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분해성계면활성제에 관한 연구(제1보)

—1, 3-Dioxlane고리를 갖는 분해성계면활성제의 합성—

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Studies on the Destructible Surfactants(1)

—Synthesis of Cleavable Surfactant with Dioxolane Ring—

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요 약

미셀반응, 유화중합, 상간이동촉매반응 등에 이용되는 계면활성제가 갖고 있는 문제점을 해결하기 위하여 반응 후 분해되는 분해성 계면활성제를 합성하였다.

케탈이나 아세탈반응에 의하여 이루워진 1, 3-디옥솔란 고리가 산수용액 중에서 불안정해 쉽게 가수분해로 계면활성을 띠지 않는 분해성 계면활성제를 합성하였다. 합성된 화합물은 백색결정상태로 얻었으며 수율은 90% 이상이었다. 그리고 이 화합물과 중간생성물은 얇은막 크로마토그래피와 컬럼 크로마토그래피로 분리하여 적외선과 수소핵자기공명 및 원소분석 스텍트라로 그 화합물들의 구조를 확인하였다.

I. INTRODUCTION

Surfactants are useful for micellar reaction, emulsion polymerization, phase-transfer reaction and other organic synthesis.[1~8] Because of troublesome emulsion formed by surfactants, however, we have frequently been confronted with the difficulty of separating desired products from the emulsions.[1~5] So the isolation of the desired products has traditionally been carried out by the addition of an appropriate metal salts.[1~3] For example, in polymerization process in the presence of surfactants, for the purpose of breaking the emulsion, metal salt such as calcium or magnesium salt has been added after the completion of the polymerization.[2~5] But this procedure often debases the water-resistance and electrical insulation of the resultant polymer.[1~5]

An alternative approch involves the use of cleavable surfactants that can be converted to surface-inactive products at the end of the reaction.[1~6] And these cleavable surfactants have come to interest about 15 years ago. The type of cleavable surfactants are disulfide link compounds, silicon-oxygen bonding compounds and 1,

3-dioxolane ring compounds which are studied in recent years in advanced nations. Their 3-type cleavable surfactants are degraded in respectively conditions.[1~11]

Silicon-oxygen bond compounds[9] and disulfide link compounds[10] have been synthesized and found to be effective as catalysts, emulsifiers, or solubilizers, but these were obtained only by the use of the complicated synthesis paths and the special reagents.[2, 3] These problems limit the use of the surfactants. But without special apparatuses and reagents, cleavable surfactant having 1, 3-dioxolane ring was expected the solution of the problems.

In this study, it was synthesized under ketalization that cleavable surfactant has 1, 3-dioxolane ring and is easily cleaved to ketone and diol in acid condition. And this surfactant and intermediates were separated through thin layer chromatography and column chromatography and their molecular strucures were confirmed from IR, ^1H-NMR and elementary analysis spectra.

Ⅱ. EXPERIMENTAL METHODS

1. Materials

Dodecanoic acid and oxamic acid ethyl ester were purchased from Tokyo Kasei Organic Chemicals. Glycidol was purchased Aldirich Co. And the special or analytical grade solvent and other reagents were used.

2. Experimental Apparatus and Instruments

In this study, rota mentle was used in heating and megnetic stirring for all reactions. The other apparatus are described in each step reaction.

Silica gel G plates(20×20cm) from E. Merck Co., were used in thin layer chromatography and melting point was given by Electrothermal Cat. No. 1A 9100. And infrared spectra, proton nuclear magnetic resonance spectra and elementary analysis were obtained by Bomem Michelson series FT-IR, Gemini 300MHz FT-NMR and Carlo Erba Instrument EA 110 respectively.

3. Synthesis of 2′, 3′-Dihydroxy propyl dodecanate(monolaurin)

In a 500mL, four-necked, round-bottom flask fitted Liebig's condenser, dropping funnel, thermometer and N_2 gas tube, dodecanoic acid(30g, 0.15mol) and tetraethylammonium iodide(0.3g, 0.01mol) were dissolved in toluene(250mL). Under the N_2 gas, glycidol(11.1g, 0.15mol) was gradually added in the solution for 20min and the solution was kept with stirring at 86~88℃ for about 1hour.[12, 13] In this time, it was identified through thin-layer-chromatography that the reaction was terminated. Then the solvent was distilled off under reduced pressure and the reaction product was extracted with diethylether.

