

คอเลสเตรอลเอสเทอร์สำหรับการเกิดฟิล์มรูพรุน



นายจิรพจน์ อโณทัย

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

**CHOLESTERYL ESTERS FOR POROUS FILM FORMING**



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for the Degree of Master of Science in Petrochemistry and Polymer Science**

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สารคอเลสเตริลเอสเทอร์สังเคราะห์ได้จากปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของเมธิลเอสเทอร์ของกรดไขมันจากน้ำมันมะพร้าวกับคอเลสเตรอล โดยใช้กรดพาราโทลูอินซัลโฟนเป็นตัวเร่งปฏิกิริยา สภาวะที่เหมาะสมสำหรับปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของน้ำมันมะพร้าวกับเมทานอลคือที่ 65 องศาเซลเซียส เป็นเวลา 4 ชั่วโมง สภาวะที่เหมาะสมของปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของเมธิลเอสเทอร์ของกรดไขมันกับคอเลสเตรอลคือที่ 69 องศาเซลเซียส เป็นเวลา 6 ชั่วโมง อัตราส่วนของคอเลสเตรอลต่อเมธิลเอสเทอร์ของกรดไขมันเป็น 3 ต่อ 33.27 โดยน้ำหนัก ศึกษาสภาวะทรานส์ชันของสารสังเคราะห์คอเลสเตริลเอสเทอร์ซึ่งแสดงสมบัติการเป็นผลึกเหลวด้วย DSC ศึกษาโครงสร้างของคอเลสเตริลเอสเทอร์ด้วย FT-IR, GC-MS และ <sup>13</sup>C-NMR คอเลสเตริลเอสเทอร์ที่ได้ถูกกระจายตัวในพอลิเอธิลีนเพื่อเตรียมผลึกเหลว-พอลิเอธิลีนคอมโพสิต หลังจากนั้นสกัดเอาส่วนที่เป็นคอเลสเตริลเอสเทอร์ออกด้วยเฮกเซนทำให้เกิดฟิล์มรูพรุน ตรวจจสอบฟิล์มรูพรุนด้วย SEM ซึ่งแสดงถึงหลุมซึ่งมีขนาดประมาณ 5 ไมโครเมตร บนฟิล์มของพอลิเอธิลีน



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จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์  
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The cholesteryl esters were synthesized from trans-esterification reaction of coconut oil fatty acid methyl esters (FAMES) with cholesterol using *p*-toluenesulfonic acid as a catalyst. The optimum condition of trans-esterification reaction of coconut oil with methanol was at 65 °C for 4 hours. The optimum condition of trans-esterification reaction of FAMES with cholesterol was at 69 °C for 6 hours with the 3:33.27 by weight ratio of cholesterol to FAMES. The synthesized cholesteryl esters, which exhibit liquid crystal property, were characterized for phase transition by DSC. Their structures were identified by FT-IR, GC-MS and <sup>13</sup>C-NMR. The obtained cholesteryl esters were dispersed in polyethylene, to form a liquid crystal-polyethylene composite. After that, the composite was extracted with hexane to remove the cholesteryl esters resulted in the formation of a porous film. The porous film was examined by SEM which indicated holes of about 5 μm on polyethylene film.

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## ABBREVIATIONS

°C	=	Celcius degree
ml	=	milliliter
g	=	gram
ppm	=	part per million
%	=	percent
% w/v	=	percent weight by volume
cm <sup>-1</sup>	=	wavenumber unit
% wt	=	percent by weight
cm	=	centimetre
FAMEs	=	Fatty acid methyl esters
DSC	=	Differential scanning calorimeter
SEM	=	Scanning electron microscope
FT-IR	=	Fourier transform-infrared spectroscopy
GC-MS	=	Gas chromatography – Mass spectroscopy
TLC	=	Thin layer chromatography
DCC	=	Dicyclohexylcarbodiimide
DMAP	=	Dimethylaminopyridine
PDLC	=	Polymer dispersed liquid crystal

# CHAPTER I

## INTRODUCTION

### *1.1 GENERAL*

Since the discovery of many of organic compounds, liquid crystal can be formed with suitable conditions. They play a very important role in many applications. Liquid crystals are a versatile material that can be used in electronic industrial equipments [1-2] such as temperature sensor, radiation sensor, trace vapor indicator, electrical display devices, pressure sensor, etc. As a result, there is a change in color when the temperature has changed or there is a change of molecular aspects when it is applied to an electric or magnetic field. In addition, it can be used in petrochemistry as a lubricating additive in the gearbox of an engine [3]. Furthermore, in the polymer industry [4], liquid crystal can be in a main chain or side-chain of a polymer and is defined as a liquid crystal polymer.

Natural fats and oils from vegetables and animals are mainly used for human nutrition. However, fats and oils are also used as materials in many branches of industry. In this connection, the technological utility of these products depends on the particular properties of the fats and oils.

As a result, coconut oil has been defined chemically as the esters of fatty acids with glycerol. The fatty acid esters of cholesterol are one of the organic components that have been found to exhibit liquid crystalline properties. Coconut oil was chosen

as the raw material for synthesizing cholesteryl derivatives by a trans-esterification reaction to transform esters of glycerol to esters of cholesterol. It is the objective of this research to prepare the ester of cholesterol from coconut oil and to apply it in the formation of porous film.

### ***1.2 Objectives***

1. To isolate and characterize liquid crystal from coconut oil.
2. To synthesize cholesteryl esters from coconut oil.
3. To prepare the porous film from liquid crystal-polymer composite.

### ***1.3 The scope of the investigations***

For the preparation of cholesteryl esters from coconut oil, the appropriate conditions were studied. The application of liquid crystals in liquid crystal-polymer composite was studied, yielding the porous film after being passed through the extraction process.

The necessary procedures are as follows:

1. Literature surveys for an in-dept study of the work.
2. Isolation and characterization of the composition of coconut oil, which was obtained through a red spot on TLC when spraying with a solution of 5% w/v phosphotungstic acid in 95% ethanol and then heating the plate.
3. Preparation of the cholesteryl esters from coconut oil by the following method.



- a) Trans-esterification of coconut oil by excess methanol using *p*-toluenesulfonic acid as a catalyst at 65 °C for various times.
  - b) Re-Trans-esterification of the fatty acid methyl esters from step a) with cholesterol and *p*-toluenesulfonic acid at about 69 and 110 °C.
  - c) Investigation of the optimum condition of trans-esterification reaction.
4. Characterization of fatty acid methyl esters and cholesteryl esters by FT-IR, <sup>13</sup>C-NMR, GC-MS, and DSC.
  5. Preparation of porous film by formation of liquid crystal-polymer composite from mixture of the cholesteryl esters with polyethylene follow by solvent extraction.
  6. Characterization of pore distribution in the porous film by SEM.
  7. Summary of the results.

## CHAPTER II

### THEORETICAL CONSIDERATION

#### 2.1 Fats and fatty oils

Fats and fatty oils constitute a well-defined class of neutral and water insoluble substances that are produced in some quantity by plants and animals [5]. They consist of triglycerides or glycerol esters and both saturated and unsaturated high molecular or long chain aliphatic acids. In general, they become progressively higher in melting point and easily solidify while the average molecular weight of the fatty acids increases and their average of unsaturation decreases. So, they may be liquid (oils) or solid (fats) at room temperature and become liquid at high temperatures.

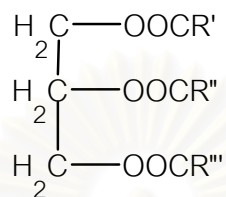
The main uses of fats and fatty oils are: (a) for food, (b) soap as a source of fatty acids, (c) paints and protective coating, and (d) industrial applications.

##### *2.1.1 Composition and properties*

A great majority of commercial oils, fats and fatty oils are composed with esters in the glyceride form (Scheme I) and a non-ester portion, which is usually less than 2% by weight. The non-ester portion may contain sterols, hydrocarbons, aliphatic alcohols, free fatty acids, and other organic compounds. Ordinarily, it consists mostly of sterols. A few oils contain ether components as part of the glyceride molecule, e.g., certain fish liver oils.

The ester portion is a complex mixture of glycerides, which are composed of several different major fatty acids and others in smaller amounts.

Scheme I



Whereas R', R'', R''' represent the hydrocarbon chain of fatty acid radicals.

Natural fats and fatty oils have similar properties to esters of high molecular weight, i.e., they are essentially neutral, relatively inert, and have very low volatility. They are soluble in most organic solvents, but insoluble in water. Some characteristic of commercial fats and fatty oils are given in Table I.

Table I Characteristic of commercial fats and fatty oils

Fats or oils	Iodine value	Saponification value	Freezing point of fatty acids, °C
Coconut	7-10	255-260	20-22
Palm	51-58	196-210	36-45
Olive	79-88	188-195	17-21
Peanut	82-99	188-196	23-29
Castor	82-90	177-187	3
Rape	97-107	168-178	12-18

Table I (continued)

Fats or oils	Iodine value	Saponification value	Freezing point of fatty acids, °C
Cottonseed	103-113	192-196	33-38
Corn	103-125	188-193	21-24
Sunflower	120-140	186-194	17-20
Soybean	125-145	189-195	15-21
Linseed	175-195	189-196	31-37
Beef tallow	32-47	190-200	41-47

Since the alcohol moiety in all common fats and oils is glycerol, the difference in chemical and physical properties of the glycerides depend on the nature of the fatty acid moiety. Fatty acids are classified mainly by chain length and degree of unsaturation. By chain length, the fatty acids are divided as short-chains (C4-C8), medium-chains (C10-C14), and long-chains (C16 and longer). The melting point and the boiling point of the fatty acids and their glycerides rises when chain length increases.

Fatty acids are classified by the degree of unsaturation as saturated types, monounsaturated types, and polyunsaturated types. The melting point of the fatty acids and their glycerides decrease from saturated to polyunsaturated types, whereas the volatility and boiling points change only slightly.

Fats and oils are freely miscible with most organic solvents at temperatures above their melting point. In controversy, fats are very slightly soluble in organic solvents at temperatures below their melting point. Generally, the relationship between solubility and temperature is linear.

### *2.1.2 Extraction and refining*

Extraction of oil from vegetable materials in which they occur is accomplished by pressing or solvent extraction [6]. Both processes are widely used. Prior to extraction by pressing, vegetable seeds must be ground finely. The ground material is adjusted to certain moisture content and warmed or cooked in a steam-jacketed vessel. It is then fed to the press. For solvent extraction the seeds are ground in such a way as to produce the flakes rather than very fine particles. The flaked material is then extracted in suitable equipment by means of a low boiling point solvent, usually a petroleum fraction.

The crude oil from either process is allowed to settle and is then filtered to remove solid material such as phospholipids. Refining of the oil is carried out to remove other colloidal matter, free fatty acid, and colored impurities. A number of processes are employed for this purpose, including treatment with alkali and absorbent materials. In a further process, known as residual solvent, certain free acids, and other substances would give undesirable taste odors. A final treatment for edible oils may consist of hydrogenation and blending of the hydrogenated product with other oils to obtain a product of the desired characteristics.

## 2.2 Coconut oil

The coconut palm, *Coco nucifera L.* [7], is one of the coconut oil groups, which is derived from the seeds of various tropical species of the Family Palmae. Two fats of this group, viz. coconut oil and palm kernel oil, are of very great commercial importance. The coconut oil is the fats derived from the kernels of the coconut palm, as shown in Figure I, which grow on all coasts and islands in the tropics. The hard shell, covered by a fibrous husk, encloses the white endosperm tissue 1-2 cm thick, the copra. To obtain a light, flavor-stable coconut oil, the fresh copra with water content of 60-70% is dried in the sun or with hot air. This treatment prevents bacterial decomposition and lypolysis of fat. Dry copra contains 60-70% of oil.

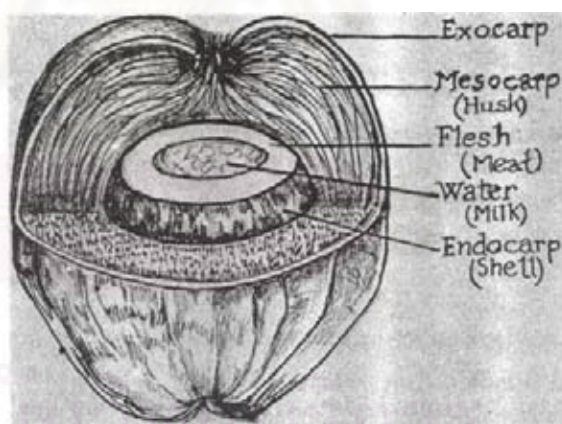


Figure I Parts of coconut

### 2.2.1 Origin and systematic

The coconut oil is obtained from the coconut palm which is supposed to have been indigenous to the Malayan Arctic pelago, from which the seeds were carried by

sea currents eastward to the Pacific Islands and the coast of Central America, and to the Africa, so that it is now found growing wild, or under cultivation, on all tropical coast. It is used largely for edible purposes in local areas, leaving no balance for exports. It is used as articles of food, margarine and soap making.

### 2.2.2 Composition and properties

The coconut oil is a white fat of bland taste having a peculiar, not unpleasant, odor of coconut meat. The odorous substances are removed in the deodorizing and refining of the coconut oil for edible purposes. The coconut oil has a range of analytic characteristics are shown in Table II [8]. It consists of a complex mixture of glycerides, which contain several different fatty acids [9]. The composition of coconut oil is shown in Table III.

Table II The ranges of analytic characteristic of coconut oil

Properties	Coconut oil
Melting point	23-28 °C
Specific gravity	ca. 0.874
Iodine value	8-10
Saponification value	250-264
Hehner value (insoluble fatty acids)	88-91%
Unsaponifiable matter	ca. 0.2%
Titre (f.p. of fatty acids)	20-23 °C



Table III The composition of coconut oil

Fatty acids	Amount (%)
Caproic	ca. 0.5
Caprylic	7.9-9.5
Capric	4.5-7.6
Lauric	45-51
Myristic	16-18.5
Palmitic	7.5-9
Stearic	2-3
Oleic	5-8
Linoleic	1-2.6

Due to glycerides presently being mixed with glyceride containing two or three different acid radicals, the chemical and physical properties of coconut oil are dependent upon the nature of the fatty acid moiety. The melting point of individual glycerides is shown in Table IV.

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Table IV The melting points of glycerides of coconut oil

Glyceride	m.p. (°C)
Caprylo-lauro-myristin	15.0
Caprylo-myristin-olein	-
Dilauro-myristin	33.0
Lauro-dimyristin	38.1
Dimyristo-palmitin	45.1
Myristo-palmitin	-
Dipalmito-stearin	55.0

### 2.2.3 Industrial Application

#### Food

The main food uses of coconut oil are for deep fat frying for doughnuts, French fries, and nuts; as an ingredient of confections, cookies, and baked products; and shorting compounds and margarine.

#### Cosmetic

Coconut oil derivatives are used in lipstick, shampoos, cream, lotions, and makeup. Fatty acids in coconut oil such as caprylic, capric, lauric, and myristic acids and many derivatives of these acids, are important cosmetic and pharmaceutical raw materials.

### Pharmaceuticals

Hydrogenated fats and high melting saturated fatty acids are employed in making tablets. These coatings can withstand the acid environment of the stomach without disintegrating and will only break down and liberate the active medication when the alkaline enzymatic intestinal tract is reached. A systematic liquid glyceride, derived from coconut oil and completely saturated in natural not only controls cholesterol level in approximately the same degree as corn oil, but also controls the deposition of cholesterol in the liver, arteries and heart.

### Lubricating oil additives

Coconut oil is used as a viscosity improver to improve the ability of the oil to lubricated over a wider temperature range. Coconut oil furnishes the lauryl component of the lauryl methacrylate monomer from which most of this type of product is made.

### Plasticizers

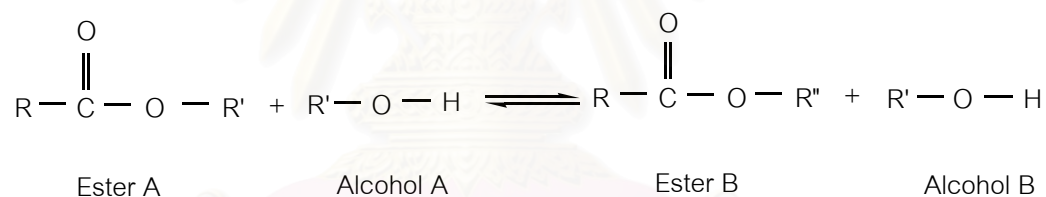
As plasticizers, the derivatives of coconut oil are added to aid in vinyl fabrication, As stabilizers, it is added to prevent discoloration and other degradation during fabrication or while in use.

### 2.3 Trans-esterification

Trans-esterification [8, 10] is a reversible reaction in which substances composed of ester functional groups react with alcohol by the interchange of the acyl group to produce a new ester. In the trans-esterification reaction, an alcohol acting as a nucleophile attacks to carbonyl functional group of ester and displaces the alkoxy functional group of the ester.

Trans-esterification is catalyzed by acid or base catalysts. The equation is shown in Scheme II.

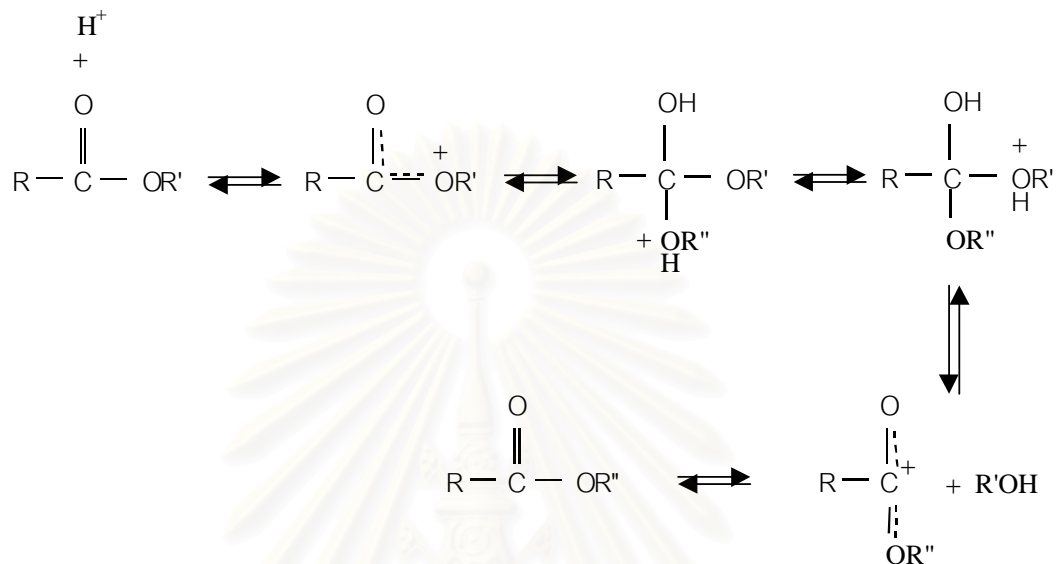
Scheme II



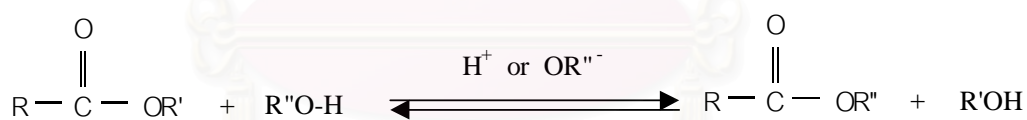
The mechanisms are shown in Scheme III for acid catalyst and in Scheme IV for basic catalyst

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Scheme III



Scheme IV



## 2.4 Liquid crystal

### 2.4.1 General

The term “Liquid Crystal” is used to describe the high anisotropic substances that have been formed to pass through states intermediate between the crystalline solid and conventional, isotropic liquid phase [1]. This phase has a long-range orientational ordering among constituent molecules that occur within certain ranges of temperature

in melts and solution. Since the ordering is sufficient to impart some solid-like properties, but the attraction forces usually are not enough to prevent flow, they flow like ordinary liquids and exhibit anisotropic properties, as do solids. They are also referred to as mesophases or mesomorphic phases or mesoforms due to their intermediate nature. Many thousands of organic compounds form liquid crystal when the solid crystal is heated above its melting point. The general molecular structure is an elongated, narrow molecular framework, which usually is depicted as a rod-, cigar-, or disk-shaped molecule. Liquid crystals are extraordinarily sensitive to external perturbations, e.g., temperature, pressure, electric or magnetic field, or foreign vapors.

#### *2.4.2 Categories and classes*

According to the means of breaking down the order of the solid states, liquid crystals can be divided into two broad categories [11]. First, lyotropic liquid crystals are multi-component mixtures, which form a mesophase when a solvent is added. The degree of order depends upon the concentration of mixture. The lyotropic liquid crystals may be transformed into an isotropic fluid by sufficiently high temperature and by increasing the amount of solvent beyond critical concentration ratio. Second, thermotropic liquid crystals may be a mixture of compounds or single compound, which forms a mesophase when the temperature is varied.

Within each category, three structural classes of liquid crystals have been denominated as smectic, nematic and cholesteric structures. These structures are related to the dimensionality and packing aspects of residual molecular order. For the first class, the smectic phase has a layer structure of a molecular center of gravity in

two-dimensional planes and a parallelism of longitudinal molecular axis. Mobility within the smectic layers may occur. Molecules may move in and out of the layers as a result of translations along the long axes involving single molecules or columns of molecules. However, the large-scale movement in any direction other than tangential to the layer surfaces is difficult. The smectic mesophase is the most solid-like of the liquid crystal modifications. In addition, there are various types of smectic mesophase denominated by the alphabet letters A through K as a result of the order of the smectic structure. The arrangement depicted in Figure II is only the simplest one of the smectic mesophase.

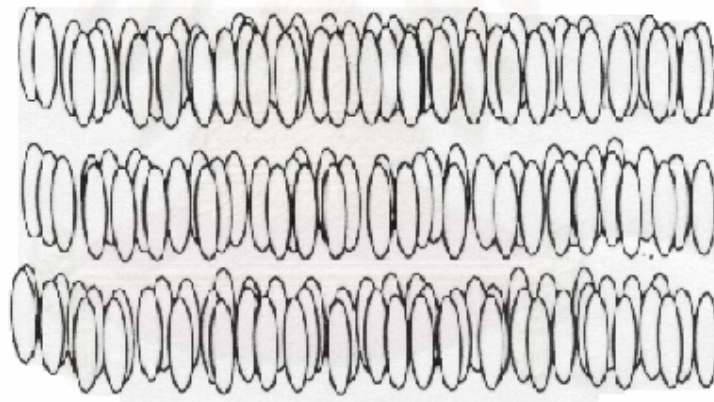


Figure II The smectic liquid crystal structure

For the second class, the nematic mesophase has a parallelism of long molecular axes of molecule as in smectic mesophase, but the molecular center of gravity is randomized as in an ordinary liquid as shown in Figure III. The molecules are allowed to rotate freely around their long axes. As a result from this structure, nematic liquid crystals are uniaxial with respect to all physical properties.

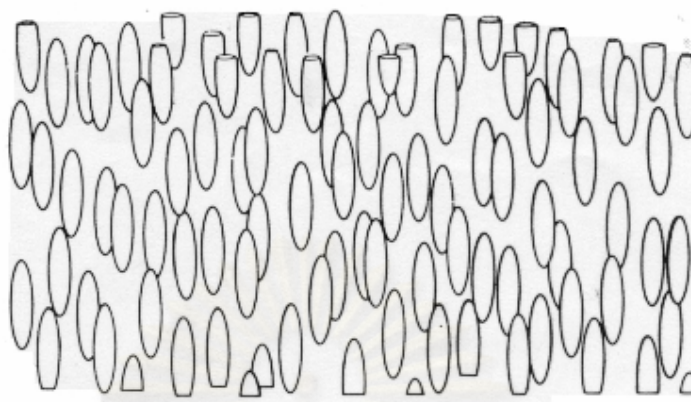


Figure III The nematic liquid crystal structure

The simple structure of many organic compounds can be formed the nematic mesophase as depicted in Figure IV.

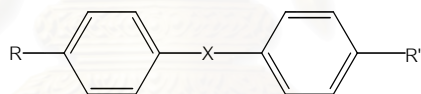


Figure IV The simple structure of nematic liquid crystal

The  $-x-$  groups linking of the two substituted phenyl rings are shown in Table V; R and R' are short chains.

Table V The important x linking groups



-x-	Name
-N=N-	Azobenzenes
-N=NO-	Azoxybenzenes
-CH=CH-	Stilbenes
-C≡C-	Tolanes
-CH=N(O)-	Nitrones
-CH=N-	Shiff bases
-O-CO-	Phenyl benzoates
-	Biphenyls

Finally, the cholesteric mesophase, the third class of liquid crystal modification, is denominated since many cholesteryl esters form this type of liquid crystals. Since cholesteric liquid crystals have a natural screw structure, the molecules are aligned parallel to a preferred direction like that of nematic liquid crystals; but, the long axes lie in a plane. The planes pile on the top of one another and are able to glide past one another. Each plane must be slightly twisted with respect to the next due to the functional groups that extend out of the molecular plane as shown in Figure V. The pitch,  $p$ , of the structure is defined as the distance that is necessary to rotate a preferred direction by  $2\pi$  when proceeding along helical axes.



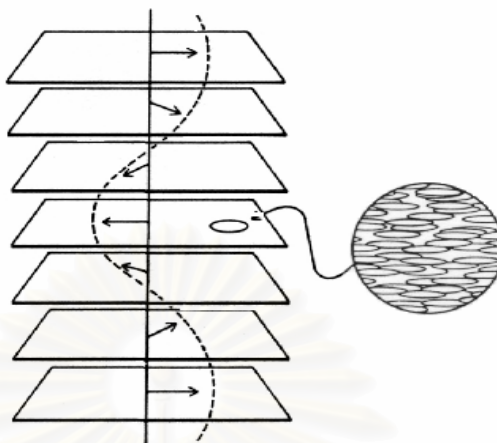
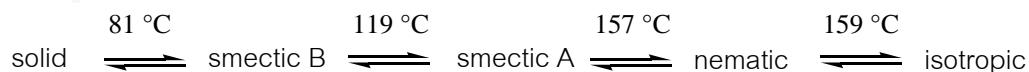


Figure V The cholesteric liquid crystal structure

### 2.4.3 Polymorphism

The liquid crystals can take on more than one modification of mesomorphic structure by once changing the conditions of temperature in the case of thermotropic liquid crystals or of solvent in the case of lyotropic liquid crystals [12]. For thermotropic liquid crystals, the transitions between various structural classes occur at definite temperatures and are accompanied by definite change in the latent heat. For example, ethyl 4-(4'-ethoxybenzylideneamino) cinnamate has three liquid crystal structures as shown in Scheme V.

Scheme V



#### 2.4.4 *Application of liquid crystals [13, 14]*

##### Temperature sensor

Based on the unique color properties and the temperature-dependent variation in the color of cholesteric liquid crystals, it has led to the use of these substances in the measurement of temperature and temperature gradients. Liquid crystals always exhibit the same color at the same temperature. Temperature variation of less than 0.01 °C can be distinguished visually with the liquid crystal temperature sensor. Liquid crystal can be employed to detect fault in electronic devices by indicating the defective area which has a change in color of the liquid crystal film at the point of excessive thermal stress. Or the liquid crystal is used to create a thermal mapping of human skin for locating veins, arteries, infection, tumor, and the fetal placenta, which has a higher temperature than the surrounding tissue.

##### Radiation sensor

As a result of change of the pitch of the twisted structure, the liquid crystal film has a change in color by local heating where an impinging, invisible radiation field is registered. Ultraviolet, infrared, microwave, ultrasonic, and ionizing radiation transducers have been devised based on this principal.

### Trace-vapor indicator

Besides the pitch of helical, cholesteric structure changing as a result of the temperature variation, its color is also affected by the percents of only a few parts per million of impurity molecules. This property has been exploited to construct trace-vapor indicators for certain chemicals.

### Electrical display devices

Liquid crystal displays are achieving great popularity as low voltage, low power devices that are visible over a wide range of ambient high levels. Liquid crystal displays consist of three parts such as the display cell, the liquid crystal layer, and a reflector or a backlight. The display cell, which is made from glass plates, has coated inner surfaces with a transparent electrode. The liquid crystal, which is about 6-12  $\mu\text{m}$  thick, is sandwiched between the plates. The devices are produced for application in wristwatches, calculators, clock, and higher information content displays.

## **2.5 Liquid crystal-polymer composites**

Liquid crystal-polymer composites are the mixture of the polymer and low molecular weight liquid crystals [15, 16]. They constitute a class of materials whose properties attract scientific and technological attention. Liquid crystal-polymer composites consist of low molecular weight liquid crystalline dispersed as micro-

droplets in a solid polymer matrix. They have been largely investigated as materials for many potential application, i.e., electro-optic application (optical display, light valve, sensor, etc.), projection television, and switchable color.

