Studies on the Surfactants of the N-Acyl Carboxylic Acid

-Synthesis of N-Acyl Amidoethyl N-Amido Carboxylic Acid Derivatives-

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N-아실 카르복시산계 계면활성제에 관한 연구
-N-아실 아미도에틸 N-아미도 카르복시산 유도체의 합성-

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요 약

2염기성 산의 모노메틸에스테르류와 에틸렌디아민을 반응시켜 얻은 아미도아민 유도체류를 고급지방산 염화물로 아실화하여 N-아실 아미도에틸 N-아미도카르복시산 유도체 9종을 합성하였다. 카르복시기와 디아미드기 그리고 소수성의 긴 알킬사슬을 갖는 모든 반응생성물들은 얇은 막 크로마토그래피와 컬럼크로마토그래피로 분리·정제하였다. 합성 수율은 74~87%였으며 그들의 구조를 FT-IR, ^{1}H-NMR, 그리고 원소 분석으로 확인하였다.

I. INTRODUCTION

Since the rise of oil prices and awareness of the effects of surfactants on ground water and waste treatment operations in environment, surfactants based on natural fats, oil and fatty acids obtained therefrom are of importance.[1] A large number of fatty acid and amide derivatives which cannot be obtained at all from petrochemical present substanced are used as surfactants in conversion industries.

The essential fields of application of fatty acid derivatives are cosmetics, detergent powders, detergent liquids, fabric softeners, corrosion inhibitors, textile auxiliaries and food stuffs. Fatty amines and amides likewise have a wide spectrum of uses.

Fatty amides are compounds that exhibit low reactivity and high thermal stability. Their chemical properties vary depending on the length of the hydrocarbon alkyl chain and the nature of the substituent on the nitrogen atom.[2] Fatty amides have many different applications.[3] These include anti-slip and anti-block additives for polyethylene films, water repellents for textiles, coatings for paper, mold-release agents, lubricant additives, printing ink additives, defoaming

agents and flow improvers.

In the previous studies, amidoamine derivatives obtained by the reaction of fatty acids or their methyl esters with hydroxyethyl ethylene diamine have textile softening properties as well as detergency.[4] It was observed that the introduction of an amido group into sulfopropylated amphoteric molecule improved water solubility.[5,6] Introduction of a second amido group into the sulfobetaine molecule will be given to enhanced water solubility. It was therefore of interest to synthesize new type surfactants based on carboxyl group and diamide group. Accordingly, a series of N-acyl amidoethyl monoamide of oxalic acid, malonic acid and succinic acid of the general structure $RCONH-CH_2CH_2NHCO(CH_2)_xCOOH$ (where $R=C_{11}H_{23}$, $C_{15}H_{31}$, $C_{17}H_{35}$ and $X=0$, 1, 2) were synthesized.

II. EXPERIMENTAL METHODS

II −1. Materials and Experimental Apparatus

Oxalic acid, malonic acid and succinic acid were obtained from Tokyo Kasei Organic Chemicals and fatty acid chlorides were purchased from Aldrich chemical Co.. These materials were used without further purification. Tetrahydrofurane, sodium methoxide and pyridine were also purchased from Aldrich Co., and all the other solvents were reagent & analytical grade.

For the reaction apparatus of esterfication, a 300mL round-bottomed flask was equiped with thermometer, dry calcium chloride column, dropping funnel and reflux condenser. The apparatus of N-acylation was equiped with a mechanical stirrer, dry calcium chloride column, thermometer and dropping funnel in a 300mL round-bottomed flask.

II −2. Synthesis of N-Acyl Amidoethyl Amine Derivatives

II −2−1. Preparation of Monomethyl Esters of Dicarboxylic Acid[7]

To a solution of the dicarboxylic acid(0.1mol) in tetrahydrofurane 80mL, pyridine 18.2g(0.23 mol) and methanol 11.8mL(0.204mol) were added and stirred, followed by cooling to 0℃. To the mixture, methanesulfonyl chloride 12.2g(0.12 mol) was added over 20 minutes and stirred for 1 hour. Then, methylene chloride 30mL and water 20mL were added. pH of the mixture was adjusted to 10~11 with 30% aqueous solution of sodium hydroxide. The mixture was separated and an aqueous layer was washed with methylene chloride 20mL three times. After adjusting pH of aqueous phase to 2.5 with 6N hydrochloric acid, the aqueous phase was extracted with methylene chloride 60mL four times. The organic phase was dried over sodium sulfate and concentrated to obtain the monomethyl esters of dicarboxylic acid.

II −2−2. Synthesis of Carboxy Amido Ethylamine[8]

To a 300mL flask equipped with a mechanical stirrer, dropping funnel and a Dean and Stark apparatus fitted with a reflux condenser, was added 12.09g(0.2mol) of ethylene diamine in 150mL of chloroform. The monomethyl esters of the dicarboxylic acid(0.2mol) in 100mL chloroform was added to the flask for 30 minutes with stirring. The methanol from the reaction was continuously removed. The mixture was refluxed for about 3 hours and evaporated. And then, the products were crystallized twice by methanol.