4. Synthesis of 2-Amido-2-ethyl carboxylate-4-methyl dodecanate-1, 3-dioxolane

In a 300mL, four-necked, round-botton flask fitted Dean-Stark receiver, thermometer and a tube to a tube to induce N_2 gas, monolaurin(2.8g, 10mmol), oxamic acid ethyl ester(1.17g, 10 mmol) and *p*-toluene sulfonic acid(0.1g, 0.5 mmol) were dissolved in toluene(40mL). The solution was refluxed with stirring for 2 hours. Then the solvent was evaporated at reduced pressure, and the residue was partitioned between chloroform(50mL) and 5% sodium carbonate aqueous solution(30mL). The organic layer was washed with distilled water(30mL) and saturated sodium chloride solution(30mL) in that order and dried by using magnesium sulfate. The solvent being evaporated under the reduce pressure, the reaction product was obtained.

5. Synthesis of Sodium 2-amido-2-carboxylate-4-methyl dodecanate-1, 3-dioxolane

In a 300mL, two-necked, round-bottom flask fitted Liebig's condenser, dropping funnel and thermometer 2-amido-2-ethyl carboxylate-4-methyl dodecanate-1, 3-dioxolane(5.6g, 15mmol) was dissoloved in methanol(30mL) then sodium hydroxide(0.6g, 15mmol)-methanol solution(10mL) was gradually added in the solution for 10min. The solution was stirred at 60~62℃ for 30min. After the solvent was evaporated, the final product was obtained.

6. Separation and Analysis

1) Chromatography

The products prepared by the methods of Ⅱ-3 and Ⅱ-4 were purified through column chromatography. First of all, silica gel 60G(Merck Co.) as the stationary phase was added to 300mm in 30×40mm column, and the products were separated by using chlorofrom-acetic acid-toluene(94:4:0.5 v/v)[12, 13] and toluene-ethanol(50:50 v/v) as mobile phases respectively. The rate of flow was about 3mL/min and eluent was parted every 3 minutes.

Meanwhile, thin layer chromatography was used in order to analyze the sample prepared by column chromatography step by step on the plate from E. Merck Co.(20×20).

The sample was dipped at the narrow end of the microsyringe into the solution of chemicals separated. The solution will be down into the capillary by capillary action. Touching the tip of the syringe to the absorbent on the thin-layer plate 25mm from the lower end in such a manner as to leave the adsorbent undisturbed, and the plate was dried and developed in the development vessel.

After the plate was dried to warm air, the spots were identified by using iodide vapor. the ratio of front(R_f) was calculated from those spots.

2) Infrared Spectra(IR)

Infrared spectra of products prepared by Ⅱ-3~Ⅱ-5 were recorded on a Bome Bomem Michelson series FT-IR using KBr plate.

3) Proton Nuclear Magnetic Resonance Spectra(^{1}H NMR)

Proton nuclear magnetic resonance spectra of products were obtained in $CDCl_3$ on a Gemini 300MHz FT-NMR by using TMS as internal standard material.

4) Elementary Analysis

The results of elementary analysis for reaction products were furnished by using Carlo Erba Instrument EA 1108(He : 100mL/min., O_2 : 29mL/min., Temp. : 1000℃) and were recorded on.

Ⅲ. RESULTS AND DISCUSSION

1. Synthesis of 2′, 3′-Dihydroxy propyl dodecanate

According to Kang's study,[13] 2′, 3′-Dihydroxy propyl dodecanate is obtained. The molecular of the product has two hydroxy group so that it has been preparated with oxamic acid ethyl ester for ketalization.

And the results of melting point, appearance and yield were listed in Table 1.

2. Synthesis of 2-Amido-2-ethyl carboxylate-4-methyl dodecanate-1, 3-dioxolane

As the ketalization, the carbonyl group of Oxamic acid ethyl ester and the two hydroxy groups of 2′, 3′-dihydroxy propyl dodecanate are reacted. The product which is obtained by the reaction has a 1, 3-dioxalane ring group so that it has decomposition property in acid condition. Accordingly, this reaction product is intermediate for cleavable surfactant.