### *2.5.1 Preparation*

Dispersion of liquid crystal in a polymer matrix can be prepared by techniques which are described as emulsion, encapsulation of the liquid crystal with water soluble polymer, or phase separation process.

#### *2.5.1.1 Emulsion process*

Liquid crystal-polymer composites obtained by emulsion process are traditionally called Nematic Curvilinear Aligned Phase, NCAP. The process starts with the emulsification of liquid crystals in an aqueous medium, which contains a water-soluble polymer and a surfactant. The emulsion is coated on a substrate and dried. A second substrate is then laminated on top of the film. The droplet size of liquid crystal in the film is controlled by mechanical agitation or maceration in the emulsification step.

The advantages of the emulsion process are that it has easy extension to industrial processes and to very different kinds of polymer. On the other hand, the disadvantage is difficulty to remove water.

### *2.5.1.2 Phase separation process*

Liquid crystal-polymer composites obtained by this process are usually called Polymer Dispersed Liquid Crystal, PDLC. They can be classified into three methods as Temperature-induced Phase Separation, TIPS, Solvent-induced Phase Separation, SIPS, and Polymerized-induced Phase Separation, PIPS.

### *2.5.2 Application*

For electro-optic displays, the nematic droplets have randomly resulted in diffuse oriented scattering in the field-off state, while their uniform alignment by an electric field or magnetic field makes the film transparent because of refractive index matching. Recently, it has been shown that cholesteric and smectic liquid crystal can be used just the as same as nematic liquid crystal.

Other applications of liquid crystal-polymer composite, such as projection television and switchable color, have recently developed. In projection television, it is made from composite containing 5 to 50 % of polymer. It has advantages over existing technologies in many points, such as simple manufacturing process, no alignment layer, no polarizer, large view angle, and low driving force. For switchable color, the cholesteric liquid crystals in the droplet are transformed from non-selectively reflecting to selectively reflecting helicoidal texture by applying an electric field.

## 2.6 Literature review

C. Leonorina[17], hydrolyzed coconut oil to form fatty acids by cold saponification process and then reacted cholesterol with the fatty acids to obtain the derivatives of cholesterol using DCC and DMAP. The liquid crystal properties were then characterized. The derivatives of cholesterol were found to exhibit the phase transition temperatures: a solid to smectic phase transition at 44.5 °C, a smectic to cholesteric phase change at 66.5 °C, and isotropization at 78.2 °C.

J.R. Quigley[18], dispersed cholesteric liquid crystals within urethane monomers, and subsequent polymerized into polyurethane elastomeric liquid crystalline dispersions. From macroscopic observation, he concluded that under suitable condition in polyurethane there is a critical size range for dispersed aggregates of cholesteric liquid crystal reflecting visible light.

G.W. Smith[19], determined the relationship between cure kinetics and the size of the liquid crystal microdroplet in PDLC films in order to control droplet size and thus optimize electrooptic performance for a given application.

D.K. Yang[20], microscopically observed the texture of very large droplets of cholesteric liquid crystal in a polymer matrix under the influence of an electric field.

## CHAPTER III

### EXPERIMENT

#### 3.1 Materials

1. Ground Coconut: commercial grade from a supermarket
2. MeOH : analytical grade; Fluka
3. Methylene chloride: analytical grade; Fluka
4. Hexane: analytical grade; Fluka
5. Cholesterol: analytical grade; Fluka
6. *p*-toluenesulfonic acid: analytical grade; Fluka
7. Phosphotungstic acid: analytical grade; Merck
8. Sodium sulfate anhydrous: analytical grade; Fluka
9. Sodium hydrogen carbonate: analytical grade; Fluka
10. Silica: analytical grade; Fluka
11. TLC plate: analytical grade: Merck
12. Cholesteryl palmitate: analytical grade; Fluka
13. Cholesteryl oleate : analytical grade ; Fluka
14. Cholesteryl stearate: analytical grade; Fluka



### 3.2 Apparatus

1. Fourier-Transform NMR Spectroscopy:

Model 1760 AC-F 200 (200MHz); Bruker Spectrospin

2. Fourier Transform-IR Spectrophotometer:

Model 1760x; Perkin Elmer

3. Gas Chromatography-Mass Spectrometer

Model MD-800 equipped with a 800 series GC; Fison Instrument

4. Differential Scanning Calorimeter:

Model DSC200; NETZSCH

5. Scanning Electron Microscope:

Model JSM-5800LV; JEOL

6. UV Lamp

### 3.3 Procedures

#### *3.3.1 Isolation and characterization of liquid crystal from coconut oil*

The ground coconut (2.5kg) was extracted with hexane (3L) for four times. The coconut oil was collected. After removing the solvent, the weight of coconut oil was determined. Then, crude coconut oil was separated by column chromatography, which was packed with silica and connected with a pump. Hexane was used as eluting agent for eluting the triglyceride portion. Then, methylene chloride was applied to elute cholesterol containing fraction which gave a red spot on a TLC plate when



spraying the plate with a solution of 5% w/v phosphotungstic acid in 95% ethanol and then heating at 100 °C. The latter fraction was pooled together and then recrystallized with methylene chloride/methanol. The products were characterized by FT-IR, <sup>13</sup>C-NMR, and GC-MS.

The condition to obtain GC-MS chromatogram was the following.

Column: DB5ms Capillary column

30 x 0.25 ID x 0.25 μm

Carrier gas: N<sub>2</sub> pressure 15 Psig.

Oven: 150 °C (1 min) to 320 °C (13 min) rate 10 °C /min.

Injection Temperature: 250 °C

Detector: MS (EI<sup>+</sup>70) eV.

### 3.3.2 Synthesis of cholesteryl ester

#### Step I. Trans-esterification of coconut oil

Coconut oil (100g) and excess methanol (150g) were mixed together in a 250ml round bottom flask equipped with magnetic stirrer. *p*-Toluenesulfonic acid(1 g) was added into the flask as a catalyst. The reaction flask was connected with condenser. The mixture was refluxed with continuous stirring for 2, 3, and 4 hours. The progress of the reaction was monitored using <sup>13</sup>C-NMR analysis. The reaction was stopped by cooling down the reaction flask to room temperature. The mixture was neutralized with saturated sodium carbonate solution. The neutralized mixture was extracted to remove glycerol with distilled water by using a 500ml separating funnel.

The organic phase was separated and dried with anhydrous sodium sulfate. The organic phase was evaporated to remove the solvent using rotary evaporator. The yield of the fatty acid methyl esters was determined by weight.

The condition to obtain GC-MS chromatogram was the following.

Column: DBwax Capillary column

30 x 0.25 ID x 0.25  $\mu\text{m}$

Carrier gas:  $\text{N}_2$  pressure 15 Psig

Oven: 80  $^{\circ}\text{C}$  (3 min) to 220  $^{\circ}\text{C}$  (3 min) rate 10  $^{\circ}\text{C}/\text{min}$

Injection Temperature: 250  $^{\circ}\text{C}$

Detector: MS ( $\text{EI}^+70$ ) eV.

#### Step II. Trans-esterification of fatty acid methyl esters with cholesterol

Cholesterol (3g), hexane (100 ml), and fatty acid methyl esters with different weight (8.30, 16.60, 24.91, 33.27, and 41.50g) were mixed together in a 250ml round bottom flask equipped with magnetic stirrer, and *p*-toluenesulfonic acid (1g) was added into the flask. The reaction flask was connected with a Deans & Stark trap and a condenser. The mixture was reflux with continuous stirring for various times during 2, 3, 4, 6 and 9 hours. The reaction was stopped by cooling down the reaction flask to room temperature. The catalyst was separated by filtration. The mixture was neutralized with saturated sodium carbonate solution and separated in a 500ml separating funnel. The organic phase was dried with anhydrous sodium sulfate and then was evaporated by using a rotary evaporator. The remains were extracted to remove excess fatty acid methyl esters with methanol. The solid were crystallized and

re-crystallized with methylene chloride/methanol. The yield of the fatty acid methyl esters was determined by weighing.

Note: the temperature of the reaction was varied by using various media such as hexane and toluene.

The condition to obtain GC-MS chromatogram was the following.

Column: DB5ms Capillary column

30 x 0.25 ID x 0.25  $\mu\text{m}$

Carrier gas:  $\text{N}_2$  pressure 15 Psig

Oven: 150  $^{\circ}\text{C}$  (1 min) to 320  $^{\circ}\text{C}$  (13 min) rate 10  $^{\circ}\text{C}/\text{min}$

Injection Temperature: 250  $^{\circ}\text{C}$

Detector: MS ( $\text{EI}^{+70}$ ) eV.

The condition to obtain a DSC thermogram is the following.

Temperature: 25  $^{\circ}\text{C}$  to 80  $^{\circ}\text{C}$ , rate 3  $^{\circ}\text{C}/\text{min}$

Atmosphere:  $\text{N}_2$ , flow rate 15 mm/sec

### 3.3.3 Preparation of porous film

Three grams of polyethylene powder and cholesteryl esters were mixed together with mechanical stirrer. The cholesteryl esters portion were used at 0.15 and 0.30g. The mixture was heated to 140  $^{\circ}\text{C}$  and then held for 5 minutes. Then it was cooled down with a cooling rate at 5  $^{\circ}\text{C}/\text{min}^{-1}$ . After that, the composite film was extracted with hexane to remove the droplet of liquid crystal. FT-IR was use to investigate of complete extraction. The

porous film was characterized in term of size and distribution of pores using SEM.



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## CHAPTER IV

### RESULTS AND DISCUSSION

The aims of this research were : a) to isolate the substances, which give a red color when spraying the TLC plate with phosphotungstic acid solution, from coconut oil; b) to prepare cholesteryl esters from cholesterol and fatty acid methyl esters of coconut oil; and c) to prepare the porous film from the liquid crystal-polymer composite.

Coconut oil was used as a main raw material throughout this research. A ground coconut meat has a moisture content of 51.75%. Its dry weight contains 47.59% of oil as shown in Table VI. The  $^{13}\text{C}$ -NMR and FT-IR spectra of coconut oil were shown in Figures B1, A1, respectively.

Table VI The percentage of oil in ground coconut meat

Day \ No.	I (2045.00g)	II (2011.20g)
2	292.97	307.55
4	109.05	88.23
6	32.32	36.89
8	33.26	31.05
Total	462.60	463.72
%oil of wet weight	22.87	23.06
%oil of dried weight	47.39	47.79

In Figure B1,  $^{13}\text{C}$ -NMR spectrum showed the important signals of triglycerides,  $-\text{CH}_2\text{O}-$ , of coconut oil at 62.11 and 68.87 ppm and the signals of carbonyl of triglyceride ( $\text{C}=\text{O}$ ) at 172.90 and 173.33 ppm.

The infrared spectrum of coconut oil is shown in Figure A1. Its characteristic indicated the signals of aliphatic C-H stretching at 2925 to 2855  $\text{cm}^{-1}$ , carbonyl ( $\text{C}=\text{O}$ ) of triglyceride at 1745  $\text{cm}^{-1}$ , C-H bending at 1461 to 1373  $\text{cm}^{-1}$ , and C-O stretching at 1228 to 1160  $\text{cm}^{-1}$ .

The  $^{13}\text{C}$ -NMR spectrum of methanol and cholesterol are shown in Figures B2 and B3, respectively. The FT-IR spectrum of cholesterol is shown in Figure A7.

Characteristics of fatty acid methyl esters and cholesteryl esters were determined by  $^{13}\text{C}$ -NMR, FT-IR and GC-MS. Furthermore, the cholesteryl ester products were also characterized for the phase transition by DSC.

#### **4.1 Isolation and characterization of liquid crystal from coconut oil**

The fraction, which gave a red spot on TLC when spraying it with 5% w/v phosphotungstic acid solution as shown in Figure VI from coconut oil, was obtained in 0.27% yield by weight. The products were characterized with  $^{13}\text{C}$ -NMR, FT-IR and GC-MS as shown in Figures B4, A6, and C3, respectively.

From Figure A6, FT-IR spectrum indicated the signal of O-H at 3416  $\text{cm}^{-1}$ , aliphatic C-H stretching at 2935 to 2869  $\text{cm}^{-1}$ , unsaturated bond ( $\text{C}=\text{C}$ ) at 1622  $\text{cm}^{-1}$ , C-H bending at 1463 and 1374  $\text{cm}^{-1}$ , and C-O stretching at 1056  $\text{cm}^{-1}$ . Its spectrum was similar to authentic cholesterol as shown in Figure A7.

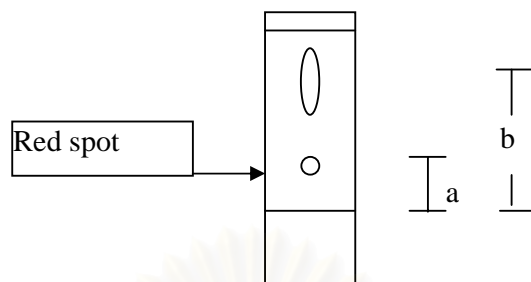


Figure VI TLC plate of coconut oil using methylene chloride as eluting agent

Where a = spot which has  $R_f = 0.17$

b = spot which has  $R_f = 0.86$

From Figure B4, the  $^{13}\text{C}$ -NMR spectrum showed the peak of paraffinic carbons ( $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$ ) at 11.85 to 56.86 ppm, and the important peaks of  $\text{C-O}$  and  $\text{C=C}$  appeared at 71.80 and 121.70 and 140.74 ppm, respectively.

From Figures C3 and D1 (GC chromatogram and mass spectrum), the results demonstrated that the fraction which has  $R_f$  equal to 0.17 was cholesterol (MW 386).

## 4.2 Synthesis of cholesteryl esters

### 4.2.1 Trans-esterification of coconut oil with methanol

The optimum reaction time of trans-esterification reaction of coconut oil with methanol was monitored by  $^{13}\text{C}$ -NMR as shown in Figures B5 to B7 from the results of reaction times of 2, 3, and 4 hours.

From Figure B7, the  $^{13}\text{C}$ -NMR spectrum of products at 4 hours reaction time indicated that the signals of  $\text{C-O}$  of coconut oil triglycerides at 62.11 and 68.87 ppm were disappeared and the important peak of  $\text{CH}_3\text{-O-}$  and  $\text{C=O}$  of methyl ester products appeared at 51.34 and 174.28 ppm, respectively.



These experimental results indicated that the trans-esterification reaction of coconut oil with methanol was completed at a reaction time of 4 hours. In this study, the product yield was 98.42%.

$^{13}\text{C}$ -NMR spectrum, FT-IR spectrum and GC-MS chromatogram in Figures B7, A8, and C1, showed the characteristics of methyl ester products from trans-esterification at an optimum condition.

From Figure A8, FT-IR spectrum showed the signal of aliphatic C-H stretching at 2926 to 2856  $\text{cm}^{-1}$ , carbonyl (C=O) of methyl ester products at 1743  $\text{cm}^{-1}$ , C-H bending at 1461 to 1366  $\text{cm}^{-1}$ , and C-O stretching at 1245 to 1113  $\text{cm}^{-1}$ .

The composition of fatty acid methyl ester products at the optimum condition was determined by GC-MS. The GC-MS chromatogram of fatty acid methyl ester products are presented in Figure C1 and mass spectrums of each peak are shown in Figures D2 to D9.

From Figure C1, GC-MS chromatogram indicated that the methyl ester product was a mixture of methyl ester of long chain fatty acids. The main composition was methyl laurate with a retention time of 8.48 min. The others were methyl caprylate, methyl caprate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate with retention times of 3.13, 5.71, 10.37, 12.13, 13.87, 13.94, and 14.24 min, respectively.

The peak area ratio of the GC-MS chromatogram was determined and calculated to get into the percentage of each composition, which is presented in Table VII.

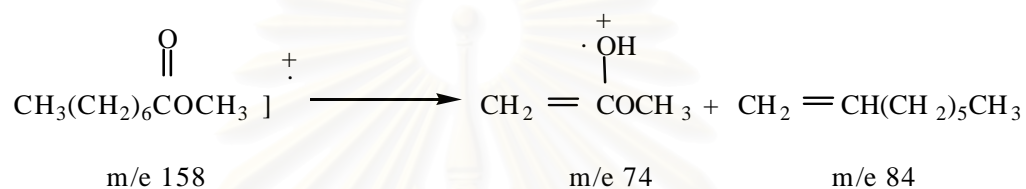
Table VII The composition of FAMES from coconut oil



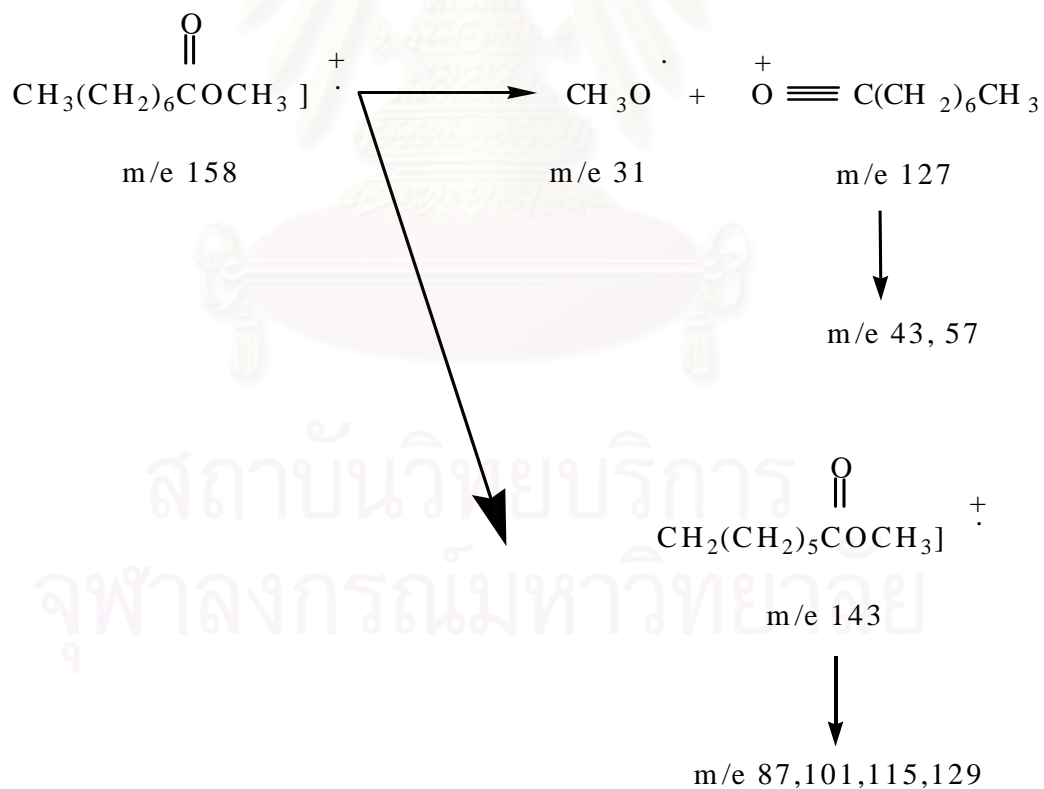
FAMEs	Retention time (min.)	Amount (%)
Methyl caprylate (C8)	3.13	3.85
Methyl caprate (C10)	5.71	3.78
Methyl laurate (C12)	8.48	66.30
Methyl myristate (C14)	10.37	15.97
Methyl palmitate (C16)	12.13	5.14
Methyl stearate (C18:0)	13.87	0.83
Methyl oleate (C18:1)	13.94	3.63
Methyl linoleate (C18:2)	14.24	0.52

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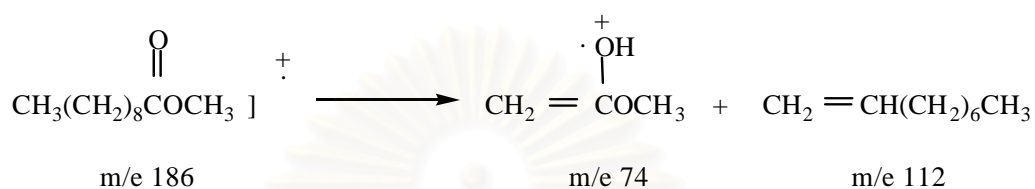
Characteristics of the fatty acid methyl esters were confirmed by mass spectrum as shown in Figures D2, D3, D4, D5, D6, D7, D8 and D9, respectively. Mass spectrum of methyl caprylate (MW 158), at a retention time of 3.13 min shown in Figure D2 showed the base peak at 74 due to McLafferty rearrangement as shown in the following equation:



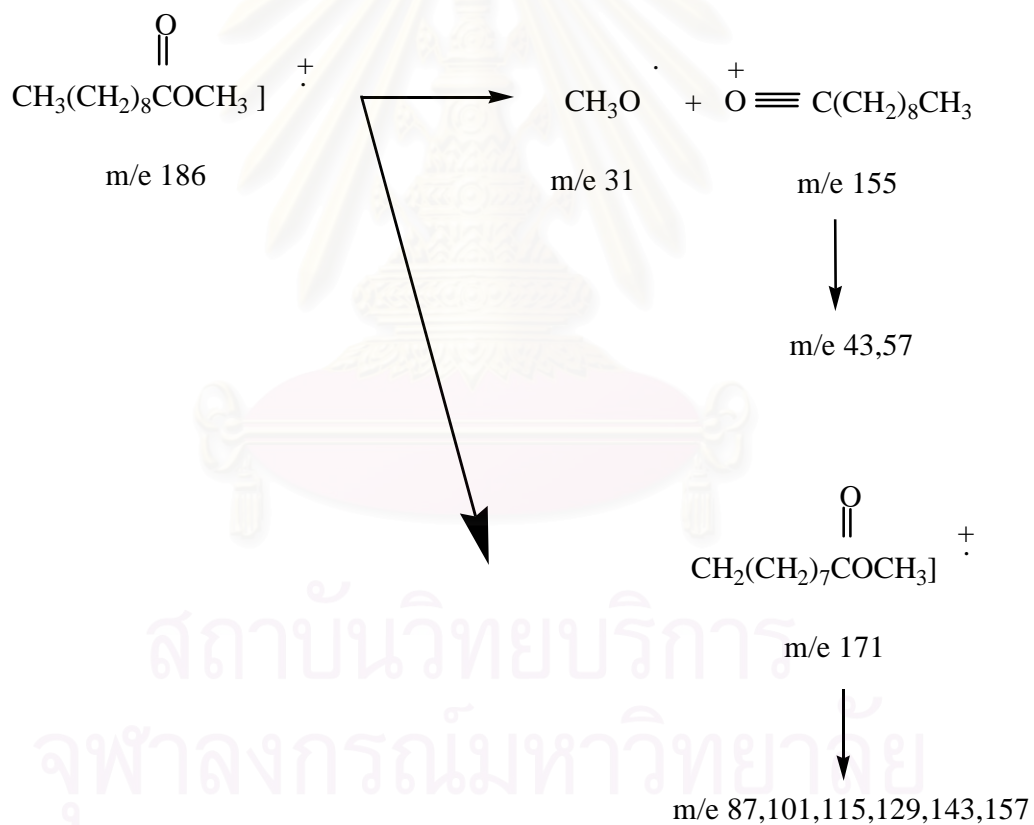
The reaction could occur as shown in the following equation:



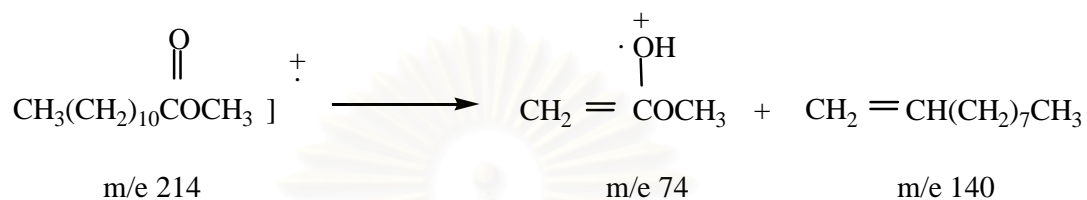
Mass spectrum of methyl caprate (MW 186), at a retention time 5.71 in Figure D3 showed the base peak at 74 due to McLafferty rearrangement as in the following equation:



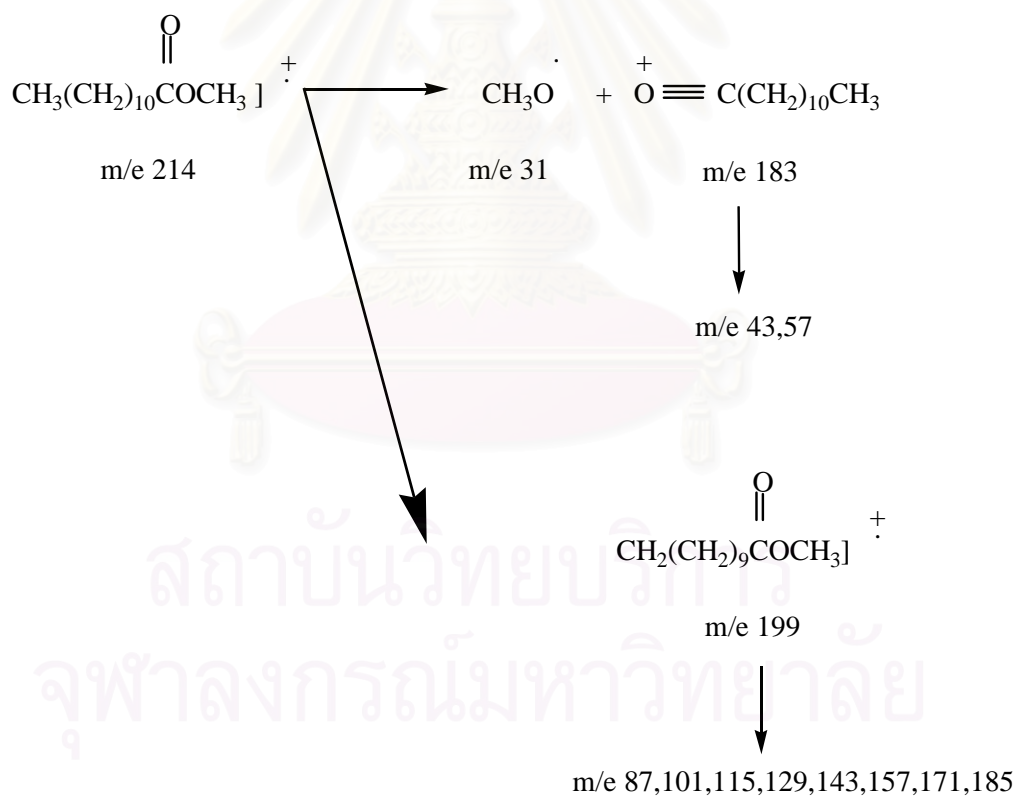
The reaction could occur as shown in the following equation:



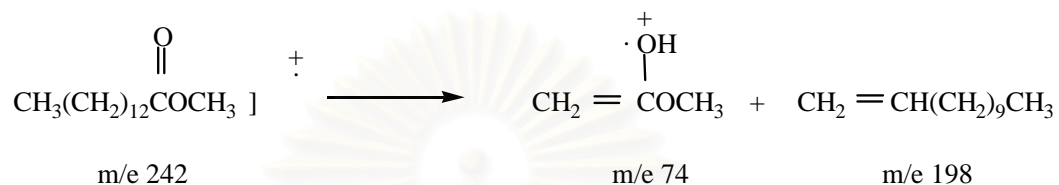
Mass spectrum of methyl laurate (MW 214), at a retention time of 8.48 min., from Figure D4 showed the base peak at 74 due to McLafferty rearrangement as in the following equation:



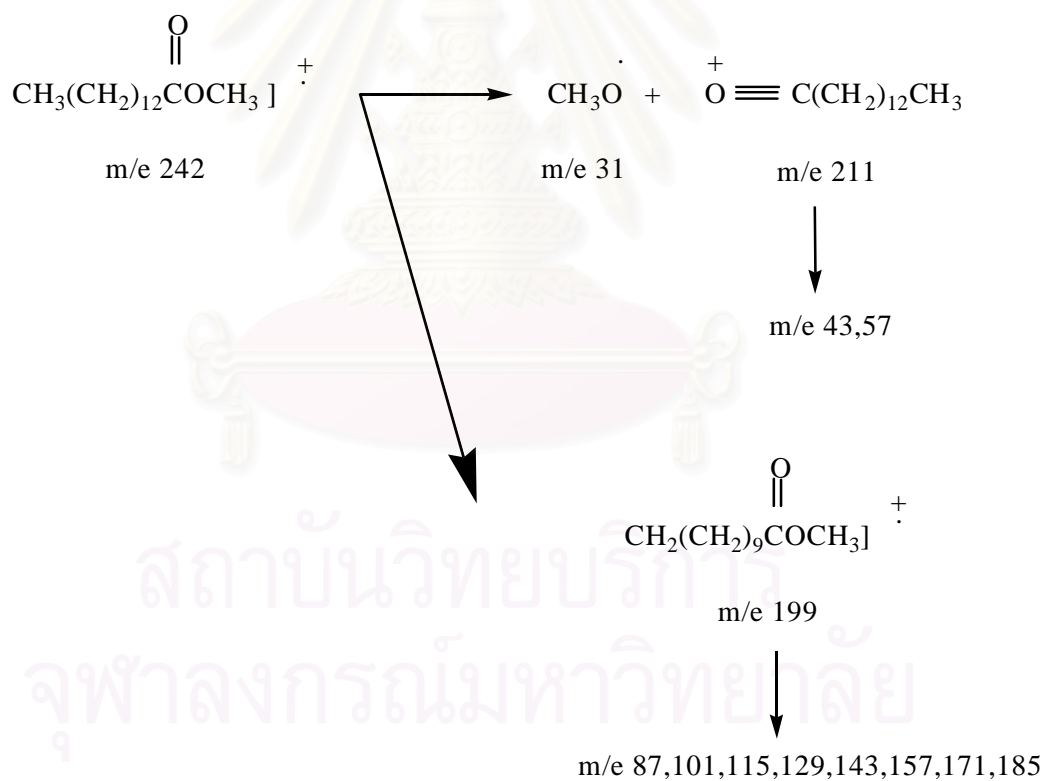
The reaction could occur as shown in the following equation:



