อนุพันธ์บาราคอลเพื่อใช้เป็นสารทำเครื่องหมายเรืองแสงในน้ำมันดีเซล

นางสาวนริศรา ห้าวหาญ

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BARAKOL DERIVATIVES AS FLUORESCENT DIESEL MARKERS

Miss Narisara Howhan

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ได้สังเคราะห์อนุพันธ์บาราคอลจากบาราคอลที่สกัดได้จากใบอ่อนและดอกของต้นขี้เหล็ก เพื่อใช้เป็นสารทำเครื่องหมายเรืองแสงในน้ำมันดีเซล โดยนำบาราคอลมาทำปฏิกิริยาเอสเทอริฟิเคชันกับแอซิดคลอไรด์ในไทรเอทิลแอมีน สารทำเครื่องหมายเรืองแสงที่สังเคราะห์ได้ คือ 7-propionyloxy-5-acetony-2-methylchromone (สารประกอบ **1**), 7-butyryloxy-5-acetony-2-methylchromone (สารประกอบ **2**), 7-(2-ethyl)-hexanoyloxy-5-acetony-2-methylchromone (สารประกอบ **3**) และ 7-lauroyloxy-5-acetony-2 methylchromone (สารประกอบ **4**) สารทำเครื่องหมายเรืองแสงที่สังเคราะห์ขึ้นเหล่านี้เมื่อนำไปเติมลงในน้ำมันดีเซลที่ระดับความเข้มข้น 2 ถึง 10 ส่วนในล้านส่วน สามารถวิเคราะห์หาปริมาณสารทำเครื่องหมายเรืองแสงในน้ำมันดีเซลด้วยเครื่องสเปกโทรฟลูออโรมิเทอร์ โดยสารประกอบ **1-4** เมื่อกระตุ้นด้วยแสงความยาวคลื่น 464 นาโนเมตร จะให้แสงฟลูออเรสเซนต์ที่มีความยาวคลื่น 612 นาโนเมตร ผลจากการทดสอบสมบัติทางกายภาพของน้ำมันดีเซลด้วยวิธี ASTM พบว่าน้ำมันดีเซลที่เติมสารทำเครื่องหมายมีสมบัติไม่แตกต่างจากน้ำมันดีเซลที่ไม่เติมสารทำเครื่องหมาย นอกจากนี้ยังพบว่าสารทำเครื่องหมายเรืองแสงที่สังเคราะห์ได้มีความคงตัวในน้ำมันดีเซลเป็นระยะเวลาไม่น้อยกว่า 3 เดือน

สาขาวิชา…ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์…. ลายมือชื่อนิสิต..
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NARISARA HOWHAN: BARAKOL DERIVATIVES AS FLUORESCENT DIESEL MARKERS. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., THESIS COADVISOR: ASSIST. PROF. NONGNUJ MUANGSIN, Ph.D., 124 pp. ISBN: 974-17-6704-8.

Fluorescent markers for diesel fuels were synthesized from esterification reaction between barakol, which was obtained from the shredded fresh young leaves and flowers of *Cassia siamea* Lamk, with acid chloride in the presence of triethylamine. These synthetic fluorescent markers were 7-propionyloxy-5-acetony-2-methylchromone (compound **1**), 7-butyryloxy-5-acetony-2-methylchromone (compound **2**), 7-(2-ethyl)-hexanoyloxy-5-acetony-2-methylchromone (compound **3**) and 7-lauroyloxy-5-acetony-2 methylchromone (compound **4**). These synthetic fluorescent markers were invisible color in diesel fuels when they were added into diesel at concentration of 2 to 10 ppm and quantitative measurement was carried out using spectrofluorometer. Compound **1-4** gave fluorescence at 612 nm when they were excited at 464 nm. The testing results of fuel properties using the ASTM test methods revealed that the physical properties of the marked diesel fuels were similar to those of the unmarked diesel fuels. Moreover, those synthetic fluorescent markers were found to be stable in diesel fuels for at least three months.

Field of study... Petrochemistry and Polymer Science... Student's signature..................
Academic year......…......2004...................… Advisor's signature.................
Co-advisor's signature.............

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ABBREVIATIONS

δ	Chemical shift
J	Coupling constant
ASTM	American Society for Testing and Materials
API	American Petroleum Institute
CFR	Cooperative Fuel Research Council
^{13}C-NMR	Carbon–13 Nuclear Magnetic Resonance
cST	Centistroke
°C	Degree Celsius
°F	Degree Fahrenheit
^{1}H-NMR	Proton Nuclear Magnetic Resonance
Hz	Hertz
mmol	Millimole
ml	Milliliter
ppm	Part per million
Sp.Gr.	Specific Gravity
s, t, p, q, m	Splitting patterns of ^{1}H-NMR (singlet, triplet , pentlet, qulet and multiplet)
cm^{-1}	Unit of wave number
%wt	Percent by weight
%yield	Percentage yield

CHAPTER I

INTRODUCTION

At present, much large quantities of fuel oils are consumed in many countries. Generally, fuel oils have to be taxed accordingly to the government rate, which is depended on the type of fuel oils. This cause the government encountered many problems such as smuggling diesel from abroad into the country, mixing of hydrocarbon solvents to fuel oils, avoidance to pay fuel fax in higher rate by using fuels with different purpose for example; using diesel, which is used for fishery, in vehicles and the addition of low–taxed light heating oil to high–taxed diesel fuel. These causes made the government lose many revenues and consumers have to use low-quality fuel oils. For these reasons, it is essential to develop the method of marking and identifying petroleum products so as to distinguish a variety of fuel available in the market.

A marker is defined herein as a substance which can be dissolved in a liquid to be identified, then subsequently detected by performing a simple chemical or physical detection on the tagged liquid. Markers in petroleum products are used for identifying the products by simple chemical analysis, prevent evading a fuel tax. Marker systems for petroleum product have been used for a long time but various drawbacks have existed. At the beginning, radioactive substance was used as markers but it had to be analyzed by special instrument. Quinizarin and diphenylamine were used as markers for heating oil in France since 1956, but both of them have the disadvantages of poor solubility in petroleum products. Later, azo dyes are utilized as marker for petroleum products and they give good color by pH change [1, 2].

Azo dyes are good markers but they are unstable in petroleum products and making them too difficult to detect after storage. Later, silent florescent markers are utilized as markers in petroleum products. Silent fluorescent markers are compounds which are utilized as markers because they are visually undetectable to the naked eye under normal lighting conditions, but they can be fluoresced which are easily detected and they are stable in petroleum products much longer than azo dyes. In 1999, Friswell had synthesized silent fluorescent petroleum markers from esterification reaction between an appropriate linear or branched C_1-C_{18} alkylcarboxylic acid or acid halide and coumarin. They may be detected in the product by extraction with an alkali aqueous solution which strongly produces fluorescence [3].

Barakol which is easily obtained from *Casia siamea* Lamk [11] is known to give fluorescence at 505 nm (excitation at 222 nm in methanol). However, barakol is insoluble in diesel fuels. Therefore, if a derivative of barakol could be made soluble in diesel feuls, a diesel marker applicable to diesel fuels would be possible.

The objective of the research

1. To synthesize barakol derivatives for use as fluorescent markers in diesel.
2. Qualitative and quantitative analysis of markers after adding into diesel, including three months stability of marker in diesel.

The scope of this research

The scope of this research covers the synthesis of barakol derivatives for use as fluorescent markers in diesel. These markers are characterized using spectroscopic techniques such as FT–IR, NMR, EA and MS. In addition, the stability and properties of markers in diesel are studied.

CHAPTER II

THEORETICAL

2.1 Fluorescence [4-6]

A molecule in the excited state can lose the absorbed energy in the following processes (a) photochemical processes and (b) photophysical processes.

Photochemical processes (e.g. rearrangements, dissociations, dimerizations, and photoadditions) generally occur in triplet states which have lifetime between 100 ns and 10 ns. The lifetime of excited singlet states (1 to 100 ns) is normally too short for chemical reaction to take place.

Photophysical processes can occur via radiations transitions which involves the spontaneous emission of a photon (e.g. fluorescence and phosphorescence) or radiationless transitions (e.g. internal conversion and intersystem crossing). All these photophysical processes must occur in a time period less than the natural radiative lifetime of the molecular. The unimolecular processes are represented by Jablonski diagram in Figure 2.1. Radiation transitions are denoted by straight arrows whereas radiationless transitions by wavy arrows.

Radiation transitions

A molecule in the ground states S_0 will be brought to the excited singlet states, either S_1 or S_2 (or higher states S_j) by absorb high-energy radiation such as UV radiation and then a molecule in the excite states drops back to the ground states by emit a photon of lower energy than was absorbed.

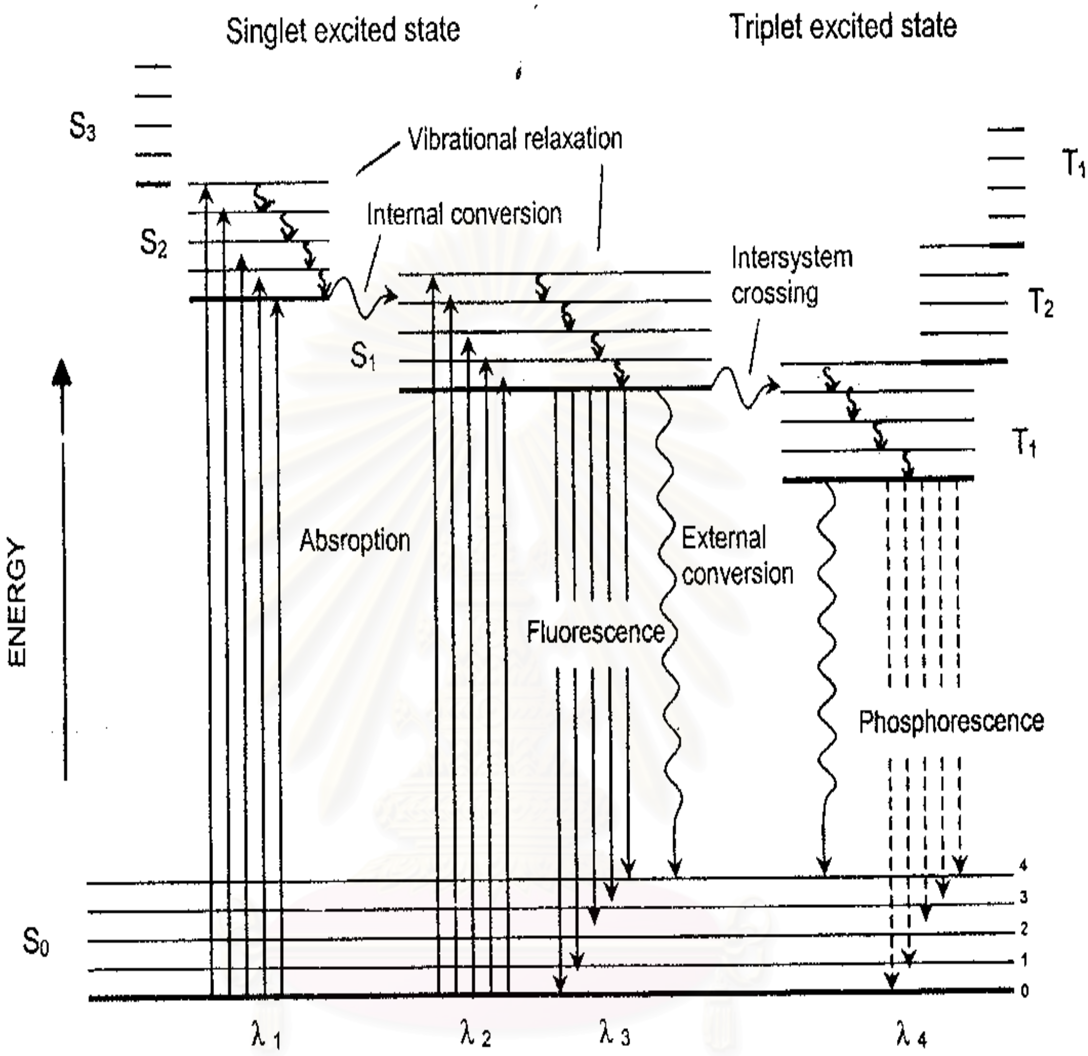


Figure 2.1 Jablonski diagram for photophysical pathways

Fluorescence

Fluorescence is the spin allowed emission of radiation from the lowest vibrational levels of the excited state S_1 to any of the vibrational levels of the ground state S_0. Fluorescence emission occurs very rapidly after excitation (10^{-6} to 10^{-9} s). Consequently, it is not possible for the eye to perceive fluorescence emission after removal of the excitation source. The fluorescence spectrum, in ideal cases, is a mirror image of the excitation spectrum but shifted to longer wavelengths (Figure 2.2).

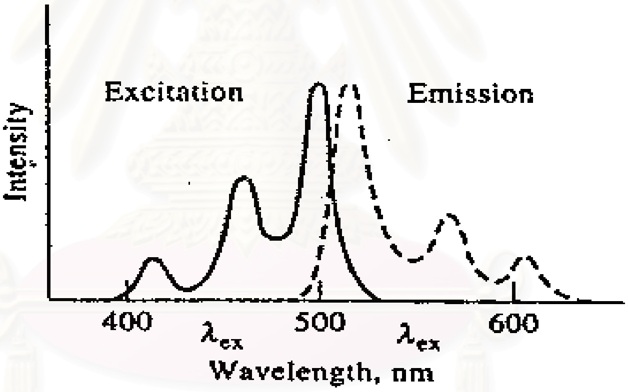


Figure 2.2 Typical mirror-image relations between excitation and fluorescence spectra

Phosphorescence

Phosphorescence is the spin forbidden emission of radiation from the lowest triplet state T_1 to the ground state S_0. The T_1 state is usually of lower energy than S_1. The phosphorescence spectrum is not a mirror image of the excitation spectrum (Figure 2.3).

In order to display phosphorescence, molecules primarily excited to the S_1 singlet state must convert to the lowest level of their triple manifold (T_1) by the radiation less process of intersystem crossing. From T_1 they can slowly emit radiation (phosphorescence), or they can return to the S_0 level without emission by intersystem crossing. The reason for this is that the energy of the triplet level T_1 is usually below that of the singlet S_1. Therefore, phosphorescence is always at a longer wavelength than fluorescence. The transition $T_1 \leftarrow S_0$ is forbidden by spin selection rule and is not observed under ordinary conditions.

A typical energy relationship between excitation, fluorescence and phosphorescence spectrum on the energy scale, fluorescence is often a mirror image of excitation spectrum, whereas phosphorescence is of even lower-energy (red-shifted) emission with respect to the fluorescence reflecting the lower electronic level of the triplet state.

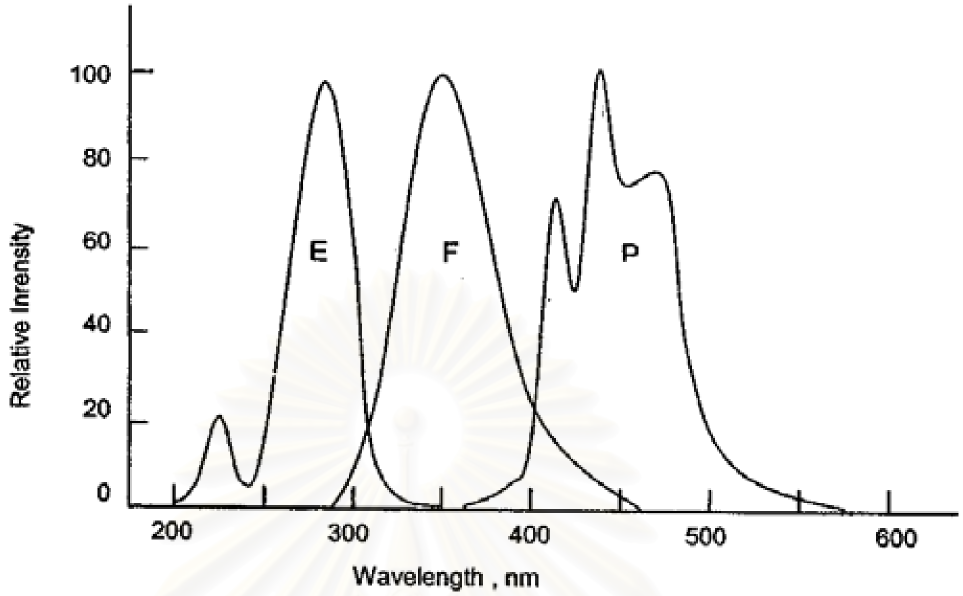


Figure 2.3 Relations of excitation, fluorescence and phosphorescence spectra

Radiationless transitions

There are two radiationless processes. The first or **internal conversion**, denotes a radiationless transitions between two states of the same multiplicity, usually $S_n \rightarrow S_{n-1}$ or $T_n \rightarrow T_{n-1}$.In the specific case being considered, this would be the ground state, and the transition would be denoted $S_1 \rightarrow S_0$. **Intersystem crossing** is a similar radiationless transitions connected with a change in multiplicity (mostly $S_1 \rightarrow T_1$, or $T_1 \rightarrow S_0$). Radiationless transitions are isoenergetic transitions to a vibrationally excited lower state, and followed by very rapid **vibrational relaxation** which occurs from any vibrational state and represents a return to the thermal equilibrium of the vibrational ground state within the same state, for instance $S^v \rightarrow S$ or $T^v \rightarrow T$. This occurs in condensed systems by energy transfer, i.e. transfer of vibrational energy to the surrounding medium.

With the exception of phosphorescence all radiation processes are vary fast. First order rate constants for these processes have the following orders of magnitude: Light absorption 10^{15} s^{-1}, Vibrational relaxation ≥ 10^{12} s^{-1}, Fluorescence 10^{6} to 10^{9} s^{-1}, Intersystem crossing 10^{-1} to 10^{5} s^{-1} and Phosphorescence 10^{-2} to 10^{4} s^{-1}.

2.1.1 Chemical structure and fluorescence

Although all molecules are capable of absorption, fluorescence is not observed in large number of compounds. Fluorescence is generally observed in those organic molecules which have rigid framework. Following structures are called fluorophores in analogy with chromophores and they are part of the molecules with conjugated system of double bonds. One or more electron-donating groups such as –OH, $-NH_2$ and $-OCH_3$ enhances the fluorescence. Polycyclic compounds such as vitamin K, purines and nucleosides and conjugated polyenes such as vitamin A are fluorescent. Groups such as $-NO_2$, –COOH, $-CH_2COOH$, –Br, –I and azo groups tend to inhibit fluorescence. The fluorescence of many molecules is greatly pH dependent because only the ionized or unionized from may be fluorescent. For example, phenol, C_6H_5OH, is fluorescent but its anion, $C_6H_5O^-$, is not.

2.1.2 Fluorescence Instrumentation

For fluorescence measurements, a spectrofluorometer, it is necessary to separate the emitted radiation from the incident radiation. This is most easily done by measuring the fluorescence at right angles to the incident radiation. The fluorescence radiation is emitted in all directions, but the incident radiation passes straight through the solution. A sample spectrofluorometer design in illustrated in figure 2.4-2.5.

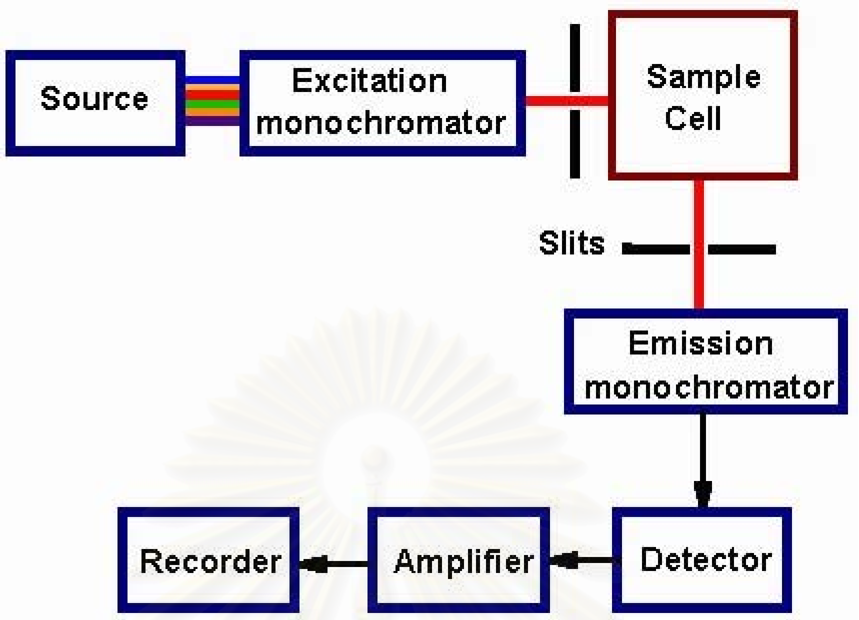


Figure 2.4 Component of a spectrofluorometer

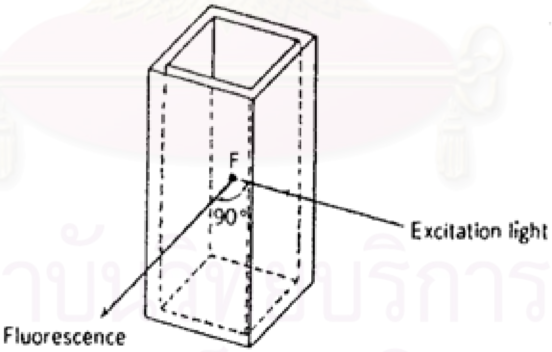


Figure 2.5 Sample cell

Most fluorescing molecule absorbs ultraviolet radiation over a band of wavelengths and so a simple line source is sufficient for many applications such as mercury vapor lamp. A spectrofluorometer incorporates two monochromators, one to select the wavelength of excitation and one to select the wavelength of fluorescence.

A beam of monochromatatic light excites the specimen in the cell and the emission is observed and analyzed at right angles to the incident beam. The output is the emission spectrum plotted by the XY recorder. The wavelength of excitation from a source can be scanned and the fluorescence measured at a set wavelength to give a spectrum of the excitation wavelengths. Then, by setting the excitation wavelength for maximum excitation, the emission wavelength can be scanned to establish the wavelength of maximum emission.