And the results of melting point, appearance and yield were listed in Table 1.

3. Synthesis of Sodium 2-amido-2-carboxyl-

Table 1. Physical properties and yield of reaction products

Compound	Formular	Appearance	M. w.	M. p. (℃)	Yeild(%)
A	$C_{15}H_{30}O_4$	White solid	274.4	63~65	95
B	$C_{19}H_{35}NO_6$	White solid	359.5	73~75	90
C	$C_{17}H_{30}NO_6Na$	White solid	353.4	−	99

A : 2′, 3′−dihydroxy propyl dodecanate(Monolaurin)
B : 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane
C : Sodium 2−amido−2−carboxylate−4−methyl dodecanate−1, 3−dioxolane
** Instrument of Elementary Analysis : Carlo Erba Instrument EA 110 **

ate−4−methyl dodecanate−1, 3−dioxolane

This reaction is trans−esterification that ethyl group is substuted to sodium. The product has a hydrophilic property, because it is sodium salt. Accordingly, the product has hydrophilic group of soap and hydrophobilc group of alkyl group from fatty acid. And the molecular of the product has a 1, 3−dioxalane ring group so that it has decomposition property in acid condition. This is, the product is cleavable surfactant as final product.

And the results of appearance and yield was listed in Table 1.

4. Separation and Analysis

1) Chromatography

The analysis by TLC of monolaurin was reported by Zlatanos[12] and Kang.[13] So these studies were quoted in synthesis of monolaurin. But trial and error method is used in synthesis of 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane. The results are listed in Table 2.

Table 2. Results of thin layer chromatography

Compound	Developer(v/v)	$R_f \times 100$
A	$CHCl_3 : CH_3COCH_3 : CH_3COOH$ (96 : 4 : 0.5, v/v)	12
B	$CH_3C_6H_5 : CH_3CH_2OH$ (50 : 50, v/v)	66

A : 2′, 3′−dihydroxy propyl dodecanate
B : 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane
Detection : UV light(254, 365nm) and I_2 vapor

2) Infrared Spectra(IR)

The infrared spectra, of products synthesized by Ⅱ−3, Ⅱ−4 and Ⅱ−5 methods, were illustrated in Fig. 1~3. In case of 2′, 3′−dihydroxy propyl dodecanate, carbonyl stretching was shown at 1733cm^{-1}, hydroxy stretching at 3289cm^{-1}, alkyl stretching at 2920cm^{-1} and bending at 1469cm^{-1}, and primary and secondary alcohol respectively at 1104 and 1047cm^{-1}. In secondary case of 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane, carbonyl stretching was shown at 1733cm^{-1}, primary amine at 3380 and 3216cm^{-1}, alkyl stretching at 2920cm^{-1} and bending at 1403cm^{-1}, and ether 1118cm^{-1}. Finally, in case of synthesis of sodium 2−amido−2−carboxylate−4−methyl dodecanate−1, 3−dioxolane, car-