II −2−3. Synthesis of N-Acyl Amidoethyl N-Amido Carboxylic Acid[8]

To a 300mL flask equipped with a mechanical stirrer, reflux condenser and dropping funnel was added 0.5mol of carboxy amido ethylamine in 100 mL of acetone. The fatty acid chloride(0.22mol) in 50mL of acetone was added dropwise at a rate to maintain gentle reflux about 30minutes while stirring mixture. The reflux was continued until

evolution of HCl ceased about 1.5hours. The solvent was distilled and the product was purified by repeated crystallization from methanol.

II −3. Separation and Analysis of the Products

II −3−1. Chromatography

The products synthesized by method of II −2−1, II −2−2 and II −2−3 identified in TLC and purified on column chromatography. Analysis by TLC method of Bilyk[9] was employed with silicagel G plates that had been prewashed in a tank of methanol for 5 min. The plates were spotted with $10\mu L$ of a 2%(v/v) concentration of sample in chloroform. The plates were developed with a mixture of chloroform-methanol-water (65:25:4, v/v) and hexane-diethylether-formic aicd(80:20:2, v/v) as developing solvent respectively. Upon drying, the spot were revealed by exposure to iodine vapors.

In the method column chromatography, silicagel 60 G as the stationary phase was added to 300mm in 30×400mm column, and the products were separated by using hexane-diethylether-formic acid(80:20:2, v/v) as the mobile phase. The flow rate was 5mL/min and the eluent were obtained by partition elute of 10mL. And then, TLC was analyzed on the plates for the sample prepared by column chromatography.

II −3−2. Amine Value

The total amine value is the number of milligram of potassium hydroxide equivalent to the basicity in 1.0g of sample. In this study, total amine value for the products were determined by A.O.C.S. official method Tf 1b-64.

Experimental procedure as follows:

1. Melt the sample if it is not already liquid, mix throughly, and weigh 0.5g.

2. Add 50mL of isopropyl alcohol, and boil for 1 minute to drive off any free ammonia that may be present. Cool to room temperature.

3. Add 5~10 drop of indicator, and titrate, while swirling the flask, with 0.2N HCl to the yellow endpoint.

$$\text{Total amine value} = (\text{mL} \times \text{N} \times 56.1)/\text{sample weight(g)} \quad \cdots\cdots (1)$$

II −3−3. Infrared Spectra and Proton Nuclear Magnetic Resonance Spectra

Infrared(IR) spectra of the products synthesized by the method of II −3−1, II −3−2, and II −3−3 were recorded on a Bomem Michelson series FT-IR using KBr plate. Proton nuclear magnetic resonance(^{1}H NMR) spectra of the products synthesized by the method of II −3−3 were obtained in $CDCL_3$ on a Gemini 200 MHz ^{1}H-NMR by using TMS as internal standard material.

II −3−4. Elementary analysis

The elementary analysis for the final products was carried out on Carlo Erba Instrument EA 1108-Element analyzer(condition=He : 100mL/min, O_2 : 20mL/min, Temp : 1000℃.

III. RESULTS and DISCUSSION

III −1. Synthesis of the Products

III −1−1. Preparation of Monomethyl Esters of Dicarboxylic Acid

The monomethyl esters of dicarboxylic acid produced by the method of II −3−1 were intermediates for the synthesis of carboxy amido ethylamine. These materials were obstained as white crystalline solid, and their purity was checked by chromatography on silicagel G thinlayer plates(R_f=0.72) using a mixture of chloroform-methanol-water(65:25:4, v/v) as developing solvent. The reaction products were synthesized with the yields of 35~40% and their melting points were 54~60℃.

III −1−2. Synthesis of Carboxy Amido Ethylamine

The products obtained by the method Ⅱ−3−2 were crystallized twice from methanol, and mixed with petroleum ether(3×25mL) for extractibg unreacted methyl ester to give yield of order of 75~80%. Their appearance was white solid and melting points were 72~77°C.

Ⅲ−1−3. Synthesis of N-Acyl Amidoethyl N-Amido Carboxylic Acid

The products obtained by the method Ⅱ−3−3 were purified by repeated crystallization from methanol. N-acyl amidoethyl N-amido carboxylic acid derivatives were obtained in 74~87% yields, and their melting points were 92~115°C. The results of the final products of melting points, appearance and yields are listed in Table 1.

Ⅲ−2. Analysis Results of The Products

Ⅲ−2−1. Chromatography and Amine Value

Thr R_f value of the nine kinds of N-acyl amidoethyl N-amido carboxylic acid derivatives by using hexane-diethylether-formic acid(80:20 :2, v/v) as a developing solvent ranged 0.29~ 0.48, and it was decreased with the increase of acyl group carbon number. The results are listed in Table 1.