2.2 Barakol

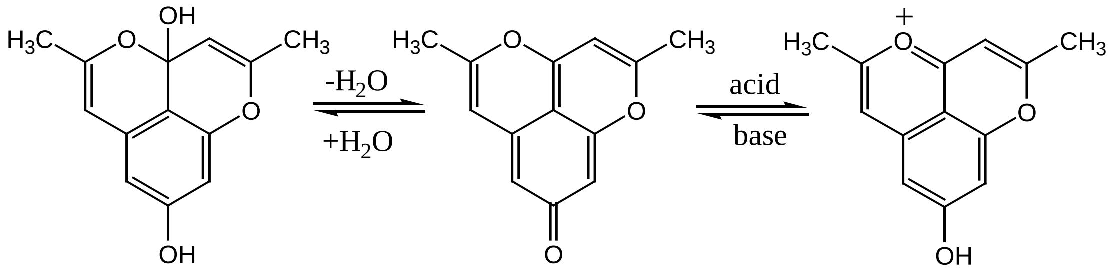
Cassia siamea is a plant widely cultivated in Southeast Asia (Figure 2.6). The different parts of the plant have been used as Thai traditional medicines [7, 8] for example for treatment of insomnia and various other medical conditions such as diabetes, hypertension, asthma, constipation and diuresis. *Cassia siamea* shows the physiological and pharmacological properties on the cardiovascular and central nervous systems [9].

Barakol (3a,4-dihydro-3a,8-dihydroxy-2,5-dimethyl-1,4-dioxaphenalene or 2,5-dimethyl-3αH-pyrano[2,3,4-de]-1-benzopyran-3a,8-diol), major active constituent extracted from the leaves and flowers of *Cassia siamea*, was first extracted in 1969 by Hassanali-Walji *et* al [10,11].

Figure 2.6 Features of Khilek tree (*Cassia siamea*)

2.2.1 The chemical nature of barakol

Barakol ($C_{13}H_{12}O_4$) is a natural compound consists of a chromone hemiacetal, therefore barakol is unstable even in ambient conditions due to a hemiacetal group easily protonated, and then loses water from its molecule to become anhydrobarakol. Anhydrobarakol is the methylene quinone derivative; it decomposes at 165°C. In hydroxylic solvents or aqueous solutions, anhydrobarakol can be reversed to barakol. Barakol is very rapidly degraded by base. In acidic conditions, barakol and anhydrobarakol can be converted to a relatively stable anhydrobarakol salt, for example anhydrobarakol bromide [9] and anhydrobarakol chloride [10]. They are stable at room temperature and in dried condition.



barakol anhydrobarakol anhydrobarakol hydrochloride

Scheme 2.1 Chemical structures of barakol, anhydrobarakol an anhydrobarakol hydrochloride [10]

2.3 Diesel Fuel [12-14]

Diesel fuel is obtained from fractional distillation of crude oil, which is a mixture of hydrocarbon such as benzene, pentane, hexane, heptane and toluene. The boiling range of distillate diesel fuel is approximately 150-370°C (300-700°F). It is a general property of hydrocarbons that the more volatile they are the higher temperatures for spontaneous ignition. It is for this reason that the less volatile middle distillate fractions of petroleum crude and even residues are more readily applicable to diesel engines than gasoline or lighter fractions. Diesel fuel has two types:

- High speed diesel (Automotive Diesel Oil (ADO)), gas oil or solar oil, used in buses, pickups and trucks.
- Low speed diesel (Industrial Diesel Oil (IDO)) used in water crafts and submarines.

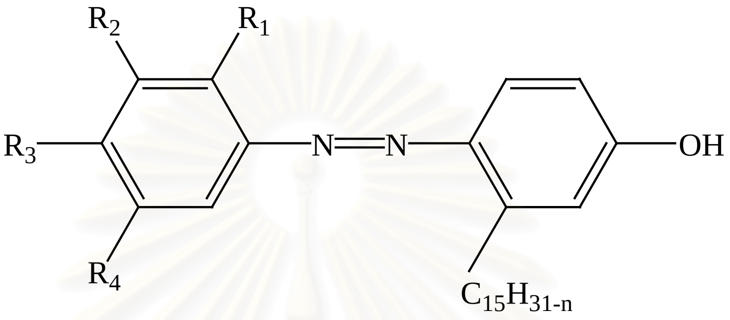
2.4 Markers [15]

A marker is defined as a substance, which can be used to tag petroleum products for subsequent detection and is colorless in the petroleum products. The marker is dissolved in a liquid to be identified and then subsequently detected by performing a simple chemical or physical test on the tagged liquid.

1. To be entirely foreign to the liquids
2. To be supplied as highly concentrated solutions in compatible solvents
3. To be easily detected by simple field test
4. To be not obscured by unstable natural components of the liquids
5. To be stable over anticipated storage lift of the tagged liquid (usually three to six months)
6. To have identities, which can be confirmed by laboratory methods

2.5 Literature reviews

Suwanprasop, S. *et al*. [16] synthesized marker dyes for gasoline and diesel fuel, having the following formula:



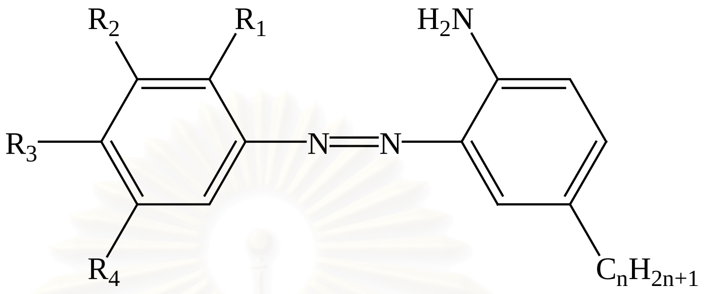
where in R_1, R_2 and R_3 are hydrogen, methyl, methoxy, chloride or nitro group.

R_4 is hydrogen or nitro group.

These marker dyes are synthesized by coupling reaction of a naturally occurring *n*-alkylphenol, cardanol, with aniline and its derivative. These marker dyes are used for tagging gasoline and high-speed diesel at levels of about 2 to 5 ppm and can be detected by extraction the tagged fuel oils with 50% (v/v) 1,2-diaminoethane in a solution containing ethane-1,2-diol and methanol (1:1, v/v), these marker dyes will give color in an extracted phase.

Suwanprasop, S. *et al*. [17] synthesized marker dyes having the following formula:

1)



where in n =10-14.

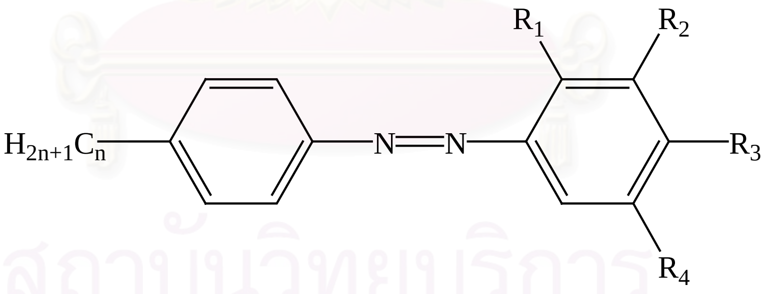
R_1 is hydrogen, nitro, chloride, methoxy group.

R_2 is hydrogen, nitro group.

R_3 is hydrogen, chloride or nitro group.

R_4 is nitro group.

2)



where in n =10-14.

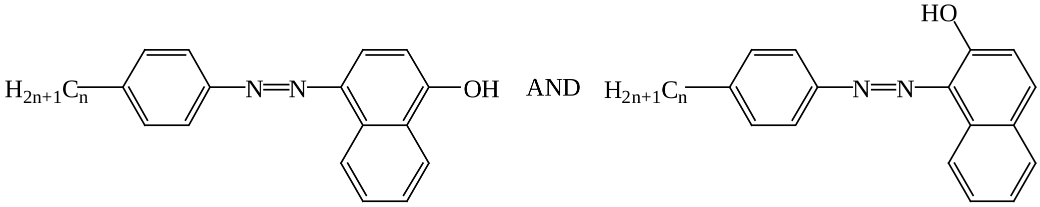
R_1 is hydrogen, nitro, chloride, methoxy or isoproply group.

R_2 is hydrogen, nitro or hydroxy group.

R_3 is hydrogen, nitro, chloride, or isoproply group.

R_4 is hydroxy and NH_2 group.

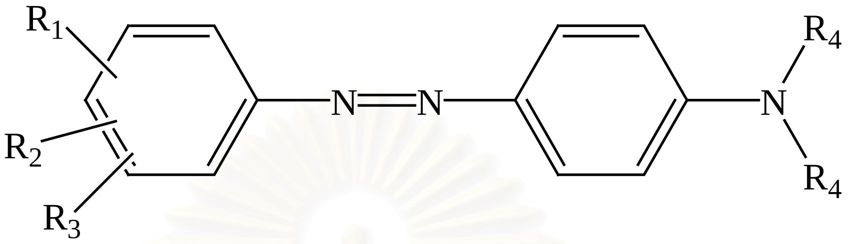
3)



where in n =10-14.

These marker dyes are synthesized either by coupling reaction of *n*-alkylaniline (which are prepareed from nitration and reductions of *n*-alkylbezene) with a diazonium salt of aniline derivatives or by a coupling reaction of a diazonium salt of *n*-alkylaniline with aniline or phenol derivatives. These marker dyes are used for high-speed diesel at levels of about 3 to 5 ppm and can be detected by extraction the tagged fuel oils with 50%(v/v) 1,2-diaminoethane in a solution containing propane-1,3-diol and methanol (2:3, v/v), these marker dyes will give color in an extracted phase.

Friswell, M.R. *et al*. [18] prepared *N*, *N*-dialkylaniline azo dyes having the following formula:



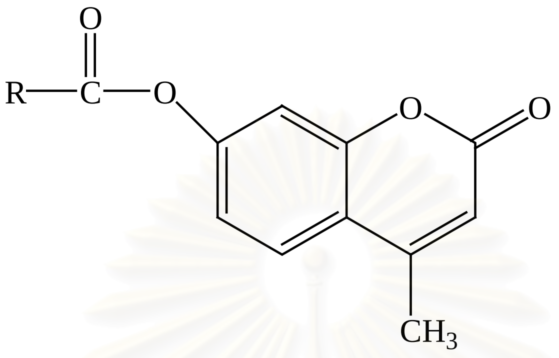
where in R_1 and R_2 are hydrogen, methyl, ethyl, isopropyl, butyl, methoxy, halogen or nitro.

R_3 is hydrogen or NH_2.

R_4 is alkyl group.

These compounds are synthesized from an *N*, *N*-dialkylaniline with aniline or substituted aniline in an aromatic solvent. These markers are used for tagging petroleum products at levels of about 0.25 to 100 ppm. They may be detected in the products by extraction with an acidic aqueous solution which produces strongly color.

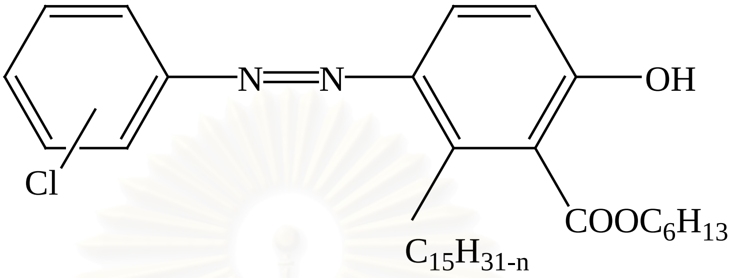
Friswell, M.R. *et al*. [3] prepared silent fluorescent markers having the following formula:



where R is selected from a linear or branched C_1-C_{18} alkyl group.

These compounds are synthesized from esterification reaction between an appropriate linear or branched C_1-C_{18} alkylcarboxylic acid or acid halide with 7-hydroxy-4-methycoumarin. These markers are used for tagging petroleum products at levels of about 0.25 to 100 ppm. They may be detected in the products by extraction with an alkali aqueous solution which produces strongly fluorescence when examine under ultraviolet light at wavelength of 365 nm.

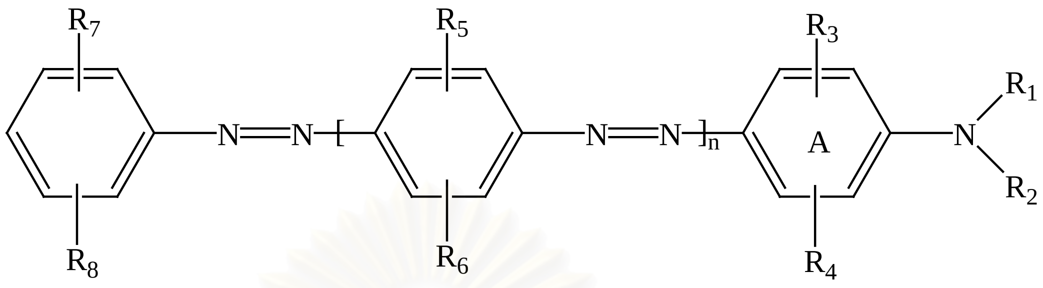
Thowongs, K. [19] synthesized marker dyes for gasoline and diesel fuel. These marker dyes having the following formula:



where n = 0, 2, 4 and 6.

These marker dyes are synthesized by esterification reaction between cashew nut shell extracted and 1-hexanol. Then, the esterified products are coupled with chloroanilines to give yellow color marker dyes. These marker dyes are used for tagging gasoline and high-speed diesel at treat rate of 30 ppm and can be detected by extraction the tagged fuel oils with 10% potassium hydroxide in methanol, these marker dyes will give yellow color in an extracted phase.

Zeidler, G. *et al*. [20] synthesized azo dyes having the following formula:



where the ring A may be benzofused,

n is 0 or 1.

R_1 is hydrogen or C_1-C_{15} alkyl, which may be interrupted by from 1 to 4 ether oxygen atoms.

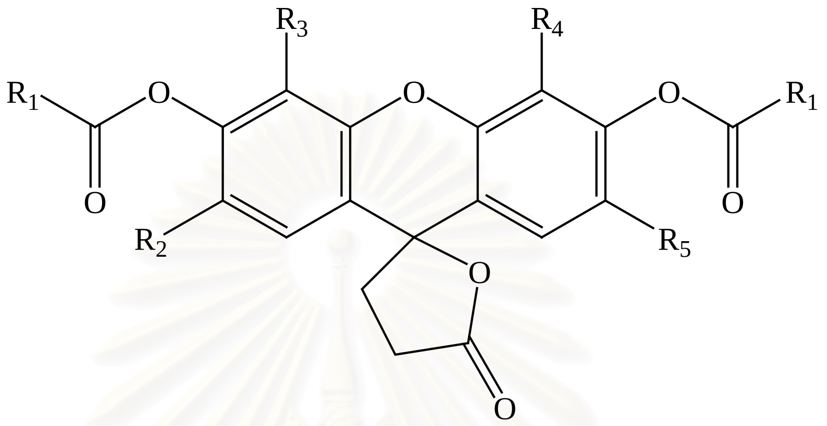
R_2 is C_1-C_{15} alkyl, which may be interrupted by from 1 to 4 ether oxygen atoms.

R_3, R_4, R_5, R6 and R_7 independently of one another are each hydrogen, C_1-C_{15} alkyl, or C_1-C_{15} alkoxy.

R_8 is hydrogen, C_1-C_{15} alkyl, or C_1-C_{15} alkoxy, cyano, nitro, or a radical of the formula $COOX_3$, where X_3 is hydrogen, C_1-C_{15} alkyl which may be interrupted by from 1 to 4 ether oxygen atoms.

These azo dyes can be used as pH-dependent markers for petroleum products and under the action of aqueous alcoholic solution of a protic acid, in the presence or absence of zinc halide, aluminum halide or tin halide; these dyes will give a color reaction, i.e. a color change, accompanied by deeping of color.

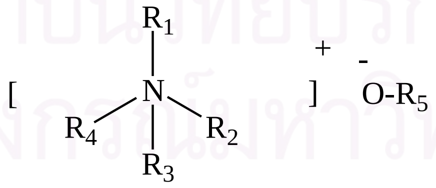
Smith, M. J. [21] developed base reactable petroleum fuel markers, which are the derivative of 2(3H) furanone having the following formula:



where in R_1 is C_1-C_{18} alkyl group or an aryl group.

R_2, R_3, R_4 and R_5 are hydrogen, chlorine, bromine or C_1-C_{12} alkyl group.

The present invention includes compositions for methods of detecting or developing base reactable fuel markers. Developing agents of its present invention contain quaternary or tetra alkyl ammonium base of the following formula:



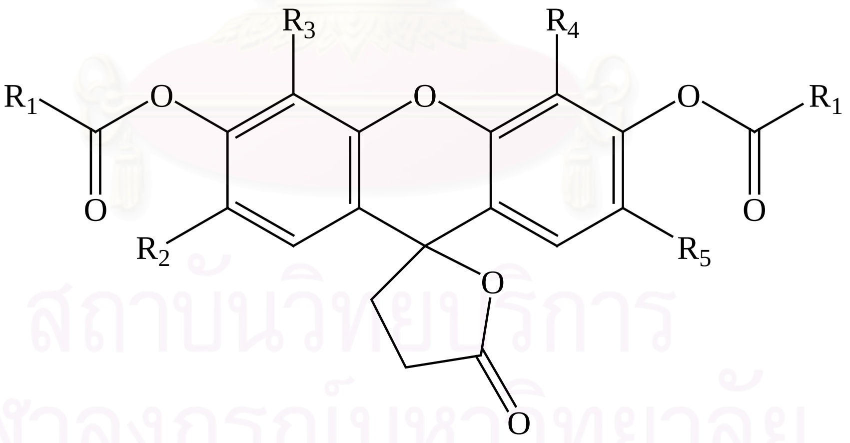
$$[NR_1R_2R_3R_4]^+ \; {}^-O\text{-}R_5$$

where in R1, R_2, R_3 and R_4 are the same or different alkyl or benzyl groups.

R_5 is hydrogen or an alkyl group.

Marker in fuel is developed as quaternary alkyl ammonium base such as tetraethyl ammonium hydroxide and extracted by solvent mixture between aprotic solvent and aromatic solvent such as formamide benzyl alcohol. These markers are synthesized by converting 2(3H) Furanone to organic diesters by the reaction of alcohols with organic anhydride or organic halide. After extraction, color of the extractant is varied up to the type of solvents and markers, e. g. green, violet and red.

Smith, M. J. [22] synthesized colorless fluorescent markers, which developed fluorescence when extracted with an appropriate basic solution. These markers, which are the derivatives of Fluoroscein, having the following formula:

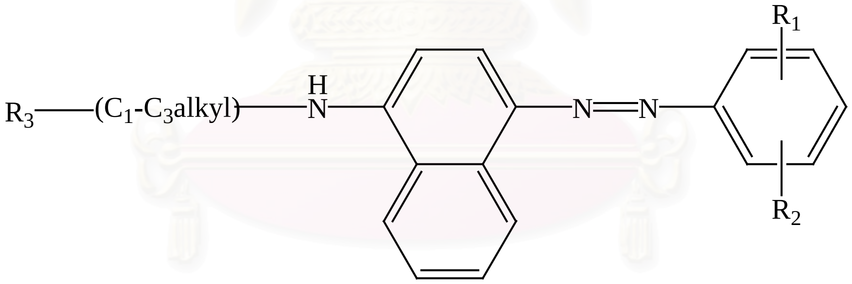


where in R_1 is C_1-C_{18} alkyl group or an aryl group.

R_2, R_3, R_4 and R_5 are hydrogen, chlorine, bromine or C_1-C_{12} alkyl group.

These markers are synthesized by converting Fluoroscein to organic diesters to eliminate any tendency to partition into water. The diester may be derived from an organic acid, its anhydride or halide containing from one to eighteen carbon atoms. The ester markers can be added to any liquid petroleum products and can be detected by reacting them with the developing reagent. Examples of the developing reagents are an aqueous solution of alkali metal hydroxide and an aqueous solution of the quaternary ammonium hydroxide. The base will hydrolyze the esters and prompt the formation of a highly fluorescent dianion, which may be exhibited variously colored.

Friswell, M. R. *et al.* [23] synthesized fuel markers having the following formula:

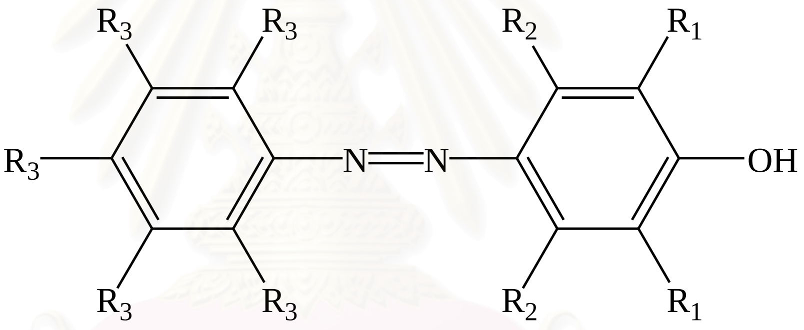


where in R_1 and R_2 are selected from hydrogen, methyl, ethyl, methoxy, halogen, cyano and nitro group.

R_3 is selected from methyl, methoxy, methoxyethoxy and morpholino group.

These markers are synthesized by azo coupling of appropriate substituted aniline to an alpha-naphthylamine. They are generally colorless or have a pale yellow color in petroleum products. On the other hand, when extracted these tagged petroleum products with acidic aqueous solution, e.g. a 10% hydrochloric or formic solution, the variously colors are developed depending on R_1, R_2 and R_3 which are substituents in the molecule.

Friswell, M.R. [2] prepared petroleum markers having the following formula:



where R_1 and R_2 are each selected from hydrogen and C_1-C_7 alkyl, provided that at least one R1 is a C_3-C_7 alkyl; and provided that R_3 are selected from hydrogen, nitro, halogen, cyano and methyl, provided that least one R_3 is selected from nitro, chloro, halogen and cyano group.