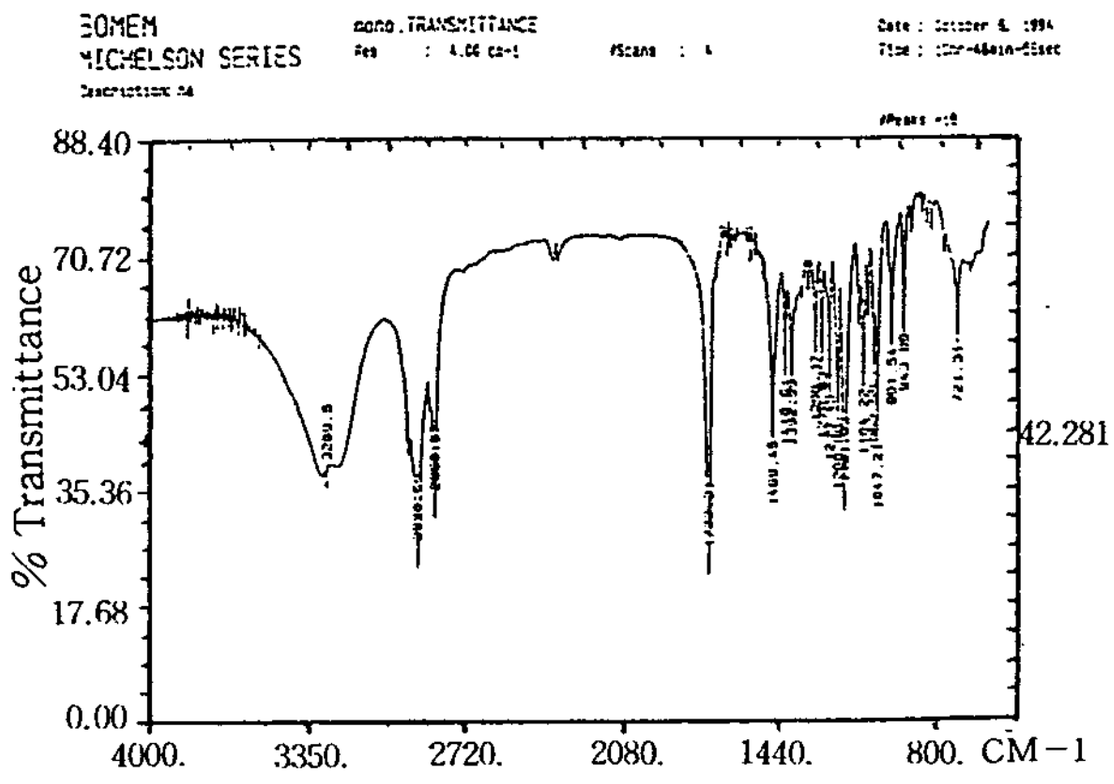

Fig. 1. Infrared spectrum of 2′, 3′−dihydroxy propyl dodecanate.

Table 3. Infrared spectra of reaction products

(cm^{-1})

Comp'd	−OH	CH(asy)	$-NH_2$	>C=O	>C=O(salt)	1°−OH	2°−OH	−CO−
A	3289	2920	−	1733	−	1104	1047	−
B	−	2920	3380~3216	1733	−	−	−	1118
C	−	2980	3381~3216	1738	1678	−	−	1117

A : 2′, 3′−dihydroxy propyl dodecanate(Monolaurin)
B : 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane
C : Sodium 2−amido−2−carboxylate−4−methyl dodecanate−1, 3−dioxolane
** Instrument of Infrared Spectrum : Bomem Michelson Series FT−IR **

bonyl stretchings were shown at 1738 and 1678 cm^{-1}, primary amine at 3381 and 3216cm^{-1}, alkyl stretching at 2980cm^{-1} and bending at 1401cm^{-1}, and ether 1117cm^{-1}. And Table 3 was recorded the results of products.