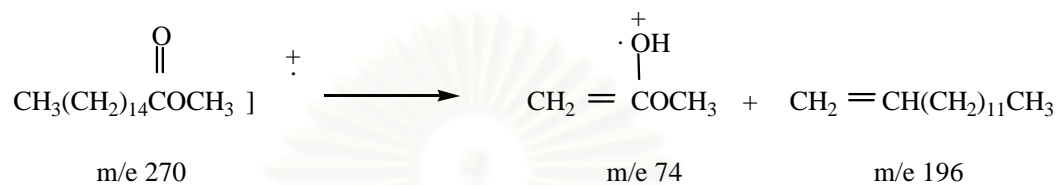
Mass spectrum of methyl myristate (MW 242), at a retention time of 10.37 min., from Figure D5 showed the base peak at 74 due to Mcafferty rearrangement as in the following equation:



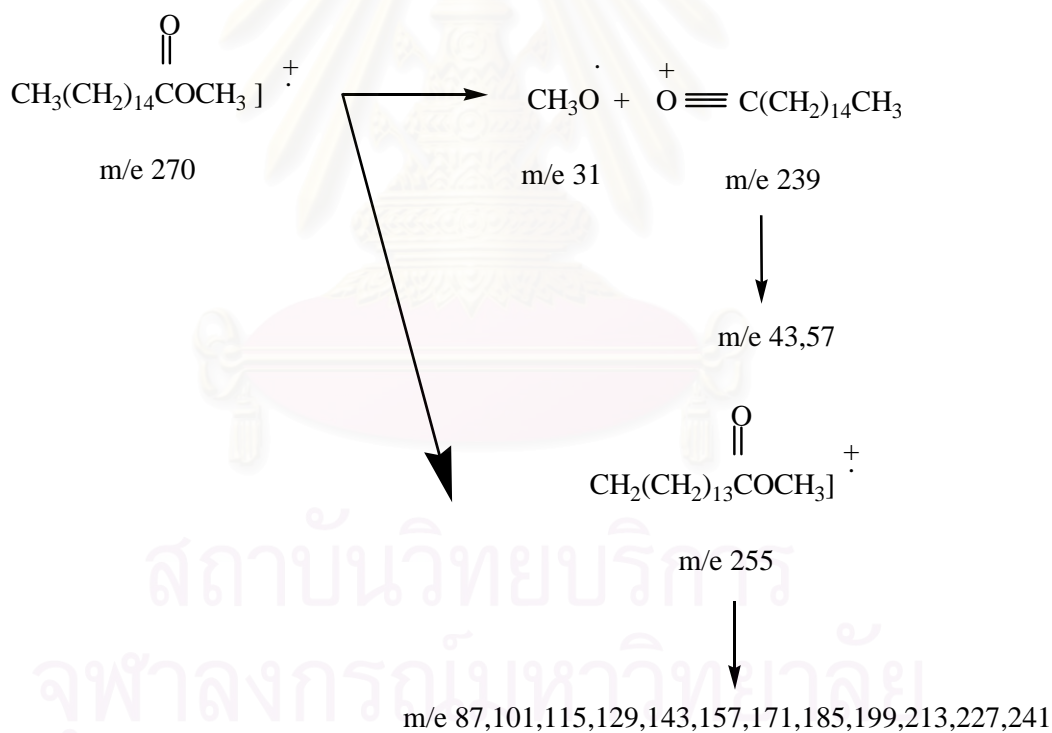
The reaction could occur as shown in the following equation:



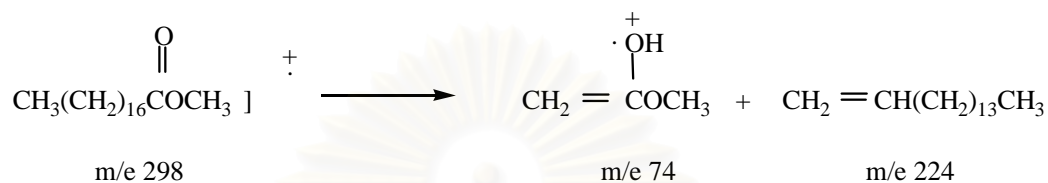
Mass spectrum of methyl palmitate (MW 270), at a retention time of 12.13 min., from Figure D6 showed the base peak at 74 due to McLafferty rearrangement as in the following equation:



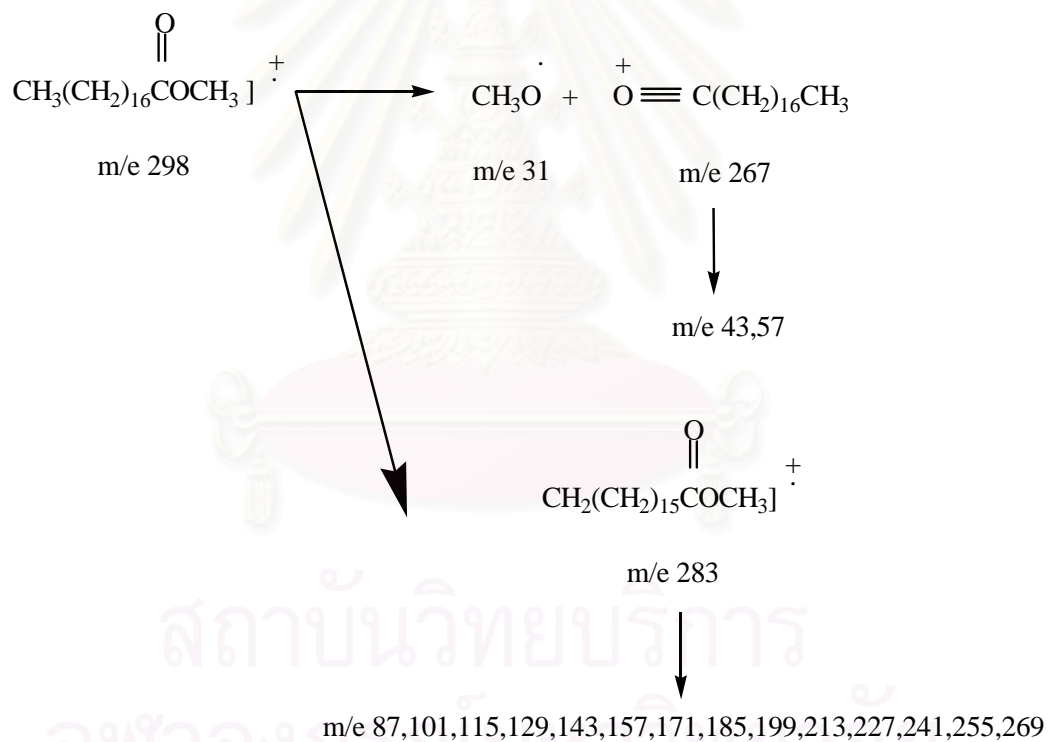
The reaction could occur as shown in the following equation:



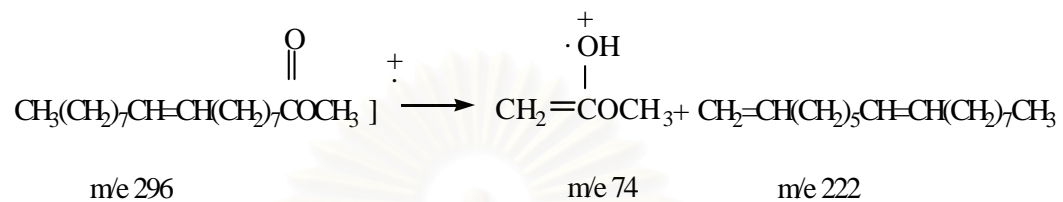
Mass spectrum of methyl stearate (MW 298), at a retention time of 13.87 min., from Figure D7 showed the base peak at 74 due to McLafferty rearrangement as in the following equation:



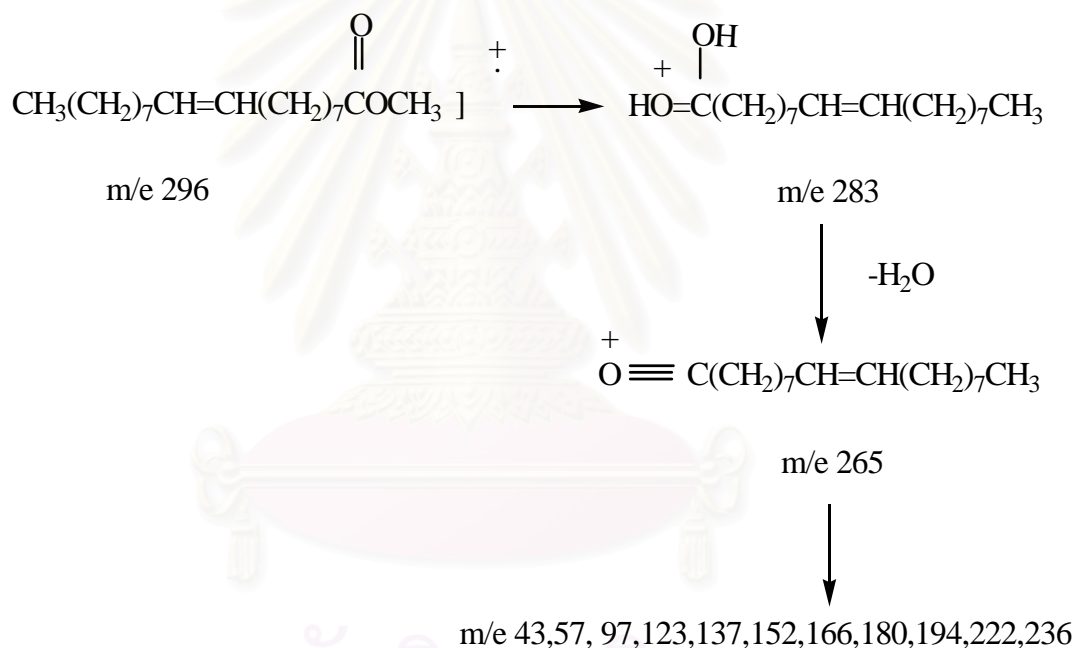
The reaction could occur as shown in the following equation:



Mass spectrum of methyl oleate (MW 296), at a retention time of 13.94 min., from Figure D8 showed the base peak at 74 due to McLafferty rearrangement as in the following equation:



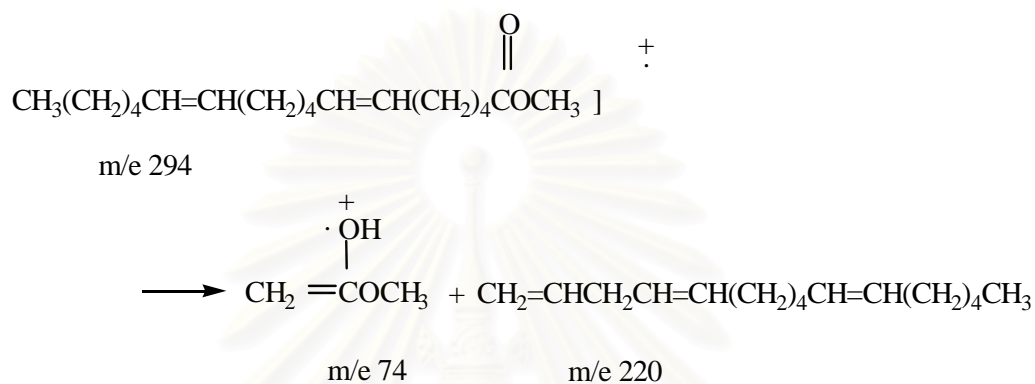
The reaction could occur as shown in the following equation:



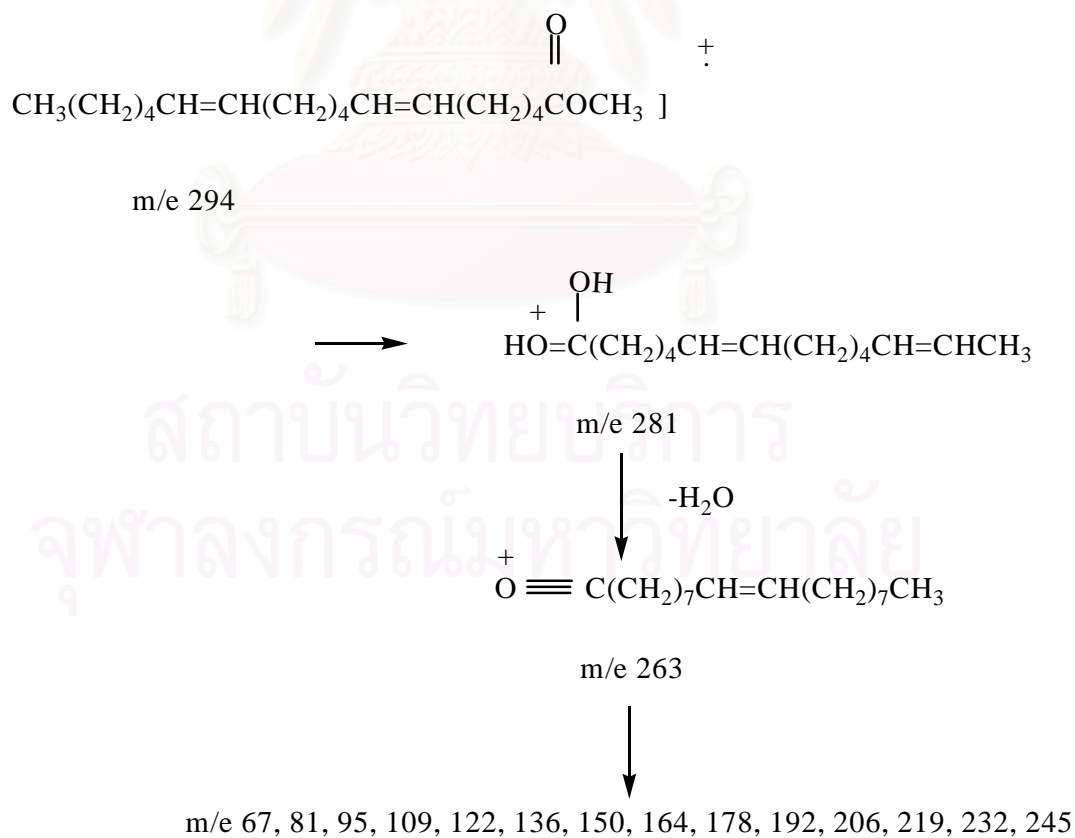
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Mass spectrum of methyl linoate (MW 294), at a retention time of 14.24 min., from Figure D9 showed the base peak at 74 due to McLafferty rearrangement as in the following equation:



The reaction could occur as shown in the following equation:



#### 4.2.2 Transesterification of fatty acid methyl esters with cholesterol

In this step, the trans-esterification reaction of fatty acid methyl esters with cholesterol was carried out. The optimum condition was obtained by varying the reaction temperature, the reaction time, and the reactant ratio of cholesterol and fatty acid methyl esters. The results of reaction temperatures are presented in Table VIII.

Table VIII The optimum reaction temperature

Medium	Bp. (°C)	Cholesterol (g)	FAMES (g)	Cholesteryl ester (g)		
				No.1	No.2	Ave.
Toluene	110	3.00	16.60	1.53	1.49	1.51
Hexane	69	3.00	16.60	3.33	3.43	3.38

Note: The reaction was carried out with reactant ratio of cholesterol and FAMES 3.00: 16.60, for 6 hours.

The results from Table VIII indicated that hexane, which has boiling point 69 °C, was suitable as a medium in the trans-esterification reaction of fatty acid methyl esters with cholesterol to give cholesteryl esters. Hexane was found to be more suitable than toluene.

The results of the reaction time, which are shown in Table IX, demonstrated that the reaction time of 6 hours was enough to converse cholesterol into cholesteryl esters.

Table IX The optimum reaction time

Time (hrs.)	Weight of Product (g)		
	No.1	No.2	Ave.
2	2.28	2.32	2.30
3	2.50	2.60	2.55
4	3.25	3.17	3.21
6	3.56	3.65	3.60
9	3.57	3.49	3.55

Note: the reaction was carried out with reactant ratio of cholesterol and FAMEs at 3.00: 24.91.

From these results, it was indicated that the weight of cholesteryl esters was increased with increasing reaction time. When the reaction was carried out for more than 6 hours, the weight of cholesteryl esters was slightly decreased.

The results of reactant ratio of cholesterol and FAMEs are shown in Table X.

Table X The optimum reactant ratio of cholesterol to FAMEs

Cholesterol (g)	FAMEs (g)	Weight of Product (g)		
		No.1	No.2	Ave.
3.00	8.30	1.70	1.58	1.64
3.00	16.60	3.34	3.42	3.38
3.00	24.91	3.56	3.65	3.60
3.00	33.27	4.88	4.80	4.84
3.00	41.50	4.21	4.11	4.16

Note: the reaction was carried out for 6 hours.

From Table X, the results demonstrated that the trans-esterification between the coconut oil fatty acid methyl esters and cholesterol was increased with increasing cholesterol to FAMES ratios. The reaction showed maximum conversion when the ratio of cholesterol to fatty acid methyl esters was 3g to 33.27g.

These experimental results indicated that the reaction reached a maximum conversion at a reactant ratio of cholesterol to FAMES of 3: 33.27 by weight, with a temperature at 69 °C and reaction time of 6 hours.

The results of cholesteryl esters from trans-esterification reaction at optimum condition were suggested by  $^{13}\text{C}$ -NMR, FT-IR and GC-MS spectrums, in Figures B8, A5, and C2, respectively.

From Figure B8, the  $^{13}\text{C}$ -NMR spectrum demonstrated that the significant peak of cholesterol at 71.05 disappeared and the important peak of  $\text{CH-O-}$ , and  $\text{C=O}$  of monoester product, appeared at 73.06 and 173.05 ppm, respectively. In addition, Figure B8 also showed peaks of unsaturated double bond at 122.54 and 139.63 ppm.

From Figure A5, the FT-IR spectrum indicated the signals of aliphatic C-H stretching at 2928 to 2855  $\text{cm}^{-1}$ , carbonyl ( $\text{C=O}$ ) of triglyceride at 1733  $\text{cm}^{-1}$ ,  $\text{C=C}$  bending at 1636  $\text{cm}^{-1}$ , C-H bending at 1465 to 1377  $\text{cm}^{-1}$ , and C-O stretching at 1172  $\text{cm}^{-1}$ .

The composition of cholesteryl ester products at the optimum condition was determined by GC-MS. The GC-MS was performed in a DB5ms capillary column. The GC-MS chromatogram of cholesteryl ester products is shown in Figure C2 and mass spectrums of each peak are shown in Figures D10 to D12.

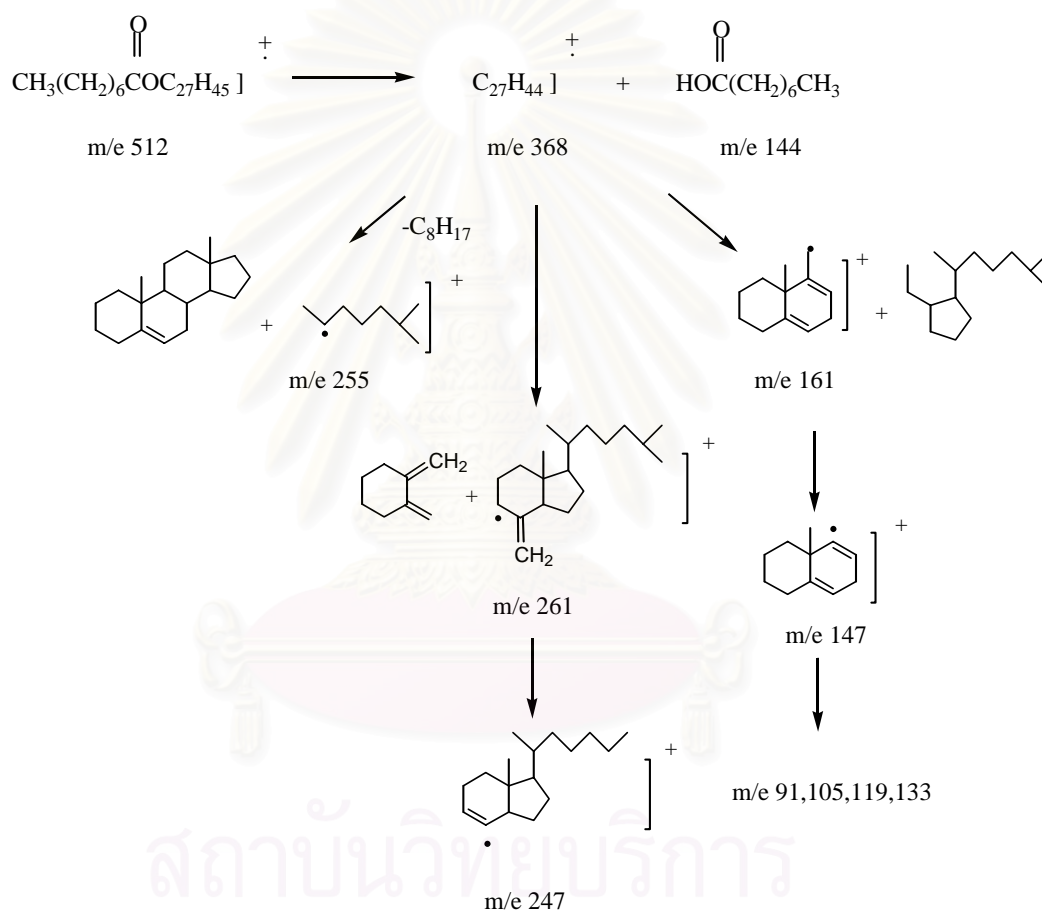
From Figure C2, GC-MS chromatogram indicated that the product was a mixture of cholesteryl ester of long chain fatty acids. The main composition was CE3 at a retention time of 18.46 min. The others were CE1 and CE2 at retention times of 17.45 and 18.16 min., respectively.

The peak area ratio of the GC-MS chromatogram was determined and calculated to obtain the percentage of each composition as shown in Table XI.

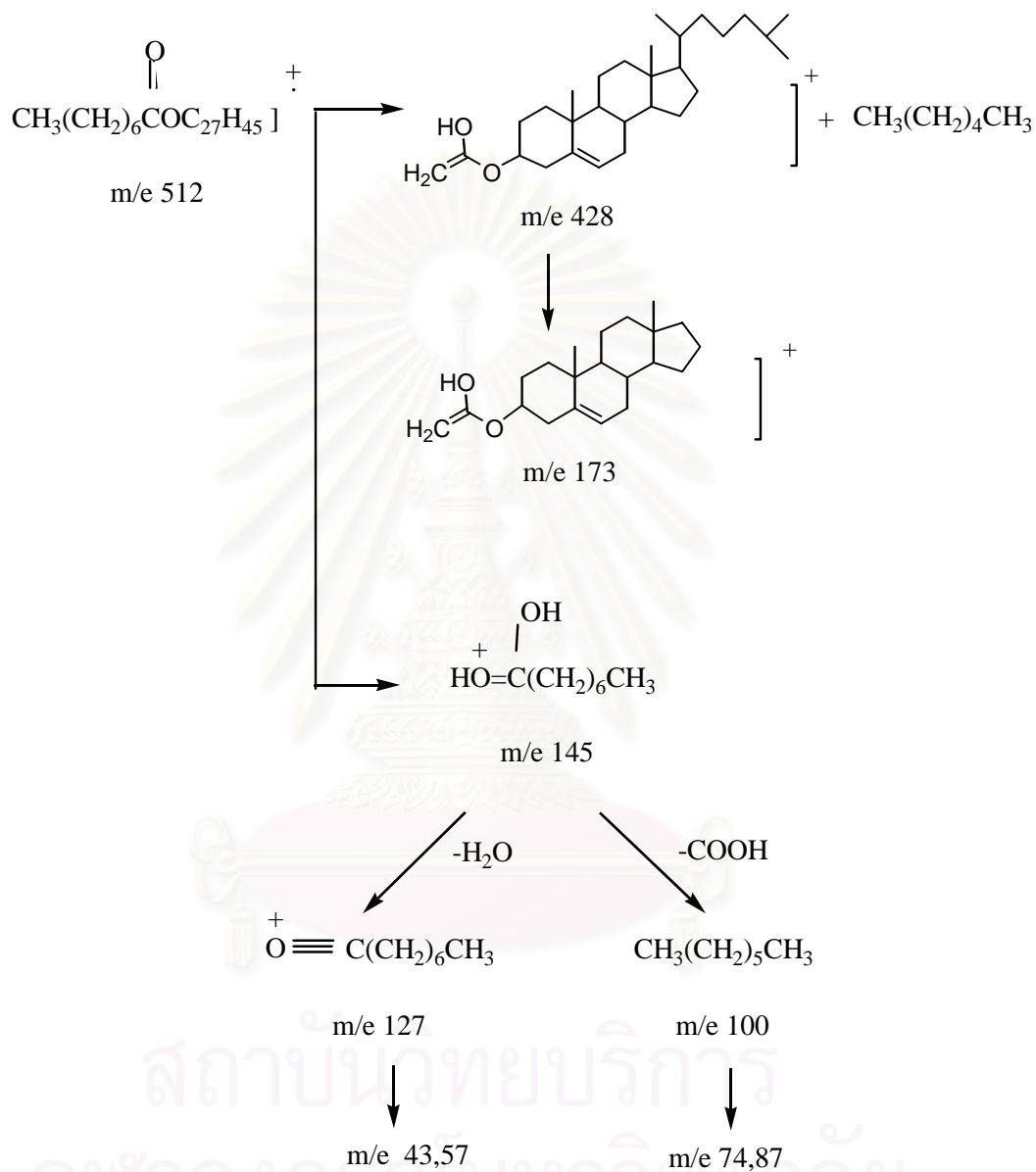
Table XI The composition of cholesteryl esters from coconut oil

Cholesteryl esters	Retention time (min.)	Amount (%)
CE1	17.45	26.41
CE2	18.18	4.76
CE3	18.46	68.83

Characteristics of their derivatives were confirmed by mass spectrum as shown in Figures D10, D11, and D12 respectively. Mass spectrum of CE1, at a retention time of 17.45 min. in Figure D10 showed the base peak at 368 due to  $\alpha$ -cleavage of ester linkage as in the following equation:



The reaction could occur as shown in the following equation:



Mass spectrum of CE2 and CE3, at a retention time of 18.18 and 18.46 min. in Figures D11 and D12, respectively, showed the base peak at 368 due to  $\alpha$ -cleavage of ester linkage similar as in the mass spectrum of CE1.

From Figure E4, the cholesteryl esters from coconut oil exhibited liquid crystal properties with phase transition temperature as followed: a solid to smectic phase transition at 44.4 °C, a smectic phase to cholesteric phase change at 66.6 °C, and cholesteric phase to a liquid phase at 78.0 °C. This result is in agreement with that reported by C. Leonorina [17].

### 4.3 Preparation of porous film

The porous film was prepared from liquid crystal-polymer composite as shown in Figures VII to XII. The completion of extraction was confirmed by FT-IR spectroscopy as shown in Figures A9 to A10 as results of before and after solvent extraction.

From Figure A10, FT-IR spectrum showed that the signal of carbonyl of cholesteryl esters at  $1735\text{ cm}^{-1}$  disappeared. It indicated that the solvent extraction with hexane was completed. Therefore, it demonstrated that the porous film could be prepared by extraction of the liquid crystal-polymer composite with hexane. The diameter of pores of film was about  $5\text{ }\mu\text{m}$ . Since this pore size was bigger more than the size of molecules of cholesteryl esters, the result correspond with the reports of Quigley and Smith which demonstrated that the aggregates of cholesteryl liquid crystal dispersed as microdroplet in the polymer matrix.