These markers are synthesized by azo coupling of appropriate substituted aniline to a 2, 6-dibutyl phenol. The markers are detected in the tagged products by extraction the tagged fuel oils with reagent comprising water, water-soluble amine and a water-miscible cosolvent. The reagent reacts with the markers resulting in developing of the colors, which identifies the petroleum products.

CHAPTER III

EXPERIMENTS

3.1 Materials

3.1.1 Plant Materials

Fresh young leaves of Khilek (*Cassia siamea* Lamk.) were obtained from Dontum farm in Nakhonpathom province, Thailand in April 2003.

3.1.2 Solvents and chemicals

Propionyl chloride, butyryl chloride, 2–ethylhexanoyl chloride, lauoryl chloride and triethylamine were purchased from Fluka. Sulphuric acid, hydrochloric acid, sodium hydrogen carbonate, sodium sulfate anhydrous, sodium carbonate, dichloromethane, ethyl acetate, hexane, methanol and aluminium oxide 90 (neutral for column chromatography) were purchased from Merck. Nitrogen gas was obtained from Thai industrial gas.

3.2 Analytical Instrument

The infrared spectra were recorded on a Nicolet Fourier Transform Infrared spectrophotometer model Impact 410. Infrared spectra were recorded between 400 cm^{-1} to 4000 cm^{-1} in transmittance mode.

The ^{1}H-NMR spectra at 400 MHz were recorded on a Varian Mercury^{+} spectrometer. The ^{13}C-NMR spectra at 100 MHz were recorded on a Varian Mercury^{+} spectrometer and at 50.32 MHz were recorded on a Bruker model ACF200 spectrometer. All chemical shifts were reported in part per million (ppm) using the residual proton or carbon signal in deuterated solvents as internal references.

The mass spectra were recorded on an Agilent 110 Series LC/MSD Electrospray mass spectrometer and a Bruker model ESQUIRE mass spectrometer.

Elemental analyses were recorded on CHNS/O Analyzer (Perkin Elmer PE2400 Series II).

The fluorescence spectra were recorded on a Perkin Elmer LS 50 luminescence spectrophotometer. Wavelength is in the range of 200-900 nm and cell width is 1 cm.

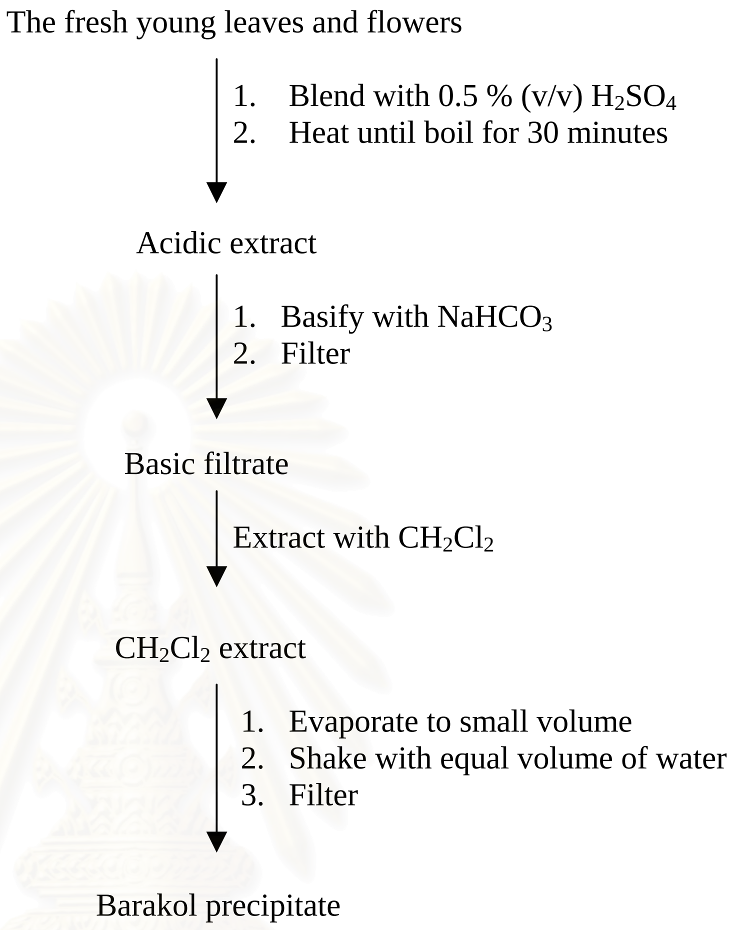
The quantities of fluorescent markers in diesel fuels were measured using a Perkin Elmer LS 50 luminescence spectrophotometer.

The kinematic viscosities of fluorescent and nonfluorescent diesel fuels were obtained with a Cannon automatic viscometer. Flash point (Pensky-Martens) of fluorescent and nonfluorescent diesel fuels were measured using an ISL (PMFP93) automatic flash point tester, while the pour points of fluorescent and nonfluorescent diesel fuels were recorded on an ISL (CPP92) automatic pour point tester. Sulfur contents in fluorescent and nonfluorescent diesel fuels were determined using Outokumpu (X-MET820) automatic sulfur content. The distillation of fluorescent and nonfluorescent diesel fuels were carried out with a Herzog (MP626) automatic distillation apparatus and the colors of fluorescent and nonfluorescent diesel fuels were observed with a Lovibond (PFX990/P) petrochemical tintometer.

3.3 Experimental

3.3.1 Extraction of barakol [9]

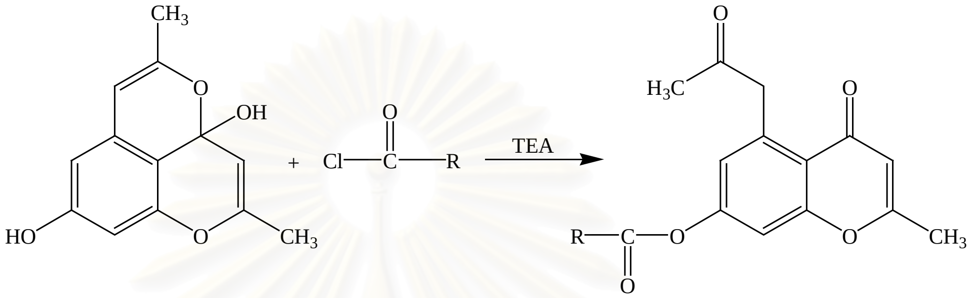
The barakol extraction and purification procedures from *Cassia siamea* Lamk are presented in Figure 3.1. Two kilograms of fresh young leaves and flowers of *Cassia siamea* Lamk were sliced into small pieces, and then boiled with 4 litres of 0.5 % (v/v) aqueous sulfuric acid for 30 minutes. It was then cooled to room temperature and filtered. The marc was re-boiled with 2 litres of 0.5% (v/v) aqueous sulfuric acid, cooled and filtered. The filtrates were combined and basified with sodium hydrogen carbonate to pH 8-9. The basic solution was extracted three times with dichloromethane (300 ml). The combined dichloromethane extracts were concentrated under reduced pressure until the volume was one-fourth of the starting volume, and mixed with the equal volume of distilled water. The mixture was shaken strongly by hand to allow precipitation of the yellow lemon needle crystals and then the solution was left in a refrigerator overnight for complete precipitation. The yield was approximately 6 g. The chemical structure of barakol was characterized by spectroscopic study such as IR, ^{1}H-NMR, ^{13}C-NMR, MS and fluorescence.



Scheme 3.1 The barakol extraction and purification procedure

3.3.2 Synthesis of barakol derivatives

General procedure for the esterification reaction of barakol with acid chloride in the presence of triethylamine was carried out as the followings:



A mixture of barakol (0.232 g, 0.001 mol), propionyl chloride (0.19 ml, 0.002 mol) and triethylamine (0.10 ml) was added in a 100 ml round bottom flask. The mixture was heated under nitrogen atmosphere at 70°C in an oil bath for 8 hours. The reaction mixture was allowed to cool to room temperature and then was dissolved in dichloromethane (15 ml). The mixture was neutralized with saturated sodium hydrogen carbonate solution and washed with distilled water (3 times, 15 ml). The organic phase was separated, dried with anhydrous sodium sulfate and filtered. Then dichloromethane was removed by vacuum to obtain crude product. This product was purified by column chromatography, which was eluted by a mixture of dichloromethane-ethyl acetate (4:1) to obtain pale yellow liquid (0.212 g, 73.87%yield).

Other acid chlorides (*e.g.* butyryl chloride, 2–ethylhexanoyl chloride and lauoryl chloride) were synthesized under the same conditions except that butyryl chloride (0.21 ml, 0.002 mol), 2–ethylhexanoyl chloride (0.33 ml, 0.002 mol) and lauoryl chloride (0.44 ml, 0.002 mol) were used instead of propionyl chloride.

3.3.3 Characterization

3.3.3.1 Characterization of barakol

The chemical structure of barakol (in section 3.3.1) was characterized by spectroscopic techniques such as FT-IR, ^{1}H-NMR, ^{13}C-NMR, MS and fluorescence.

3.3.3.2 Characterization of fluorescent markers

Fluorescent markers (in section 3.3.2) were characterized by spectroscopic techniques such as FT-IR, ^{1}H-NMR, ^{13}C-NMR, MS, EA and fluorescence.

3.3.4 Preparation of stock solution of fluorescent markers

Each 1,000 ppm stock fluorescent marker solution was prepared by dissolving 0.05 g of fluorescent markers (Section 3.3.2) with diesel fuels and made up to 50 ml in volumetric flask. The stock solution of fluorescent markers in solvent (white spirit No.0340) was prepared in a similar manner to the prepraration of the stock solution of fluorescent markers in diesel, except that the solvent (white spirit No.0340) was used instead of diesel.

3.3.5 Effect of fluorescent markers on the physical properties of diesel fuels

The physical properties of fluorescent and nonfluorescent diesel were studied according to the ASTM methods described in Table3.1.

Table 3.1 The ASTM testing methods of fluorescent and nonfluorescent diesel

Test items	Test methods ASTM
API gravity @ 60°C	D 1298
Specific gravity @ 15.6/15.6°C	D 1298
Calculated cetane index	D 976
Kinematic viscosity @40°C, cst	D 445
Pour point, °C	D 97
Flash point, °C	D 93
Sulfur content, % wt	D 4294
Distillation	D 86
Color	D 1500

3.3.6 Quantitative determination of fluorescent markers in diesel fuels

The method for quantitative determination of fluorescent markers in diesel fuels and solvent (white spirit No.0340) could be made by using spectrofluorometer.

The standard calibration curve of fluorescent markers in diesel was prepared at concentration from 0-10 ppm of fluorescent markers by the following procedure.

The stock fluorescent markers solution (1,000 ppm) was pipetted into a 50 ml volumetric flask and made up with diesel. The volume of the stock solution for each concentration is shown in Table 3.2.

Table 3.2 The volume of the stock solution (1,000 ppm) for each 0-10 ppm concentration

Concentration (ppm)	Volume of 1,000 ppm stock solution (ml)
0	0
2	0.10
4	0.20
6	0.30
8	0.40
10	0.50

The fluorescent diesel was drawn off and recorded in a spectrofluorometer at its λ_{ex} and λ_{em}. The calibration curve was a plot between intensity and the concentration of fluorescent markers in diesel.

The standard calibration curve of fluorescent markers in solvent (white spirit No.0340) was prepared at concentration from 0-10 ppm of fluorescent markers by the same procedure of fluorescent markers in diesel, except that the solvent (white spirit No.0340) was used instead of diesel.

The fluorescent solvent (white spirit No.0340) was drawn off and recorded in a spectrofluorometer at its λ_{ex} and λ_{em}. The calibration curve was a plot between intensity and the concentration of fluorescent markers in solvent (white spirit No.0340).

3.3.7 Stability of fluorescent markers in diesel fuels

The fluorescent diesel and fluorescent solvent (white spirit No.0340) at 0-10 ppm concentration of fluorescent markers were prepared and stored for 3 months. The quantity of fluorescent markers contained in diesel and solvent (white spirit No.0340) were measured by spectrofluorometer.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization and physical properties

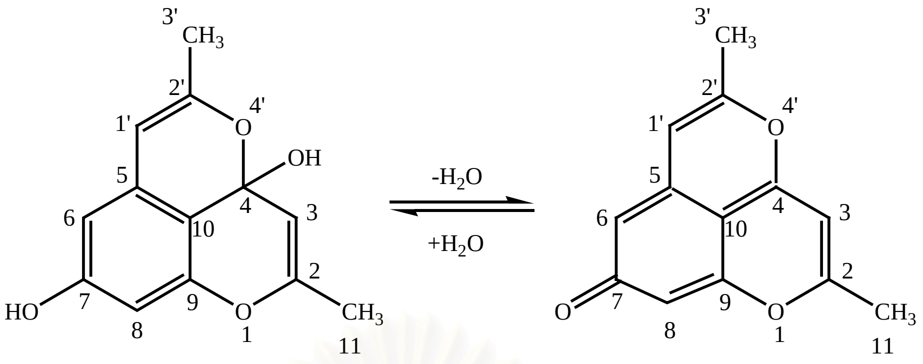
4.1.1 Characterization of barakol

The extraction of shredded fresh young leaves and flowers of *Cassia siamea* Lamk. with 0.5% sulphuric acid followed by alkalinization with sodium hydrogen carbonate gave 0.20% yield of yellow solid compound, presumably barakol.

The structure of yellow compound, presumably barakol (Figure 4.1) was characterized by TLC, FT-IR, NMR, and mass spectroscopic data as followings:

The R_f value was 0.32 and 0.53 when using an aluminum plate as the absorbent and mixtures of chloroform and methanol (9:1) and chloroform and acetone (6:4) as solvent systems, respectively.

The infrared spectrum of extracted barakol (yellow compound) (Figure 4.2) exhibited broad absorption bands at 3444 and 3295 cm^{-1} (O-H stretching of phenol). The absorption peaks at 1676 cm^{-1}(C=O stretching of ketone) and 1267 and 1188 cm^{-1} (C-O stretching), indicating barakol is unstable and can be converted to anhydrobarakol (Figure 4.1).



Barakol Anhydrobarakol

Figure 4.1 Chemical structures of barakol and anhydrobarakol with atomic numbering

The ^{1}H-NMR spectrum ($CDCl_3$) of extracted barakol (Figure 4.3) indicated two methyl groups (C11 and C3′) at δ_H 2.23 and 2.36 ppm, four protons (H3, H6, H8 and H1′) at δ_H 6.26(1H), 6.30(1H), 6.42(1H) and 6.00(1H) ppm, respectively. The ^{13}C-NMR spectrum ($CDCl_3$+MeOH-d_4) of extracted barakol (Figure 4.4) exhibited carbon signals which were aromatic carbons at 92.2-183.1 ppm and methyl groups at 19.6 ppm and 21.2 ppm. The assignments are shown in Table 4.1.

Table 4.1 The NMR spectrum assignments of barakol (1) and barakol (2) reported by Bycroft [11]

Position	Carbon type	^{1}H-NMR (ppm)		^{13}C-NMR (ppm)	
		1^a (Howhan)	2^a (Bycroft)	1^b (Howhan)	2^a (Bycroft)
2	C	-	-	168.7	168.2
3	CH	6.00 (s,1H)	5.77 (s,1H)	104.6	105.1
4	C	-	-	161.7	161.8
5	C	-	-	132.1	132.0
6	CH	6.30 (s,1H)	6.07 (s,1H)	113.3	113.8
7	C	-	-	183.1	183.7
8	CH	6.42 (s,1H)	6.17 (s,1H)	105.5	106.2
9	C	-	-	158.8	159.0
10	C	-	-	99.3	99.2
11	CH_3	2.36 (s,3H)	2.16 (s,3H)	20.5	21.2
1′	CH	6.26 (s,1H)	6.03 (s,1H)	108.0	108.0
2′	C	-	-	154.8	154.6
3′	CH_3	2.23 (s,3H)	2.05 (s,3H)	19.0	19.6

[a] In $CDCl_3$ [b] In $CDCl_3$+MeOH-d_4

The mass spectrum of extracted barakol (yellow compound) (Figure 4.5) indicated a molecular ion (m/e) (%relative intensity) 233(M)$^+$ ($C_{13}H_{12}O_4$, ≤ 1.0%) which was consistent to that of barakol reported, while anhydrobarakol (m/e) (%relative intensity) 215(M)$^+$ ($C_{13}H_{10}O_3$, 100%) is the major molecular ion presented in mass spectrum. From IR and MS spectrum data, the yellow compound obtained from the extraction of *Cassia siamea* Lamk. is considered to be a mixture of barakol and anhydrobarakol.

4.1.2 Characterization of barakol derivatives

Reaction of barakol and acid chloride (*e.g.* propionyl chloride, butyryl chloride, 2–ethylhexanoyl chloride and lauoryl chloride) using triethylamine as a catalyst, gave barakol derivatives in good yield (Table 4.2). The optimum condition for esterification reaction was obtained at 70°C and 8 hours.

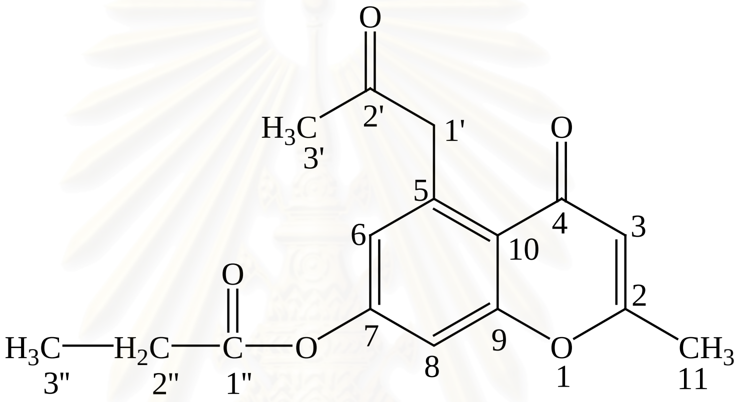
Table 4.2 The percentage yield of barakol derivatives

Acid chloride	Yield (%)
propionyl chloride (compound **1**)	73.87
butyryl chloride (compound **2**)	71.19
2-ethylhexanoyl chloride (compound **3**)	77.16
lauoryl chloride (compound **4**)	71.26

4.1.2.1 Characterization of compound 1

Compound **1** was prepared by the esterification reaction of barakol and propionyl chloride. It was pale yellow liquid (Found: C 66.01 %, H 6.01 % calculated for $C_{16}H_{16}O_5$: C 66.67 %, H 5.56 %).

The structure of compound **1** is shown below:



The infrared spectrum of compound **1** (Figure 4.6) showed absorption peaks at 2973 and 2932 cm^{-1} (C-H stretching of aliphatic), 1764 cm^{-1} (C=O stretching of ester), 1719 and 1645 cm^{-1} (C=O stretching of ketone), 1610 cm^{-1} (C=C ring stretching of aromatic) and 1383 and 1139 cm^{-1} (C-O stretching).

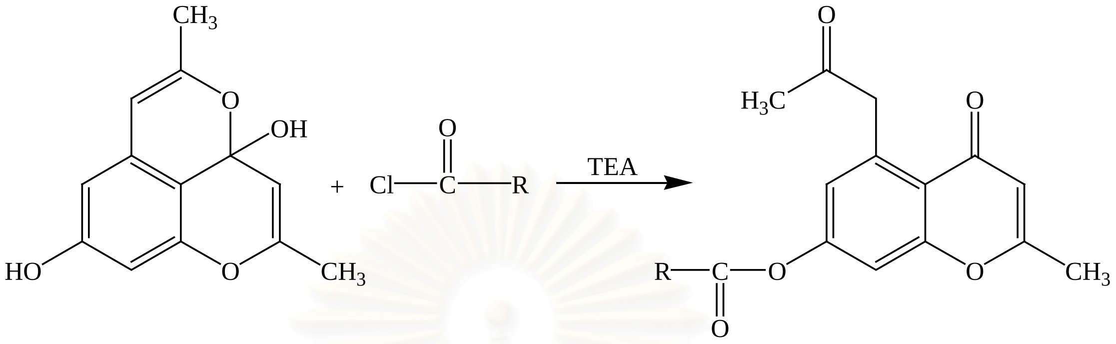
The ^{1}H-NMR spectrum ($CDCl_3$) of compound **1** (Figure 4.7) exhibited proton signals which were aromatic protons at δ_H 5.96-7.13 ppm and methylene and methyl groups at δ_H 1.18-4.17 ppm. The ^{13}C-NMR spectrum ($CDCl_3$) of compound **1** (Figure 4.8) exhibited carbon signals which were carbonyls of ketone at 179 ppm and 204.6 ppm, carbonyl of ester at 172.0 ppm, aromatic carbon at 110.3-165.2 ppm, and methylene and methyl groups at 9.1-49.6 ppm. The assignments are shown in Table 4.3.

Table 4.3 The NMR spectrum assignment of compound **1**

Position	Carbon type	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
2	C	-	165.2
3	CH	5.96 (s,1H)	110.3
4	C	-	179.0
5	C	-	138.0
6	CH	7.13 (s,1H)	119.2
7	C	-	158.4
8	CH	6.75 (s,1H)	111.6
9	C	-	153.4
10	C	-	122.5
11	CH_3	2.26 (s,3H)	20.0
1′	CH_2	4.17 (s,2H)	49.6
2′	C	-	204.6
3′	CH_3	2.30 (s,3H)	28.2
1″	C	-	172.0
2″	CH_2	2.62 (q, *J* = 7.4 Hz,2H)	30.0
3″	CH_3	1.20 (t, *J* = 7.4 Hz,3H)	9.1

The mass spectrum of compound **1** (Figure 4.9) indicated a molecular ion (m/e) (%relative intensity): 311 $(M+Na)^{+}$ (100).