The amine value by the method of Ⅱ−3−2 for the final products are listed in Table 1. The results of amine value were within 2.2% those of theoretical values.

Ⅲ−2−2. Infrared Spectra

The Infrared spectra of all the products obtained by method of Ⅱ−2−1, Ⅱ−2−2 and Ⅱ −2−3 were determined by method of Ⅱ−3−3. The results of these compounds are given in Fig. 1~3. The infrared spectra show much complexity, because the products consist of diamide group and long alkyl chain group.

Table 1. Synthetic result of N-acyl amidoethyl N-amido carboxylic acid derivatives

Comp'd	Appearance	Mp.	Yield(%)	$R_f \times 100$	Amine value	
					Calc'd.	Found
LAF	white solid	92~93	82	48	209.0	208.8
PAF	white solid	94~95	80	40	147.5	147.1
SAF	white solid	95~96	82	34	128.2	128.1
LAA	pale yellow solid	97~98	76	47	195.9	196.2
PAA	pale yellow solid	97~98	76	40	143.6	142.9
SAA	pale yellow solid	100~101	74	31	120.2	119.7
LAP	white solid	110~111	84	44	154.8	153.3
PAP	white solid	113~114	86	38	128.2	128.1
SAP	white solid	114~115	87	29	118.2	118.0

Thin layer plate : E. Merck Co.(20×20cm), Silicagel 60G
Developer : hexane-diethylether-formic acid(80:20:2, v/v)

LAF : N-lauroyl amidoethyl N-amido formic acid
PAF : N-palmitoyl amidoethyl N-amido formic acid
SAF : N-stearoyl amidoethyl N-amido formic acid

LAA : N-lauroyl amidoethyl N-amido acetic acid
PAA : N-palmitoyl amidoethyl N-amido acetic acid
SAA : N-stearoyl amidoethyl N-amido acetic acid

LAP : N-lauroyl amidoethyl N-amido propionic acid
PAP : N-palmitoyl amidoethyl N-amido propionic acid
SAP : N-stearoyl amidoethyl N-amido propionic acid

Fig. 1 showed the FT-IR spectra of mono-methylester of succinic acid. The absorption due to stretching vibration of carbonyl group was shown at 1,703cm^{-1}, and stretching vibration of CH$^-$ group was shown at 2,949cm^{-1}.

In Fig. 2 for propionic amido ethylamine, primary amine gave two sharp absorption peaks in the region of 3,380~3,260cm^{-1}. And stretching vibration of carbonyl group was shown at 1,694 cm^{-1}.

In spectrum of Fig. 3 for the final products, N-stearoyl amidoethyl N-amido propionic acid, stretching vibration of alkyl chain was shown at 1,694cm^{-1}, carbonyl group at 1,695cm^{-1}, and primary amine at 3,380~3,250cm^{-1}.

The functional groups of each step products were identified by the IR spectrum and these results were listed in Table 2.

III -2-3. Proton Nuclear Magnetic Resonance Spectra

^{1}H NMR spectra of the products by method of II -3-3 are shown in Fig. 4~5 and Table 3 respectively.

In Fig. 4, the spectrum of the N-lauroyl amidoethyl N-amido formic acid showed characteristic absorption band, a strong band at 1.28 ppm due to the methylene groups of the acyl chain, a triplet at 0.9ppm due to the adjacent methyl group, a chemical shift at 2.7~3.1ppm (4H) of the two methylene groups between the two amide groups. Chemical shift by acid amide (H) appeared at a broad low hump at 8.1ppm.

Table 2. Infrared adsorption bands of N-acyl amidoethyl N-amido carboxylic acid derivatives

Comp'd.	>NH$_2$	C=O	C-N	C-O	-CH$_2$-	-CH$_3$
SA	—	1,705	—	1,200	1,470	—
SAM	—	1,703	—	1,200	1,470	1,308
PAA	3,380~3,260	1,694	1,222	1,205	1,470	—
LAF	3,370~3,250	1,700	1,223	1,200	1,465	1,310
PAF	3,370~3,250	1,700	1,223	1,200	1,465	1,310
SAF	3,375~3,250	1,700	1,223	1,200	1,465	1,310
LAA	3,380~3,260	1,695	1,224	1,205	1,465	1,310
PAA	3,380~3,260	1,695	1,224	1,205	1,465	1,310
SAA	3,380~3,260	1,695	1,224	1,205	1,465	1,310
LAP	3,375~3,250	1,695	1,223	1,200	1,465	1,308
PAP	3,380~3,260	1,695	1,223	1,200	1,465	1,308
SAP	3,380~3,260	1,695	1,223	1,200	1,465	1,308

SA : succinic acid
SAM : succinic acid methylester
PAA : propionic amidoethyl amine