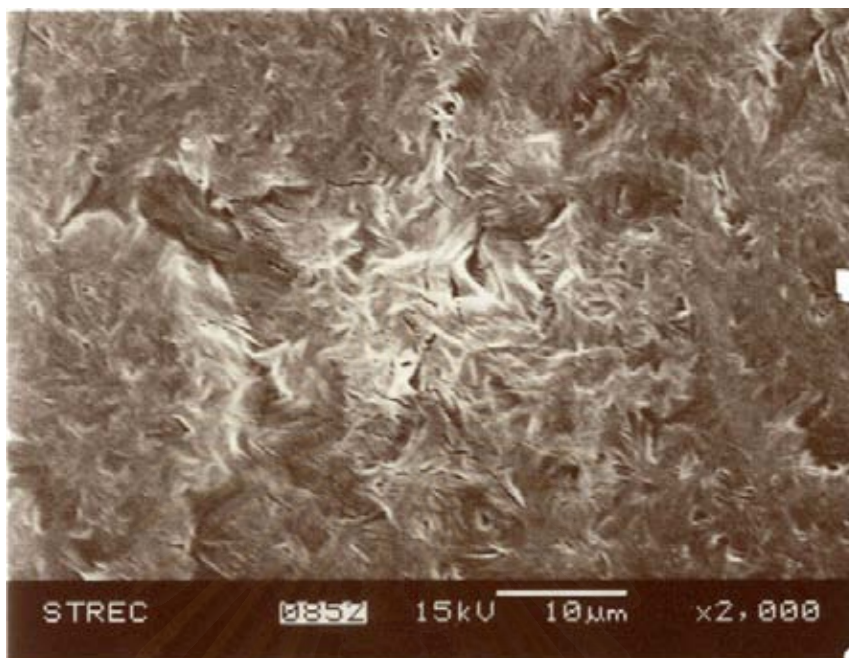


Figure VII SEM micrograph of liquid crystal-polymer composite (5% CE), magnification X2000

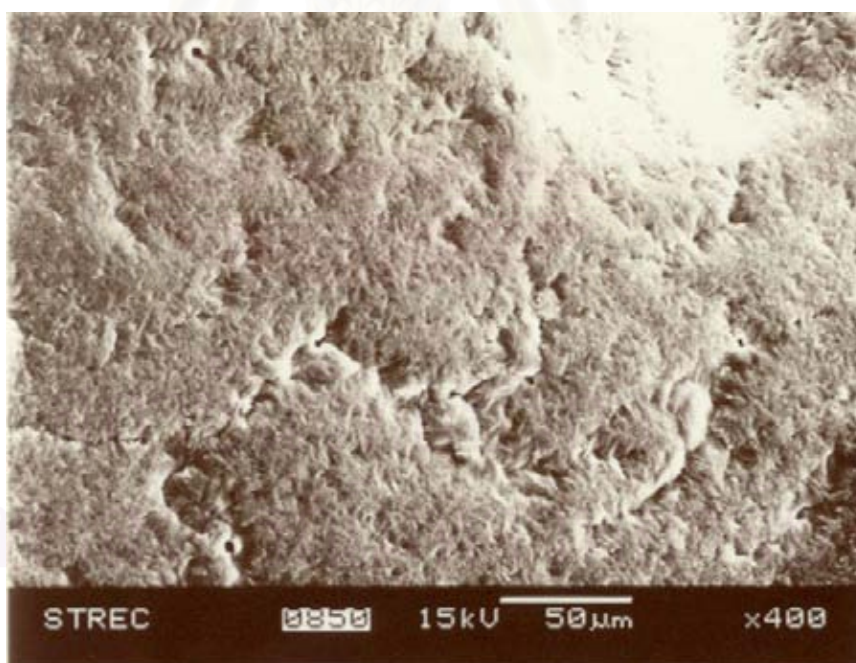


Figure VIII SEM micrograph of porous film from liquid crystal-polymer composite (5% CE), magnification X400

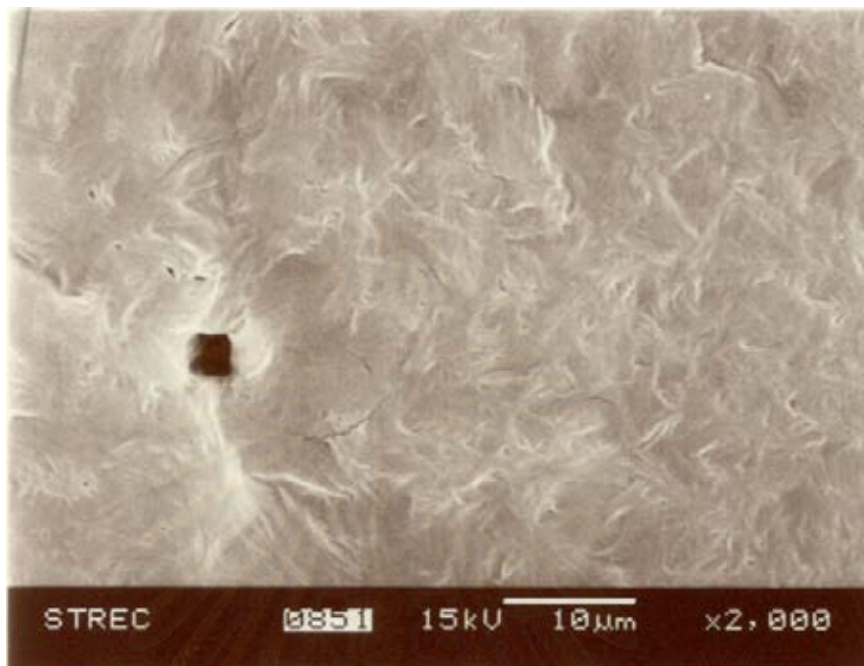


Figure IX SEM micrograph of porous film from liquid crystal-polymer composite (5% CE), magnification X2000

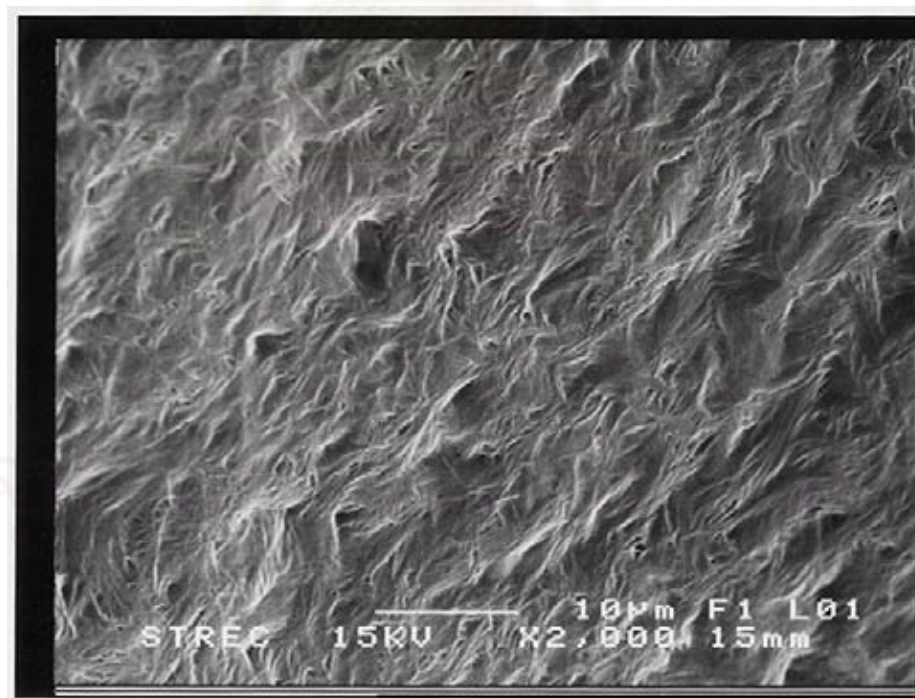


Figure X SEM micrograph of liquid crystal-polymer composite (10% CE), magnification X2000



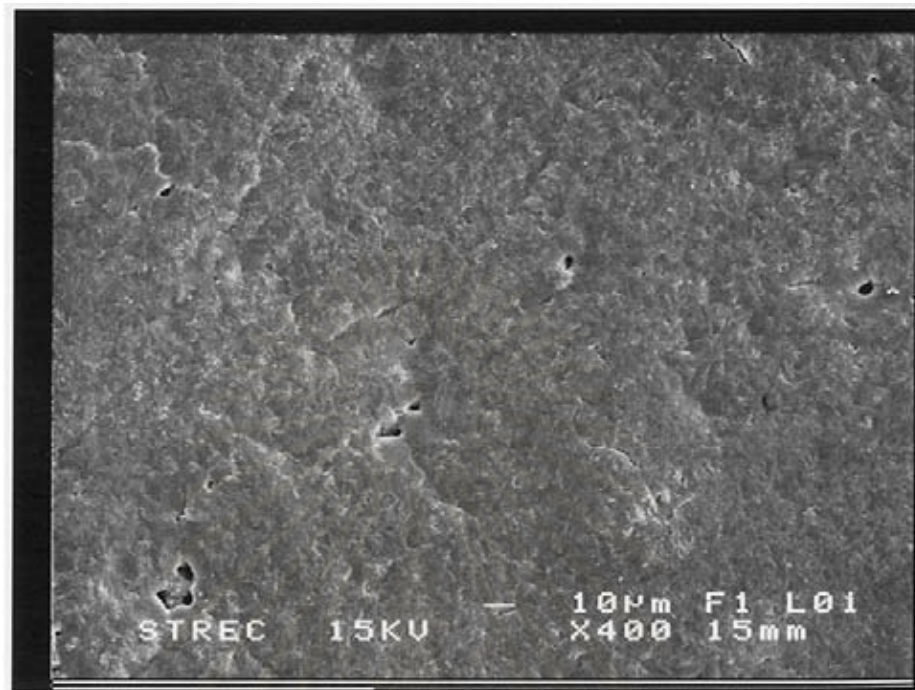


Figure XI SEM micrograph of porous film from liquid crystal-polymer composite (10% CE), magnification X400

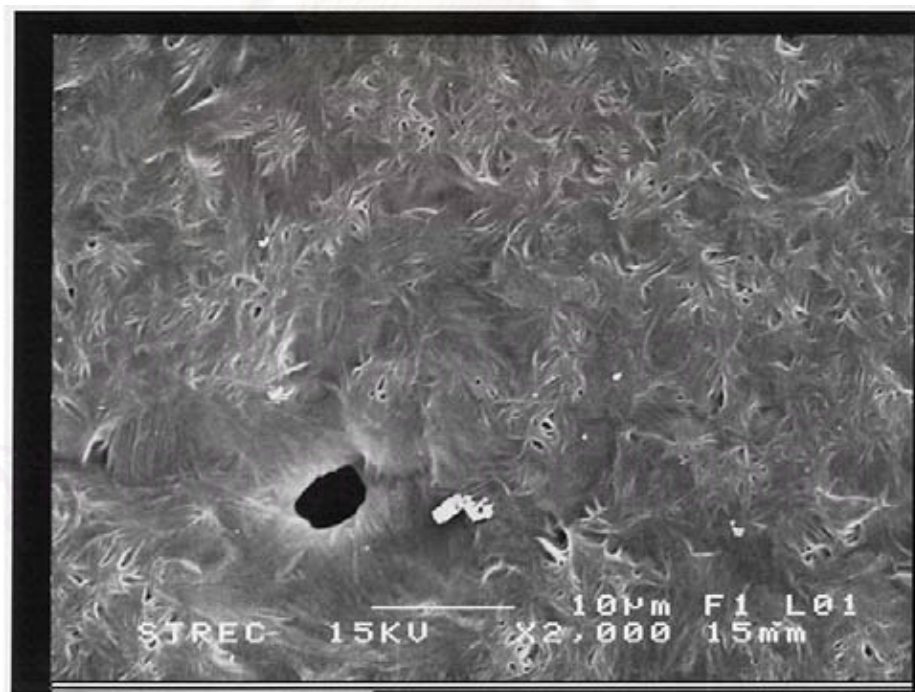


Figure XII SEM micrograph of porous film from liquid crystal-polymer composite (10% CE), magnification X2000

## CHAPTER V

### CONCLUSION

From this study, it could be concluded that the coconut was composed of about 47.6% by weight oil, based on the dry weight of coconut meat. It also contained 0.27% by weight of free cholesterol.

A trans-esterification reaction was used for synthesizing cholesteryl esters from coconut oil by using *p*-toluenesulfonic acid as a catalyst in two steps, consisting of trans-esterification of coconut oil with methanol and trans-esterification of FAMES with cholesterol. The optimum condition for trans-esterification of coconut oil and methanol was carried out at 65 °C for 4 hours. The product yield was 98.4%. The optimum conditions for trans-esterification of fatty acid methyl esters with cholesterol had a maximum conversion when the reaction was carried out with the 3: 33.27 by weight ratio of cholesterol to fatty acid methyl esters. The reaction temperature was 69 °C and the reaction time was 6 hours.

The phase transition temperatures of synthesized cholesteryl esters were from a solid phase to a smectic phase at 44.4 °C, from a smectic phase to a cholesteric phase at 66.6 °C, and from a cholesteric phase to a liquid phase at 78.0 °C. From these results, it could be concluded that the cholesteryl esters could be used as liquid crystals.

This study uses the cholesteryl esters from coconut oil to blend with polyethylene to form liquid crystal–polymer composites at 5 and 10% of cholesteryl

esters. The porous film was prepared by solvent extraction by removing the cholesteryl esters from liquid crystal–polymer composites. The results demonstrated that cholesteryl esters could be used for porous film application. From this study, it yielded porous film that had a diameter of pores of about 5  $\mu\text{m}$ .

### **SUGGESTION FOR FUTURE WORK**

In future work, we should study other parameters such as cooling rates or mixing condition that affect the size and distribution of microdroplet of liquid crystal in polyethylene film, and physical properties of the porous polyethylene film.



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12. F.M. Herman, G.O. Charles, F.O Donald and T.S. Glenn. Encyclopedia of Chemical Technology. 3<sup>rd</sup> ed. Vol. 14. London: John Wiley & Sons, 1979, pp. 395-427.
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14. S. Martin. "The History of the Liquid Crystal Display and Liquid Crystal Material Technology, " Liq. Cryst. 5(1989): pp. 57-71.
15. L. Bouteiller and P. Le Barny. "Polymer-Dispersed Liquid Crystals: Preparation, Operation and Application, " Liq. Cryst. 21(1996): pp. 157-174.
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APPENDIX

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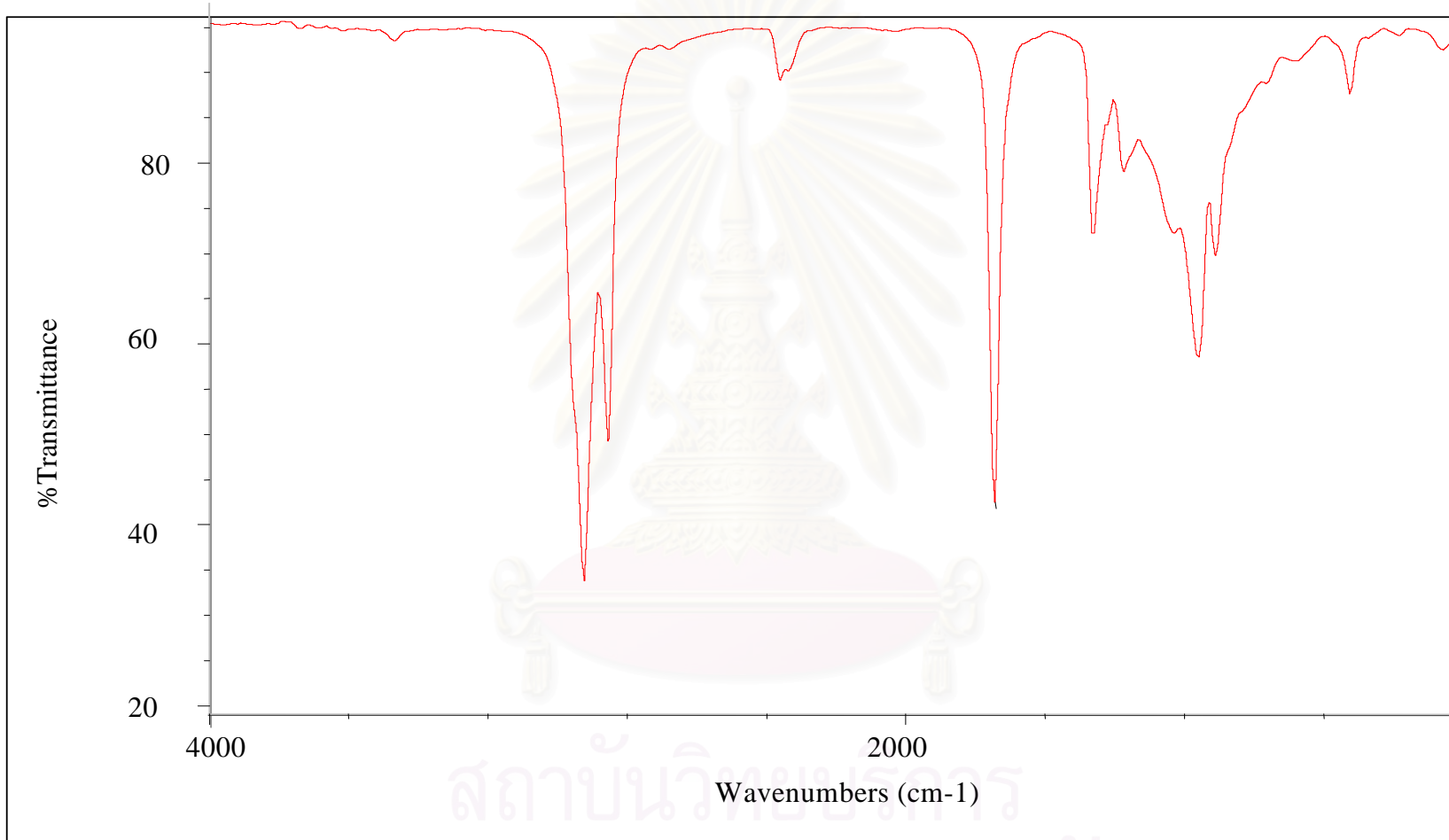