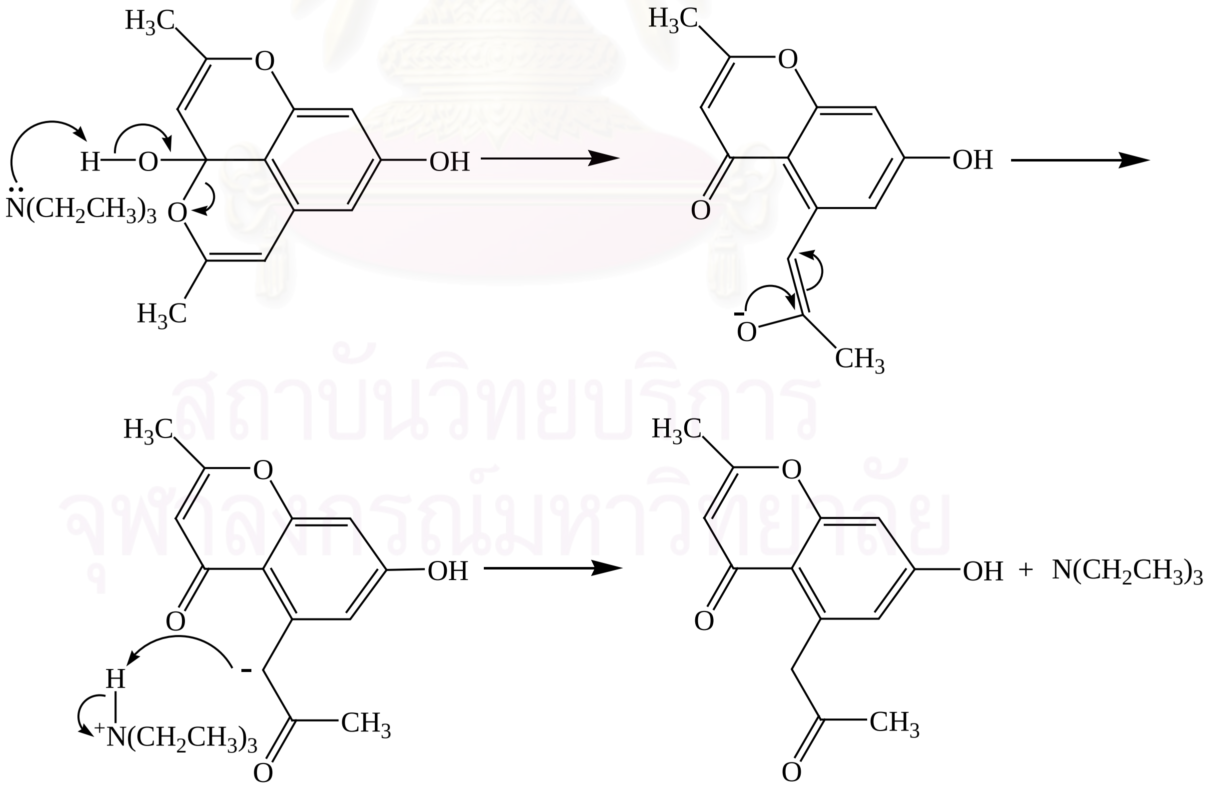
MECHANISM OF REACTION

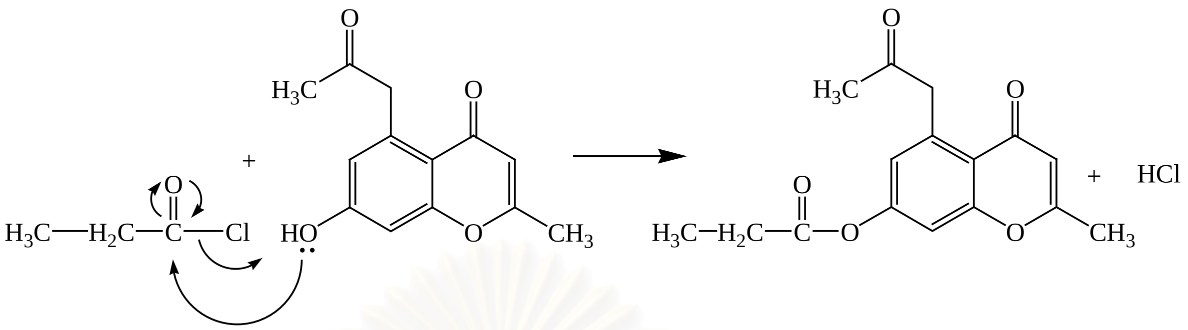


where R is selected from a linear or branched C_2-C_{11} acid chloride

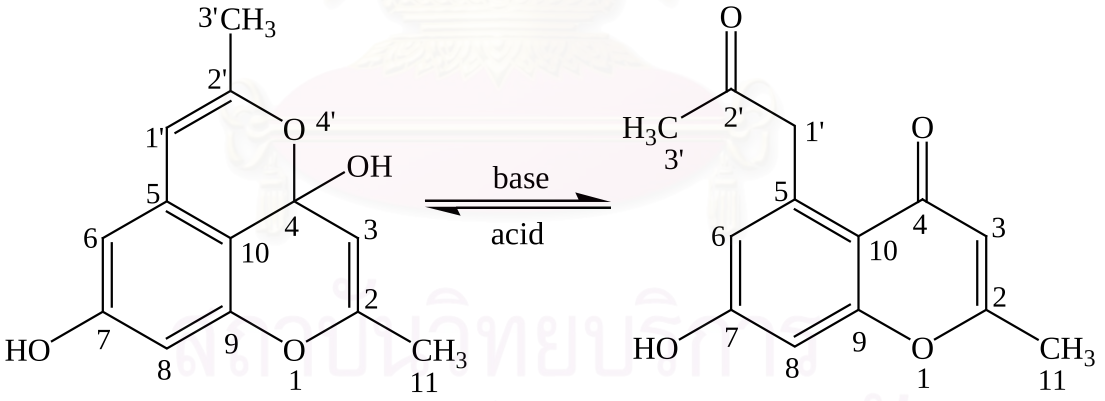
Reaction of barakol with propionyl chloride in the presence of triethylamine

: $-R = -CH_2-CH_3$





Mild basic condition, barakol was an unstable compound. It can be converted into 5-acetonyl-7-methoxy-2-methylchromone ($C_{13}H_{11}O_4$) and 5-acetonyl-7-methoxy-2-methylchromone can be reconverted into barakol in acid condition [11].

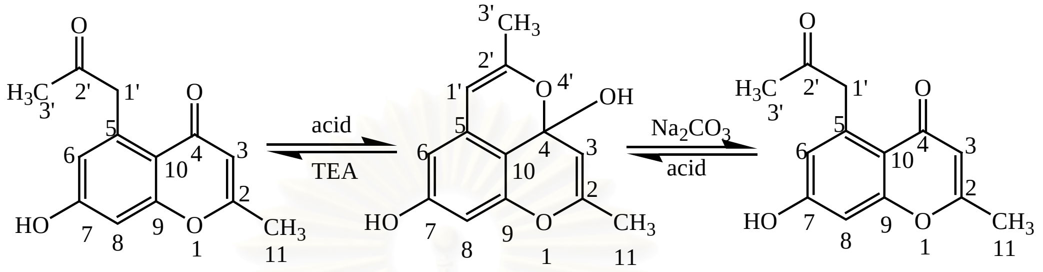


Barakol

5-acetonyl-7-methoxy-
2-methylchromone

5-Acetonyl-7-methoxy-2-methylchromone

5-Acetonyl-7-methoxy-2-methylchromone was synthesized from reaction between barakol with base such as sodium carbonate [11] and triethylamine.



compound **a** barakol compound **b**

Synthesis of compound a

Barakol (0.232 g, 0.001 mol) was added into triethylamine (1.00 ml) in a 100 ml round bottom flask. The mixture was heated at 70°C in an oil bath for 8 hours. The reaction mixture was allowed to cool to room temperature and then was dissolved in ethyl acetate (15 ml). The mixture was neutralized with hydrochloric acid and washed with distilled water (3 times, 15 ml). The organic phase was separated, dried with anhydrous sodium sulfate and filtered. Then ethyl acetate was removed in vacuum to obtain compound **a**. It was a pale red liquid.

Synthesis of compound b [11]

Barakol (0.232 g, 0.001 mol) was added into 2 M sodium carbonate (5.00 ml) in a 100 ml round bottom flask. The mixture was heated at 50°C in an oil bath for 20 minutes. The reaction mixture was allowed to cool to room temperature. The mixture was neutralized with hydrochloric and then was dissolved in ethyl acetate (3 times, 50 ml). The organic phase was separated, dried with anhydrous sodium sulfate and filtered. Then ethyl acetate was removed in vacuum to obtain compound **b**. It was a pale red liquid.

The infrared spectra of compounds **a** and **b** are shown in Figures 4.10 and 4.11, respectively and the details of absorption peaks are shown in Table 4.4.

Table 4.4 The FT-IR absorption peak of 5-acetonyl-7-methoxy-2-methylchromone (compounds **a** and **b**) and 5-acetonyl-7-methoxy-2-methylchromone reported by Bycroft [11] (compound **b)**

FT-IR (cm^{-1})	Compound		
	compound **a** (Howhan)	compound **b** (Howhan)	compound **b** (Bycroft)
O-H str.	3096, 2926	3108, 2926	-
C=O str.	1713, 1645	1713, 1645	1708, 1645
C=C str.	1575	1575	1625, 1575

The ^{1}H-NMR spectrum ($CDCl_3$) of compound **a** (Figure 4.12) exhibited protons on methyl groups (H11 and H3′) at δ_H 2.28 and 2.38 ppm, proton on methylene group (H1′) at δ_H 4.17 ppm and protons on aromatic ring (H3, H6 and H8) at δ_H 5.96, 6.66 and 6.52 ppm, respectively. The ^{13}C-NMR spectrum ($CDCl_3$) of compound **a** (Figure 4.13) exhibited carbon signals which were carbonyls of ketone at 179.8 ppm and 205.1 ppm, aromatic carbons at 102.3-164.7 ppm, and methylene and methyl groups at 19.6-49.7 ppm. The assignments are shown in Table 4.5.

The ^{1}H-NMR spectrum ($CDCl_3$) of compound **b** (Figure 4.14) exhibited protons on methyl groups (H11 and H3′) at δ_H 2.28 and 2.38 ppm, proton on methylene group (H1′) at δ_H 4.17 ppm and protons on aromatic ring (H3, H6 and H8) at δ_H 5.97, 6.66 and 6.52 ppm, respectively. The ^{13}C-NMR spectrum ($CDCl_3$) of compound **b** (Figure 4.15) exhibited carbon signals which were carbonyl of ketone at 179.2 ppm and 205.1 ppm, aromatic carbons at 102.3-165.0 ppm, and methylene and methyl groups at 19.9-49.7 ppm. The assignments are shown in Table 4.5.

Table 4.5 The NMR spectrum assignments of 5-acetonyl-7-methoxy-2-methylchromone (compounds **a** and **b**) and 5-acetonyl-7-methoxy-2-methylchromone reported by Bycroft [11] (compound **b)**

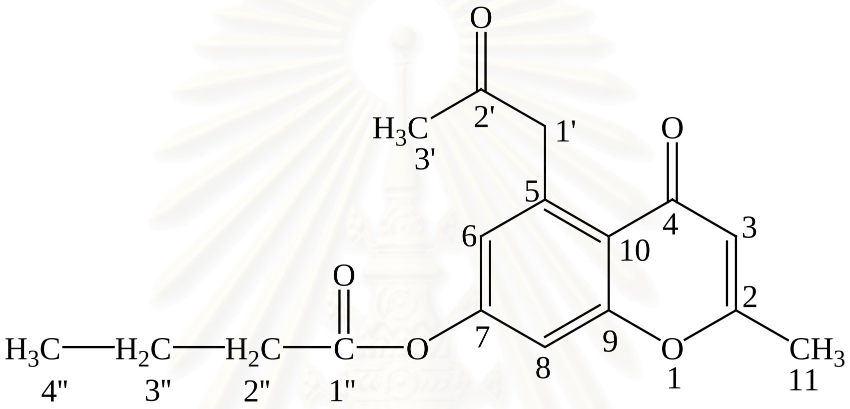
Position	Carbon type	^{1}H-NMR (ppm)			^{13}C-NMR (ppm)	
		compound **a**[1] (Howhan)	compound **b**[1] (Howhan)	compound **b**[2] (Bycroft)	compound **a**[1] (Howhan)	compound **b**[1] (Howhan)
2	C	-	-	-	164.7	165.0
3	CH	5.96(s,1H)	5.97(s,1H)	5.96(s,1H)	110.2	110.2
4	C	-	-	-	179.8	179.2
5	C	-	-	-	137.2	137.2
6	CH	6.66(s,1H)	6.66(s,1H)	6.70(s,1H)	114.1	114.0
7	C	-	-	-	161.0	161.1
8	CH	6.52(s,1H)	6.52(s,1H)	6.62(s,1H)	102.3	102.3
9	C	-	-	-	160.0	159.6
10	C	-	-	-	118.9	118.9
11	CH$_3$	2.28(s,3H)	2.28(s,3H)	2.18(s,3H)	19.9	19.9
1′	CH$_2$	4.17(s,2H)	4.17(s,2H)	4.12(s,2H)	49.7	49.7
2′	C	-	-	-	205.1	205.1
3′	CH$_3$	2.38(s,3H)	2.38(s,3H)	2.28(s,3H)	29.6	29.7

[1] In CDCl$_3$ [2] In DMSO-d$_6$

4.1.2.2 Characterization of compound 2

Compound **2** was prepared by the esterification reaction of barakol and butyryl chloride. It was pale yellow liquid (Found: C 67.66%, H 6.05% calculated for $C_{17} H_{18}O_5$: C 67.55%, H 5.96 %).

The structure of compound **2** is shown below:



The infrared spectrum of compound **2** (Figure 4.16) exhibited absorption peaks at 2967 and 2934 cm^{-1} (C-H stretching of aliphatic), 1765 cm^{-1} (C=O stretching of ester), 1720 and 1650 cm^{-1} (C=O stretching of ketone), 1610 cm^{-1} (C=C ring stretching of aromatic) and 1390 and 1137 cm^{-1} (C-O stretching).

The ^{1}H-NMR spectrum ($CDCl_3$) of compound **2** (Figure 4.17) exhibited proton signals which were aromatic protons at δ_H 5.96-7.13 ppm and methylene and methyl groups at δ_H 0.96-4.17 ppm. The ^{13}C-NMR spectrum ($CDCl_3$) of compound **2** (Figure 4.18) exhibited carbon signals which were carbonyls of ketone at 179 ppm and 205.1 ppm, carbonyl of ester at 171.2 ppm, aromatic carbons at 110.2-165.2 ppm, and methylene and methyl groups at 13.6-49.6 ppm. The assignments are shown in Table 4.6.

Table 4.6 The NMR spectrum assignment of compound **2**

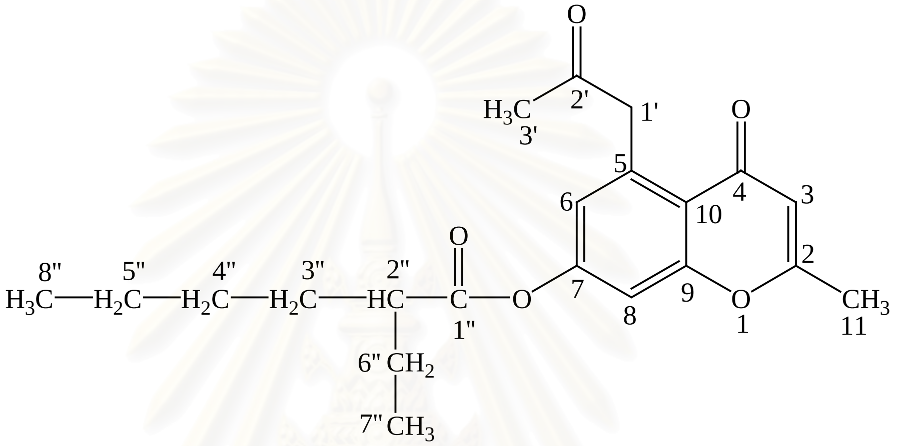
Position	Carbon type	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
2	C	-	165.2
3	CH	5.96 (1H,s)	110.3
4	C	-	179.0
5	C	-	138.0
6	CH	7.13 (1H,s)	119.0
7	C	-	158.4
8	CH	6.75 (1H,s)	111.5
9	C	-	153.3
10	C	-	122.5
11	CH_3	2.26 (3H,s)	19.0
1′	CH_2	4.17 (2H,s)	49.6
2′	C	-	205.1
3′	CH_3	2.30 (3H,s)	28.8
1″	C	-	171.2
2″	CH_2	2.50 (t, *J* = 7.2 Hz,2H)	36.2
3″	CH_2	1.72 (m,2H)	19.5
4″	CH_3	0.99 (t, *J* = 7.2 Hz,3H)	13.6

The mass spectrum of compound **2** (Figure 4.19) indicated a molecular ion (m/e) (%relative intensity): 325 $(M+Na)^{+}$ (100).

4.1.2.3 Characterization of compound 3

Compound **3** was prepared by the esterification reaction of barakol and 2-ethylhexanoyl chloride. It was pale yellow liquid (Found: C 69.86%, H 7.54% calculated for $C_{21}H_{26}O_5$: C 70.39%, H 7.27%).

. The structure of compound **3** is shown below:



The infrared spectrum of compound **3** (Figure 4.20) exhibited absorption peaks at 2960 and 2933 cm^{-1} (C-H stretching of aliphatic), 1760 cm^{-1} (C=O stretching of ester), 1724 and 1653cm^{-1} (C=O stretching of ketone), 1612 cm^{-1} (C=C ring stretching of aromatic) and 1388 and 1134 cm^{-1} (C-O stretching).

The ^{1}H-NMR spectrum ($CDCl_3$) of compound **3** (Figure 4.21) exhibited proton signals which were aromatic protons at δ_H 5.96-7.13 ppm and methylene and methyl groups at δ_H 0.79-4.17 ppm. The ^{13}C-NMR spectrum ($CDCl_3$) of compound 3 (Figure 4.22) exhibited carbon signals which were carbonyls of ketone at 178.9 ppm and 204.6 ppm, carbonyl of ester at 174.0 ppm, aromatic carbons at 110.0-165.0 ppm, and methylene and methyl groups at 13.6-49.6 ppm. The assignments are shown in Table 4.7.

Table 4.7 The NMR spectrum assignment of compound **3**

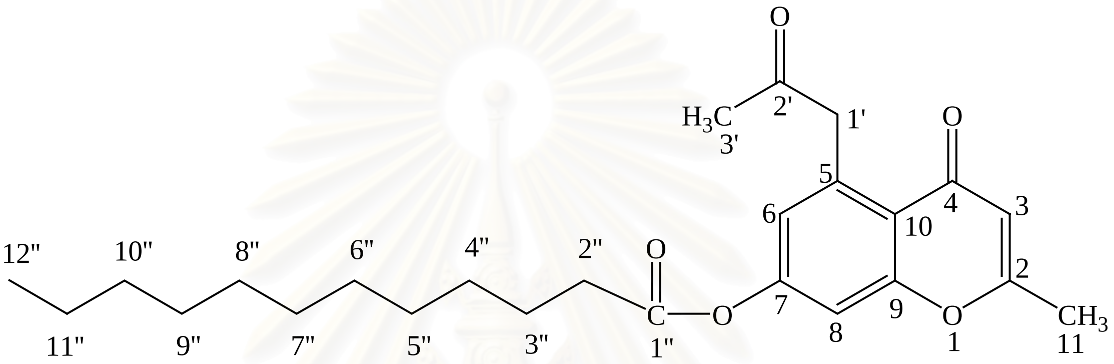
Position	Carbon type	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
2	C	-	165.0
3	CH	5.96 (s,1H)	110.0
4	C	-	178.9
5	C	-	138.0
6	CH	7.13 (s,1H)	119.2
7	C	-	158.2
8	CH	6.75 (s,1H)	111.4
9	C	-	153.4
10	C	-	122.4
11	CH$_3$	2.26 (s,3H)	20.0
1′	CH$_2$	4.17 (s,2H)	49.6
2′	C	-	204.6
3′	CH$_3$	2.30 (s,3H)	29.0
1″	C	-	174.0
2″	CH	2.46 (p,1H)	47.0
3″-6″	CH$_2$	1.55-1.72 (m,8H)	20.1-32.0
7″-8″	CH$_3$	0.79-0.96 (m,6H)	10,14

The mass spectrum of compound **3** (Figure 4.23) indicated a molecular ion (m/e) (%relative intensity): 381(M+Na)$^+$ (100).

4.1.2.4 Characterization of compound 4

Compound **4** was prepared by the esterification reaction of barakol and lauoryl chloride. It was pale yellow liquid (Found: C 72.63%, H 9.01% calculated for $C_{25}H_{34}O_5$: C 72.46%, H 8.21%).

The structure of compound **4** is shown below:



The infrared spectrum of compound **4** (Figure 4.24) exhibited absorption peaks at 2925 and 2855 cm^{-1} (C-H stretching of aliphatic), 1765 cm^{-1} (C=O stretching of ester), 1724 and 1653 cm^{-1} (C=O stretching of ketone), 1613 cm^{-1} (C=C ring stretching of aromatic) and 1384 and 1134 cm^{-1} (C-O stretching).

The ^{1}H-NMR spectrum ($CDCl_3$) of compound **4** (Figure 4.25 exhibited proton signals which were aromatic protons at δ_H 5.96-7.13 ppm and methylene and methyl groups at δ_H 0.87-4.17 ppm. The ^{13}C-NMR spectrum ($CDCl_3$) of compound **4** (Figure 4.26) exhibited carbon signals which were carbonyls of ketone at 179.0 ppm and 205.0 ppm, carbonyl of ester at 171.4 ppm, aromatic carbons at 110.2-165.2 ppm, and methylene and methyl groups at 13.6-49.6 ppm. The assignments are shown in Table 4.8.