LAF : N-lauroyl amidoethyl N-amido formic acid
PAF : N-palmitoyl amidoethyl N-amido formic acid
SAF : N-stearoyl amidoethyl N-amido formic acid

LAA : N-lauroyl amidoethyl N-amido acetic acid
PAA : N-palmitoyl amidoethyl N-amido acetic acid
SAA : N-stearoyl amidoethyl N-amido acetic acid

LAP : N-lauroyl amidoethyl N-amido propionic acid
PAP : N-palmitoyl amidoethyl N-amido propionic acid
SAP : N-stearoyl amidoethyl N-amido propionic acid

BOMEM
MICHELSON SERIES

sa1.TRANSMITTANCE
Res   : 4.00 cm-1   #Scans : 4

Date : October 6, 1994
Time : 11hr-29min-29se

HO−C−(CH₂)₂−C−O−CH₃

(with O double-bonds above both C)

2949.47

−CH Aliphatic

30.133

1703.08

C=O

CH₃
C−O

% Transmittance

62.21
49.77
37.33
24.88
12.44
0.00

4000.   3360.   2720.   2090.   1440.   800.   CM−1
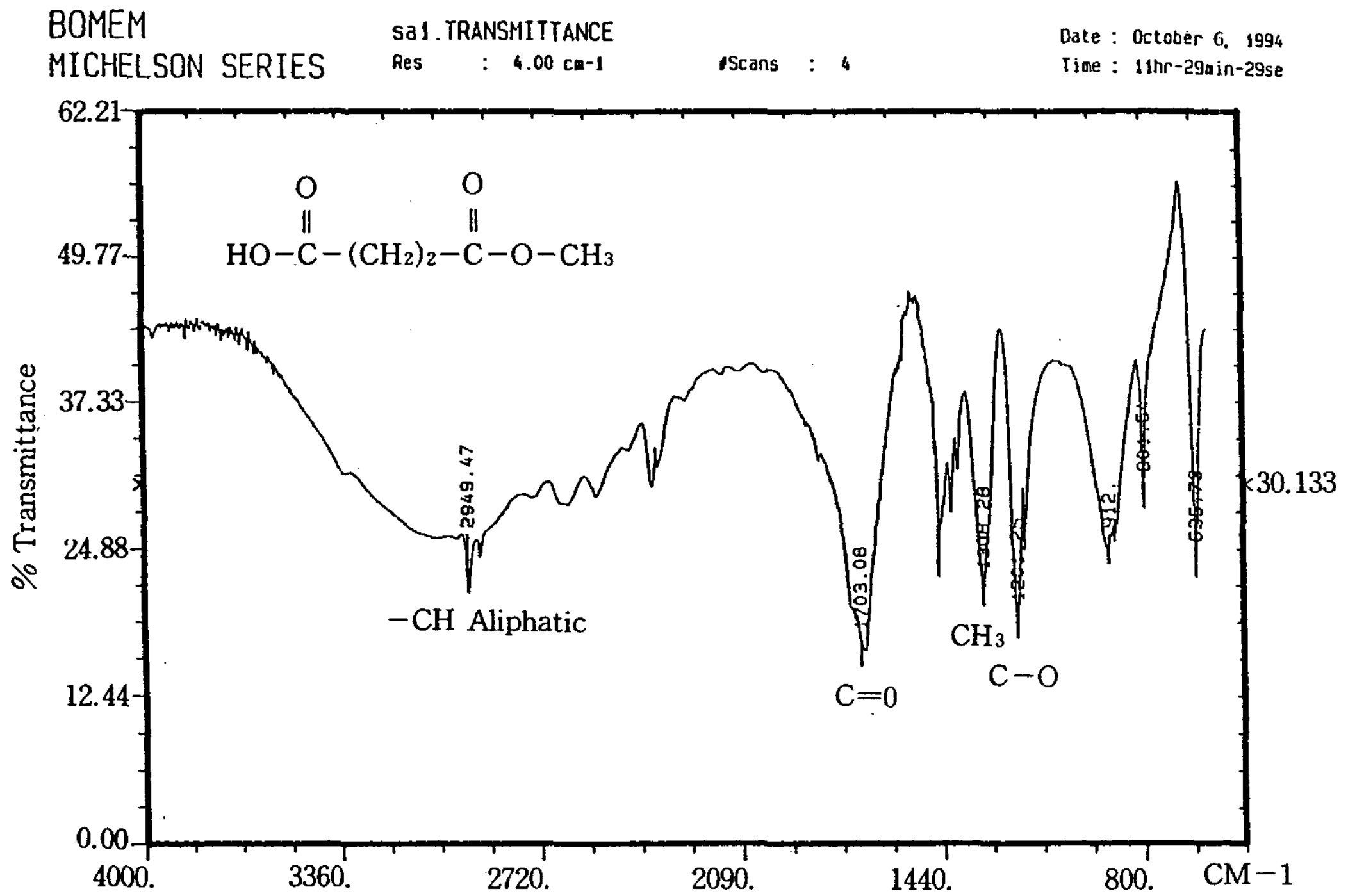
Fig. 1. Infrared spectrum of monoethyl ester of succinic acid.