Figure A1 FT-IR spectrum of the coconut oil

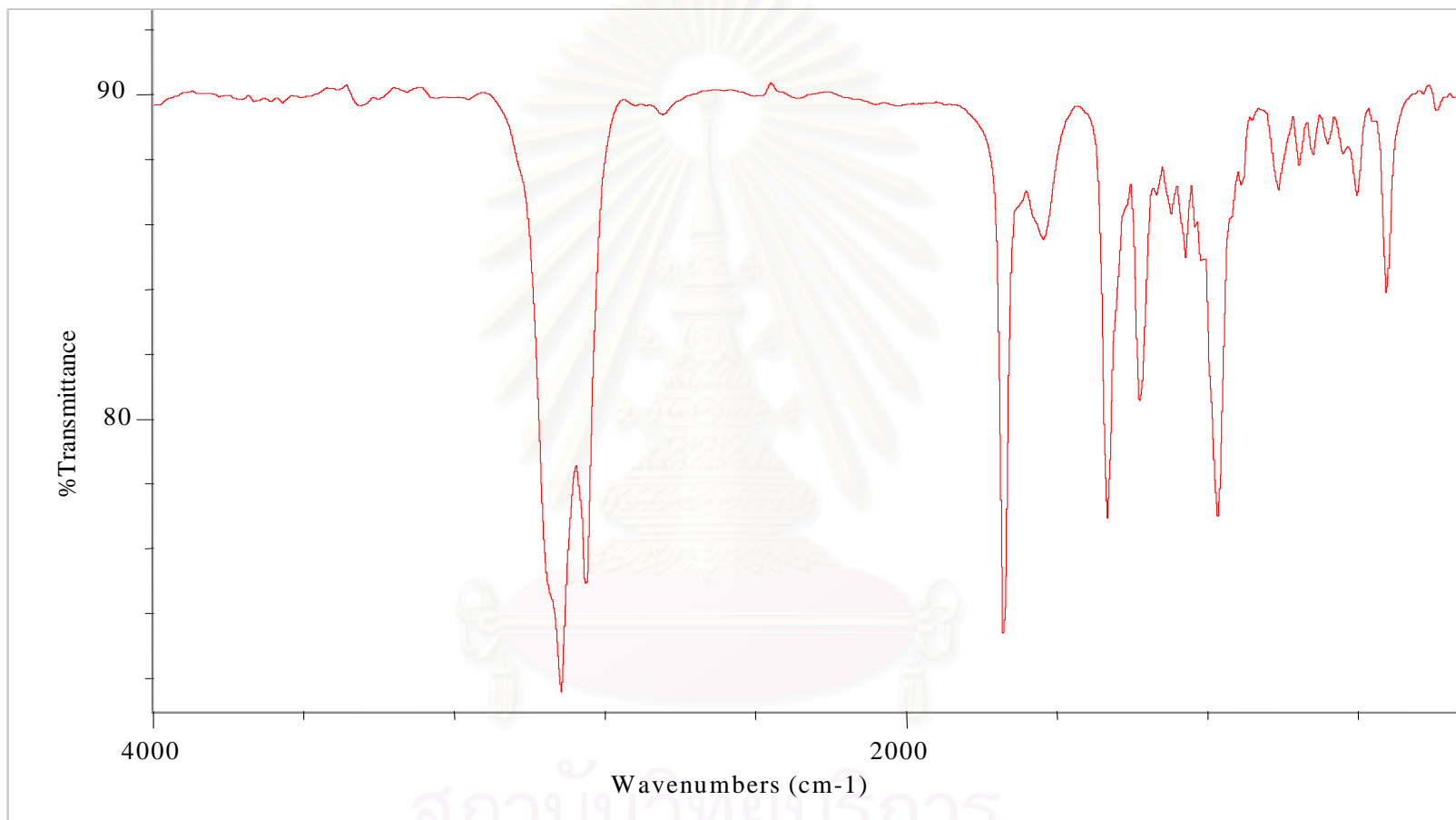


Figure A2 FT-IR spectrum of the cholesteryl stearate

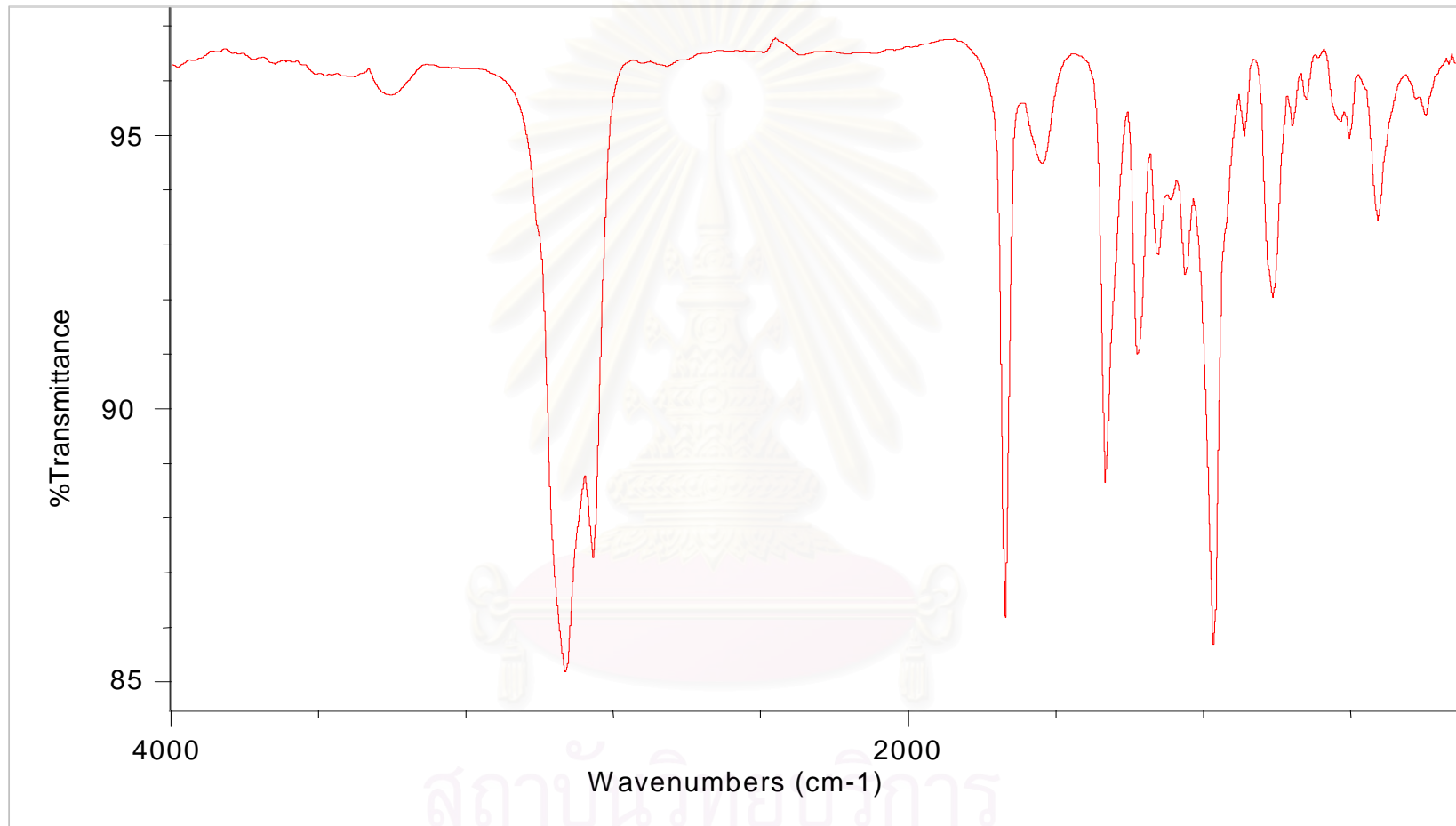


Figure A3 FT-IR spectrum of the cholesteryl oleate

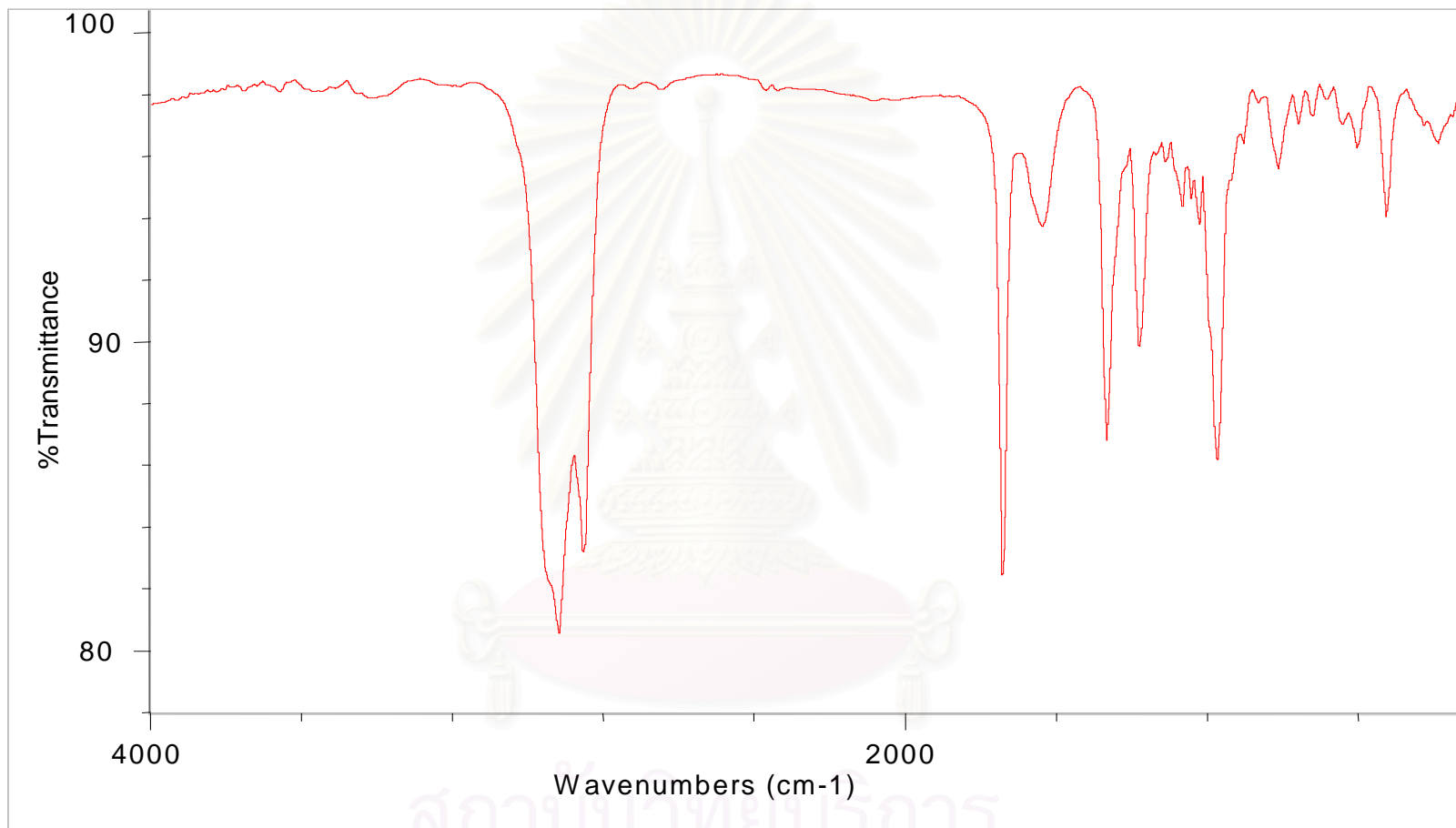


Figure A4 FT-IR spectrum of the cholesteryl palmitate

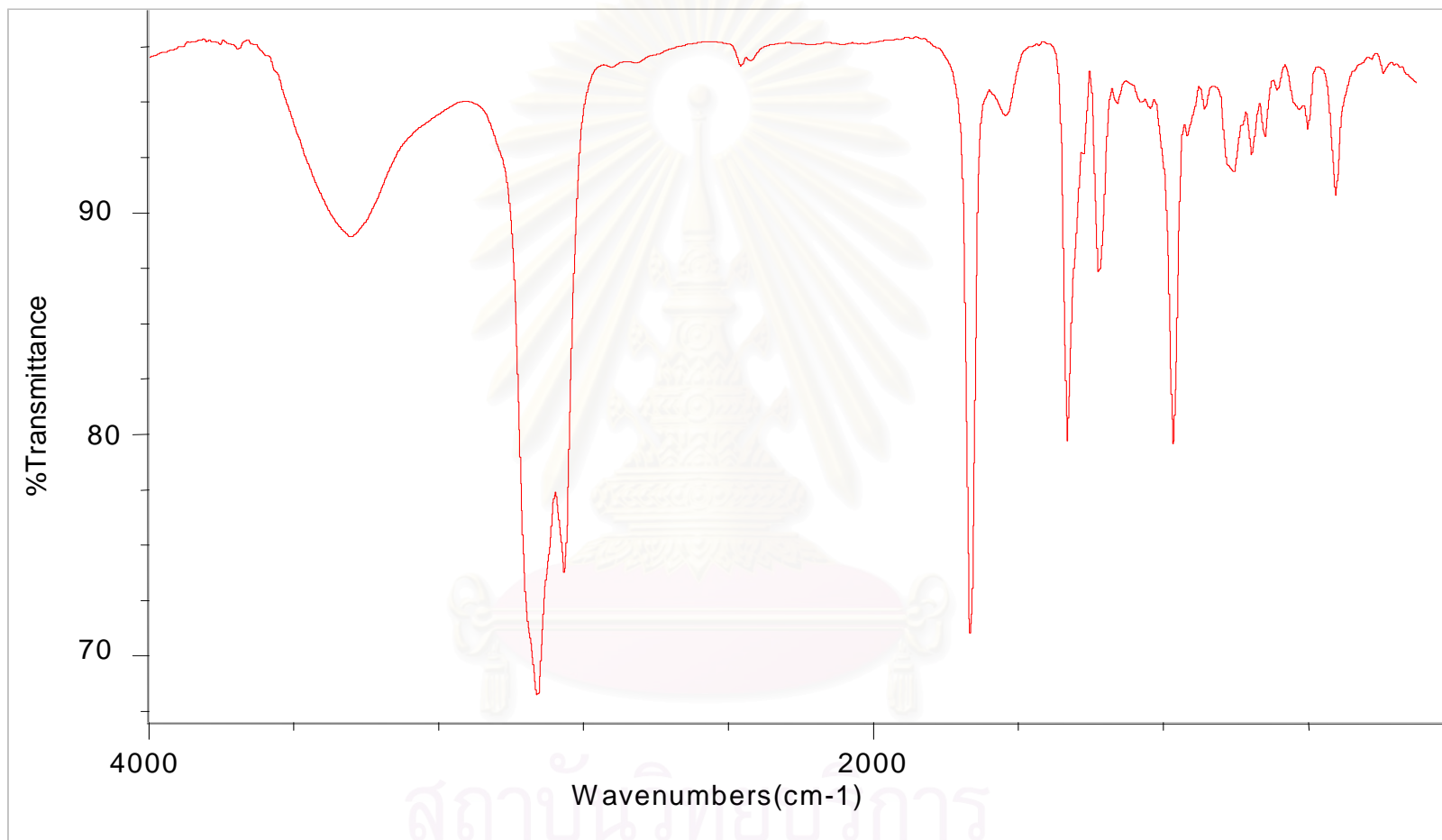


Figure A5 FT-IR spectrum of the cholesteryl ester from coconut oil

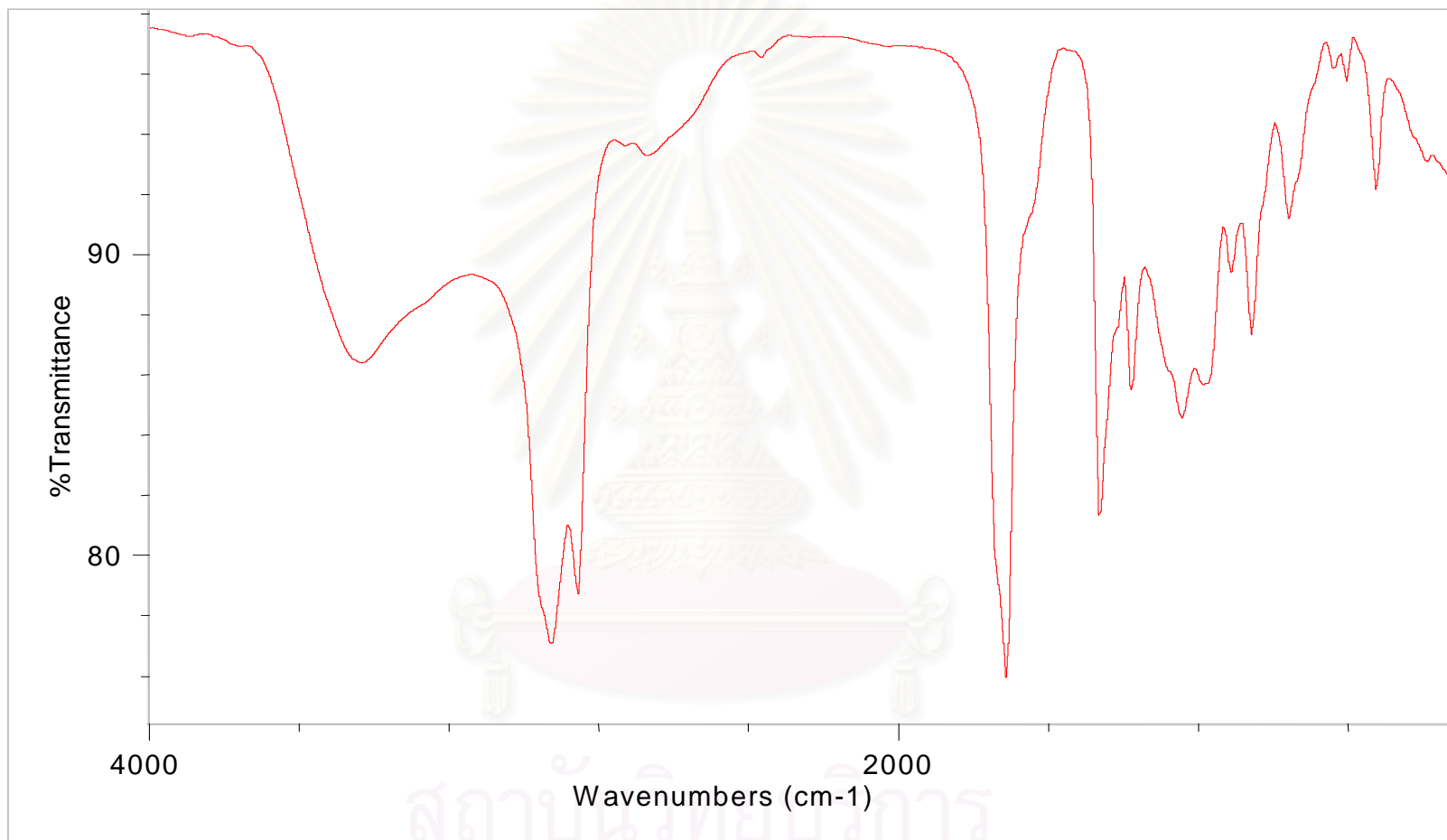


Figure A6 FT-IR spectrum of the cholesterol from coconut oil

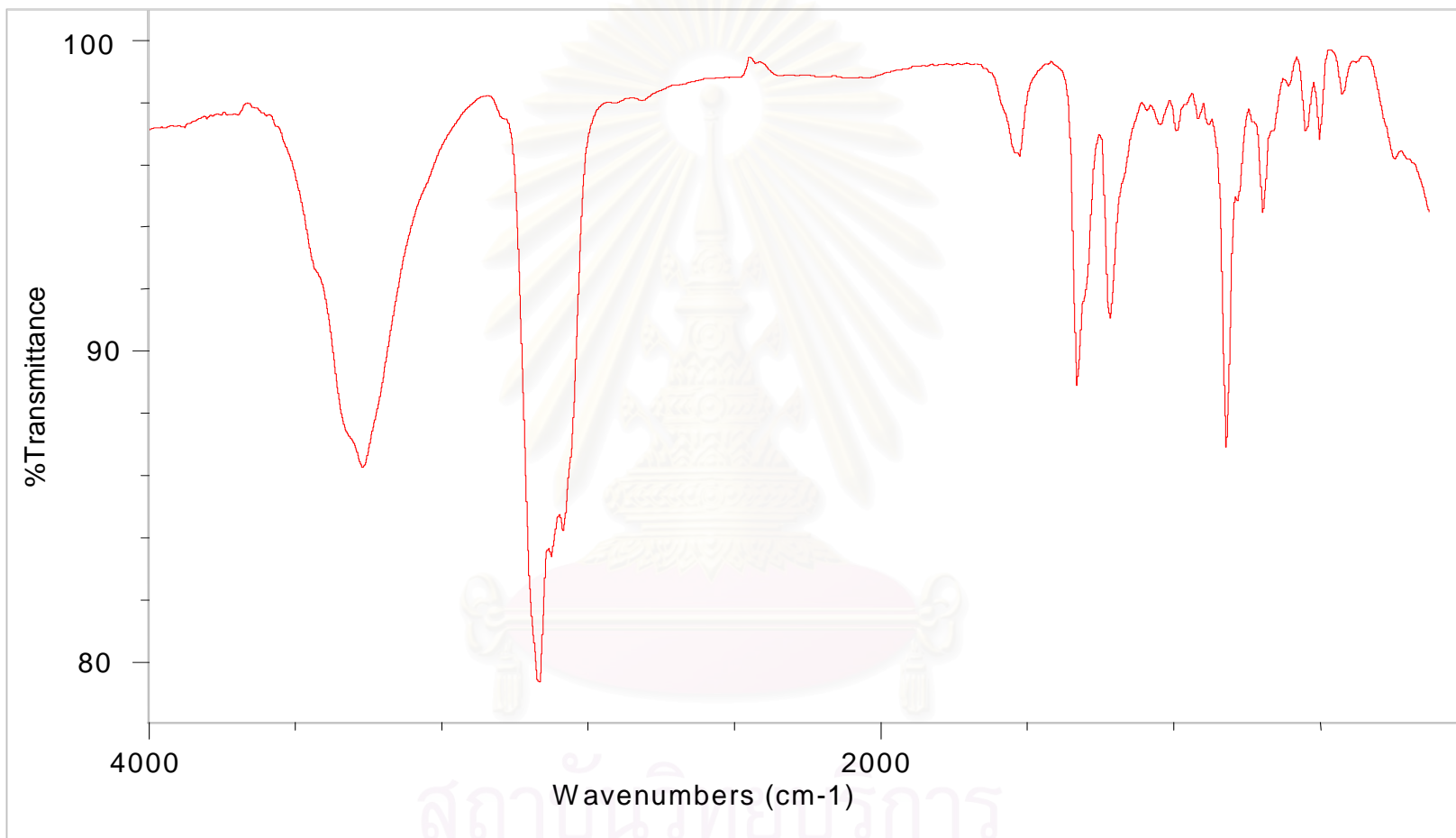


Figure A7 FT-IR spectrum of the authentic cholesterol

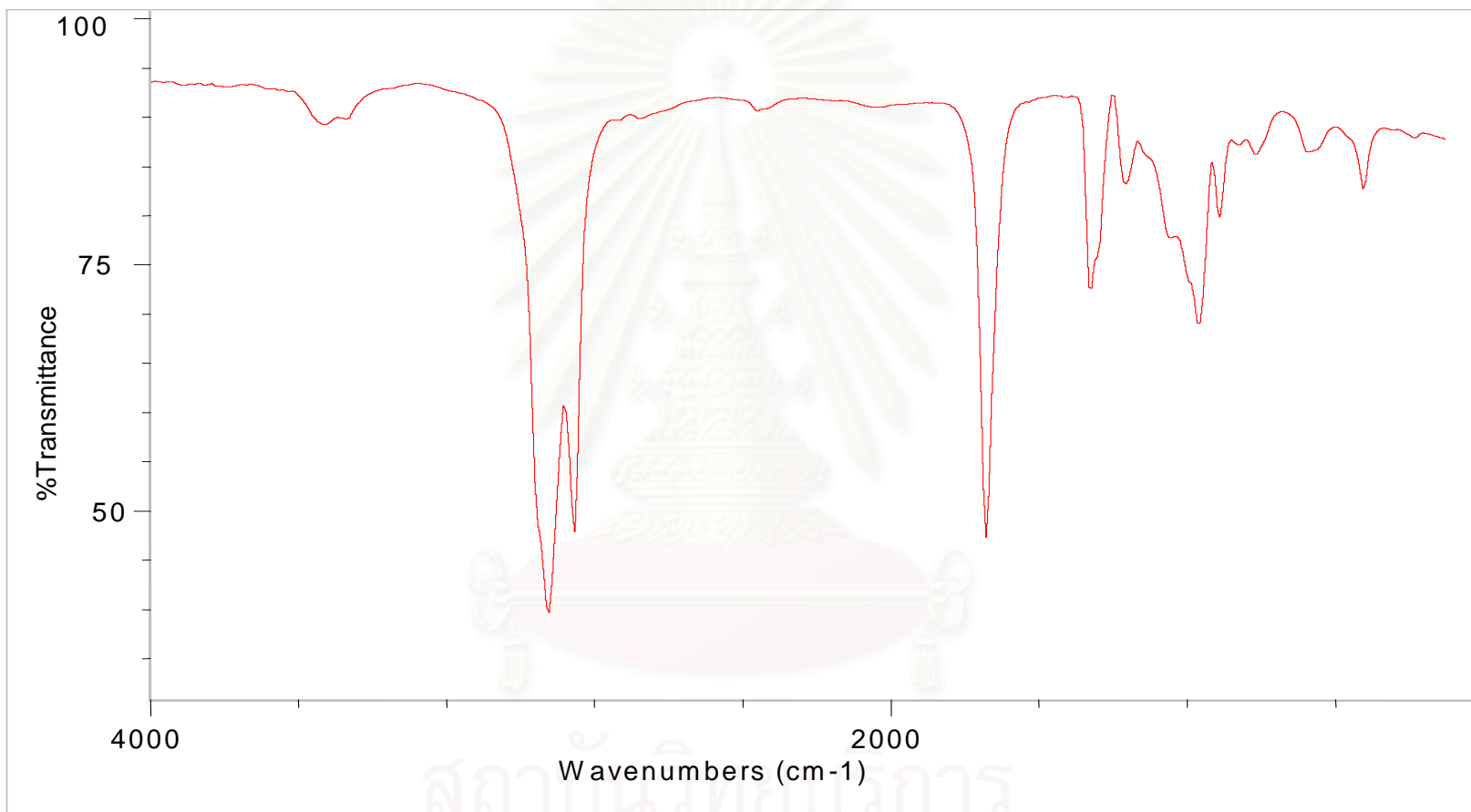
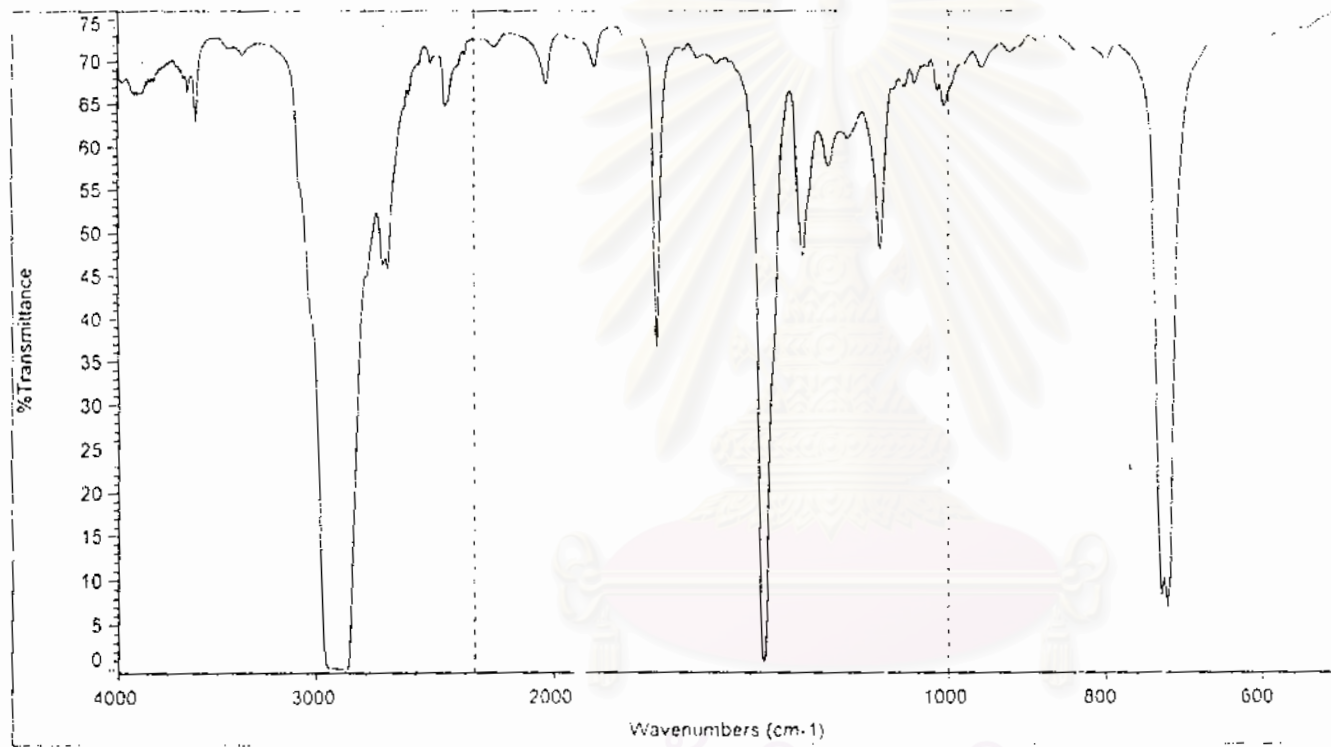


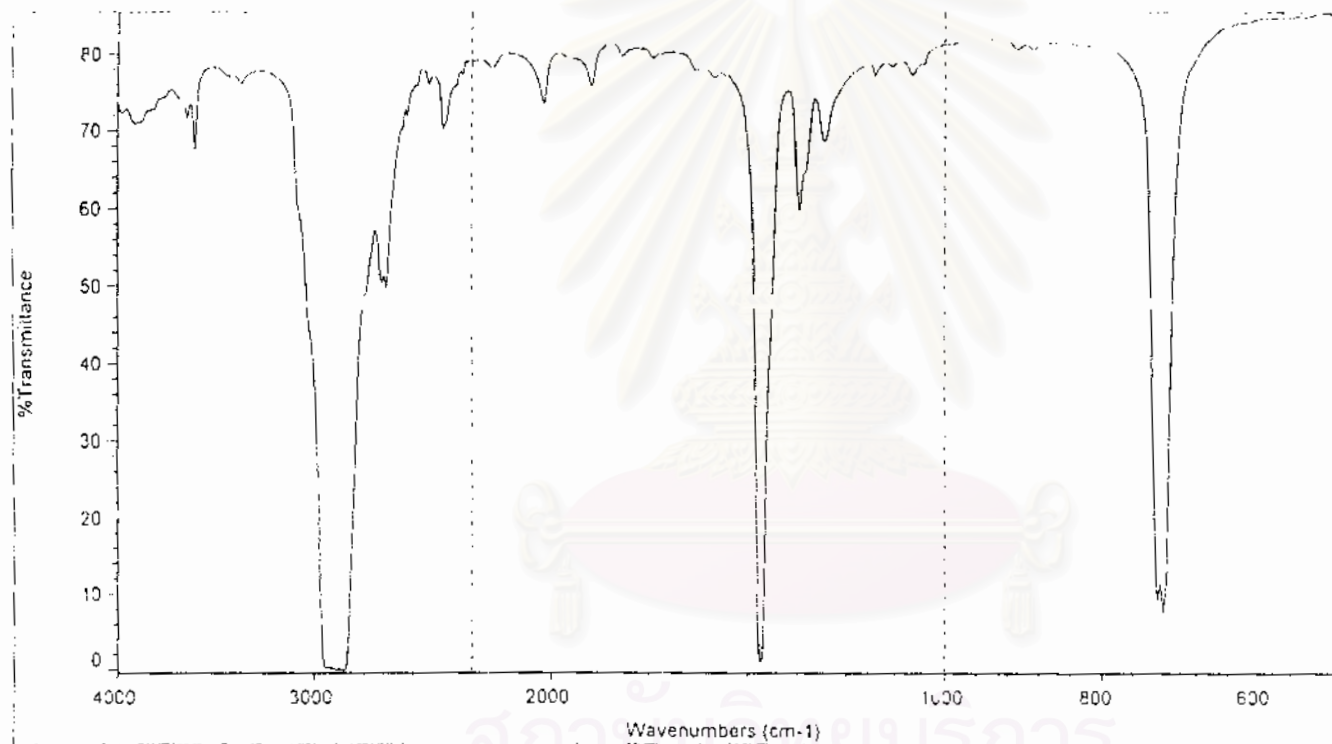
Figure A8 FT-IR spectrum of the fatty acid methyl esters





A9 FTIR spectrum of liquid crystal-polymer composite before extraction

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A10 FTIR spectrum of liquid crystal-polymer composite after extraction

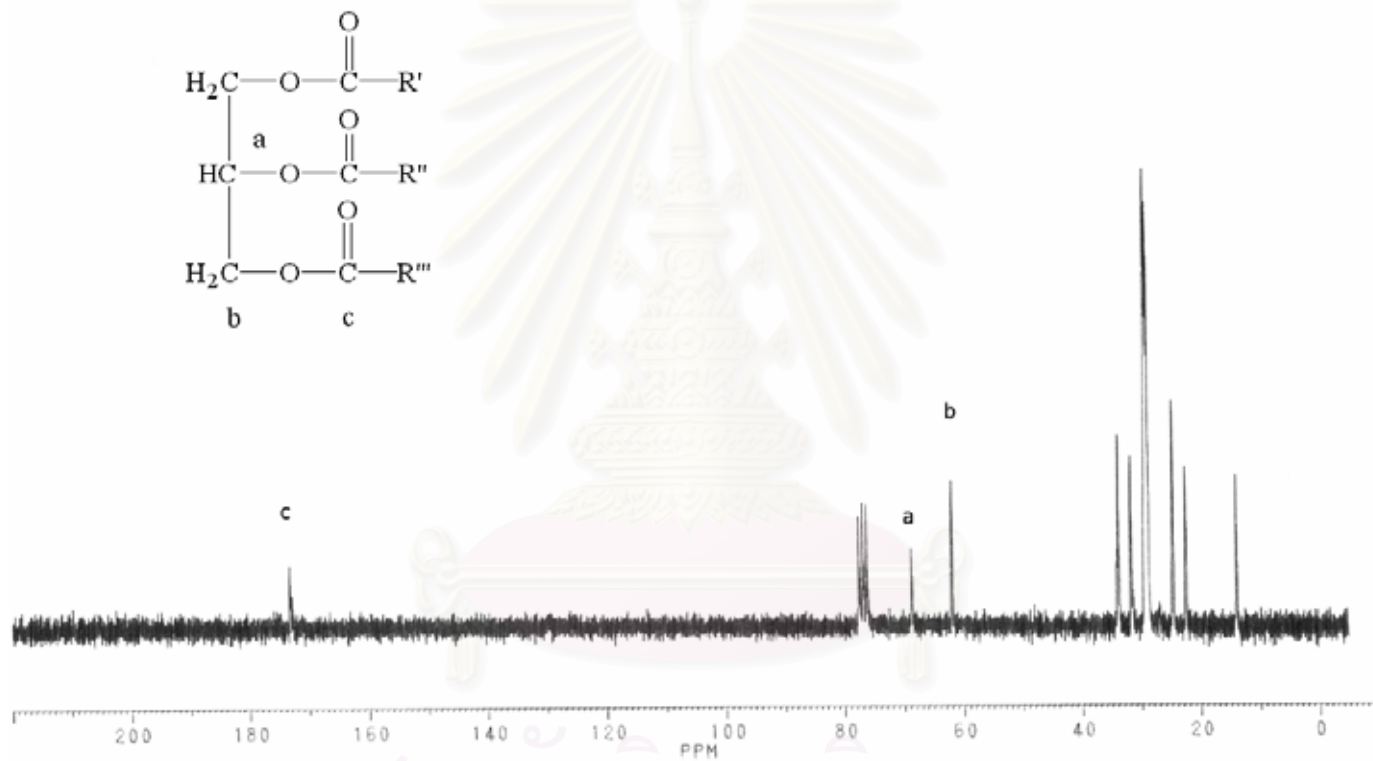


Figure B1  $^{13}\text{C}$ -NMR spectrum of the coconut oil

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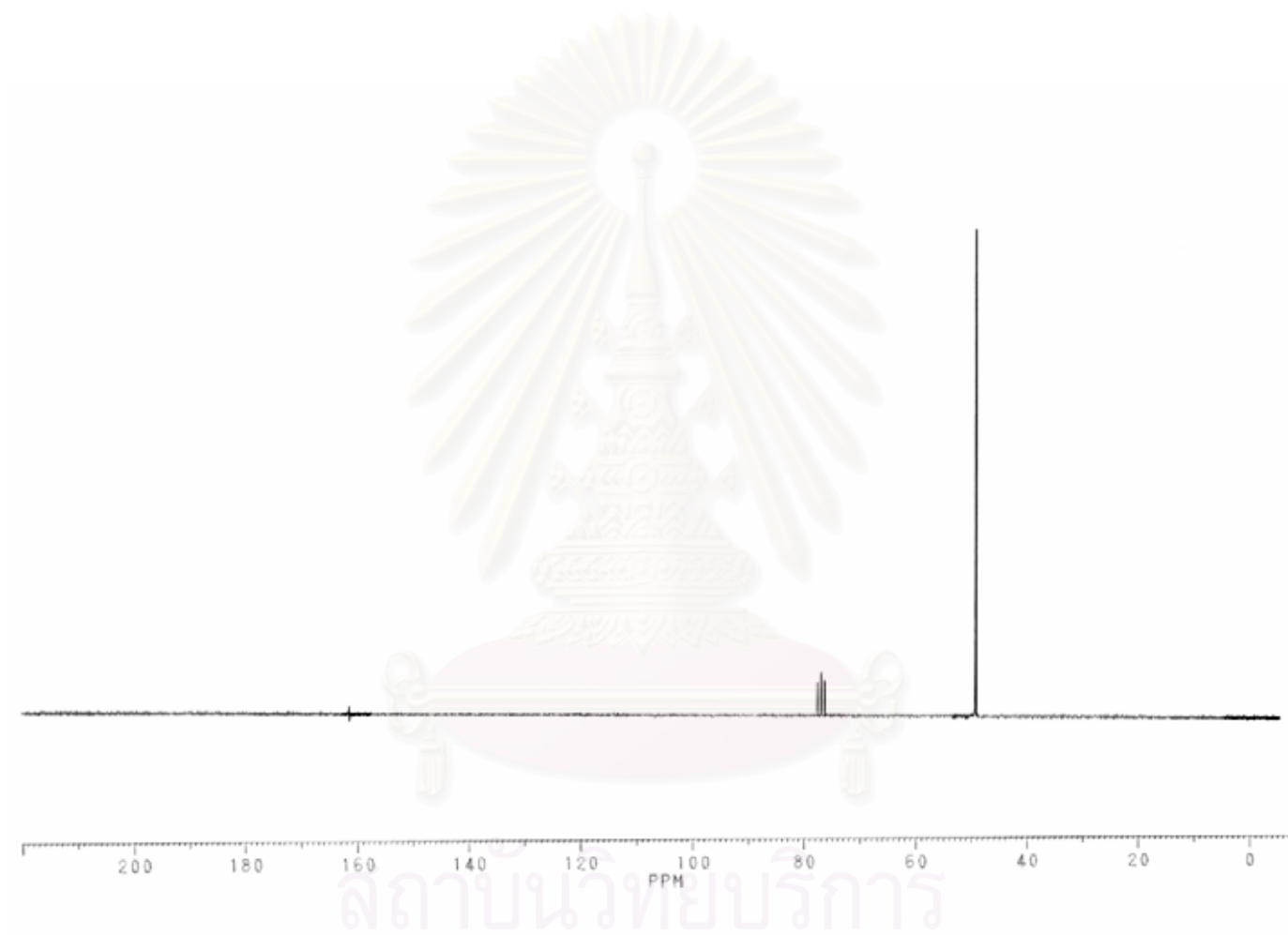