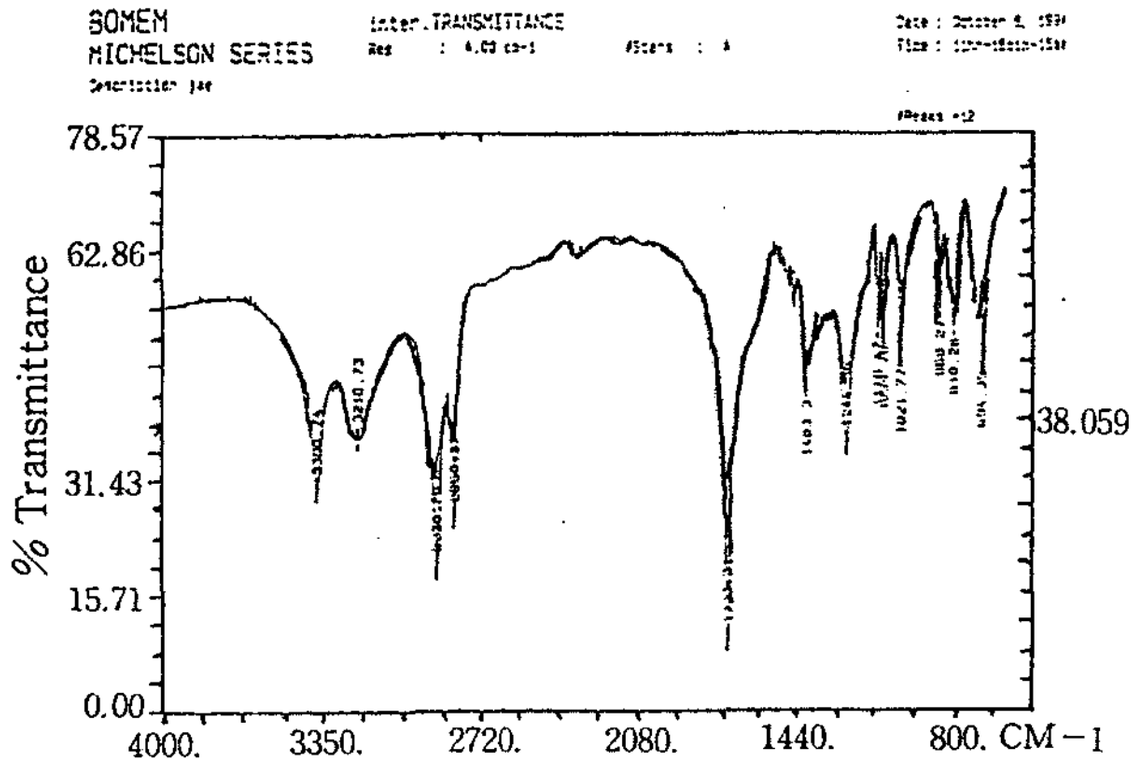

Fig. 2. Infrared spectrum of 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane.

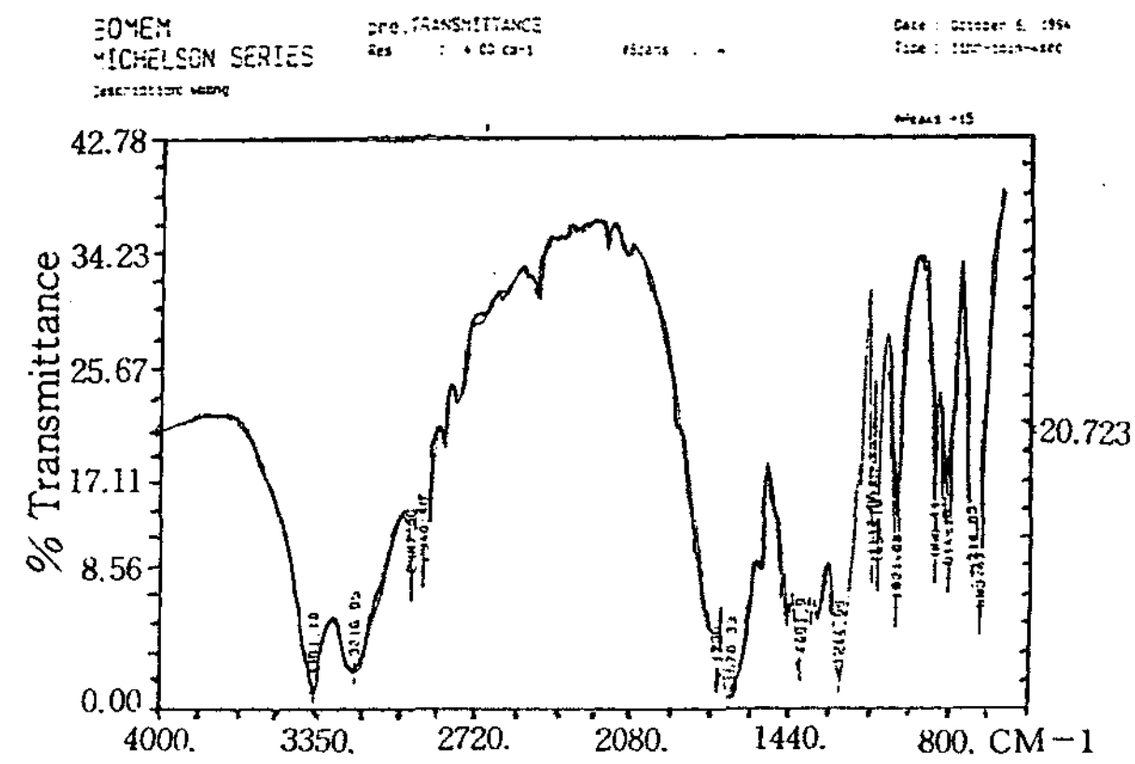

Fig. 3. Infrared spectrum of sodium 2−amido−2−carboxylate−4−methyl dodecanate−1, 3−dioxolane.