BOMEM
MICHELSON SERIES

oaea3.TRANSMITTANCE
Res   : 4.00 cm-1   #Scans : 4

Date : October 6, 1994
Time : 12hr-36min-58sec

HO−C−(CH₂)₂−C−N−CH₂−CH₂−NH₂

(with O double-bonds above both C, H above N)

34.378

791.95
947.81
1059.08
1081.85

N−H stretch

−CH Aliphatic

N−H
Bend   C−N

C=O

% Transmittance

70.97
56.78
42.58
28.39
14.19
0.00

4000.   3360.   2720.   2080.   1440.   800.   CM−1
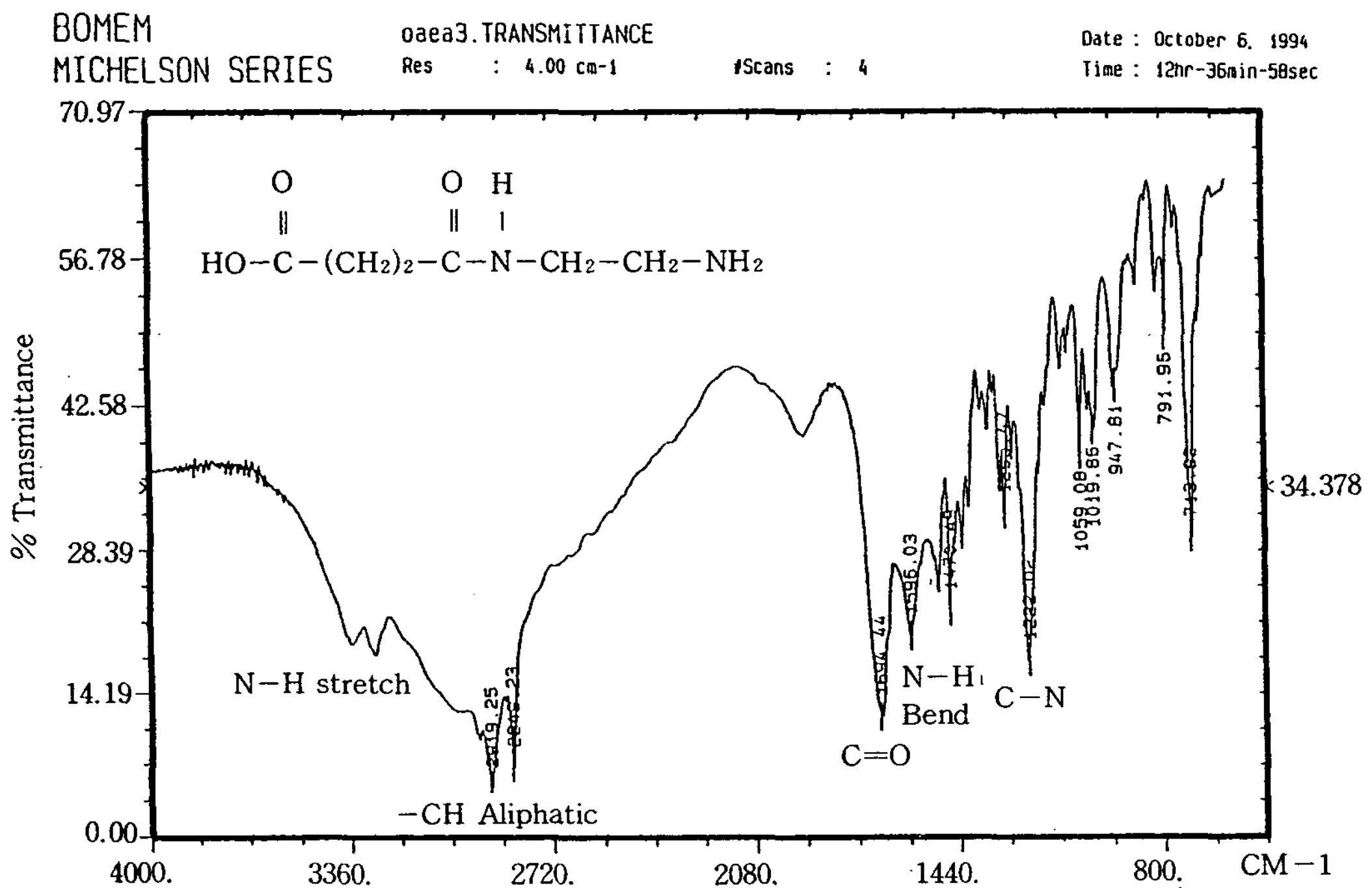
Fig. 2. Infrared spectrum of propionic amido ethylamine.