Table 4.8 The NMR spectrum assignment of compound **4**

Position	Carbon type	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
2	C	-	165.1
3	CH	5.96 (1H,s)	110.2
4	C	-	179.0
5	C	-	138.0
6	CH	7.13 (1H,s)	119.2
7	C	-	158.4
8	CH	6.75 (1H,s)	111.5
9	C	-	153.3
10	C	-	122.5
11	CH_3	2.26 (3H,s)	20.0
1′	CH_2	4.17 (2H,s)	49.6
2′	C	-	205
3′	CH_3	2.30 (3H,s)	29.0
1″	C	-	171.4
2″	CH_2	2.58 (t, *J* = 7.2 Hz,2H)	34.4
3″-11″	CH_2	1.27-1.78 (m,16H)	20.1-31.9
12″	CH_3	0.88 (t, *J* = 7.2 Hz,3H)	14.1

The mass spectrum of compound **4** (Figure 4.27) indicated a molecular ion (m/e) (%relative intensity): 437(M+Na)$^{+}$ (100)

The summarized FT-IR, ^{1}H-NMR ^{13}C-NMR and fluorescence of barakol and barakol derivatives are shown in Tables 4.9-4.11.

Table 4.9 The summarized FT-IR spectrum assignment of barakol and barakol derivatives

Barakol derivatives	FT-IR (cm^{-1})	
	C=O str.	C-O str.
Barakol	1676	1267, 1188
Compound **1**	1764, 1719,1647	1383, 1139
Compound **2**	1765, 1720,1650	1390, 1137
Compound **3**	1760, 1724,1653	1388, 1134
Compound **4**	1765, 1724,1654	1384, 1134

Table 4.10 The summarized ^{1}H-NMR spectrum assignment of barakol and barakol derivatives

Position	Chemical shift (ppm)				
	Barakol	Compound **1**	Compound **2**	Compound **3**	Compound **4**
3	6.00	5.96	5.96	5.96	5.96
6	6.30	7.13	7.13	7.13	7.13
8	6.42	6.75	6.75	6.75	6.75
11	2.26	2.26	2.26	2.26	2.26
1′	6.26	4.17	4.17	4.17	4.17
3′	2.23	2.30	2.30	2.30	2.30
2″	-	2.62	2.50	2.46	2.58
3″	-	1.20	1.72	1.55-1.72	1.27-1.78
4″	-	-	0.99		
5″	-	-	-		
6″	-	-	-		
7″	-	-	-	0.79-0.96	
8″	-	-	-		
9″	-	-	-	-	
10″	-	-	-	-	
11″	-	-	-	-	
12″	-	-	-	-	0.88

Table 4.11 The summarized ^{13}C-NMR spectrum assignment of barakol and barakol derivatives

Position	Chemical shift (ppm)				
	Barakol	Compound **1**	Compound **2**	Compound **3**	Compound **4**
2	168.7	165.2	165.2	165.0	165.1
3	104.6	110.3	110.3	110.0	110.2
4	161.7	179.0	179.0	178.9	179.0
5	132.1	138.0	138.0	138.0	138.0
6	113.3	119.2	119.0	119.2	119.2
7	183.1	158.4	158.4	158.2	158.4
8	105.5	111.6	111.5	111.4	111.5
9	158.8	153.4	153.3	153.4	153.3
10	99.3	122.5	122.5	122.4	122.5
11	20.5	20.0	19.0	20.0	20.0
1′	108.0	49.6	49.6	49.6	49.6
2′	154.8	204.6	205.1	204.6	205.0
3′	19.0	28.2	28.8	29.0	29.0
1″	-	172.0	171.2	174.0	171.4
2″	-	30.0	36.2	47.0	34.4
3″	-	9.1	19.5	20.1-32.0	20.1-31.9
4″	-	-	13.6		
5″	-	-	-		
6″	-	-	-		
7″	-	-	-	10.0,14.1	
8″	-	-	-		
9″	-	-	-	-	
10″	-	-	-	-	
11″	-	-	-	-	
12″	-	-	-	-	14.1

4.1.2.5 Fluorescent properties of barakol and barakol derivatives

Fluorescent properties of barakol and barakol derivatives were studied in four solvents of different polarity: hexane, dichloromethane, ethyl acetate and methanol and summarized in Table 4.12.

The measuring parameters for fluorescent measurement were set as the followings:

- The wavelength of the excitation monochromator (λ_{ex}) was set.
- The response was set for one second.
- The photomultiplier tube voltage level (PMT Grain) was set a medium.
- The spectrum bandwidth of the emission monochromator (Em SBW) was set at 10.
- The spectrum bandwidth of the excitation monochromator (Ex SBW) was set at 10.

Table 4.12 The summarized excitation wavelength (λ_{ex}; nm) and emission wavelength (λ_{em}; nm) of barakol and barakol derivatives in solvent

Compound	Excitation wavelength (λ_{ex}; nm)	Emission wavelength (λ_{em}; nm)
Barakol		
Dichloromethane	246	491
Ethyl acetate	285	504
Methanol	222	505
Compound **a**		
Dichloromethane	250	498
Ethyl acetate	282	492
Methanol	225	495
Compound **1**		
Dichloromethane	250	500
Ethyl acetate	281	492
Compound **2**		
Dichloromethane	250	500
Ethyl acetate	281	492
Compound **3**		
Hexane	252	455
Dichloromethane	250	500
Ethyl acetate	281	492
Compound **4**		
Hexane	252	455
Dichloromethane	250	500

The excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of barakol in dichloromethane, ethyl acetate and methanol are shown in Figures 4.28-4.30, the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of compound **a** in dichloromethane, ethyl acetate and methanol are shown in Figures 4.31-4.33, the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of compound **1** in dichloromethane and ethyl acetate are shown in Figures 4.34-4.35, the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of compound **2** in dichloromethane and ethyl acetate are shown in Figures 4.36-4.37, the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of compound **3** in hexane, dichloromethane and ethyl acetate are shown in Figures 4.38-4.40 and the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of compound **4** in hexane and dichloromethane are shown in Figures 4.41-4.42, respectively.

4.2 Effect of fluorescent markers on physical properties of fluorescent diesel

Fluorescent markers, compounds **1** and **2** were insoluble in diesel fuels, compound **3** was poor soluble in diesel fuels and compound **4** was high soluble in diesel fuels. Therefore, this research chose compound **4** as a fluorescent marker model because it was easily dissolved in diesel.

Diesel containing 5 ppm of compound **4** was used for physical properties testing, using the ASTM methods. The physical properties of fluorescent and nonfluorescent diesel were compared. The results are shown in Table 4.13.

Table 4.13 The effects of fluorescent marker on physical properties of fluorescent and nonfluorescent diesel

Test items	ASTM	Limit	Result	
			fluorescent	nonfluorescent
API gravity @ 60°C	D 1298	report	38.64	38.64
Specific gravity @ 15.6/15.6°C	D 1298	0.81-0.87	0.83168	0.83168
Calculated cetane index	D 976	47 min	56.0	56.0
Kinematic viscosity @ 40°C, cst	D 445	1.8-4.1	2.994	2.989
Pour point, °C	D 97	10 max	-4.0	-5.0
Flash point, °C	D 93	52 min	65.0	65.0
Sulfur content, % wt	D 4294	0.035 max	0.030	0.030
Distillation (Correct Temp.)	D 86			
IBP, °C		report	173.0	173.0
10% rec, °C		report	201.8	202.4
50% rec, °C		report	280.1	279.7
90% rec , °C		357 max	353.3	353.2
Color	D 1500	2.0 max	<0.5	<0.5

The physical properties of fluorescent diesel were not significantly different from nonfluorescent diesel (Table 4.13). Both fluorescent and nonfluorescent diesel provided similar specific gravity, calculated cetane index, pour point, flash point, distillation properties and colors. The results revealed this compound did not have any effect on the physical properties of diesel. Therefore it is possible to use this fluorescent marker as the marker in diesel.

4.3 Quantitative determination of fluorescent marker in diesel

The standard calibration curve of fluorescent marker (compound **4)** in diesel was prepared by adding fluorescent marker into diesel at different concentrations. The standard calibration curve was a plot between intensity and concentration of fluorescent marker in diesel.

The standard calibration equation of compound **4** in diesel is shown in Table 4.14 and the standard calibration curve of compound **4** is shown in the Appendix section (Figure 4.43).

Table 4.14 The calibration equation for quantitative determination of fluorescent marker (compound **4**) in diesel

Fluorescent marker	Standard calibration equation	Correlation coefficient (r)
Compound **4**	$Y = 0.7300X + 0.0259$	0.999

From Table 4.14 it was concluded that fluorescent marker in this research gave the precisely quantitative determinations since its correlation coefficient (r) in the standard equation was closed to 1. Therefore, the fluorescent marker in this research could be used as marker in diesel fuel.

The measuring parameters for fluorescent measurement were set as the followings:

- The wavelength of the excitation monochromator (λ_{ex}) was set 464 nm.
- The response was set for one second.
- The photomultiplier tube voltage level (PMT Grain) was set a medium.
- The spectrum bandwidth of the emission monochromator (Em SBW) was set at 10.
- The spectrum bandwidth of the excitation monochromator (Ex SBW) was set at 10.

The wavelength of the emission monochromator (λ_{em}) of compound **4** was 612 nm. The excitation wavelength and emission wavelength of compound **4** in diesel is shown in the Appendix section (Figure 4.45).

Because of the possible interference from diesel fuel, diesel fuel was measured and set as a blank. The excitation wavelength and emission wavelength of diesel fuel is shown in the Appendix section (Figure 4.44).

Fluorescent markers, compounds **1** and **2** were insoluble in solvent (white spirit No. 0340), compound **3** was poor soluble in solvent (white spirit No. 0340) and compound **4** was high soluble in solvent (white spirit No. 0340). Therefore, this research chose compound **4** as a fluorescent marker model because it was easily dissolved in solvent (white spirit No. 0340).

The standard calibration curve of fluorescent marker (compound **4**) in solvent (white spirit No. 0340) was prepared by adding fluorescent marker into solvent (white spirit No. 0340) at different concentrations. The standard calibration curve was a plot between intensity and concentration of fluorescent marker in solvent (white spirit No. 0340).

The standard calibration equation compound **4** in solvent (white spirit No. 0340) is shown in Table 4.15 and the standard calibration curve of compound **4** is shown in the Appendix section (Figure 4.46).

Table 4.15 The calibration equation for quantitative determination of fluorescent marker (compound **4**) in solvent (white spirit No. 0340)

Fluorescent marker	Standard calibration equation	Correlation coefficient (r)
Compound **4**	Y = 2.0243x + 0.0952	0.9989

From Table 4.15 it was concluded that fluorescent marker in this research gave the precisely quantitative determinations since its correlation coefficient (r) in the standard equation was closed to 1. Therefore, the fluorescent marker in this research could be used as marker in solvent (white spirit No. 0340) as well.

The measuring parameters for fluorescent measurement were set as the followings:

- The wavelength of the excitation monochromator (λ_{ex}) was set 481 nm.
- The response was set for one second.
- The photomultiplier tube voltage level (PMT Grain) was set a medium.

- The spectrum bandwidth of the emission monochromator (Em SBW) was set at 10.
- The spectrum bandwidth of the excitation monochromator (Ex SBW) was set at 10.

The wavelength of the emission monochromator (λ_{em}) of compound **4** was 560 nm. The excitation wavelength and emission wavelength of compound **4** in solvent (white spirit No. 0340) is shown in the Appendix section (Figure 4.48).

Because of the possible interference from solvent (white spirit No. 0340), solvent (white spirit No. 0340) was measured and set as a blank. The excitation wavelength and emission wavelength of solvent (white spirit No. 0340) is shown in the Appendix section (Figure 4.47).

Fluorescent markers, compounds **1** and **2** were insoluble in gasoline, compound **3** was poor soluble in gasoline and compound **4** was high soluble in gasoline. Therefore, this research chose compound **4** as a fluorescent marker model because it was easily dissolved in gasoline.

The measuring parameters for fluorescent measurement were set as the followings:

- The wavelength of the excitation monochromator (λ_{ex}) was set 396 nm.
- The response was set for one second.
- The photomultiplier tube voltage level (PMT Grain) was set a medium.
- The spectrum bandwidth of the emission monochromator (Em SBW) was set at 10.
- The spectrum bandwidth of the excitation monochromator (Ex SBW) was set at 10.

The wavelength of the emission monochromator (λ_{em}) of compound **4** was 570 nm. The excitation wavelength and emission wavelength of compound **4** in gasoline is shown in the Appendix section (Figure 4.50).

Because of the possible interference from gasoline, gasoline was measured and set as a blank. The excitation wavelength and emission wavelength of gasoline is shown in the Appendix section (Figure 4.49).

4.4 Stability of fluorescent marker in diesel

The stability of fluorescent marker which was compound **4** (5 ppm) in diesel was studied by monitoring its quantities in diesel for 3 months using spectrofluorometer. The results of the stability of compound **4** in diesel are shown in Table 4.16.

Table 4.16 The stability of compound **4** (5 ppm) in diesel

Month	Concentration in diesel (ppm)		
	1st	2nd	Average
1	4.99±0.01	5.02±0.01	5.00±0.01
2	5.00±0.02	5.01±0.01	5.00±0.01
3	5.00±0.03	5.01±0.02	5.00±0.01

From Table 4.16 the concentration of marker in diesel was slightly different from the original concentrations. The results indicated that the fluorescent marker has stability at least for 3 months. Generally, diesel is consumed within 3 months after released to the market. Therefore it was possible that the compound **4** could be used as a marker in diesel fuel.

The stability of fluorescent marker which was compound **4** (5 ppm) in solvent (white spirit No. 0340) was studied by monitoring its quantities in solvent (white spirit No. 0340) for 3 months using spectrofluorometer. The results of the stability of compound **4** in solvent (white spirit No. 0340) are shown in Table 4.17.

Table 4.17 The stability of compound **4** (5 ppm) in solvent (white spirit No. 0340)

Month	Concentration in solvent (white spirit No. 0340) (ppm)		
	1st	2nd	Average
1	5.01±0.02	5.02±0.01	5.01±0.01
2	5.00±0.01	5.03±0.01	5.01±0.01
3	5.02±0.02	5.01±0.03	5.01±0.01

From Table 4.17 the concentration of marker in solvent (white spirit No. 0340) was slightly different from the original concentrations. The results indicated that the fluorescent marker has stability at least for 3 months. Therefore it was possible to use compound **4** as a marker in solvent (white spirit No. 0340).

CHAPTER V

CONCLUSION

The extraction of shredded fresh young leaves and flowers from *Cassia siamea* Lamk gave barakol as a yellow solid compound. Barakol could be fluoresced but does not dissolve in oil. This research involved the synthesis of barakol derivatives for use as fluorescent markers in diesel fuels. Barakol derivatives are synthesized from esterification reaction between barakol and acid chloride. The optimum condition for reaction in most case was 70°C, 8 hours and triethylamine as a catalyst. These synthetic fluorescent markers were 7-propionyloxy-5-acetony-2-methylchromone (compound **1,** 73.87 % yield), 7-butyryloxy-5-acetony-2-methylchromone (compound **2**, 71.19 % yield), 7-(2-ethyl)-hexanoyloxy-5-acetony-2-methylchromone (compound **3,** 77.16 % yield) and 7-lauroyloxy-5-acetony-2 methylchromone (compound **4,** 71.26 % yield). These synthetic fluorescent markers were invisible color in diesel fuels when they were added into diesel at concentration of 2 to 10 ppm and quantitative measurement was carried out using spectrofluorometer. The excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of fluorescent markers in diesel were 464 and 612 nm, respectively. The physical properties of diesel fuels, which were tested according to ASTM method, revealed that they were unaffected. Moreover, those synthetic fluorescent markers were found to be stable in diesel fuels for at least three months.

Suggestion for further studies:

1. Since barakol derivative have good fluorescence, therefore, it is possible to synthesize barakol derivatives from the reaction between barakol and isocyanate for use as fluorescent markers.
2. It is interesting to study biological and chemical properties of barakol derivatives.
3. Fluorescent property of barakol derivatives at various pH should be investigated.

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APPENDICES

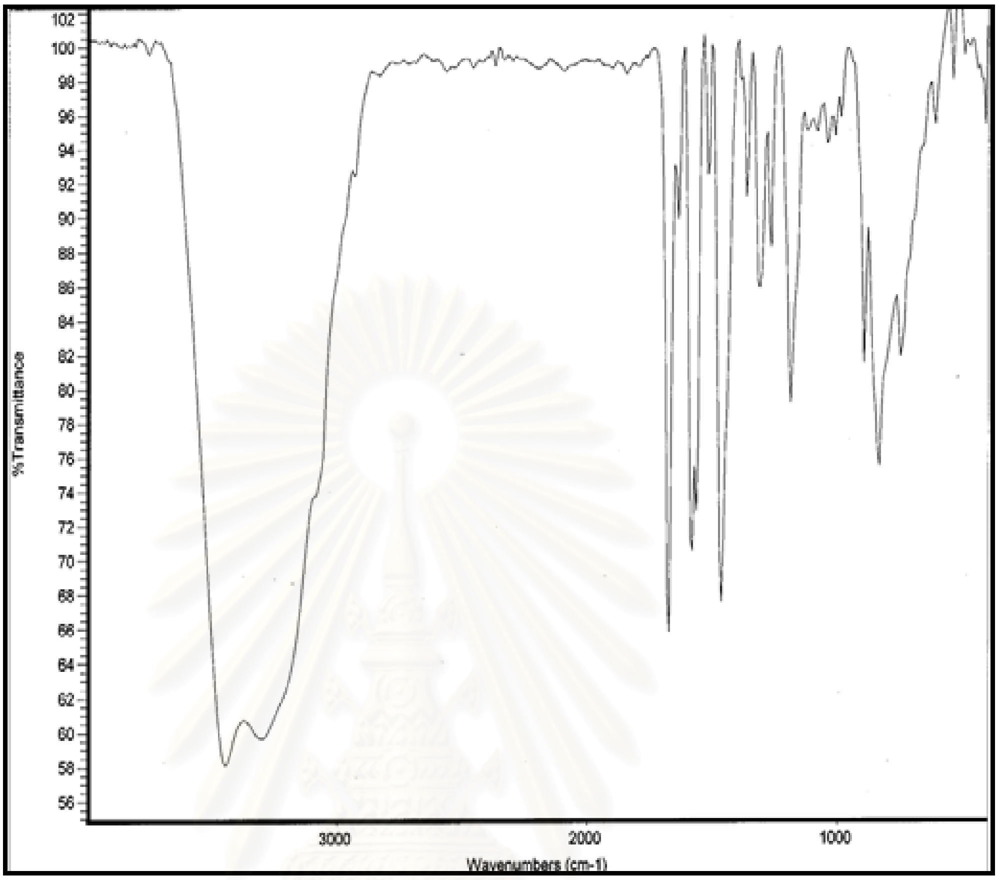

Figure 4.2 The FT-IR (KBr) spectrum of barakol

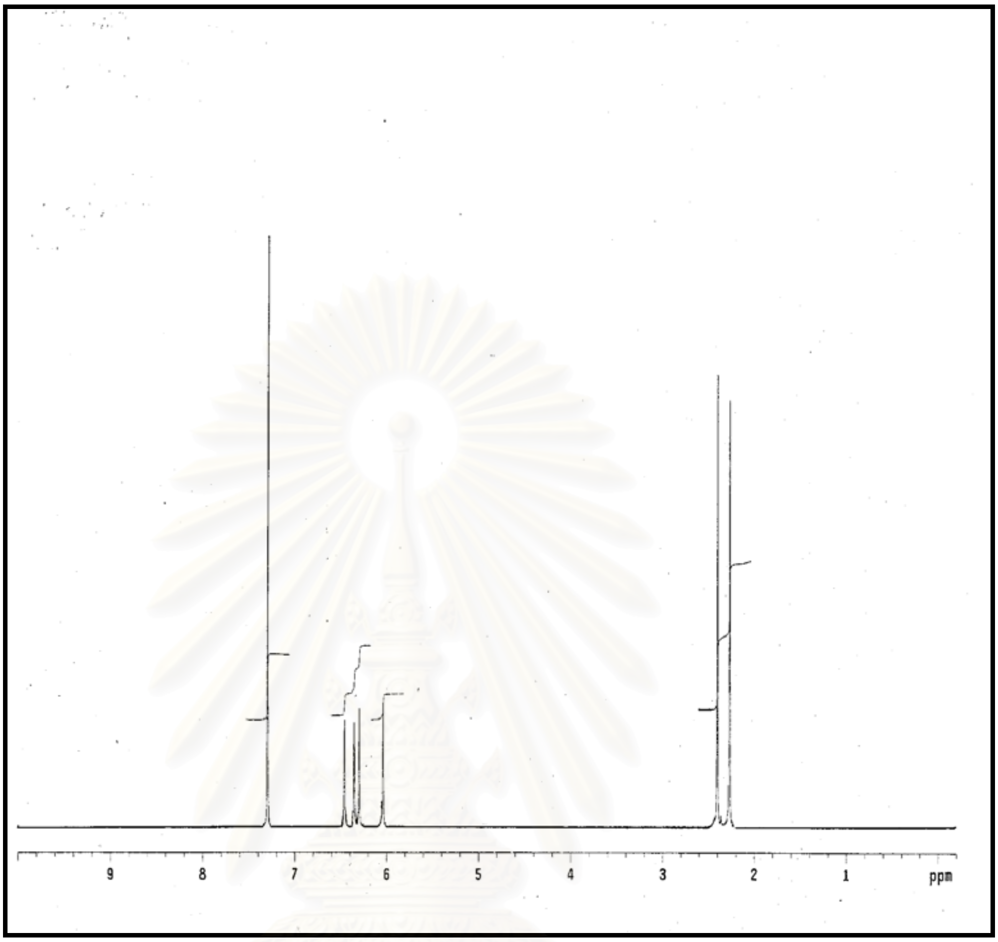

Figure 4.3 The ^{1}H-NMR ($CDCl_3$, 400MHz) spectra of extracted barakol

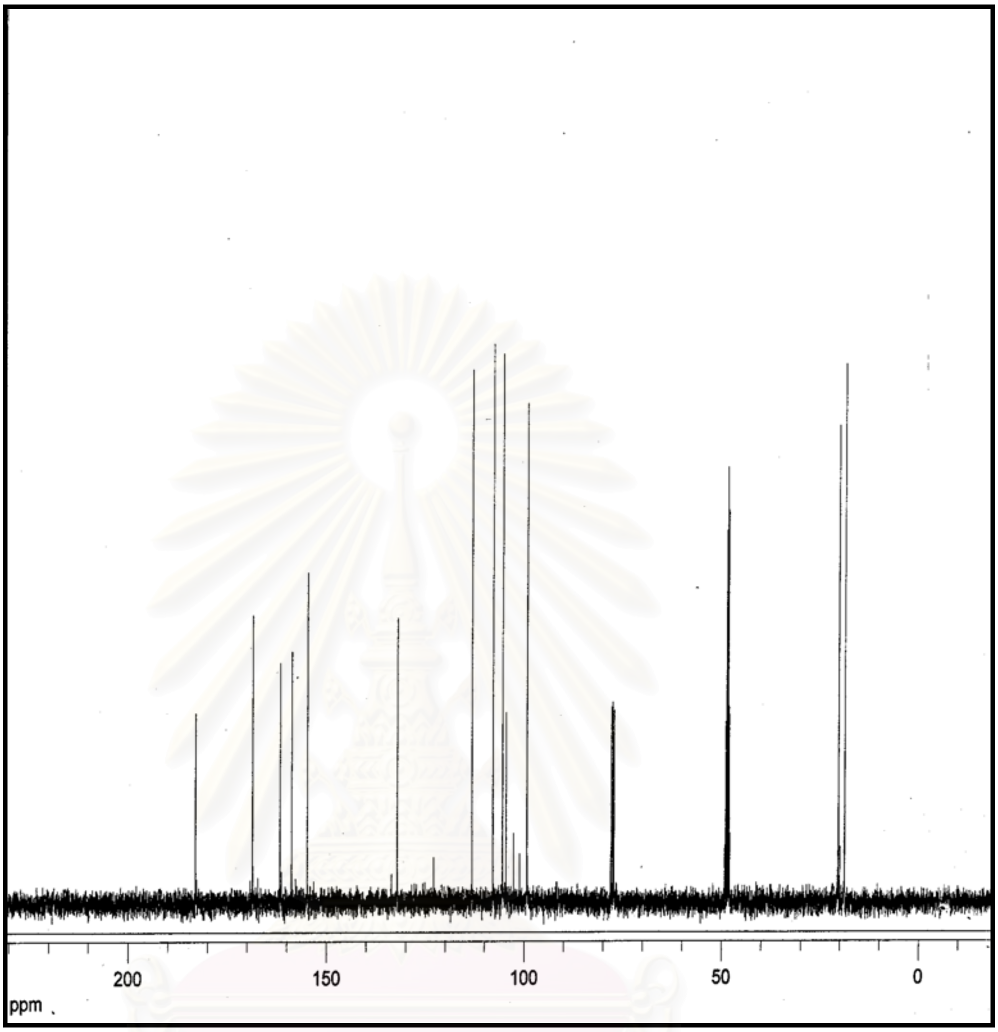

Figure 4.4 The ^{13}C-NMR ($CDCl_3$+ MeOH-d_4, 100 MHz) spectra of extracted barakol