Therefore, identifying for structure of step products by infrared spectrum was posibility.

3) Proton Nuclear Magnetic Resonance Spectra(^1H NMR)

The Proton nuclear magnetic resonance spectra(^1H NMR) of oxamic acid ethylester, 2′, 3′−dihydroxy propyl dodecanate and 2−amido−2−ethyl carboxylate −4−methyl dodecanate−1, 3−dioxolane were illustrated in Fig. 4~6.

^1H NMR spectrum interpretations of the compounds were represented in Table 4. Therefore the ratios of chemical shift intensity for all the products were known for distribution of pro-

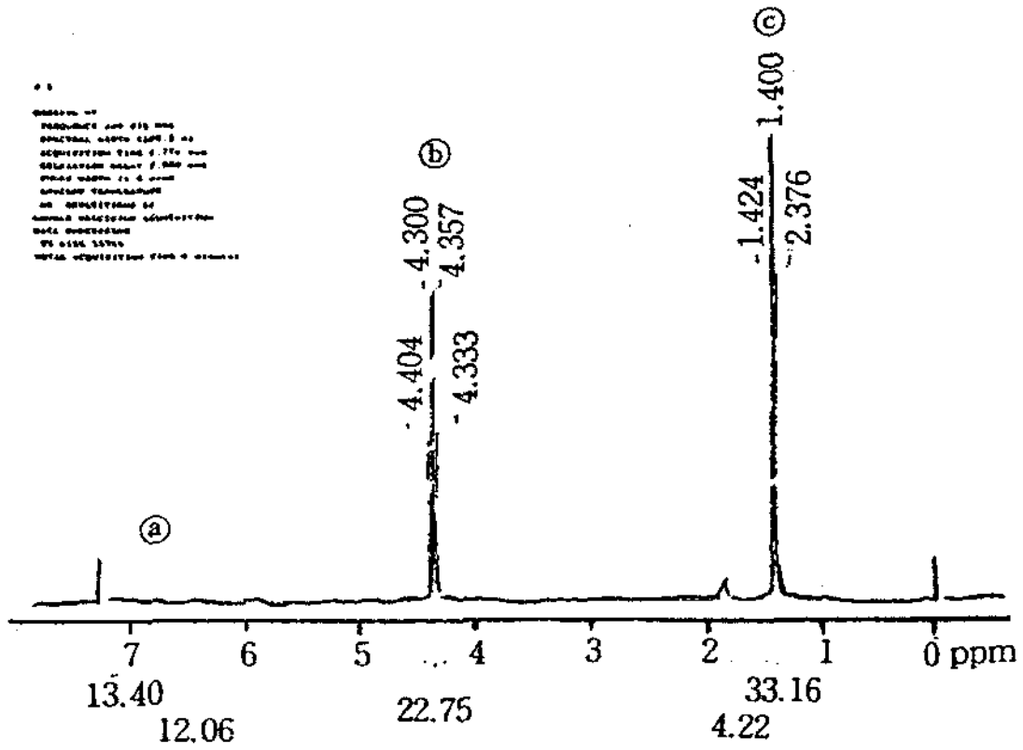

Fig. 4. ^1H−NMR spectrum of oxamic acid ethyl ester.

$$NH_2-\overset{\overset{O}{\|}}{C}-COO-\underset{ⓑ}{CH_2}-\underset{ⓒ}{CH_3}$$
ⓐ

