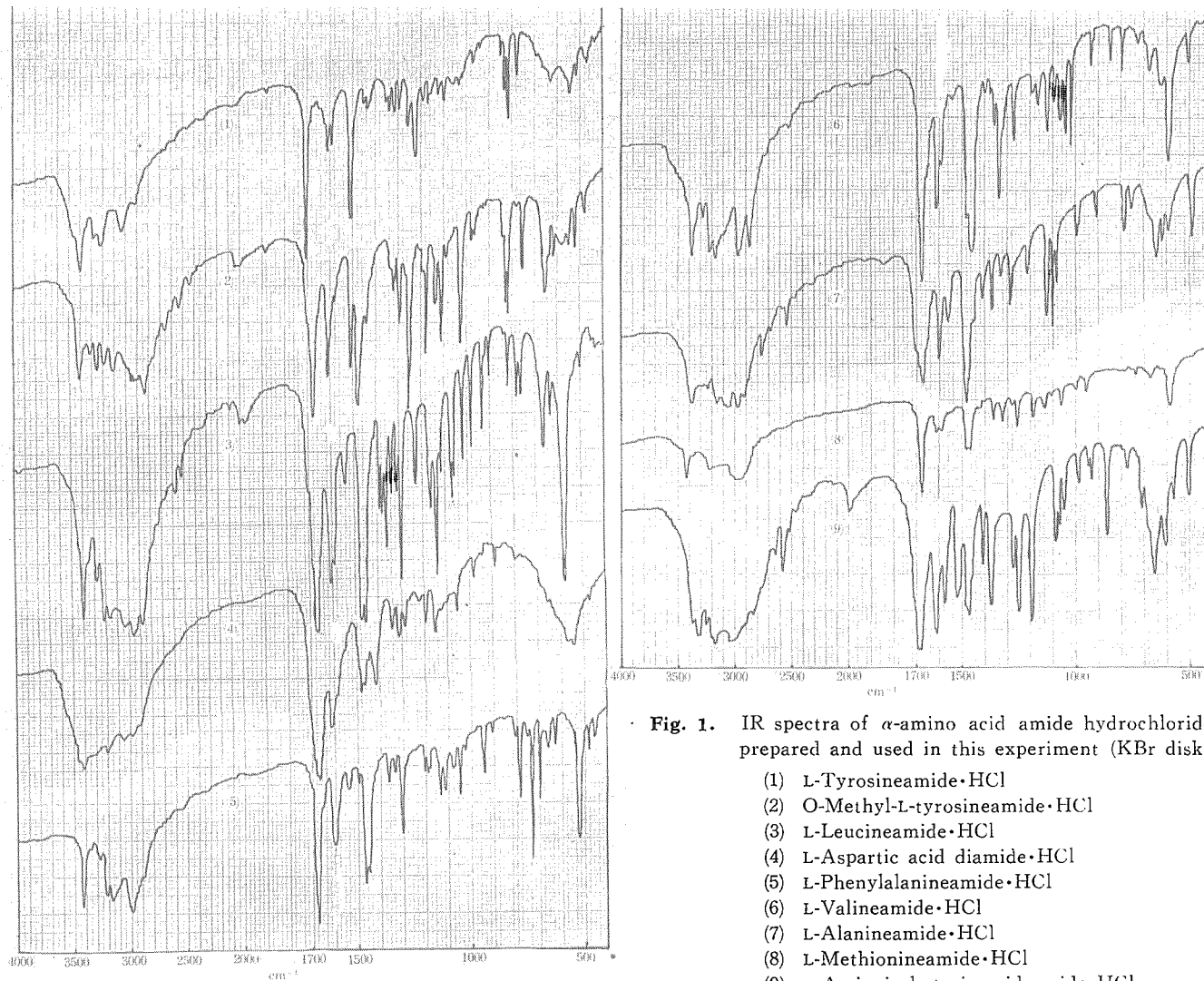


Fig. 1. IR spectra of α -amino acid amide hydrochlorides prepared and used in this experiment (KBr disks).

- (1) L-Tyrosineamide \cdot HCl
- (2) O-Methyl-L-tyrosineamide \cdot HCl
- (3) L-Leucineamide \cdot HCl
- (4) L-Aspartic acid diamide \cdot HCl
- (5) L-Phenylalanineamide \cdot HCl
- (6) L-Valineamide \cdot HCl
- (7) L-Alanineamide \cdot HCl
- (8) L-Methionineamide \cdot HCl
- (9) α -Aminoisobutyric acid amide \cdot HCl