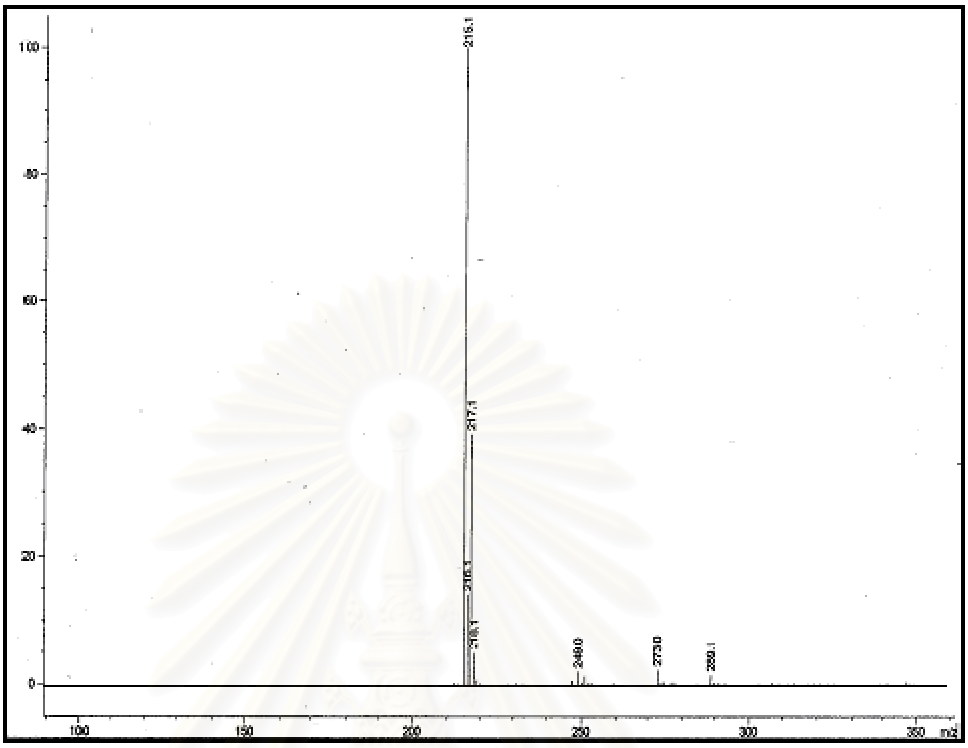

Figure 4.5 The Mass spectrum of extracted barakol

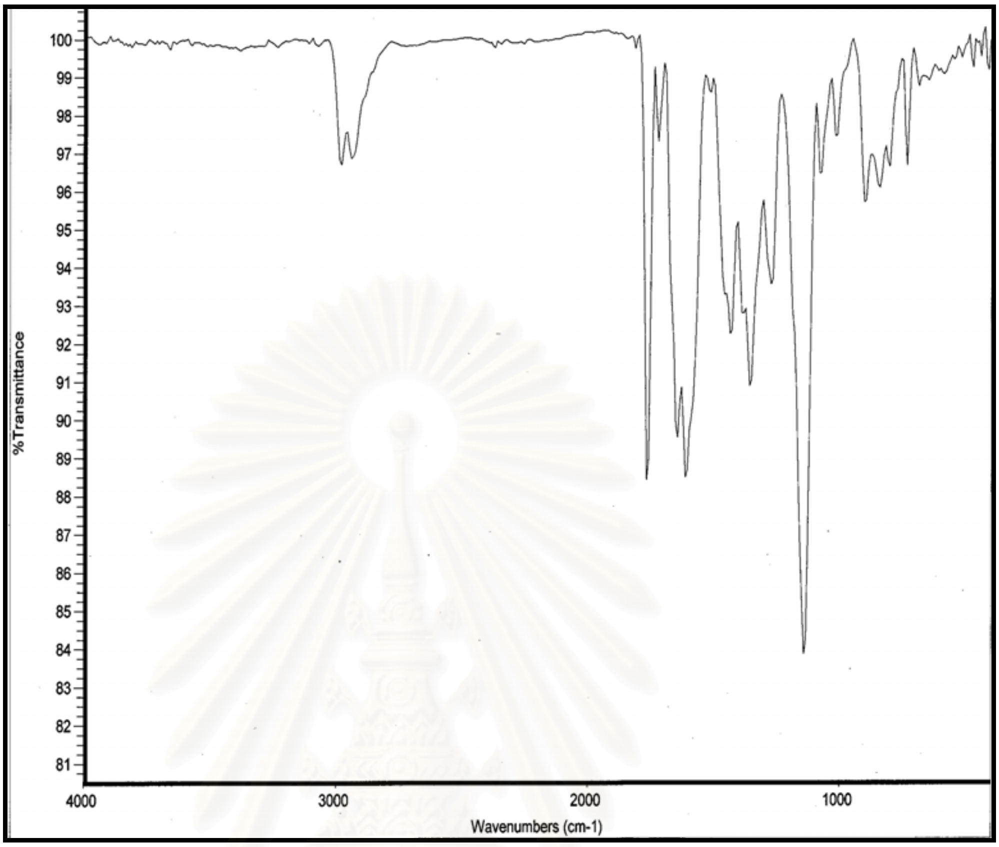

Figure 4.6 The FT-IR (NaCl) spectrum of compound **1**

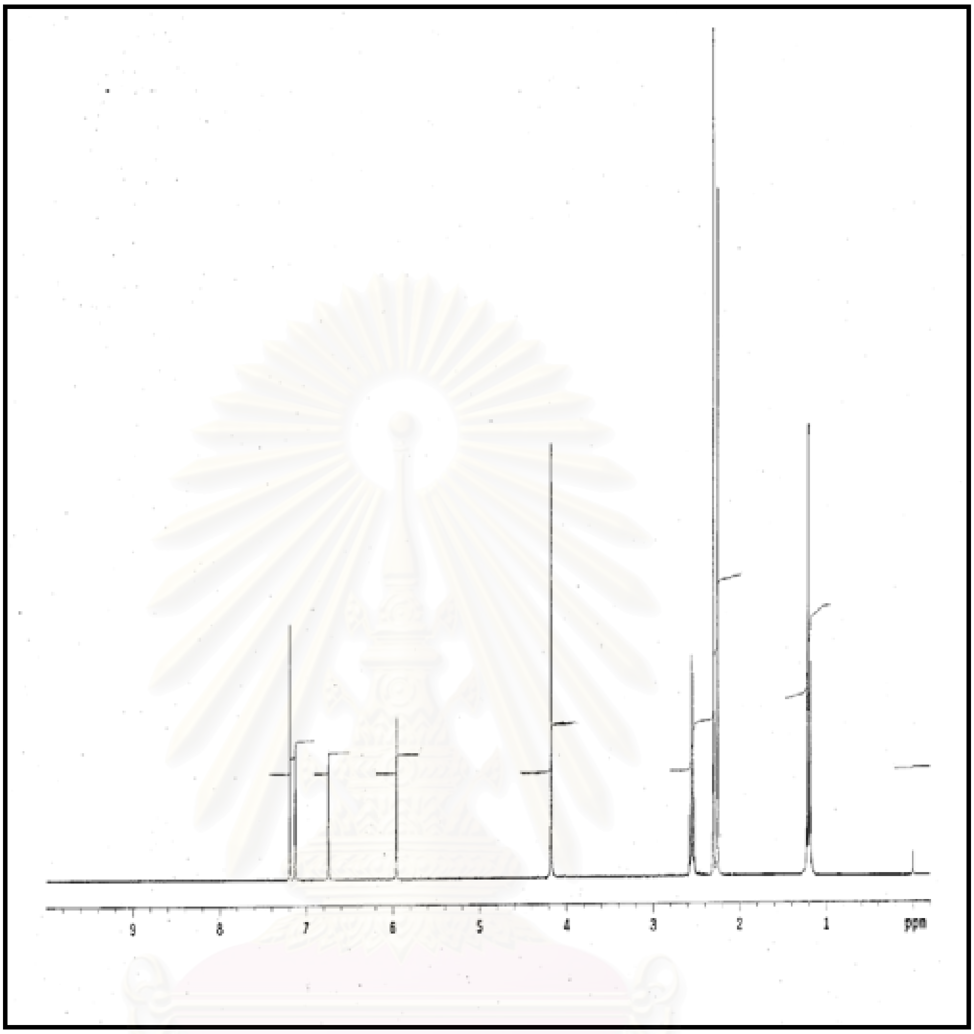

Figure 4.7 The ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of compound **1**

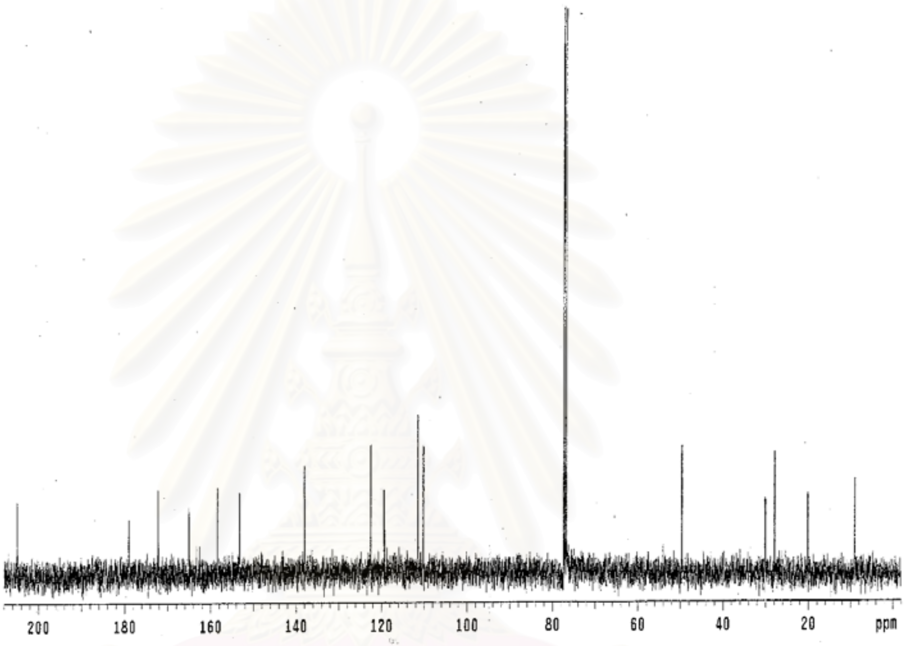

Figure 4.8 The ^{13}C-NMR (CDCl$_3$, 100 MHz) spectrum of compound **1**

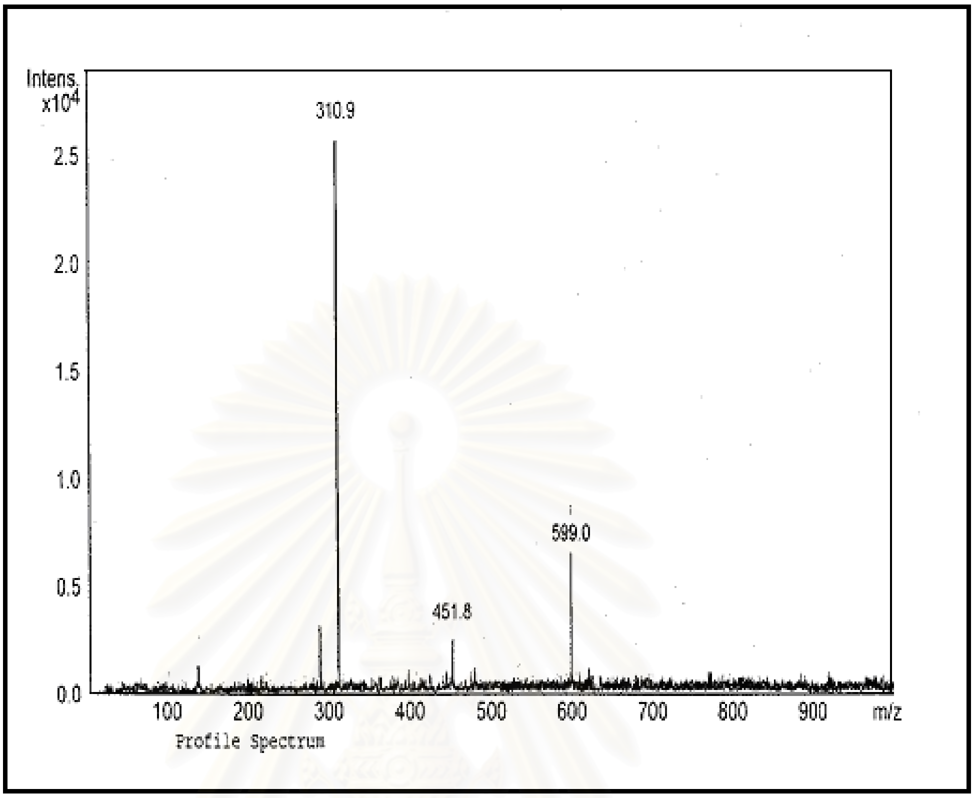

Figure 4.9 The Mass spectrum of compound **1** [M+Na]$^+$

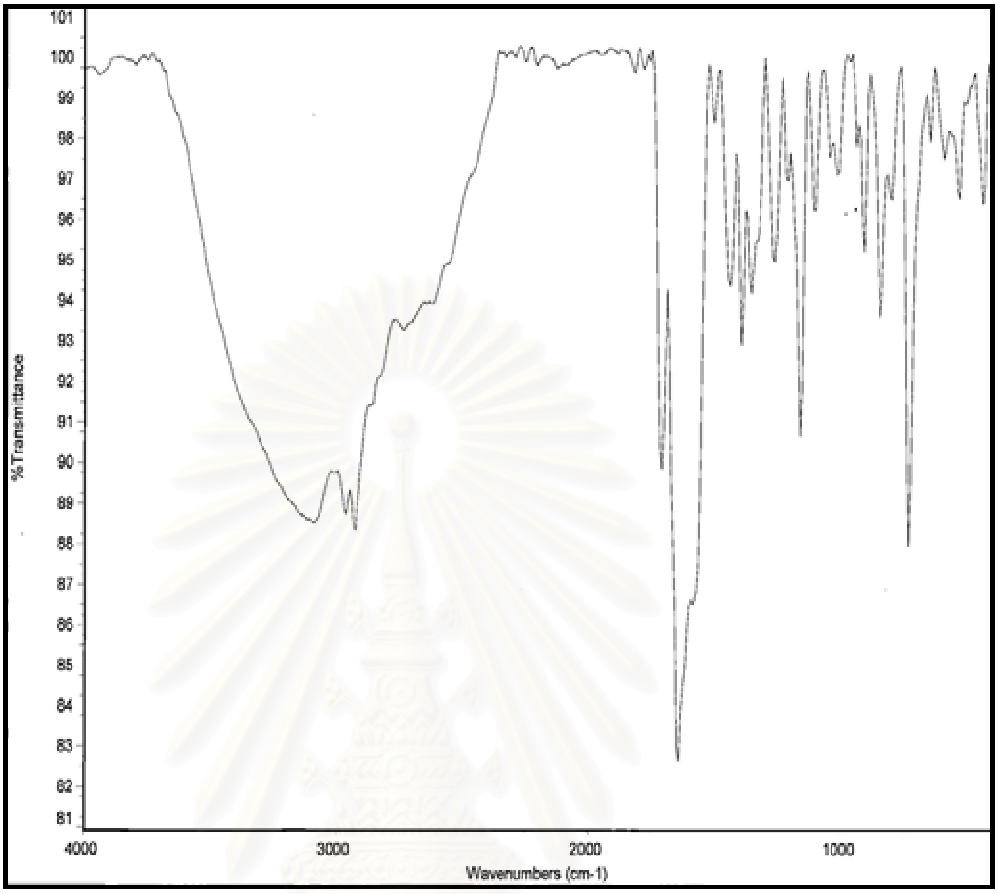

Figure 4.10 The FT-IR (NaCl) spectrum of compound **a**

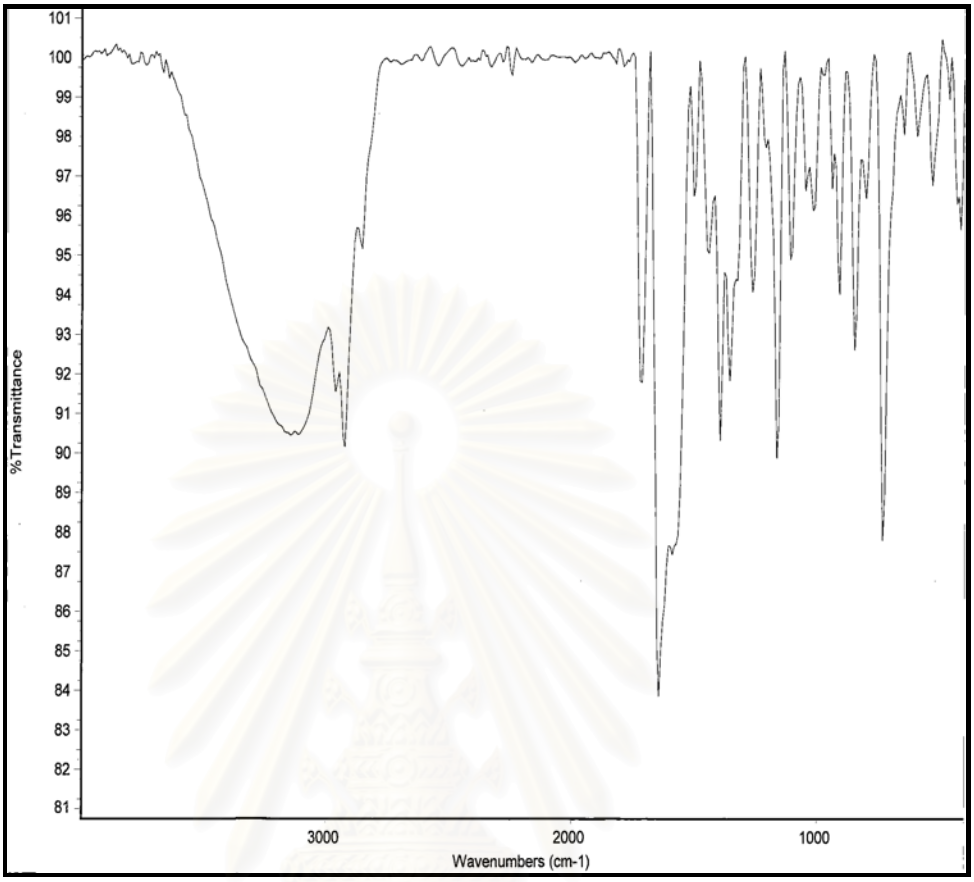

Figure 4.11 The FT-IR (NaCl) spectrum of compound **b**

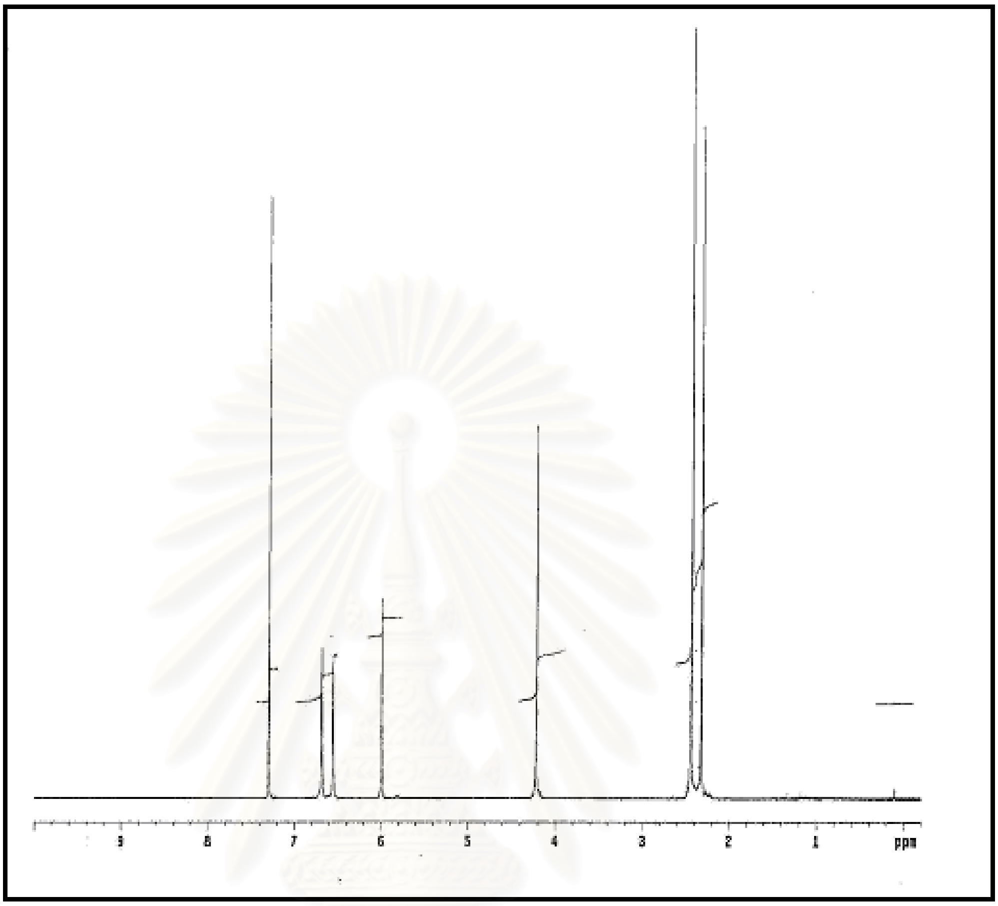

Figure 4.12 The ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of compound **a**