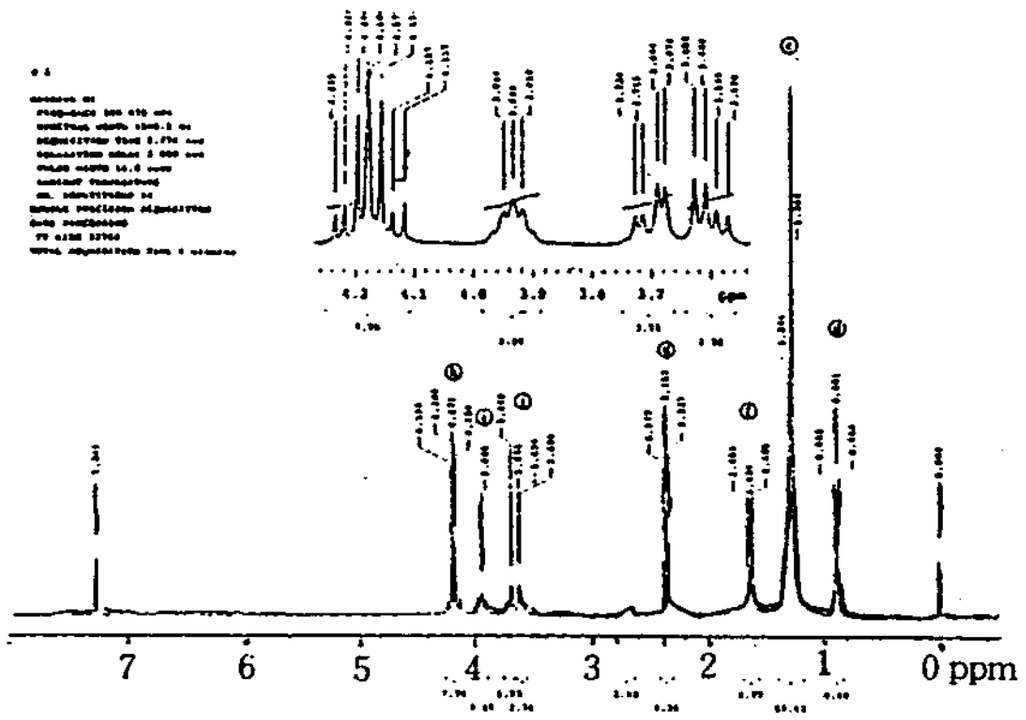

Fig. 5. ^{1}H−NMR spectrum of 2′, 3′−dihydroxy propyl dodecanate.

ⓓ ⓔ ⓕ ⓖ ⓗ ⓘ ⓙ

$CH_3-(CH_2)_8-CH_2-CH_2-COO-CH_2-CH-CH_2$

OH OH

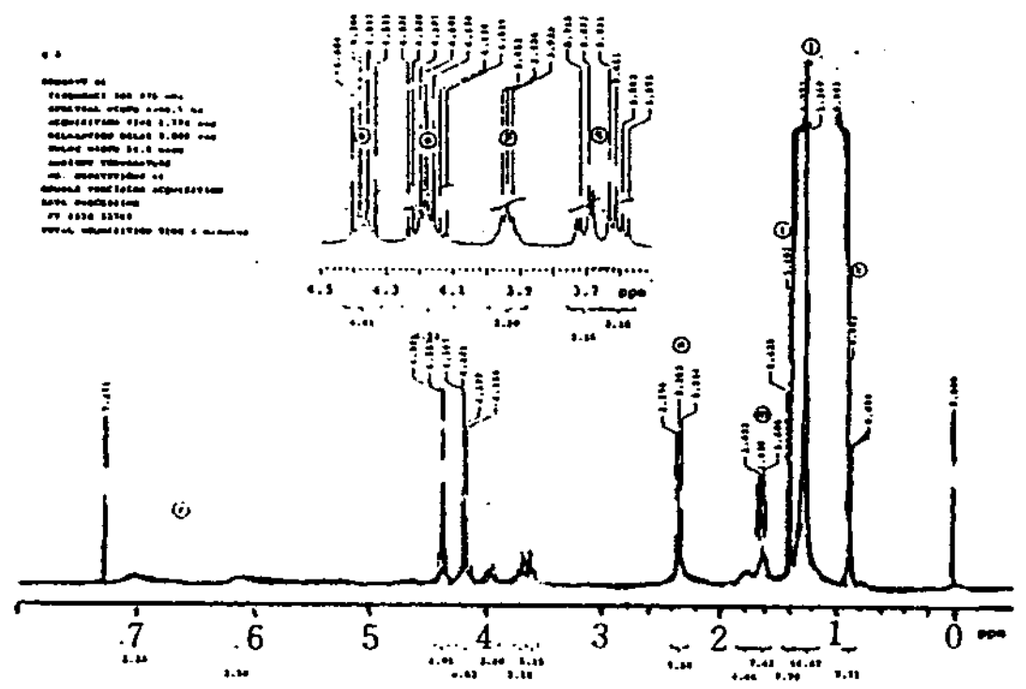

Fig. 6. ^{1}H−NMR spectrum of 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane.