Figure B2  $^{13}\text{C}$ -NMR spectrum of methanol

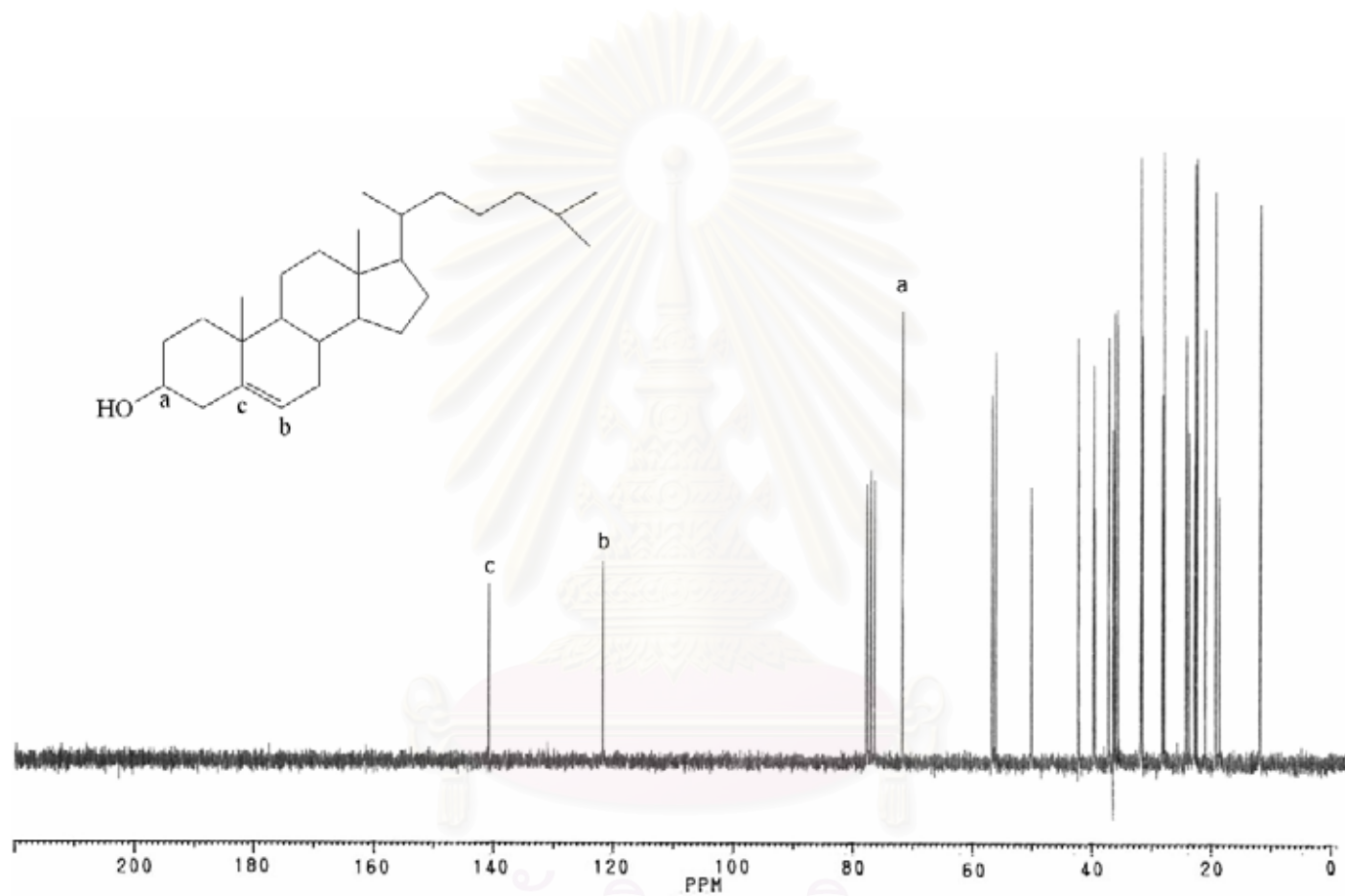


Figure B3  $^{13}\text{C}$ -NMR spectrum of authentic cholesterol

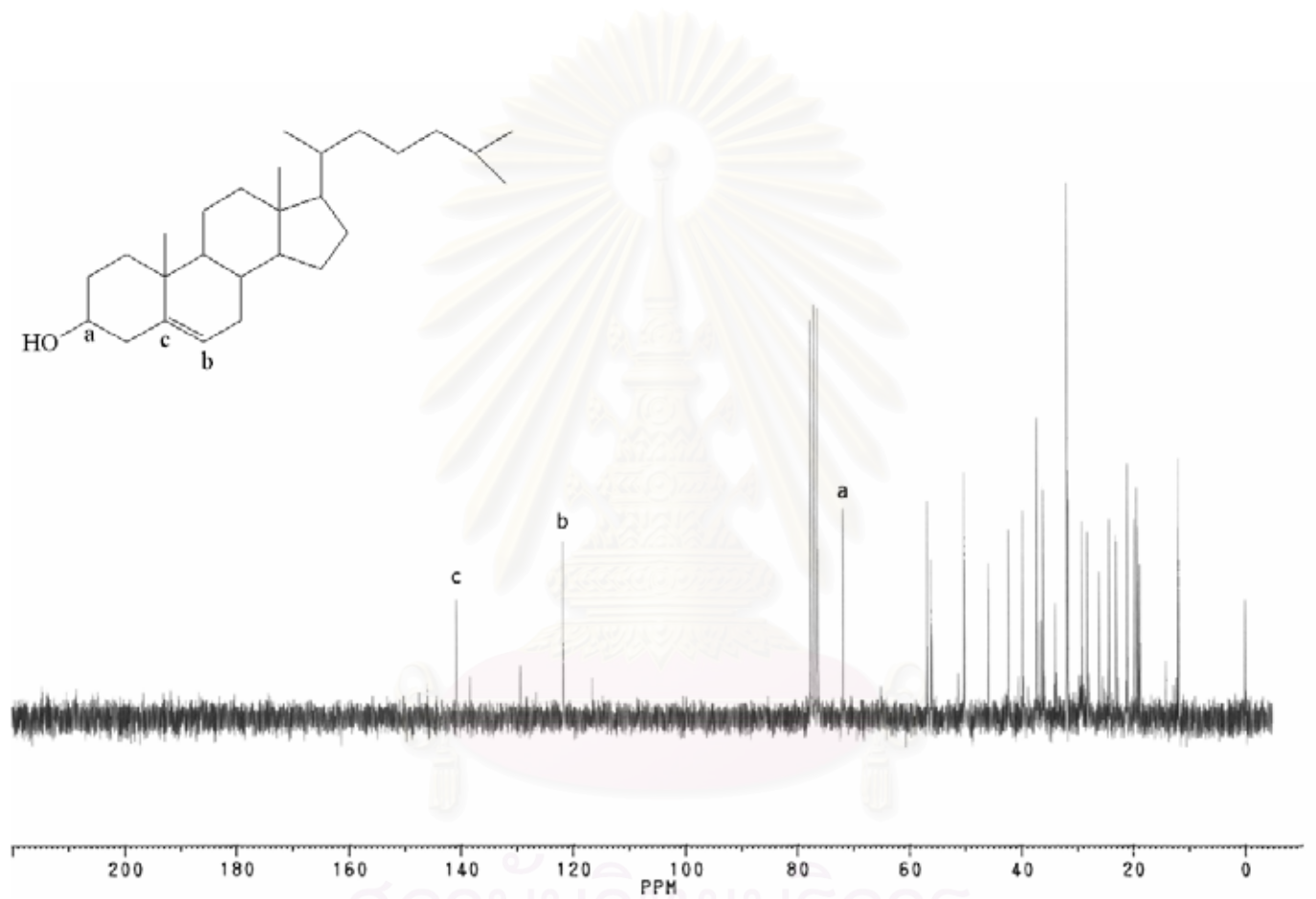


Figure B4  $^{13}\text{C}$ -NMR spectrum of cholesterol from coconut oil

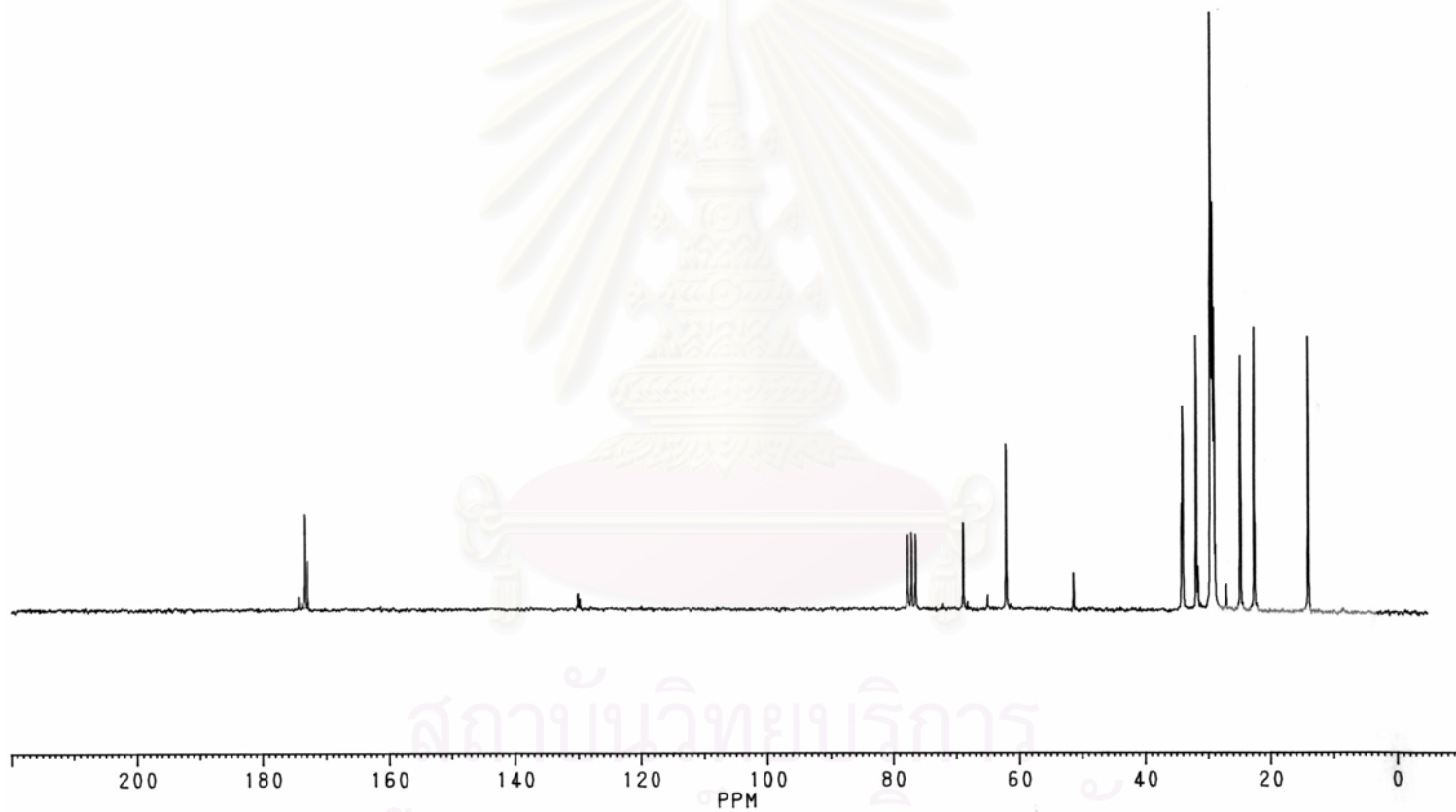


Figure B5  $^{13}\text{C}$ -NMR spectrum of the fatty acid methyl esters at 2 h.

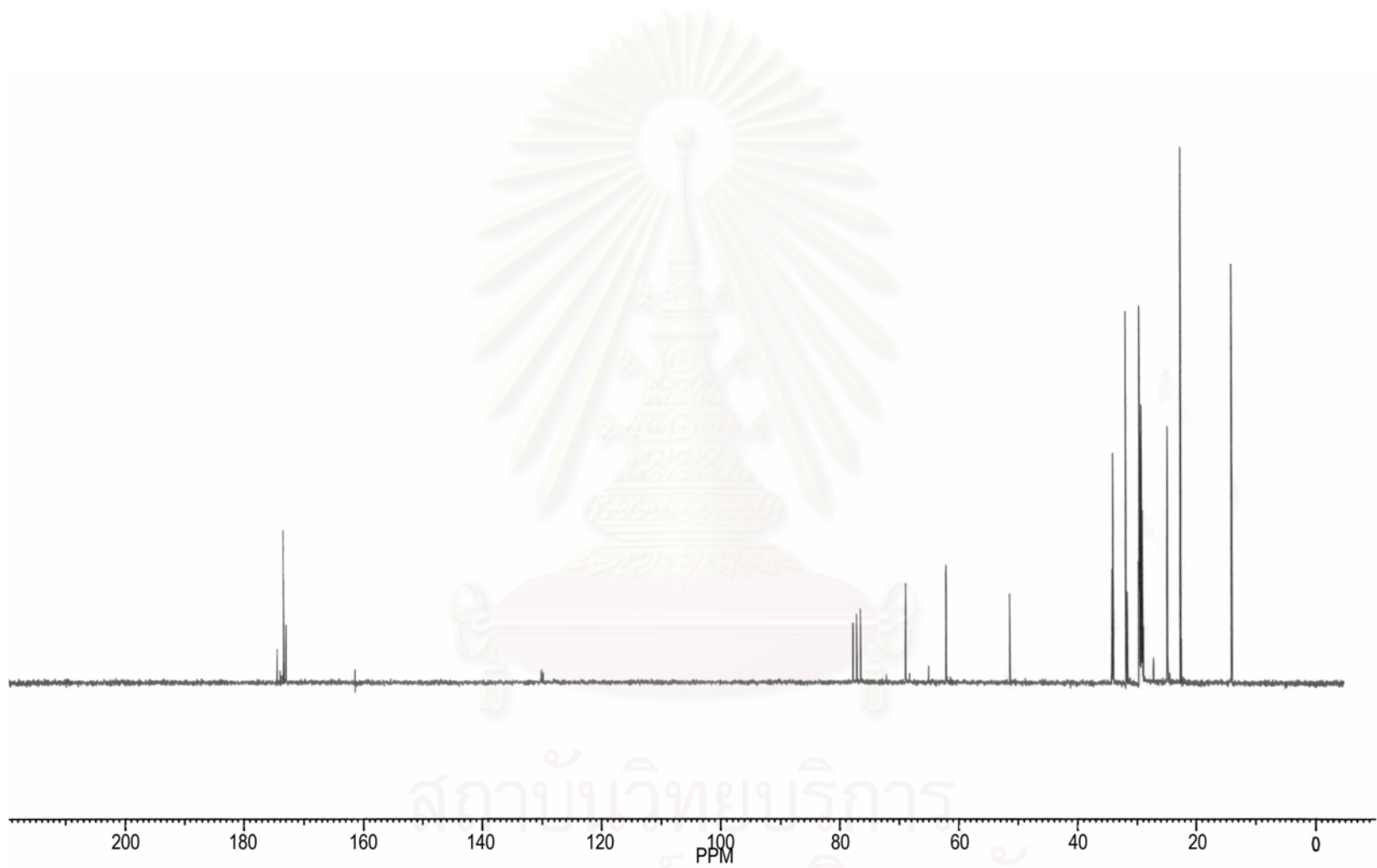


Figure B6  $^{13}\text{C}$ -NMR spectrum of the fatty acid methyl esters at 3 h.



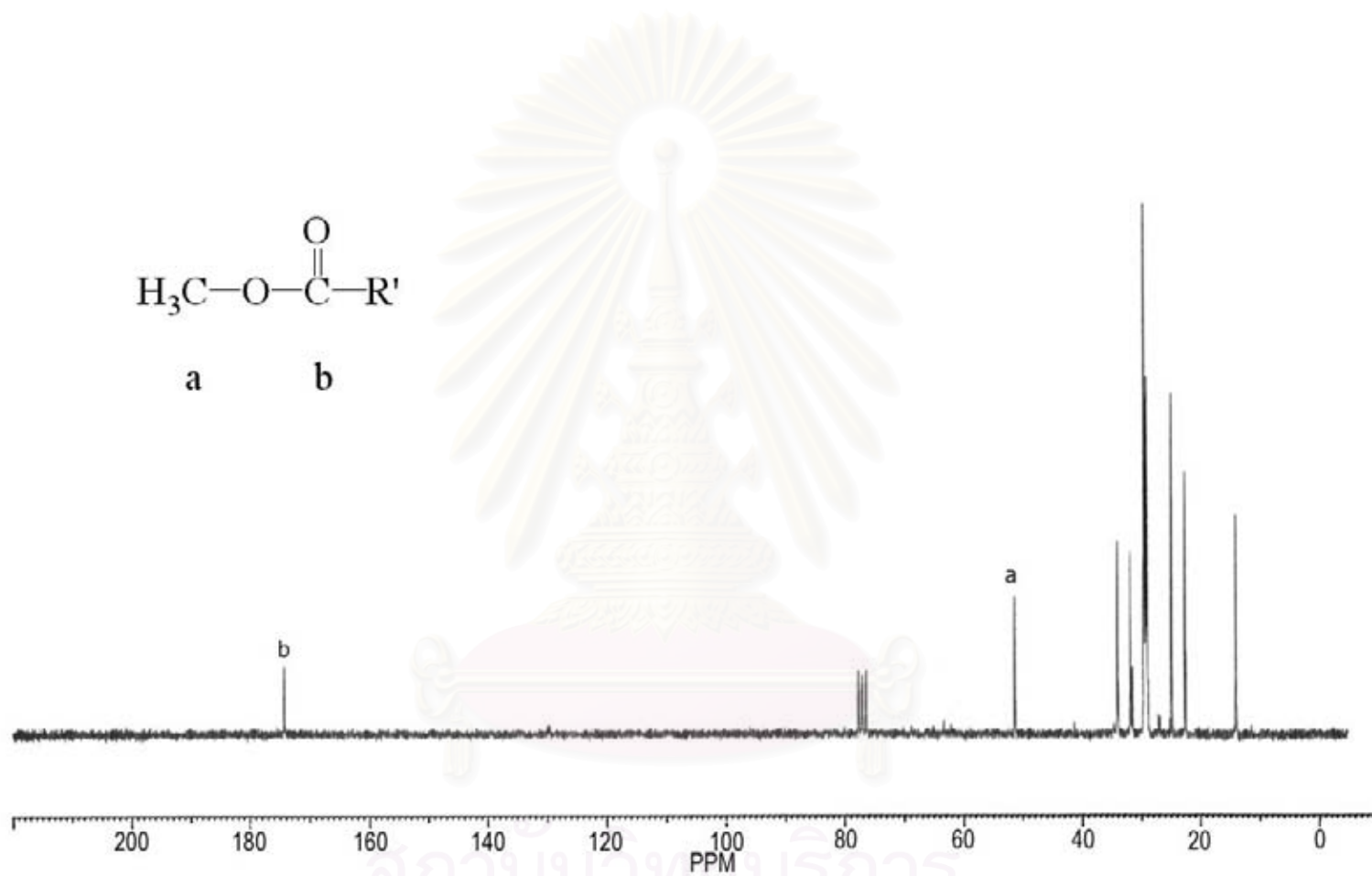
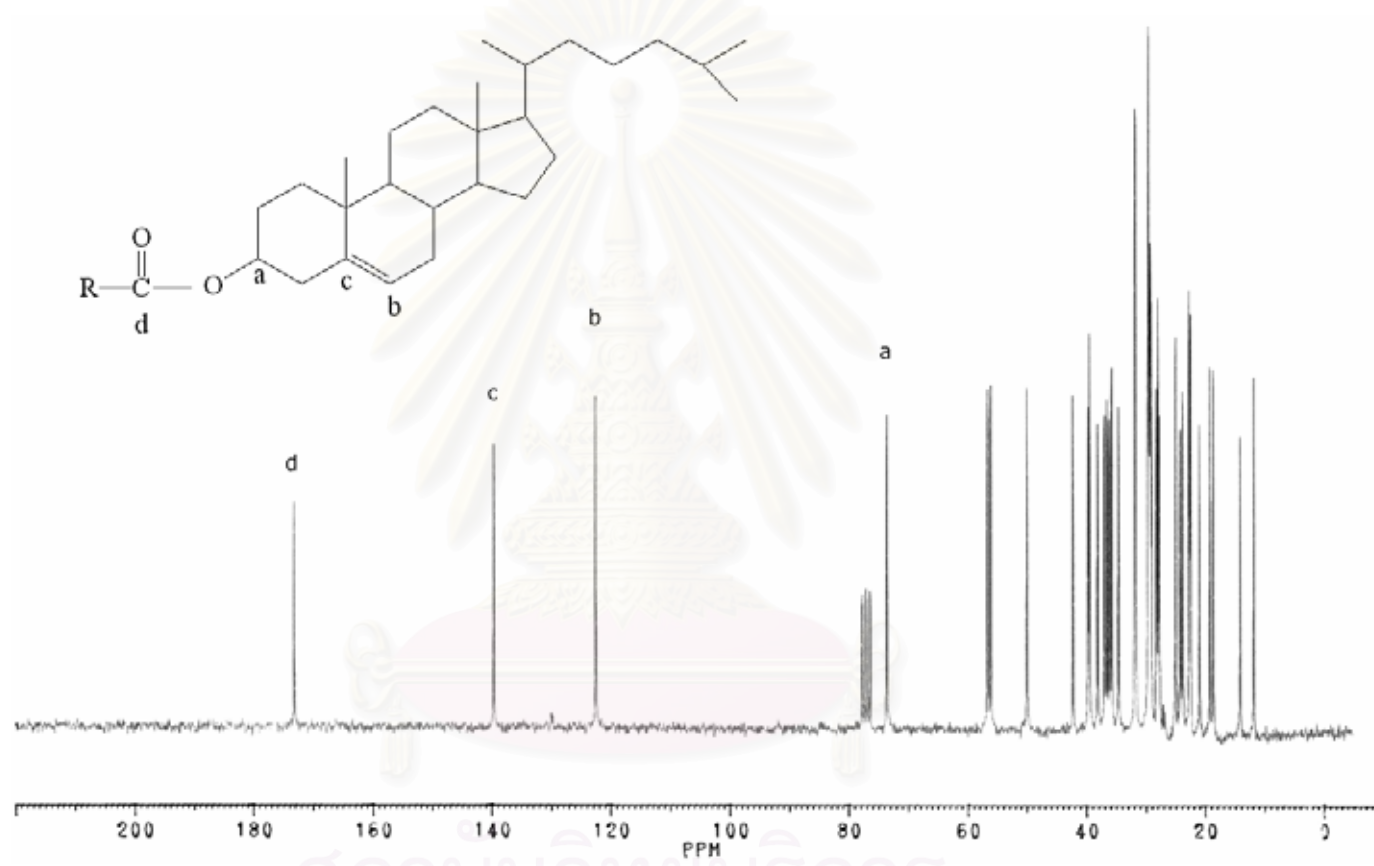


Figure B7  $^{13}\text{C}$ -NMR spectrum of the fatty acid methyl esters at 4 h.



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Figure B8  $^{13}\text{C}$ -NMR spectrum of the cholesteryl ester

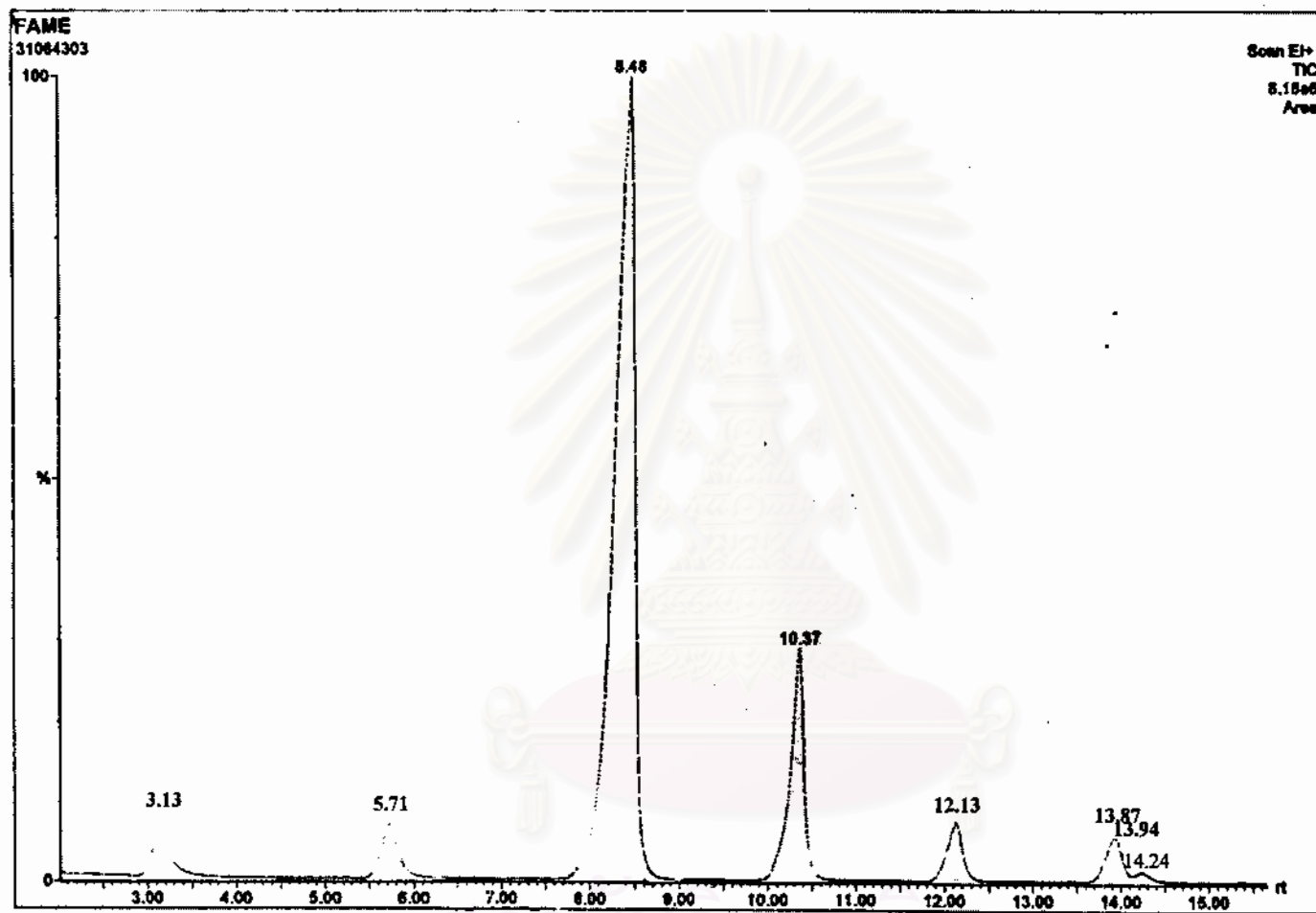


Figure C1 GC chromatogram of fatty acid methyl esters

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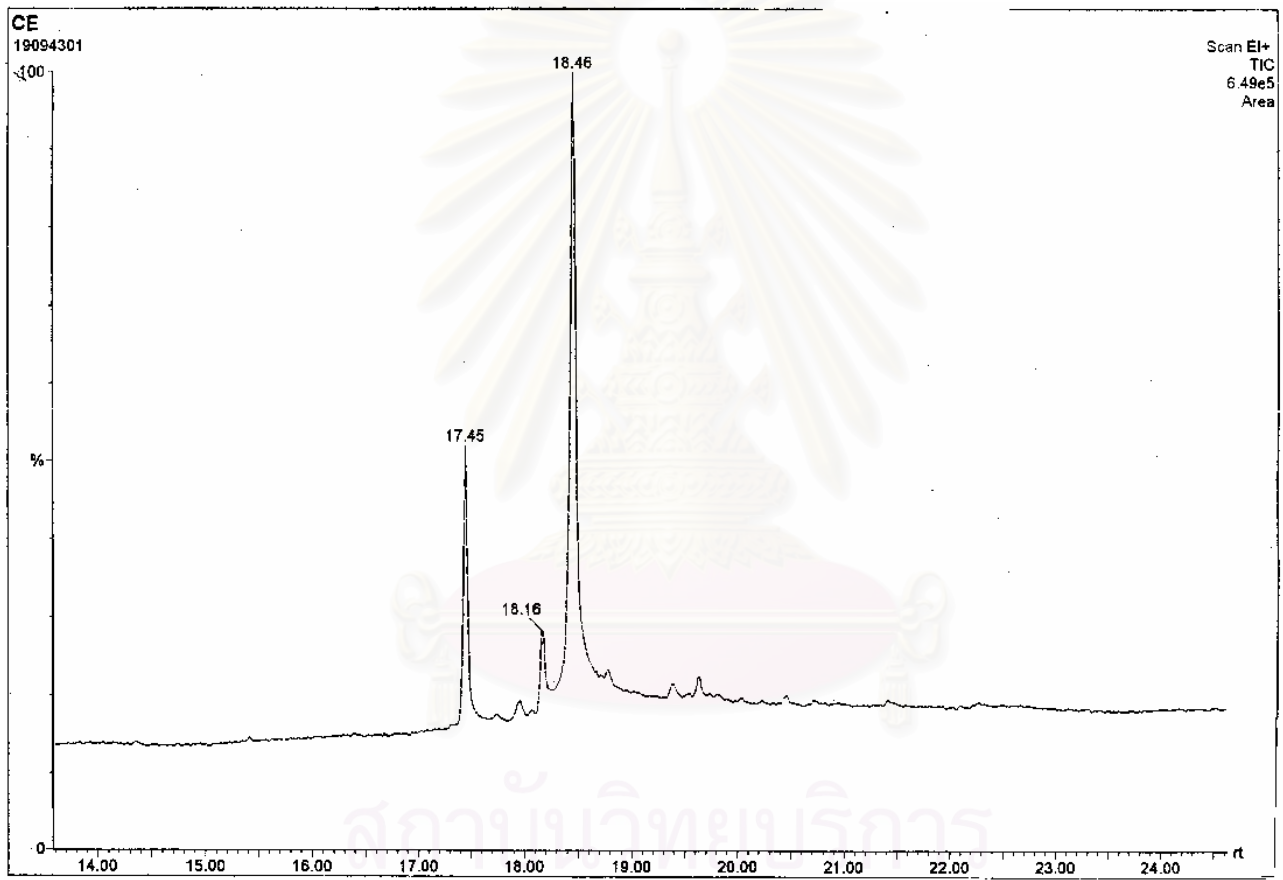