BOMEM
MICHELSON SERIES
Description: psy

4-1.TRANSMITTANCE
Res　　: 4.00 cm-1　　　　　#Scans　: 4

Date : October 6, 1994
Time : 12hr-44min-54sec

#Peaks =13

O　　　　　O H　　　　　H O
‖　　　　　‖ │　　　　　│ ‖
HO−C−(CH₂)₂−C−N−CH₂−CH₂−N−C−CH₂−(CH₂)₁₄−CH₂−CH₃

N−H stretch

−CH Aliphatic

N−H
Bend CH₃
C=O　　C−N

% Transmittance

66.59
53.27
39.95
26.63
13.32
0.00

4000.　　3360.　　2720.　　2080.　　1440.　　800.　CM−1
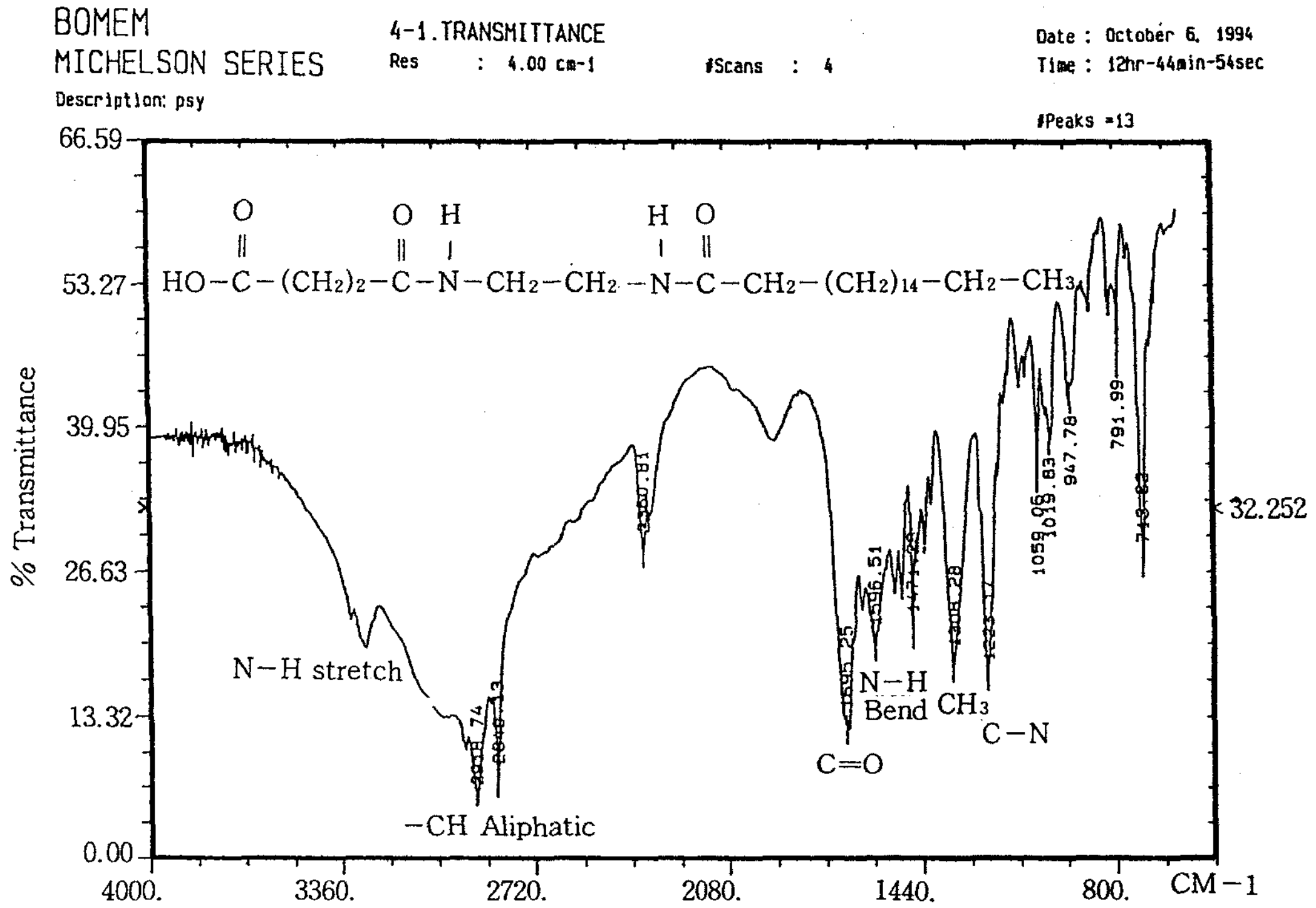
Fig. 3.　Infrared　spectrum　of　N−stearoyl　amidoethyl　N−amido propionic acid.

h　　　　　e
O O H　　　　　H O
‖ ‖ │ g f │ ‖ d c　　　　b　a
HO-C—C-N-CH₂-CH₂-N-C-CH₂-CH₂-(CH₂)₇-CH₂-CH₃

he

b
g f
d　　c　a

9　　8　　7　　6.　　5　　4　　3　　2　　1　　ppm

Fig. 4.　¹H NMR spectra of N−lauroyl amidoethyl N−amido formic acid.