ⓚ ⓛ ⓜ ⓝ

$CH_3-(CH_2)_8-CH_2-CH_2-COO-$

ⓞ ⓟ ⓠ

$CH_2-CH-CH_2$

O O

$NH_2-C-COO-CH_2-CH_3$

ⓡ ⓢ ⓣ

ton number in each reacted products, which idensities of ^{1}H NMR signals can be identified for the desired compounds.

4) Elementary Analysis

Table 4. ^{1}H−NMR Spectra of Reaction Products

Comp'd	δ (Chemical Shift)
A	1.40(t, 3H), 4.38(qd, 2H), 6.59(s, 1H), 7.02(s, 1H)
B	0.88(t, 3H), 1.26~1.28(m, 16H), 1.63(t, 2H), 2.35(t, 2H), 3.60(qu, 1H), 3.71(qu, 1H), 3.94(q, 1H), 4.18(o, 2H)
C	0.88(t, 3H), 1.26~1.28(m, 16H), 1.40(t, 3H), 1.63(t, 2H), 2.35(t, 2H), 3.61(qu, 1H), 3.69(qu, 1H), 3.94(q, 1H), 4.18(o, 2H), 6.58(s, 1H), 7.05(s, 1H)

s : singlet t : triplet qu : quartet q : quintet
o : octalet m : mutiplet
A : Oxamic acid ethyl ester
B : 2′, 3′−dihydroxy propyl dodecanate(Monolaurin)
C : 2−amido−2−ethyl carboxylate−4−methyl dodecanate−1, 3−dioxolane
** Insrument of ^{1}H−NMR Spetrum : GEMINI 300MHz FT−NMR **

The results of elementary analysis for reaction products were recorded Table 5. And it were the differences of found values and calculated values that were not about a lot of.

Ⅳ. CONCLUSION

In this study, sodium 2−amido−2−carboxylate −4−methyl dodecanate−1, 3−dioxolane of the cleavable sufactant was synthesized with high yield. The important results of this study is followed as:

1. Sodium 2−amido−2−carboxylate−4−methyl dodecanate−1, 3−dioxolane and it's intermendiates were could be synthesized with a high yield of about 90~99%.

2. They were separated through thin layer chromatography and column chromatography and their molecular structures were confirmed from IR, ^{1}H−NMR and elementary analysis spectra.

Ⅴ. ABSTRACT

Table 5. Elementary Analysis of Reaction Product

Comp'd	Formular	MW	Elemetary Analysis					
			Found			Calcd.		
			C	H	N	C	H	N
A	$C_{15}H_{30}O_4$	274.4	65.4	11.2	–	65.6	10.9	–
B	$C_{19}H_{35}NO_6$	359.5	63.7	9.68	3.93	63.4	9.74	3.89
C	$C_{17}H_{30}NO_6Na$	353.4	57.8	8.47	4.02	57.7	8.49	3.96

A : 2′, 3′–dihydroxy propyl dodecanate
B : 2–amido–2–ethyl carboxylate–4–methyl dodecanate–1, 3–dioxolane
C : Sodium 2–amido–2–carboxylate–4–methyl dodecanate–1, 3–dioxolane
** Instrument of Elementary Analysis : Carlo Erba Instrument EA 1108 **

As the surfactants that were used in micellar reaction, emulsion polymerization and phase–transfer reaction etc. have the problems, the cleavable surfactant that was converted to inactive compound after such as the reaction was synthesized to above 90% yield. And this surfactant and intermediates were separated through thin layer chromatography and column chromatatography and their molecular structures were confirmed from IR, ^{1}H–NMR and elementary analysis spectra. And its surface–active properties and acid hydrolysis will be serialized in Ⅱ.

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