Figure C2 GC chromatogram of cholesteryl esters

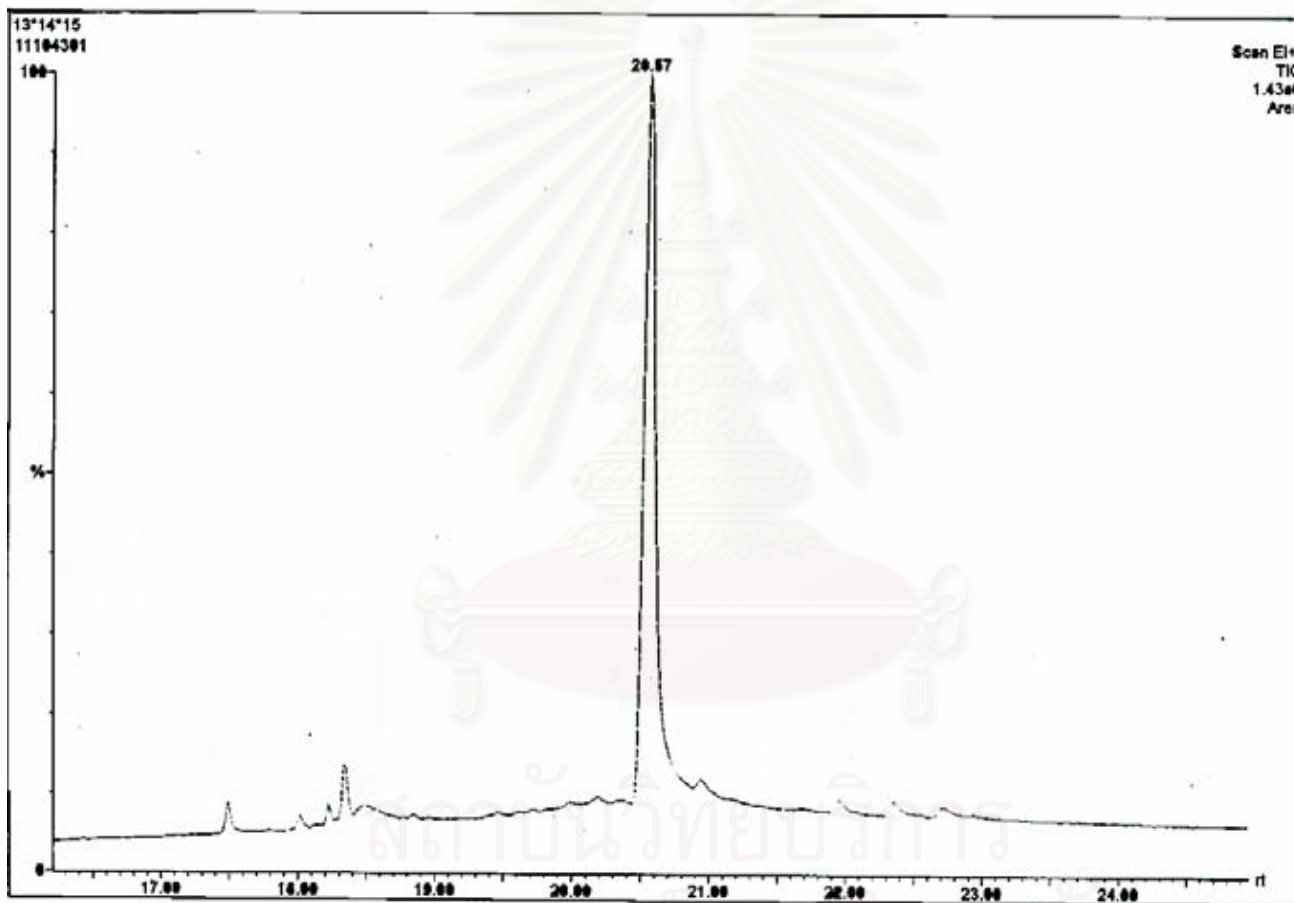


Figure C3 GC chromatogram of cholesterol

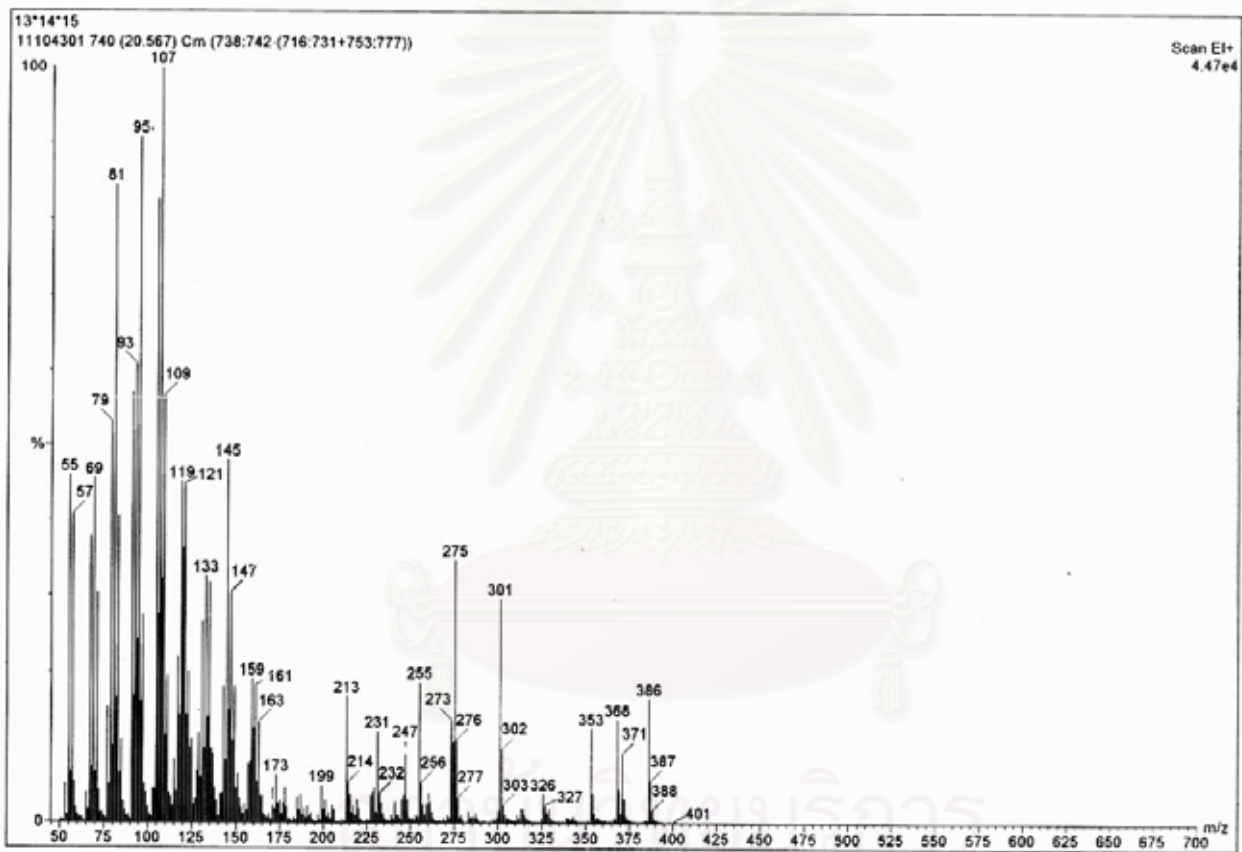


Figure D1 Mass spectrum of cholesterol from coconut oil.

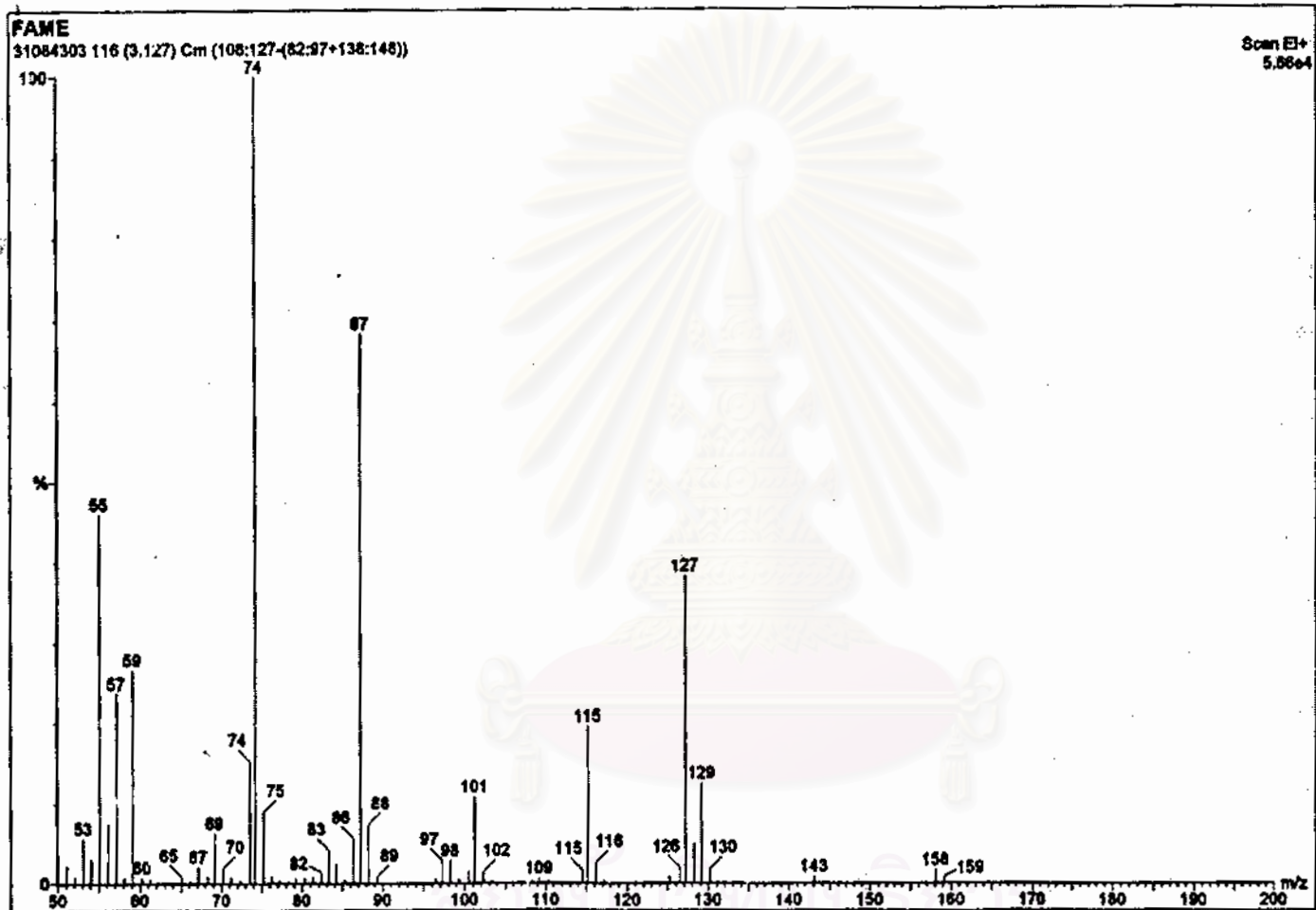


Figure D2 Mass spectrum of methyl caprylate at retention time of 3.13 min.



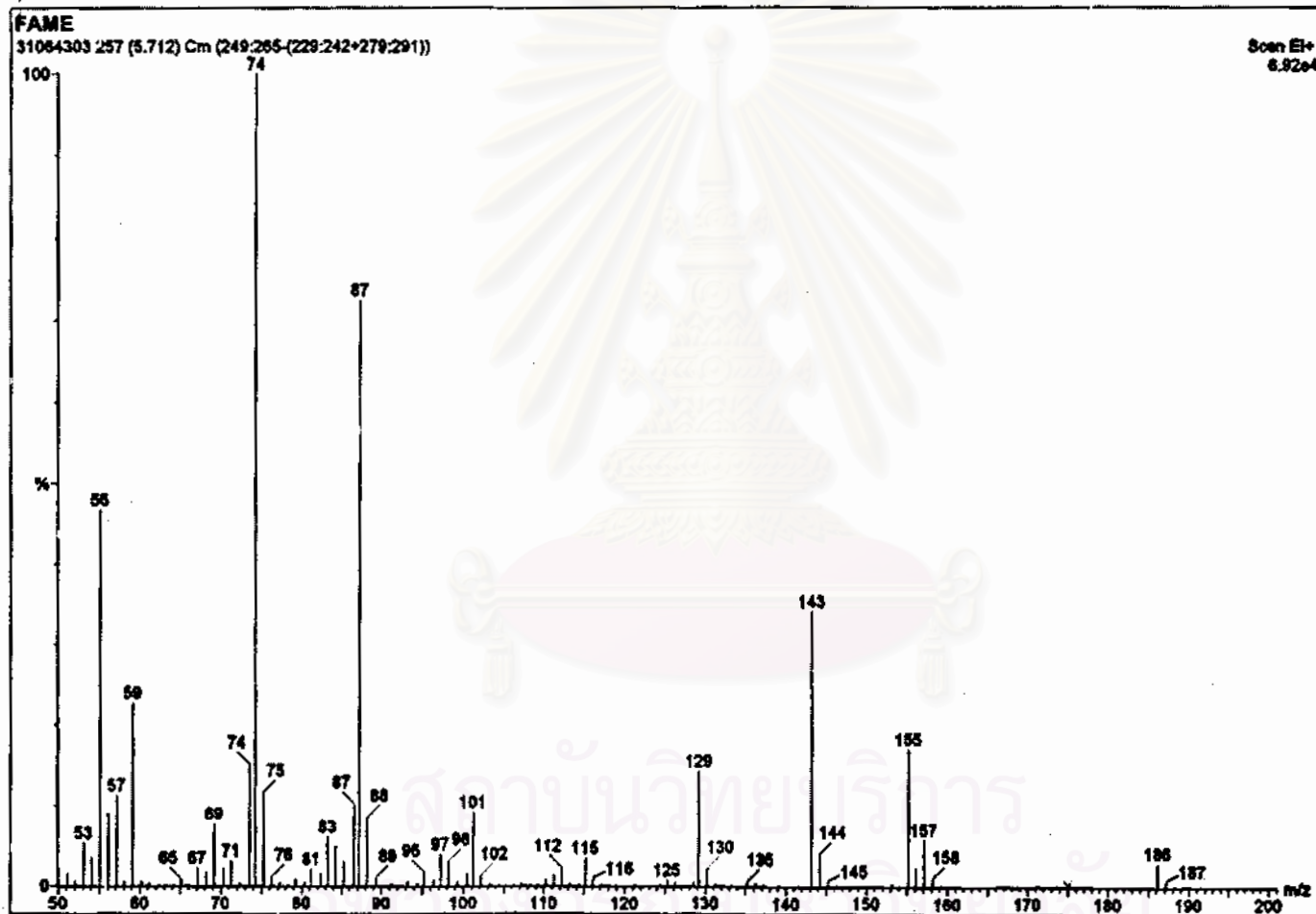


Figure D3 Mass spectrum of methyl caprate at retention time of 5.71 min.

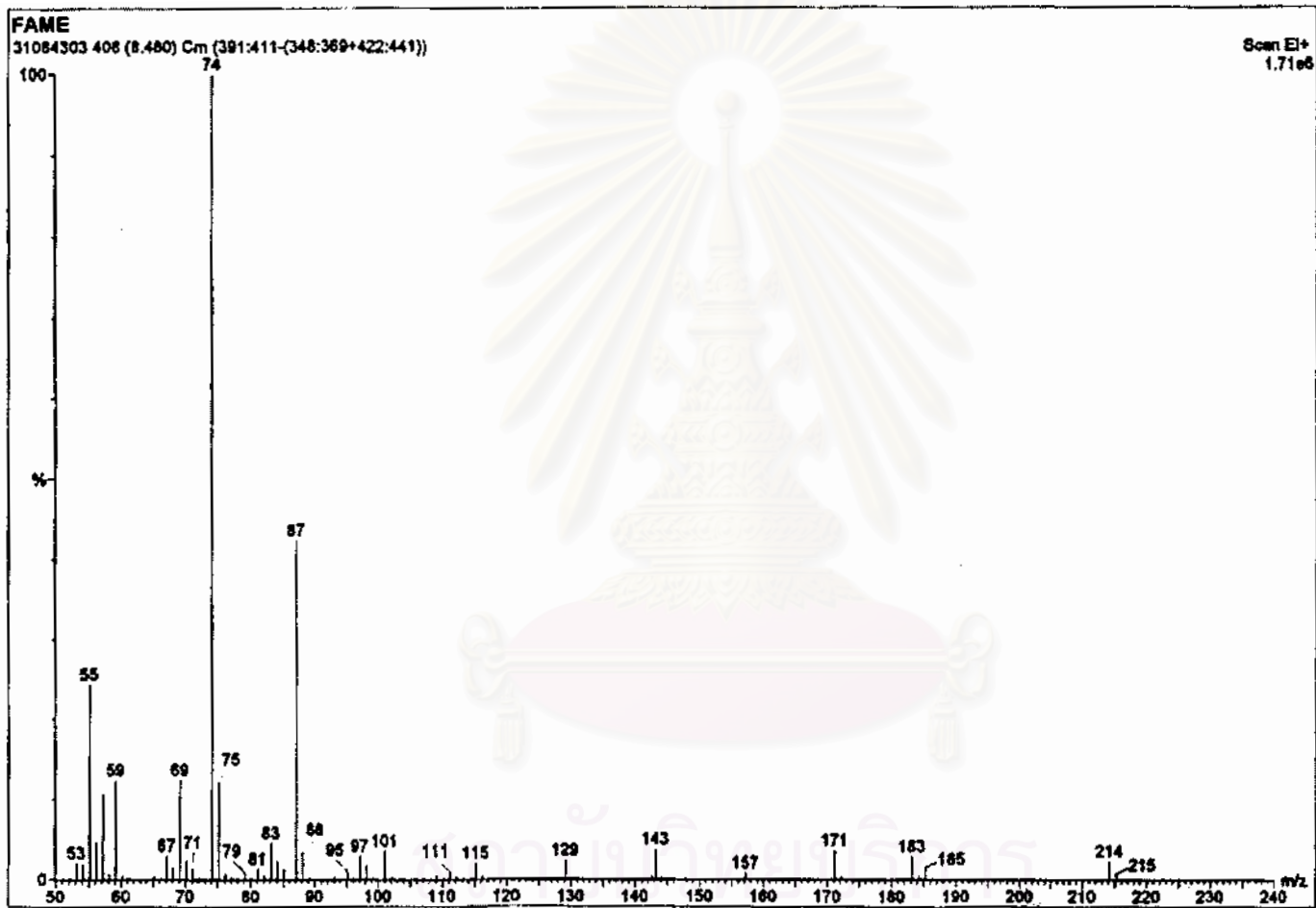


Figure D4 Mass spectrum of methyl laurate at retention time of 8.48 min.

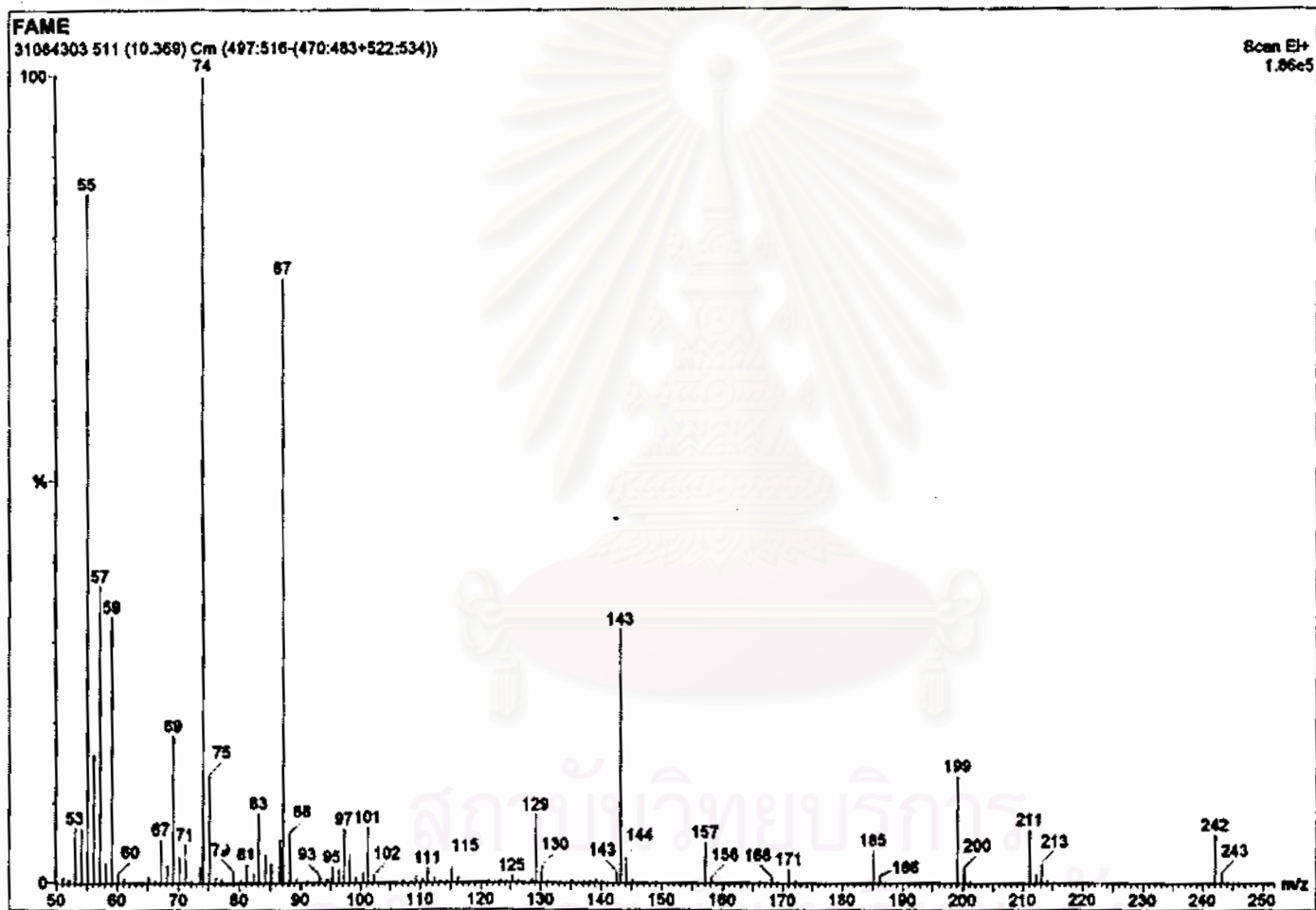


Figure D5 Mass spectrum of methyl myristate at retention time of 10.37 min.

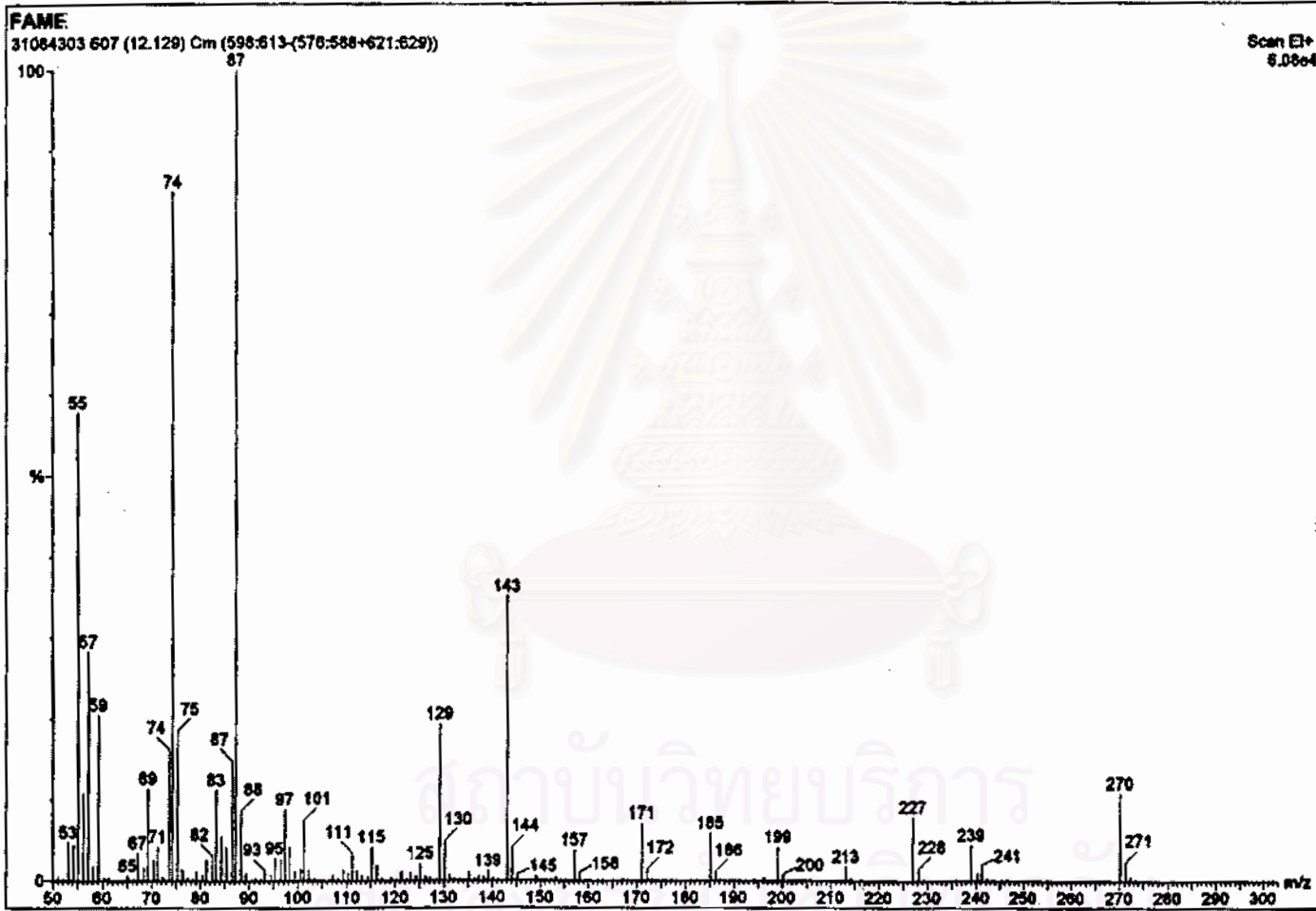


Figure D6 Mass spectrum of methyl palmitate at retention time of 12.13 min.