Table 3. Chemical shifts of ^{1}H-NMR spectral characteristics for N-acyl amidoethyl N-amido carboxylic acid derivatives

Comp'd	Group	δ (Chemical shift)	Comp'd	Group	δ (Chemical shift)
	a : CH₃−	0.9(3H)		a : CH₃−	0.9(3H)
	b : −CH₂−(CH₂)₇−	1.3(16H)		b : −CH₂−(CH₂)₁₁−	1.3(24H)
	c : −CH₂−	1.5(2H)		c : −CH₂−	1.6(2H)
	d : −CH₂−	2.4(2H)		d : −CH₂−	2.4(2H)
[I] LAF	e : −NH−	7.9(1H)	[II] PAA	e : −NH−	7.9(1H)
	f : −CH₂−	2.7(2H)		f : −CH₂−	2.9(2H)
	g : −CH₂−	3.1(2H)		g : −CH₂−	3.2(2H)
	h : −NH−	8.1(1H)		h : −NH−	8.2(1H)
	i : −COOH	10.3(1H)		i : −CH₂−	3.5(1H)
				j : −COOH	10.3(1H)

[I]

```
        h                    e
    O   O H              H O
i   ‖   ‖ |   g    f     | ‖   d    c              b    a
HO-C--C-N-CH2-CH2-N-C-CH2-CH2-(CH2)7-CH2-CH3
```