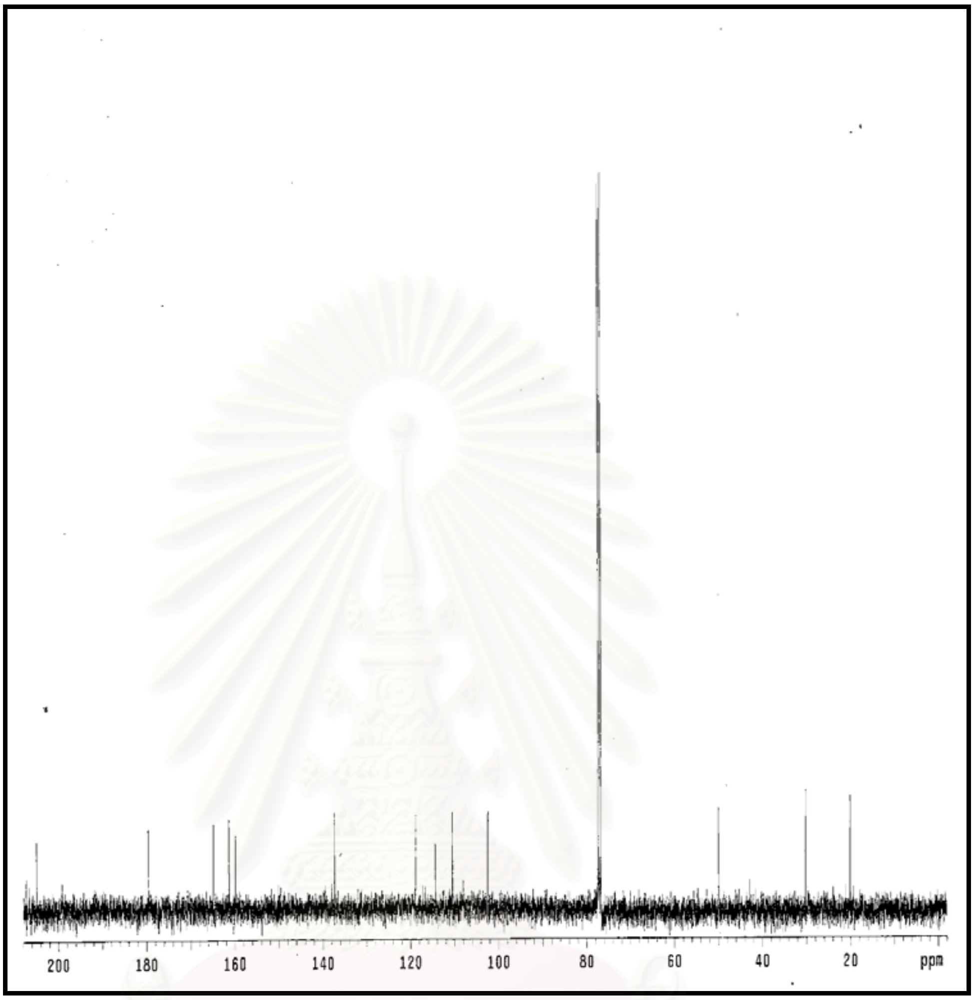

Figure 4.13 The ^{13}C-NMR ($CDCl_3$, 100 MHz) spectrum of compound **a**

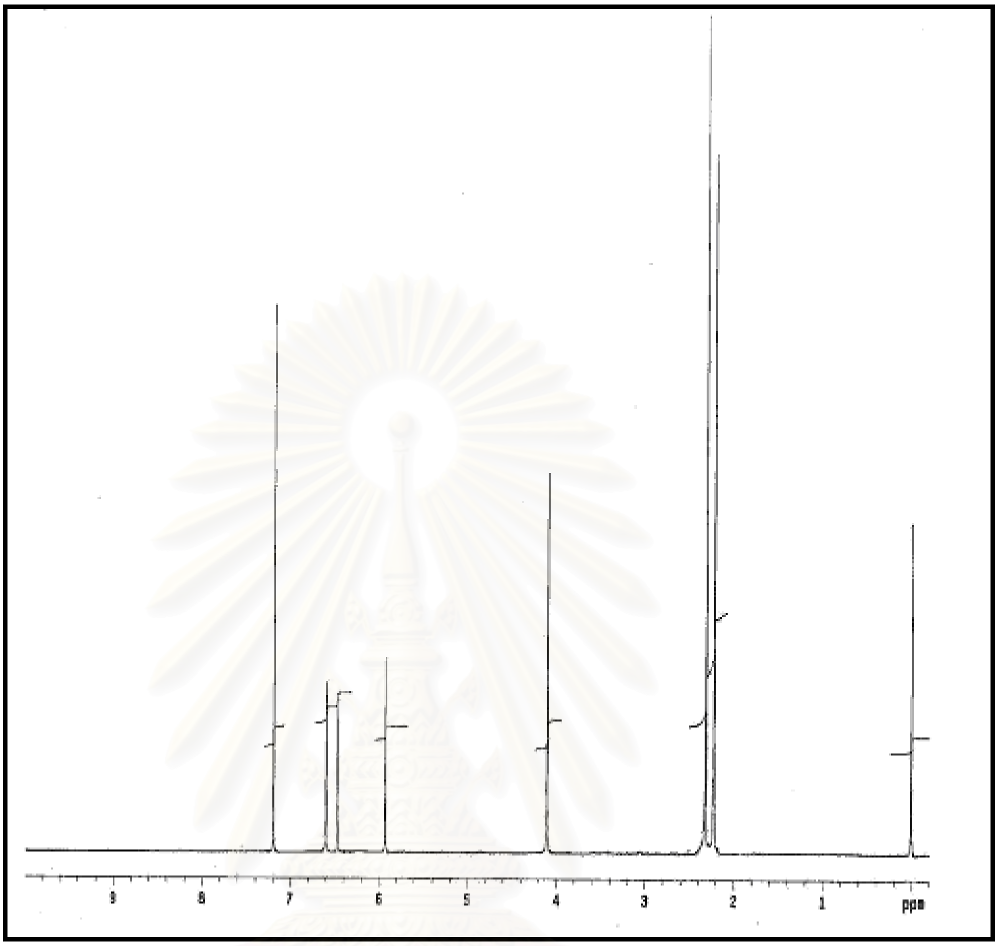

Figure 4.14 The ^{1}H-NMR (CDCl$_3$, 400 MHz) spectrum of compound **b**

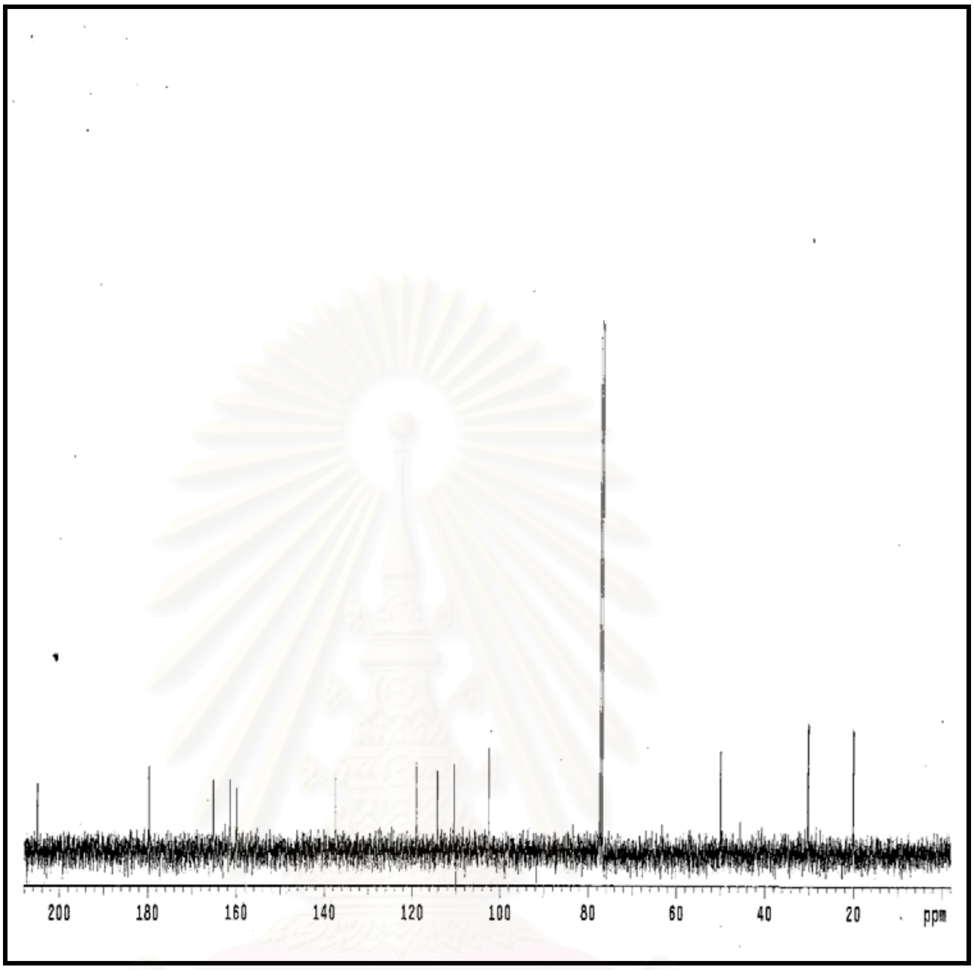

Figure 4.15 The ^{13}C-NMR (CDCl$_3$, 100 MHz) spectrum of compound **b**

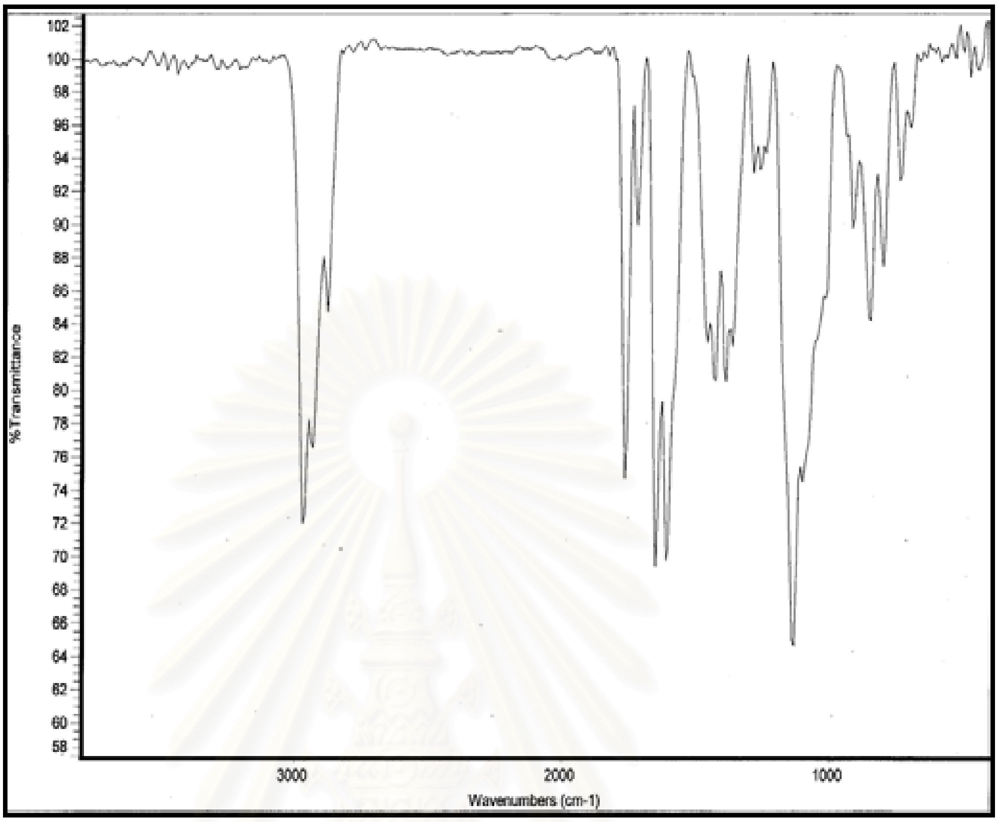

Figure 4.16 The FT-IR (NaCl) spectrum of compound **2**

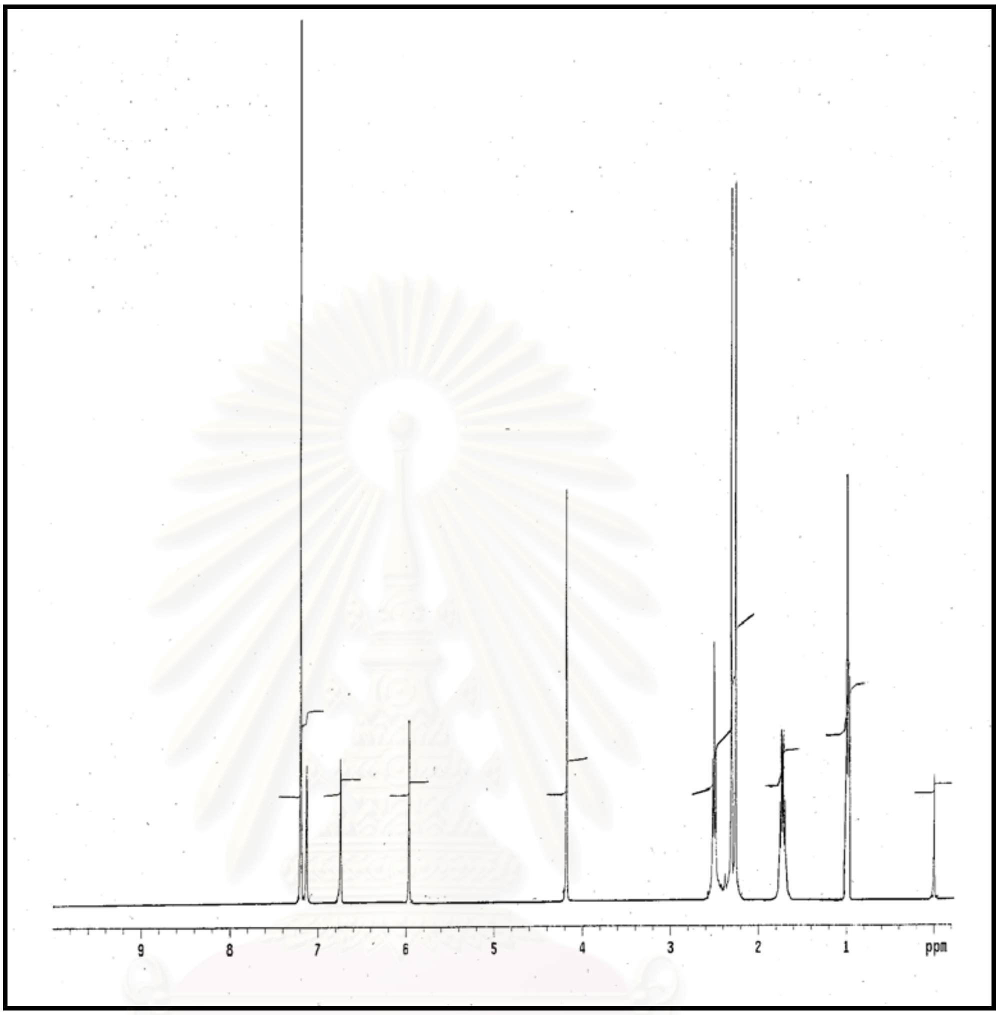

Figure 4.17 The ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of compound **2**