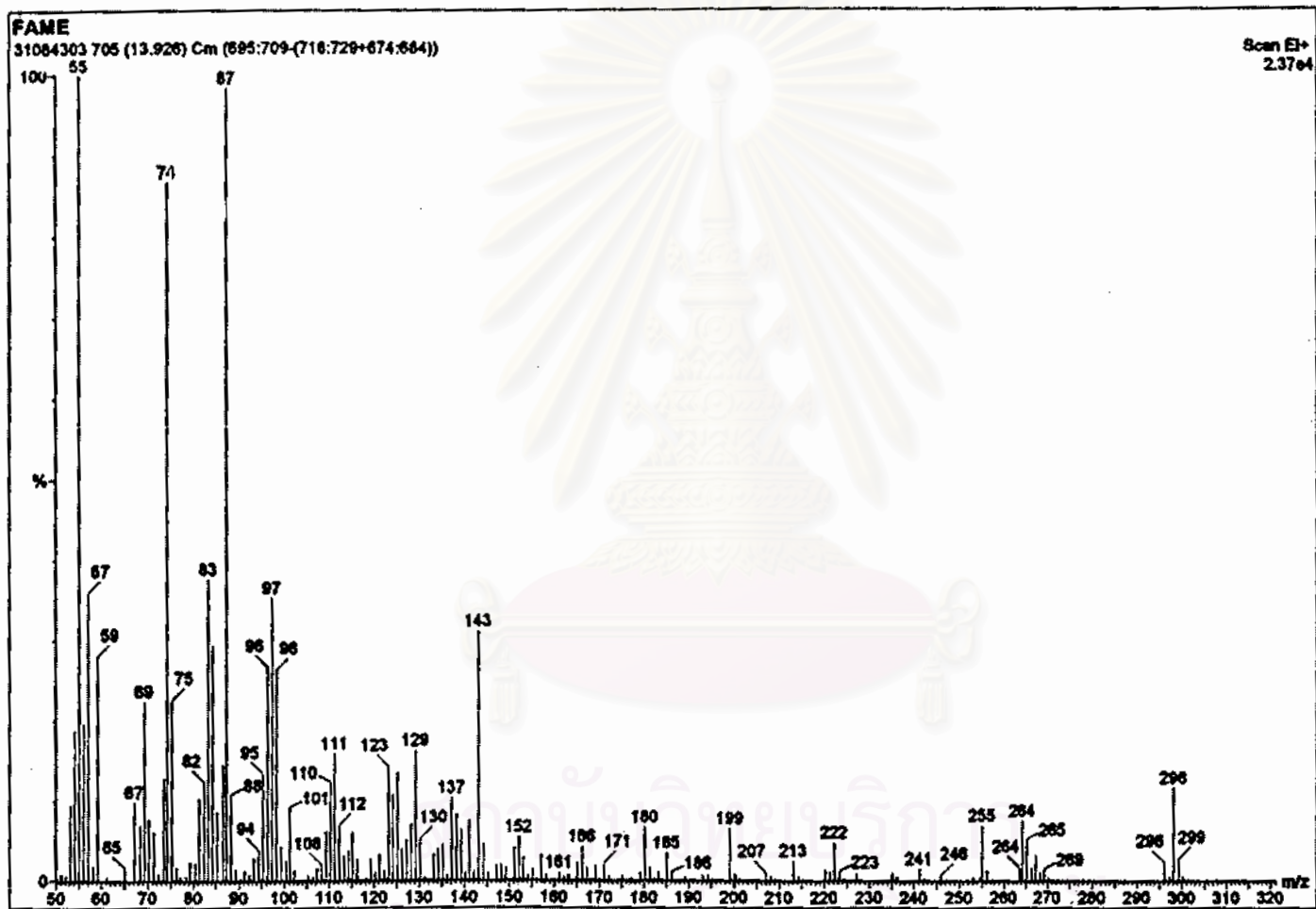


Figure D7 Mass spectrum of methyl stearate at retention time of 13.87 min.

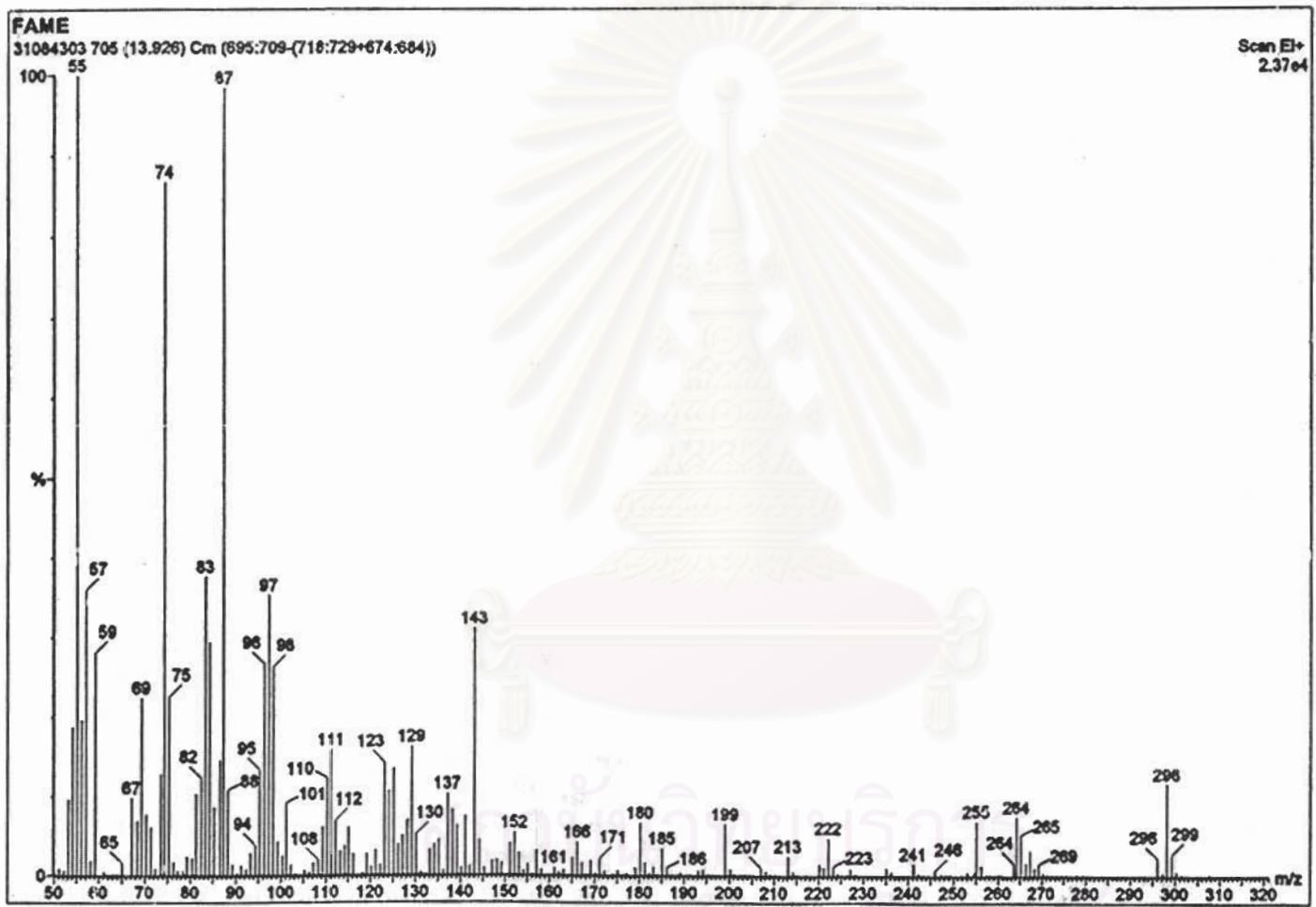


Figure D8 Mass spectrum of methyl oleate at retention time of 13.94 min.

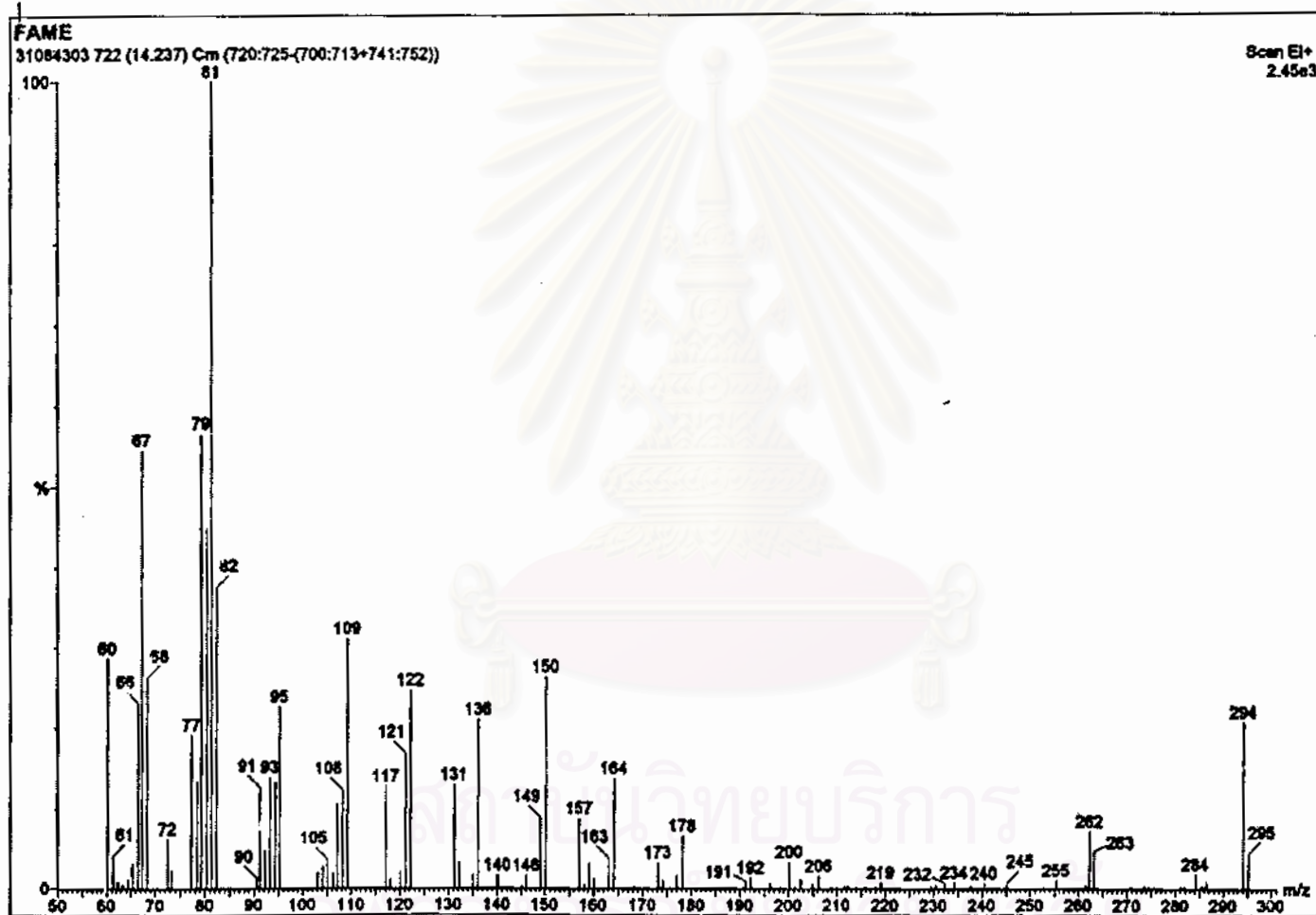


Figure D9 Mass spectrum of methyl linoleate at retention time of 14.24 min.

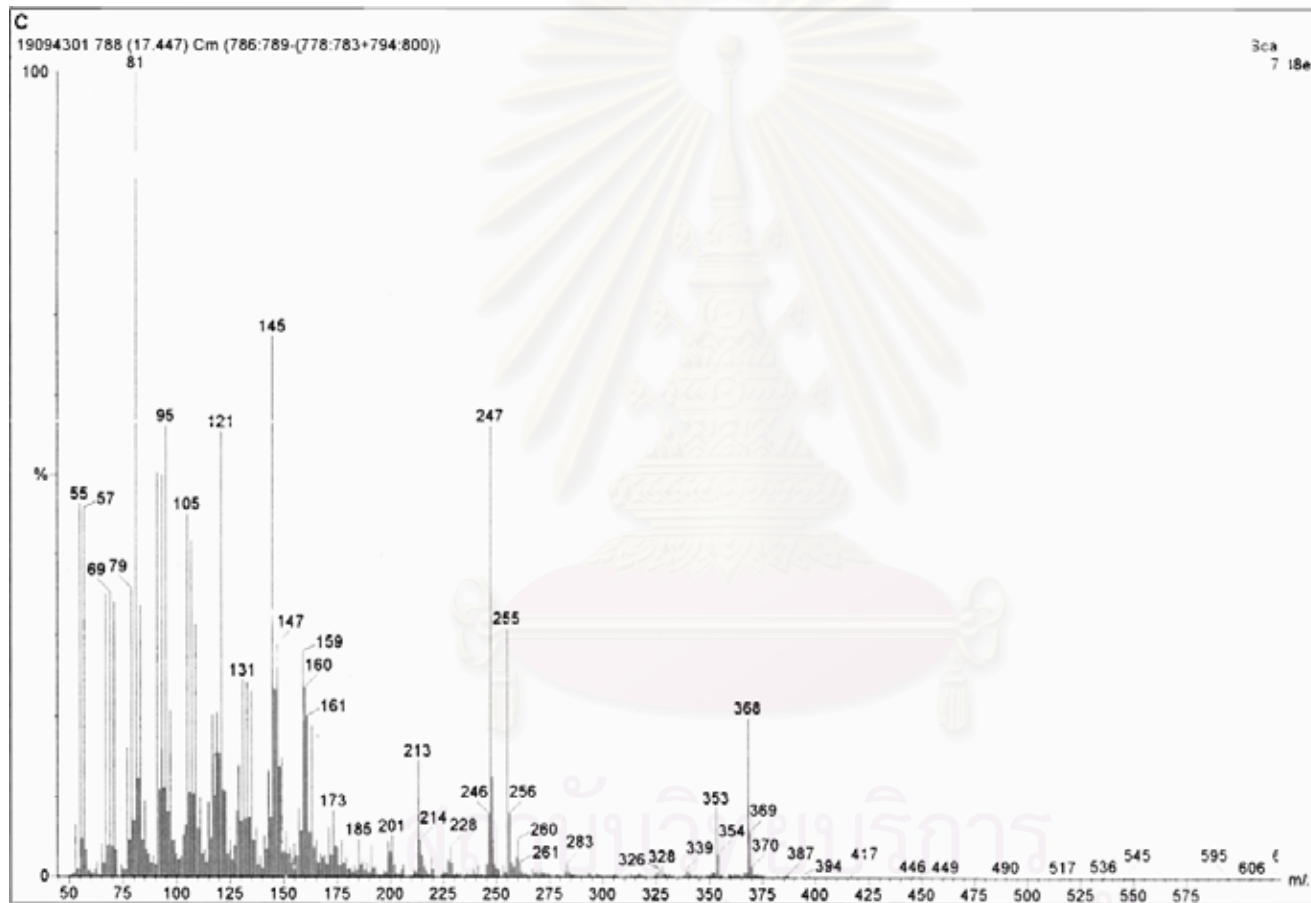


Figure D10 Mass spectrum of CE1 at retention time of 17.45 min.



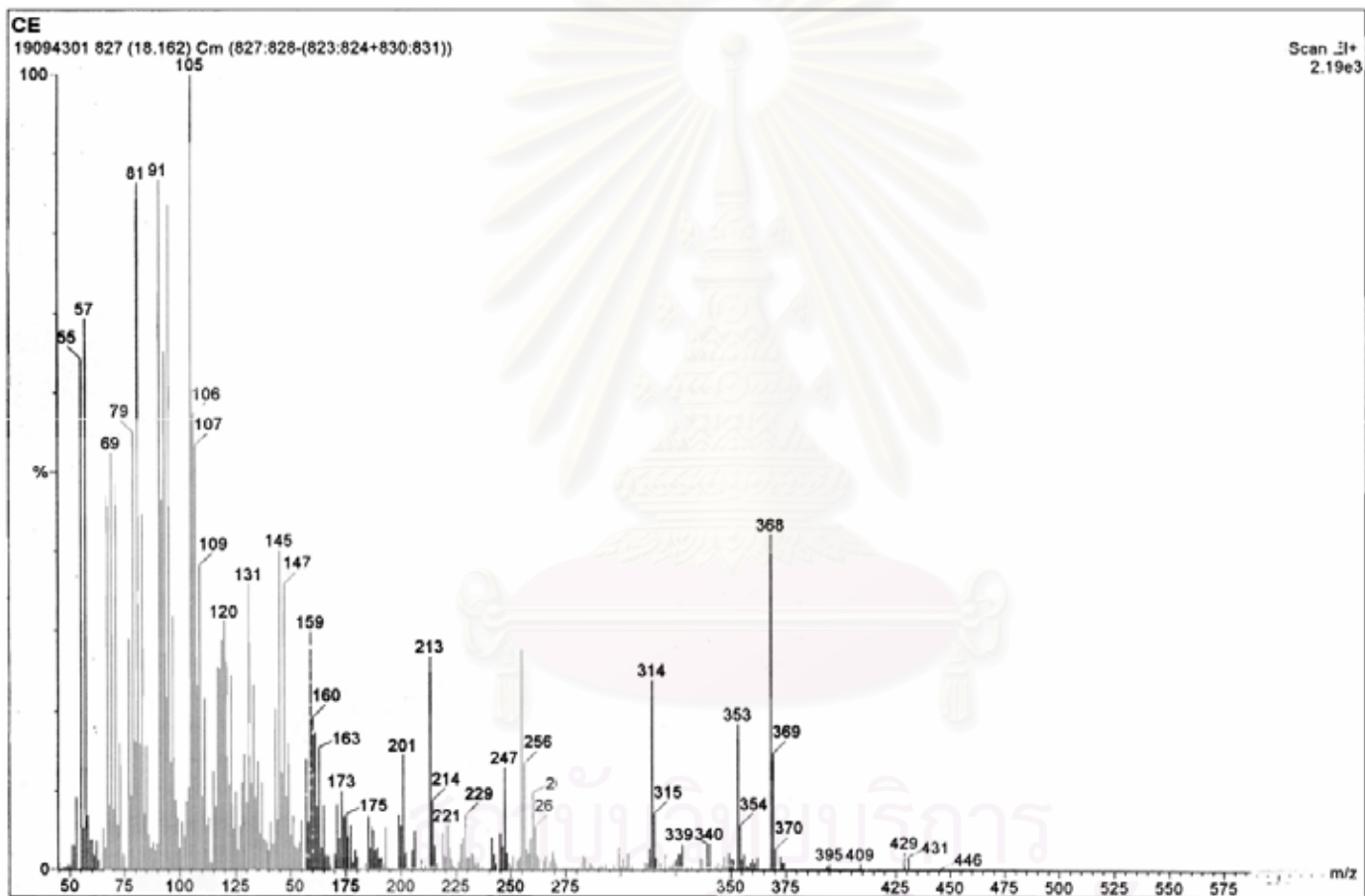


Figure D11 Mass spectrum of CE2 at retention time of 18.16 min.

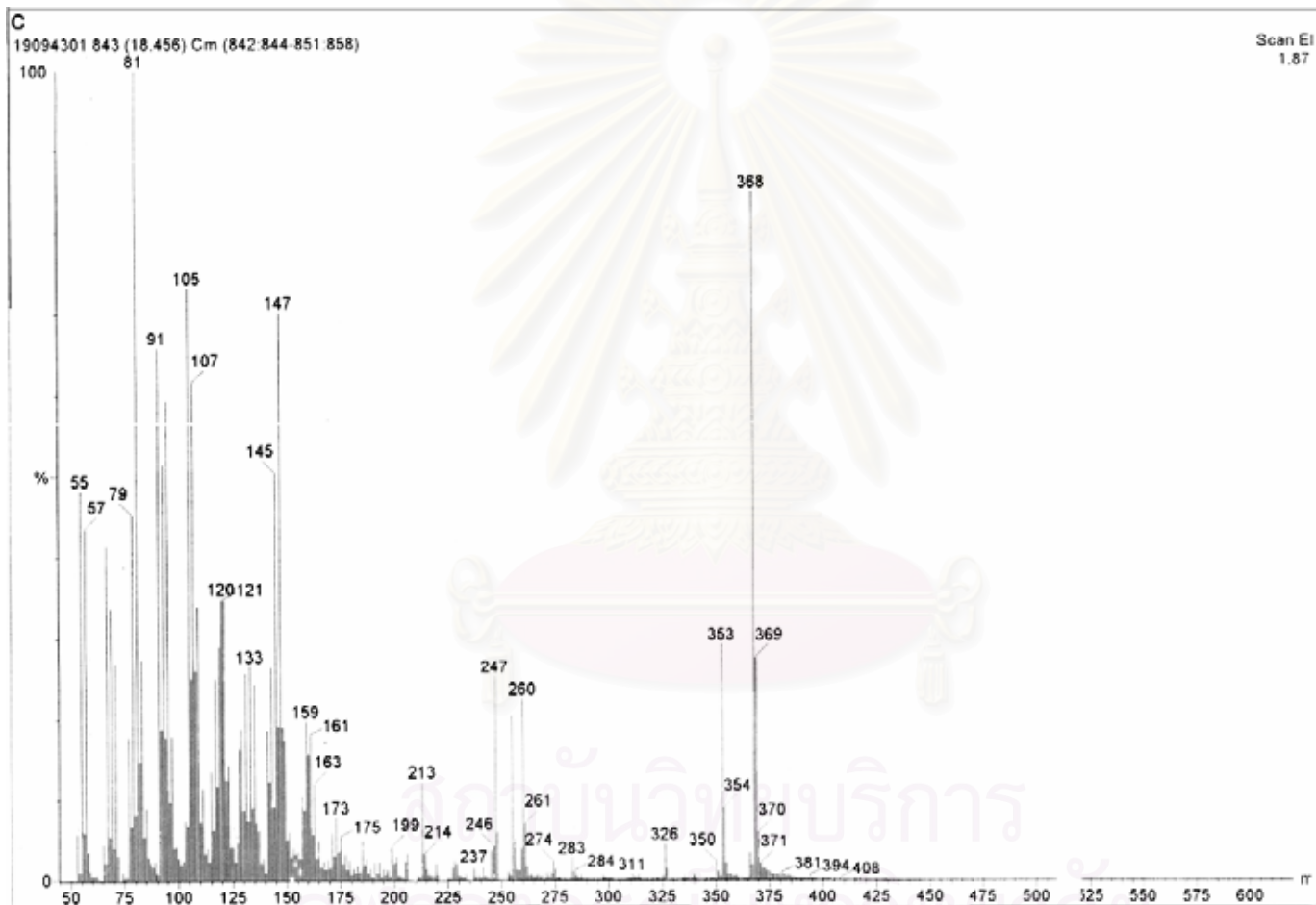


Figure D12 Mass spectrum of CE3 at retention time of 18.46 min.

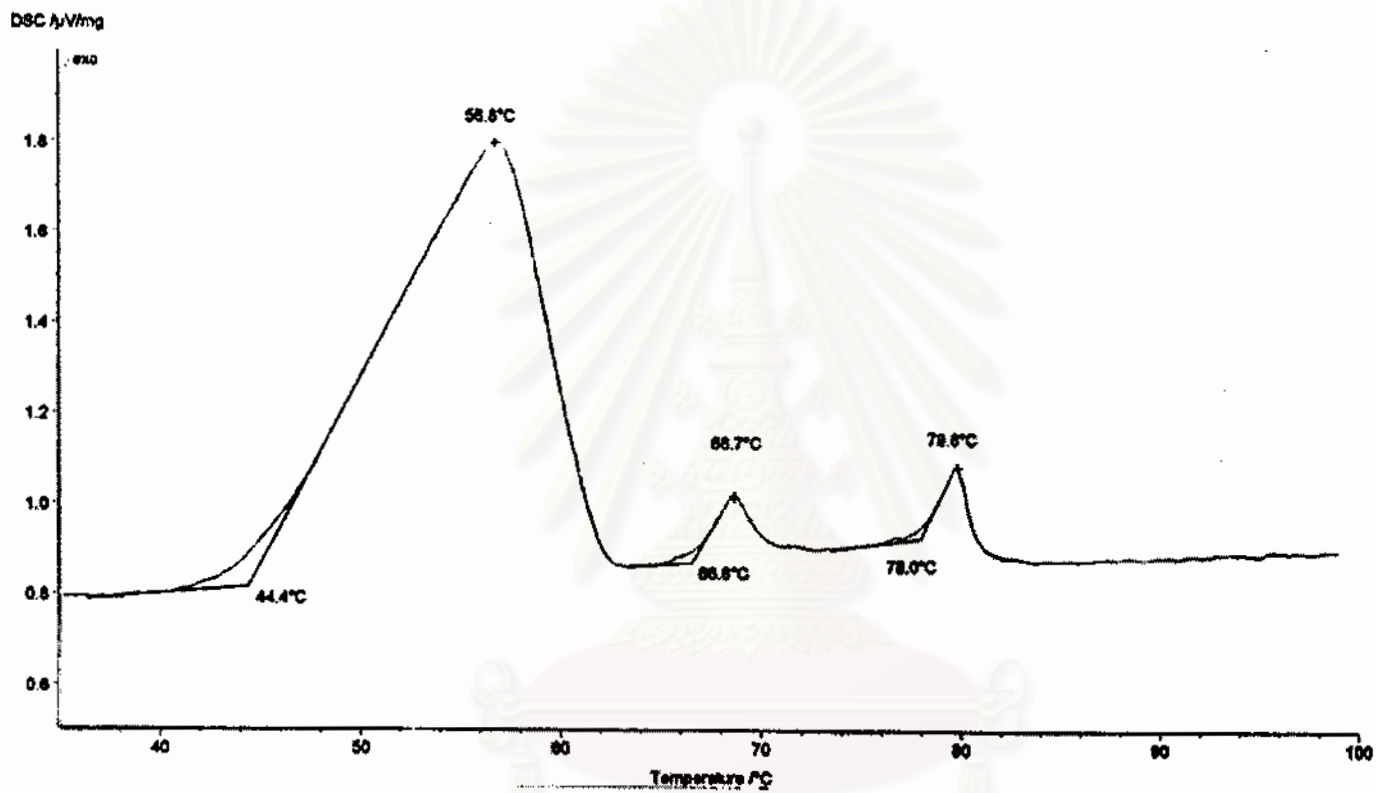
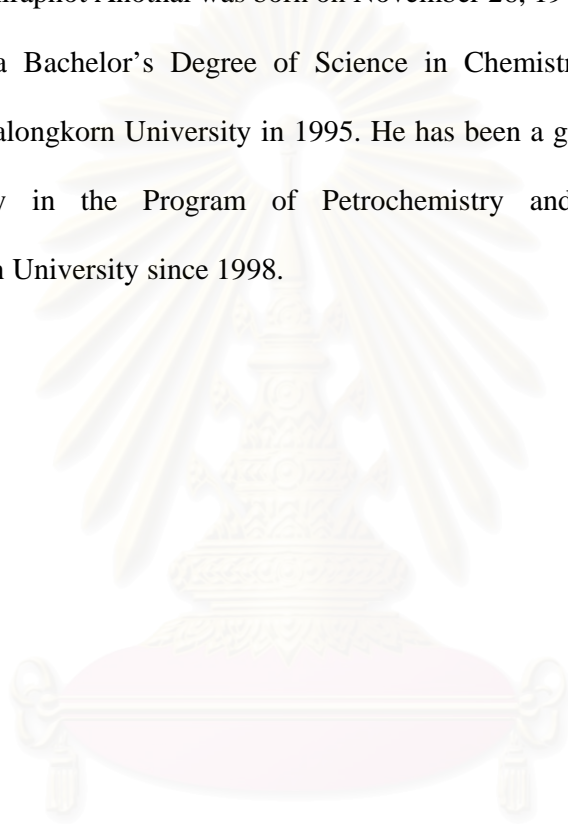


Figure E1 DSC thermogram of cholesteryl esters from coconut oil

จุฬาลงกรณ์มหาวิทยาลัย

## VITA

Mr. Chiraphot Anothai was born on November 26, 1973 in Songkhla province. He received a Bachelor's Degree of Science in Chemistry from the Faculty of Science, Chulalongkorn University in 1995. He has been a graduate student studying Petrochemistry in the Program of Petrochemistry and Polymer Science at Chulalongkorn University since 1998.



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