[II]

```
         h                     e
     O   O H               H O
j    ‖   ‖ |  i   ‖  |   g    f   | ‖   d    c              b    a
HO-C-(CH2)-C-N-CH2-CH2-N-C-CH2-CH2-(CH2)11-CH2-CH3
```



```
         h                     e
     O   O H               H O
j    ‖   ‖ |  i   ‖  |   g    f   | ‖   d    c              b    a
HO-C-(CH2)-C-N-CH2-CH2-N-C-CH2-CH2-(CH2)11-CH2-CH3
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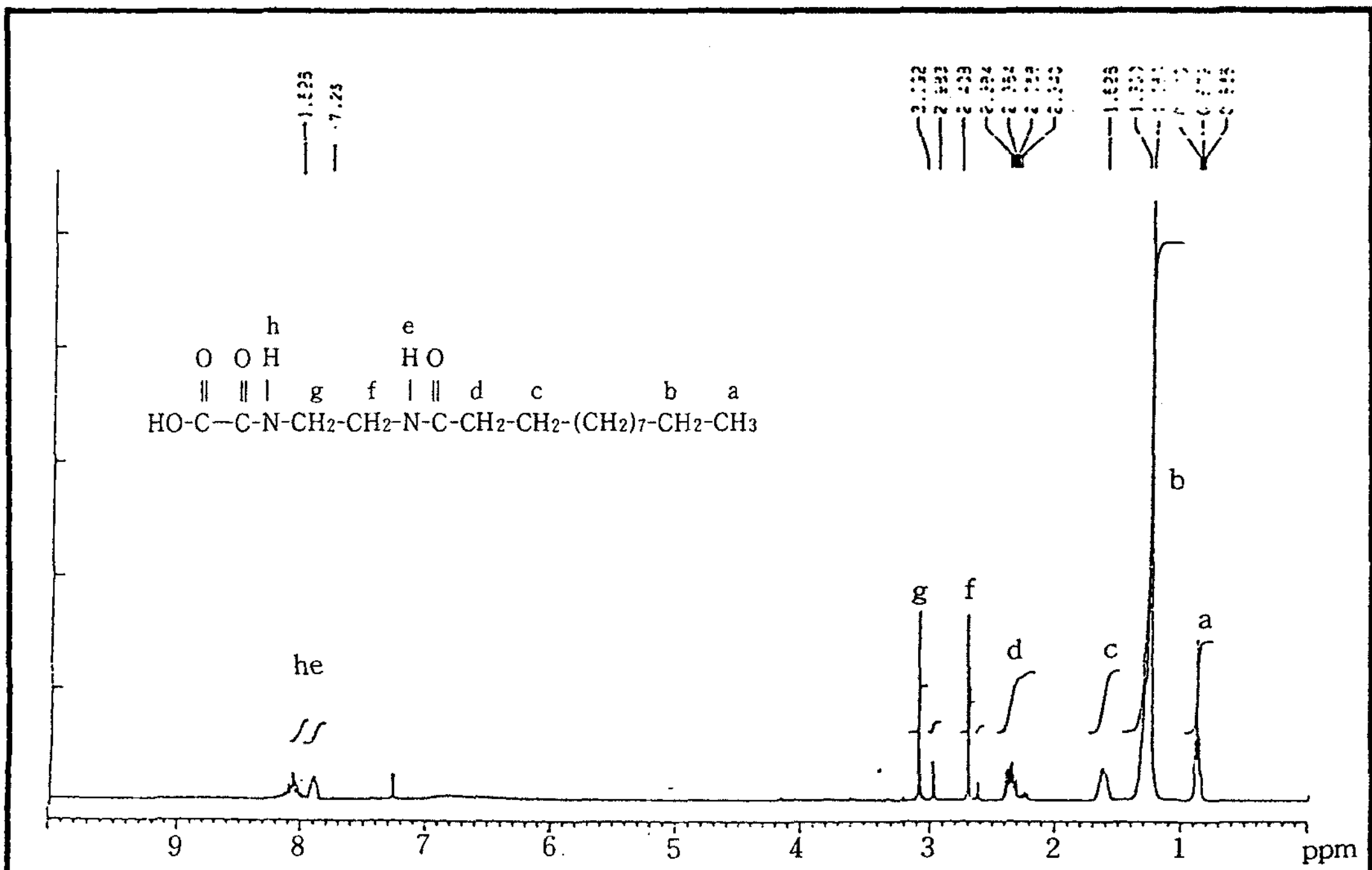
Fig. 5. ^{1}H NMR spectra of N-palmitoyl amidoethyl N-amido acetic acid.

Table 4. Elementary analysis of N-acyl amidoethyl N-amido carboxylic acid derivatives

Comp'd.	Formular	MW	Elementary analysis					
			Found			Calcd.		
			C	H	N	C	H	N
LAF	$C_{16}H_{30}N_2O_3$	298.5	64.3	10.0	9.9	64.5	10.2	9.4
PAF	$C_{20}H_{38}N_2O_3$	354.6	67.9	10.6	8.0	67.7	10.8	7.9
SAF	$C_{22}H_{42}N_2O_3$	382.6	68.9	11.3	7.4	69.1	11.1	7.3
LAA	$C_{17}H_{32}N_2O_3$	312.4	65.6	10.1	8.9	65.4	10.3	8.9
PAA	$C_{21}H_{40}N_2O_3$	368.6	68.5	11.0	7.5	68.4	10.9	7.6
SAA	$C_{23}H_{44}N_2O_3$	396.7	69.4	11.2	7.2	69.6	11.2	7.1
LAP	$C_{18}H_{34}N_2O_3$	326.5	66.3	10.6	8.4	66.2	10.5	8.6
PAP	$C_{22}H_{42}N_2O_3$	382.6	68.9	11.2	7.4	69.1	11.1	7.3
SAP	$C_{24}H_{46}N_2O_3$	410.7	70.1	11.4	6.8	70.2	11.3	6.8

LAF : N-lauroyl amidoetyl N-amido formic acid
PAF : N-palmitoyl amidoethyl N-amido formic acid
SAF : N-stearoyl amidoethyl N-amido formic acid

LAA : N-lauroyl amidoethyl N-amido acetic acid
PAA : N-palmitoyl amidoethyl N-amido acetic acid
SAA : N-stearoyl amidoethyl N-amido acetic acid

LAP : N-lauroyl amidoethyl N-amido propionic acid
PAP : N-palmitoyl amidoethyl N-amido propionic acid
SAP : N-stearoyl amidoethyl N-amido propionic acid

In Fig. 5, the ^1H NMR spectrum of the N-palmitoyl amidoethyl N-amido acetic acid showed one different signal group around 3.5ppm. The chemical shift at 3.5ppm was due to the methylene group(X) between the carboxylic acid and the nearest amide group.

III－2－4. Elementary Analysis

The results of elementary analysis by the method of II－3－4 for the reaction products were listed in Table 4. The elementary analysis for C, H and N was within 1.2% of theoretical values. As the analytical result, it is found that the products were synthesized.·

IV. CONCLUSION

The long chain N-acyl amidoethyl N-amido carboxylic acids were synthesized in with high yields in the present study. All the products were separated and analyzed for their structures. The important results from this study were;

1. The nine kinds of N-acyl amidoethyl N-amido formic acid, N-acyl amidoethyl N-amido acetic acid, and N-acyl amidoethyl N-amido propionic acid derivatives were synthesized with yields of in the range of 74~87%.

2. All the products were separated by means of thin layer chromatography and column chromatography, The results of amine value were within 2.2% those of theoretical values. and the structure of them was identified by FT-IR, ^1H-NMR spectra. The elementary analysis for C, H and N was within 1.2% of theoretical values.

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