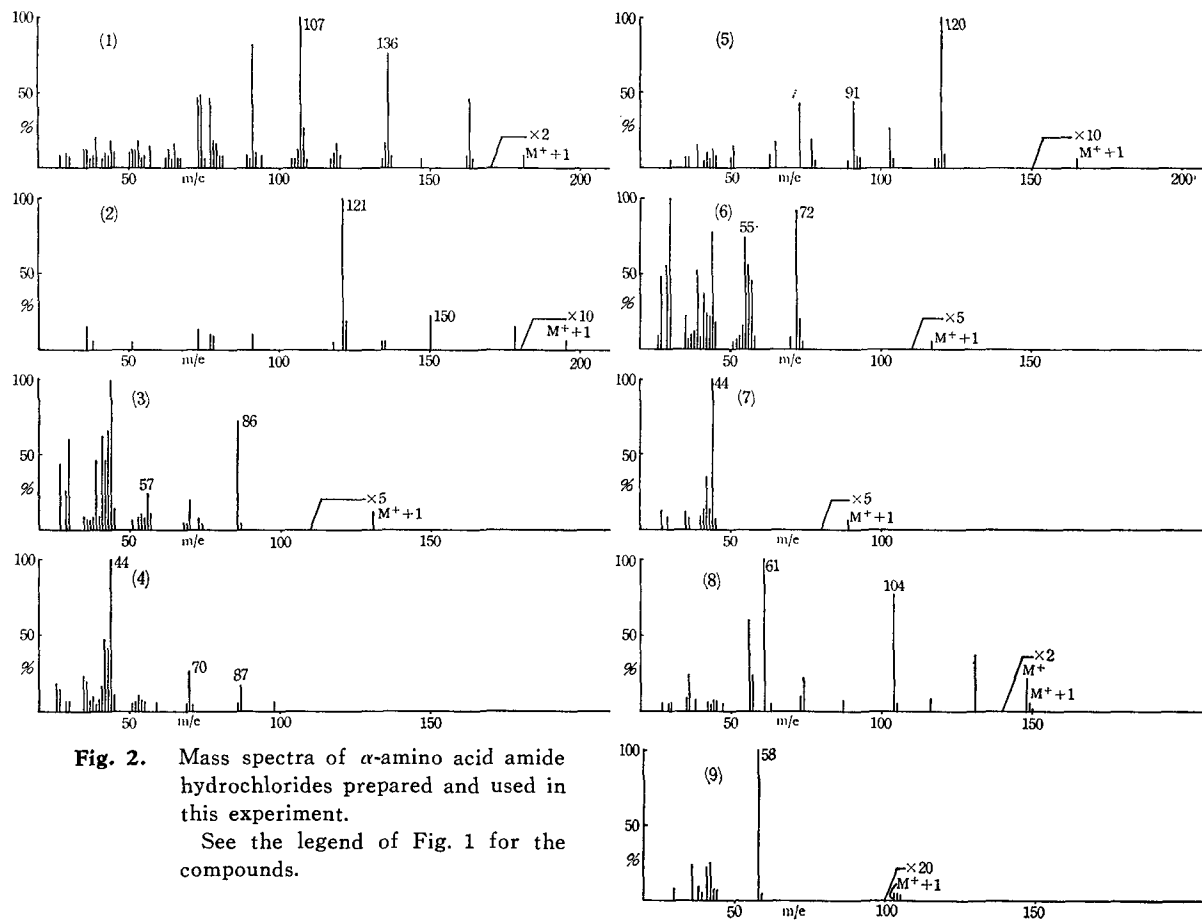


Fig. 2. Mass spectra of α -amino acid amide hydrochlorides prepared and used in this experiment.

See the legend of Fig. 1 for the compounds.

TABLE 1. IR and Mass Spectra of α -Amino acid Amide Hydrochlorides

	IR (KBr)	Mass (m/e) (Relative Intensity, %)		
	(cm^{-1})	M^+	$M^+ + 1$	Others*
	CO Stretching (amide I)			
L-Tyrosineamide·HCl	1705	—	1.3	136 (70, a), 107 (100, b)
L-O-Methyltyrosineamide·HCl	1680	—	0.5	150 (22, a), 121 (100, b)
L-Leucineamide·HCl	1670	—	2.2	86 (73, a), 57 (12, b)
L-Aspartic acid diamide·HCl	1675	—	—	87 (17, a), 44 (100, c+1), 43 (43, c)
L-Phenylalanineamide·HCl	1675	—	0.5	120 (100, a), 91 (43, b)
L-Valineamide·HCl	1680	—	1.1	72 (92, a), 44 (77, b+1), 43 (22, b)
L-Alanineamide·HCl	1675	—	1.2	44 (100, a)
L-Methionineamide·HCl	1675	11	3.0	104 (78, a), 61 (100, b-14)
α -Aminoisobutyric acid amide·HCl	1690	—	0.3	58 (100, a)

* a= $M^+ - \text{CONH}_2$, b= $M^+ - \text{CH}(\text{NH}_2)\text{CONH}_2$, c= $M^+ - 2\text{CONH}_2$.

Instruments; Hitachi Model 285 for IR spectra. Hitachi RMS-4 for mass spectra. Hitachi R-22 (90 MHz) for NMR spectra. IR spectra were all measured as KBr disks.

IR and mass spectra of the compounds prepared are given in Fig. 1 and 2. Carbonyl stretching vibration (amide I) in IR spectra and relative intensity of M^+ and $M^+ + 1$ ions in mass spectra of those compounds are summarized in Table 1. Carbonyl stretching vibration of all α -amino acid amide hydrochlorides except tyrosineamide hydrochloride and α -aminoisobutyric acid amide hydrochloride were in normal range ($1680 \sim 1670 \text{ cm}^{-1}$) experimented so far. Amide I band of O-methyltyrosineamide hydrochloride was also in this region. Stretching vibration of amide carbonyl group appears generally at lower wave number than that of other carbonyl group because of the effect of nitrogen bonded directly to carbonyl carbon⁹. As one of the reasons for the fact that amide I band of tyrosineamide appears at uncommonly higher region, it is assumed that the effect of nitrogen to the carbonyl bond becomes weaker than in the case of other amide groups by occurrence of intermolecular hydrogen bond between amide N and phenolic OH, because amide I band of tyrosineamide moves down into normal region by methylation of its phenolic group.

In mass spectra, M^+ ion could not be observed except methionineamide, but very weak $M^+ + 1$ ion was always recognized except aspartic acid diamide. This result, however, does not seem to be characteristic of α -amino acid

amides, because relative intensities of those $M^+ + 1$ ions are very small and nitrogen containing compounds often give small $M^+ + 1$ peak.

From those results described above, it is obvious that, in IR spectra, α -amino acid amides except tyrosineamide have their amide I band in normal wave length region and, in mass spectra, most of α -amino acid amides do not give parent peak, but very small $M^+ + 1$ peak of little significance, in samples experimented so far.

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