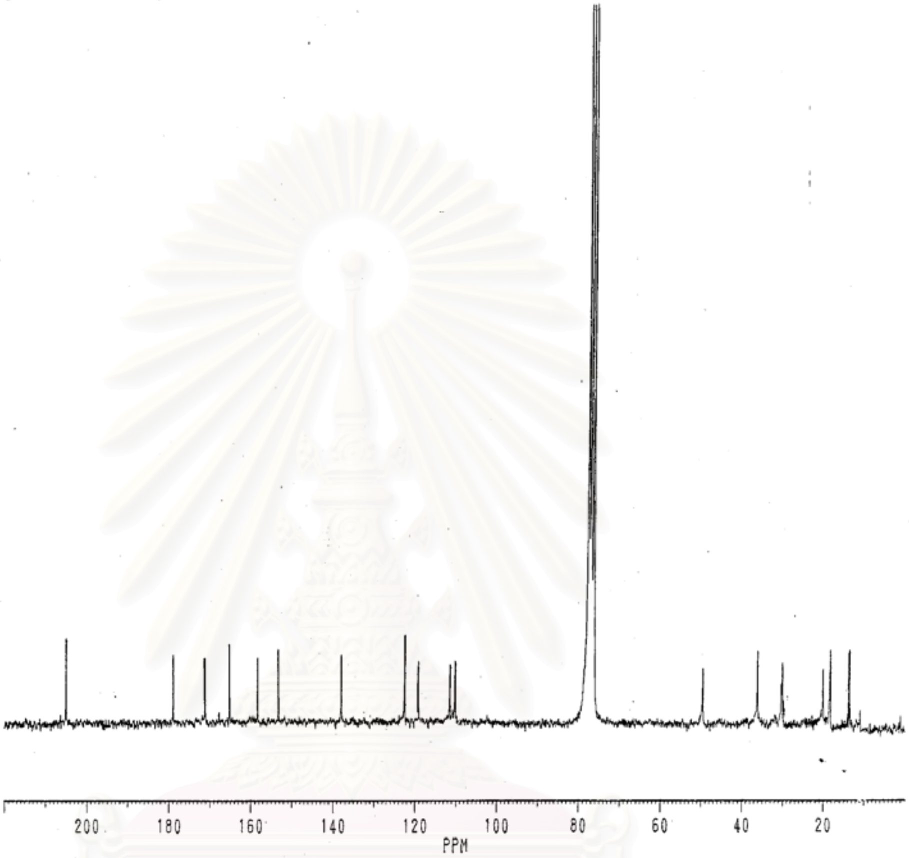

Figure 4.18 The ^{13}C-NMR (CDCl$_3$, 50.32 MHz) spectrum of compound **2**

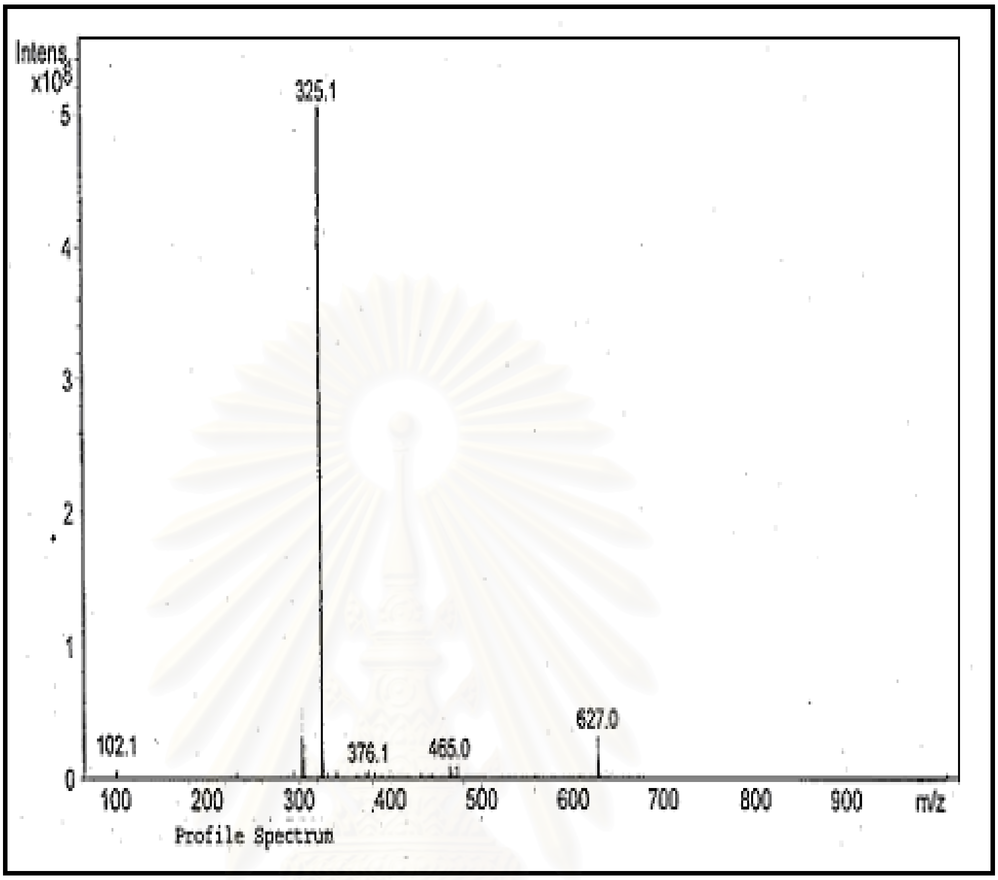

Figure 4.19 The Mass spectrum of compound **2** $[M+Na]^+$

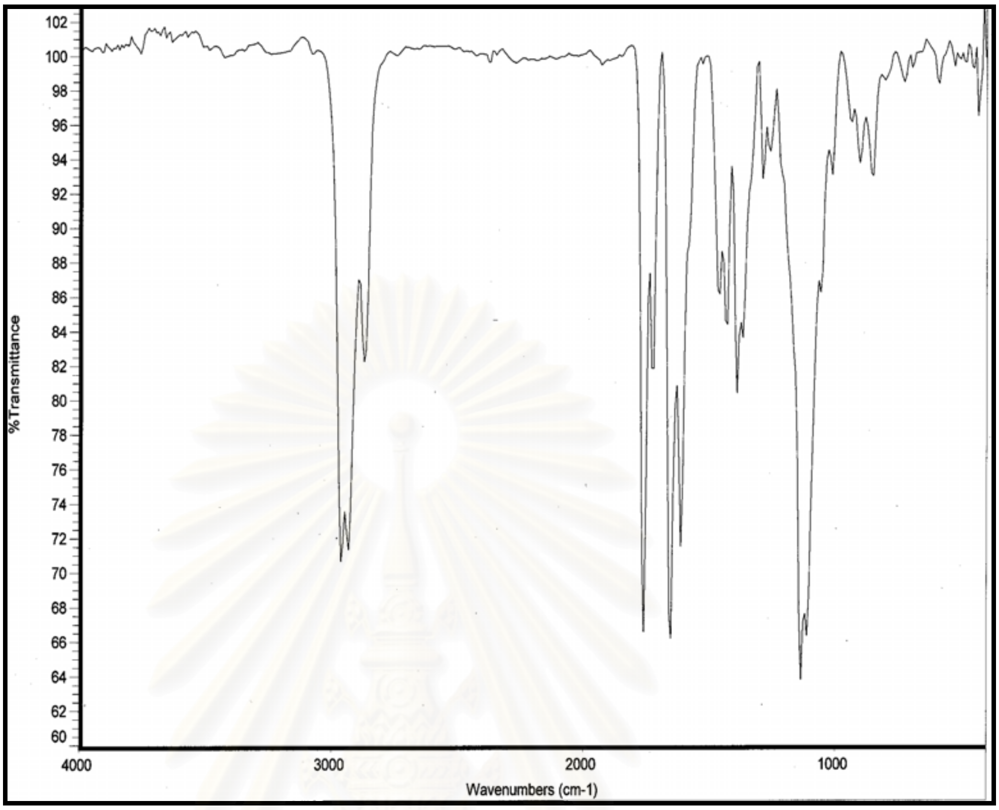

Figure 4.20 The FT-IR (NaCl) spectrum of compound **3**

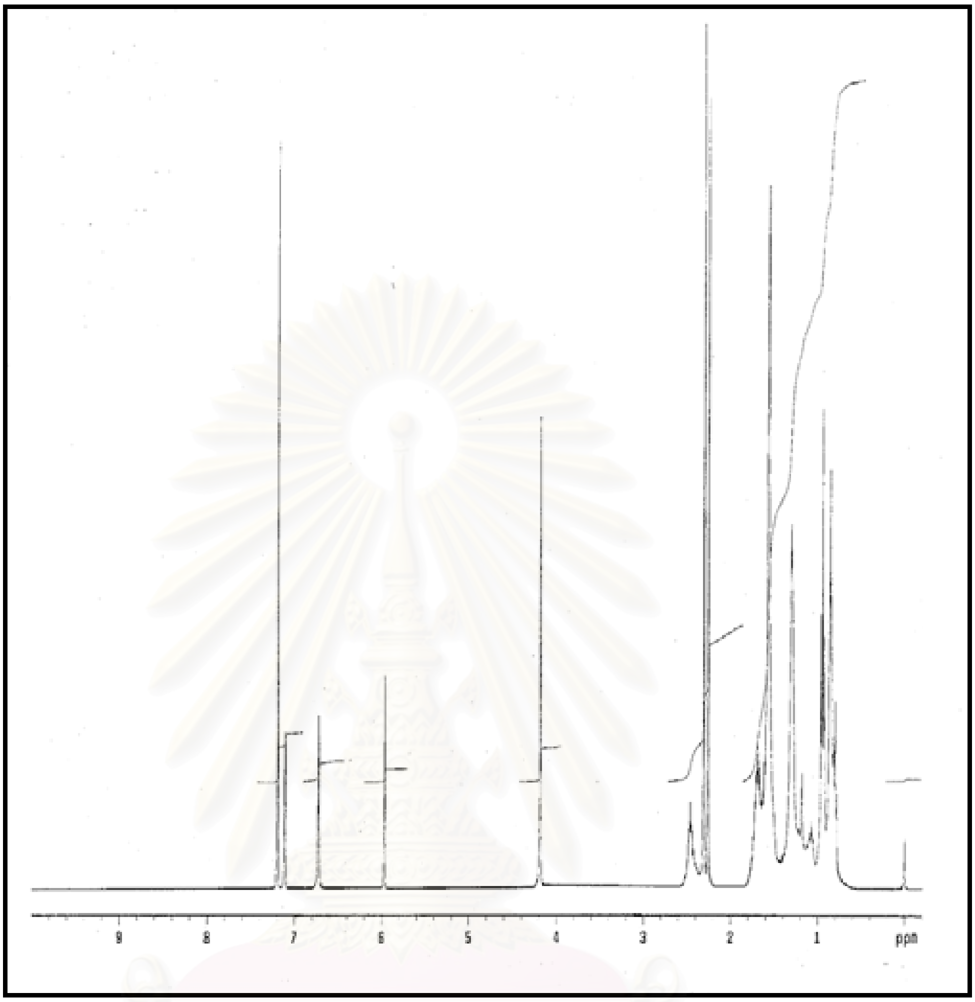

Figure 4.21 The ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of compound **3**

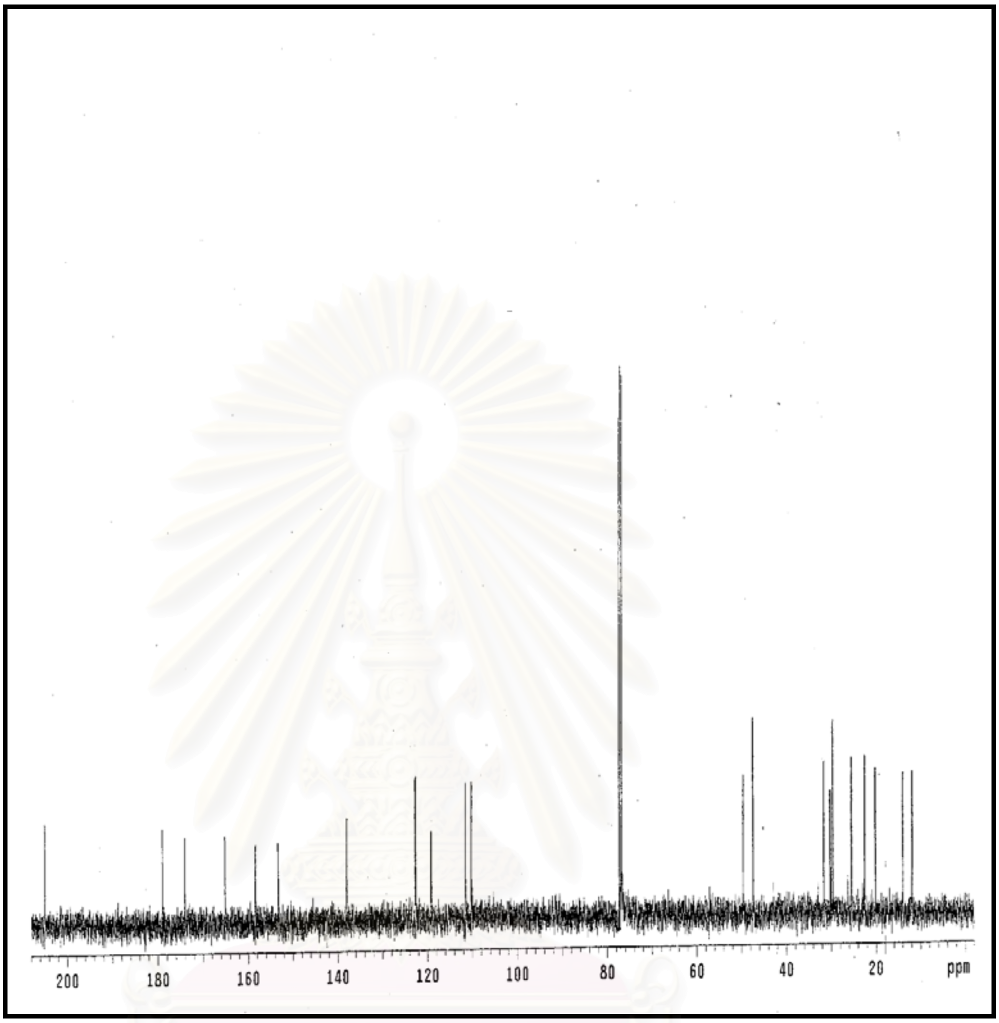

Figure 4.22 The ^{13}C-NMR ($CDCl_3$, 100 MHz) spectrum of compound **3**

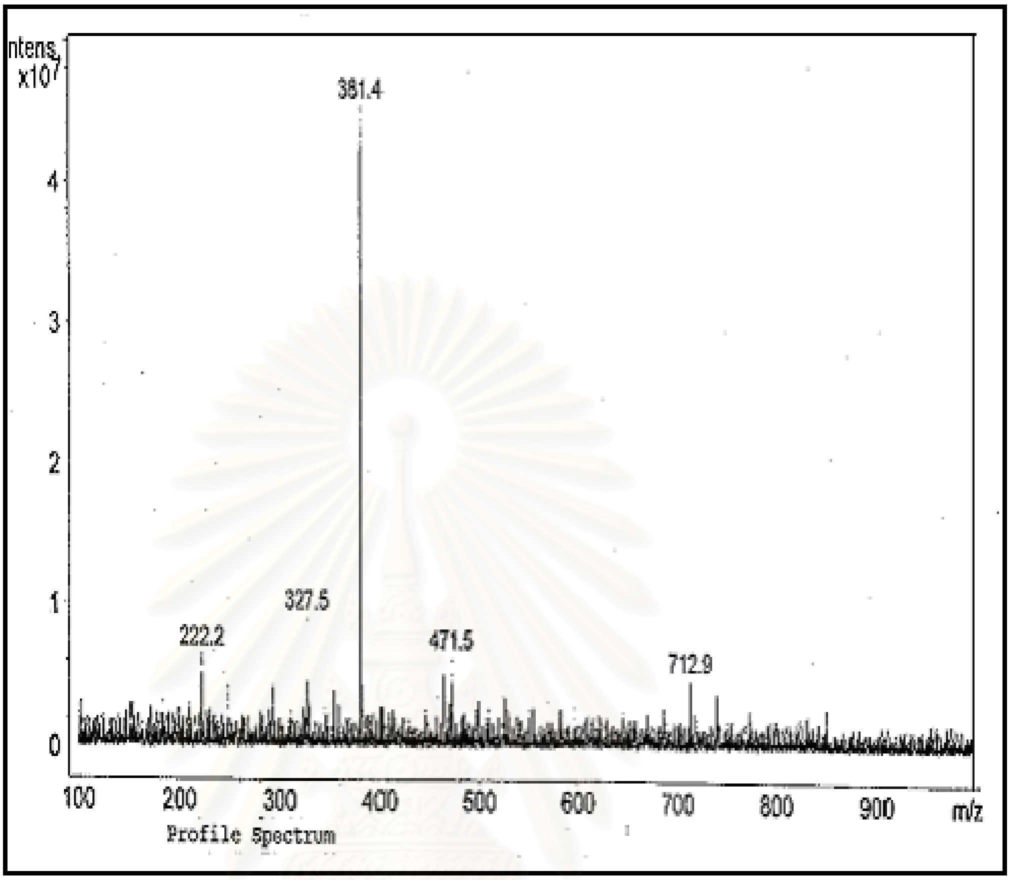

Figure 4.23 The Mass spectrum of compound **3** $[M+Na]^+$

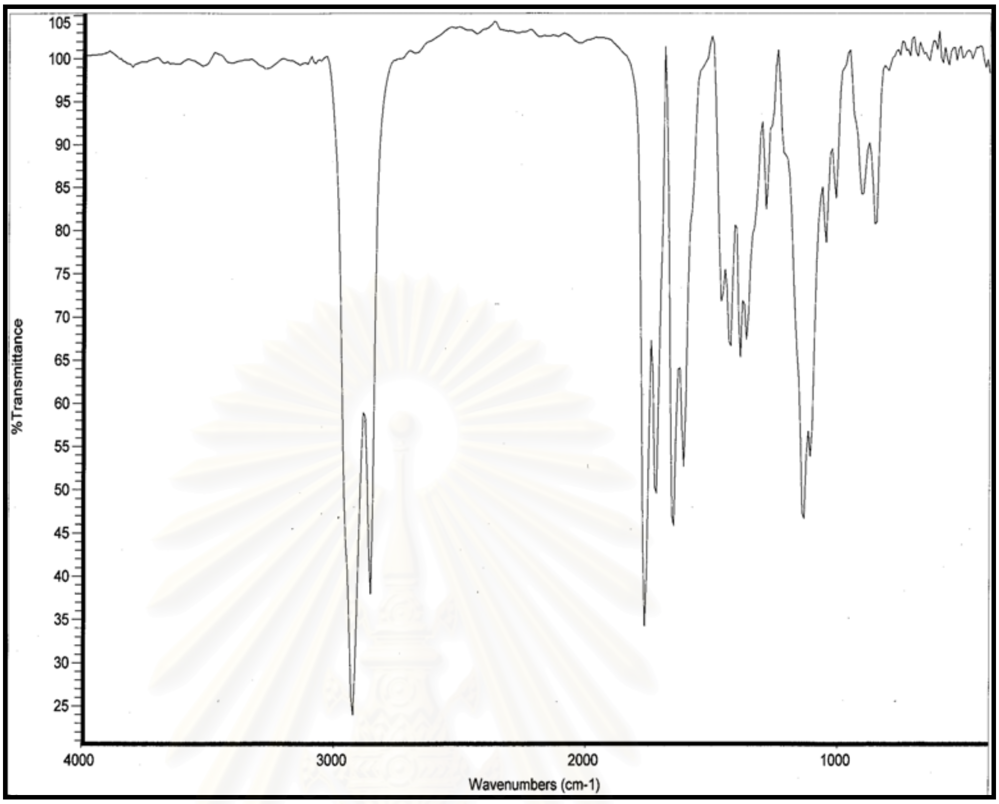

Figure 4.24 The FT-IR (NaCl) spectrum of compound **4**

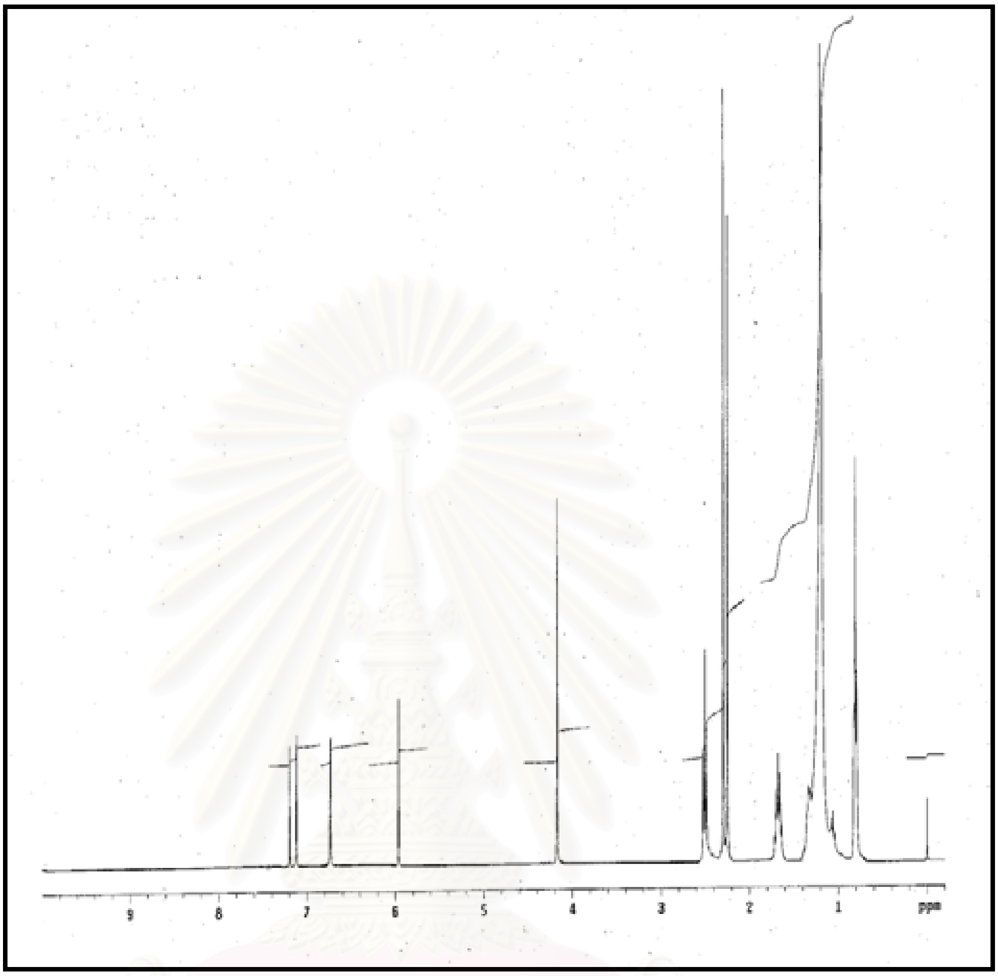

Figure 4.25 The ^{1}H-NMR (CDCl$_3$, 400 MHz) spectrum of compound **4**

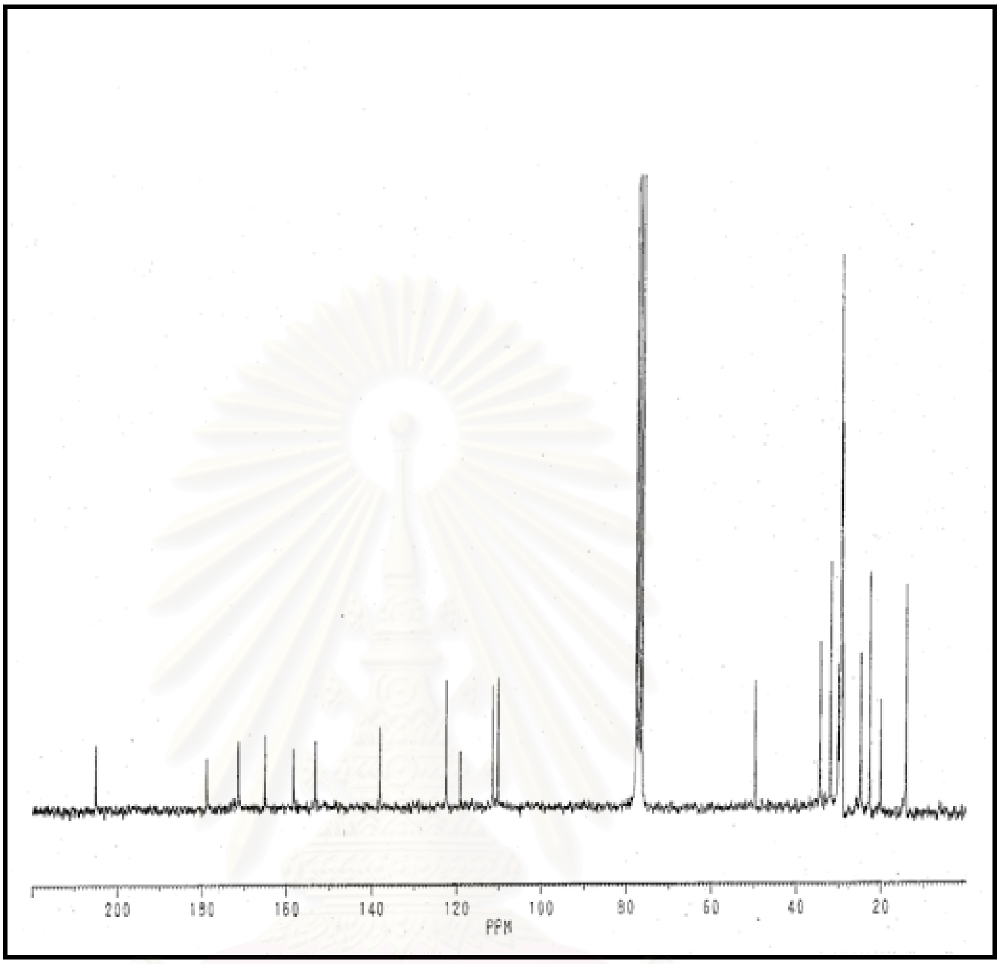

Figure 4.26 The ^{13}C-NMR ($CDCl_3$, 50.32) spectrum of compound **4**

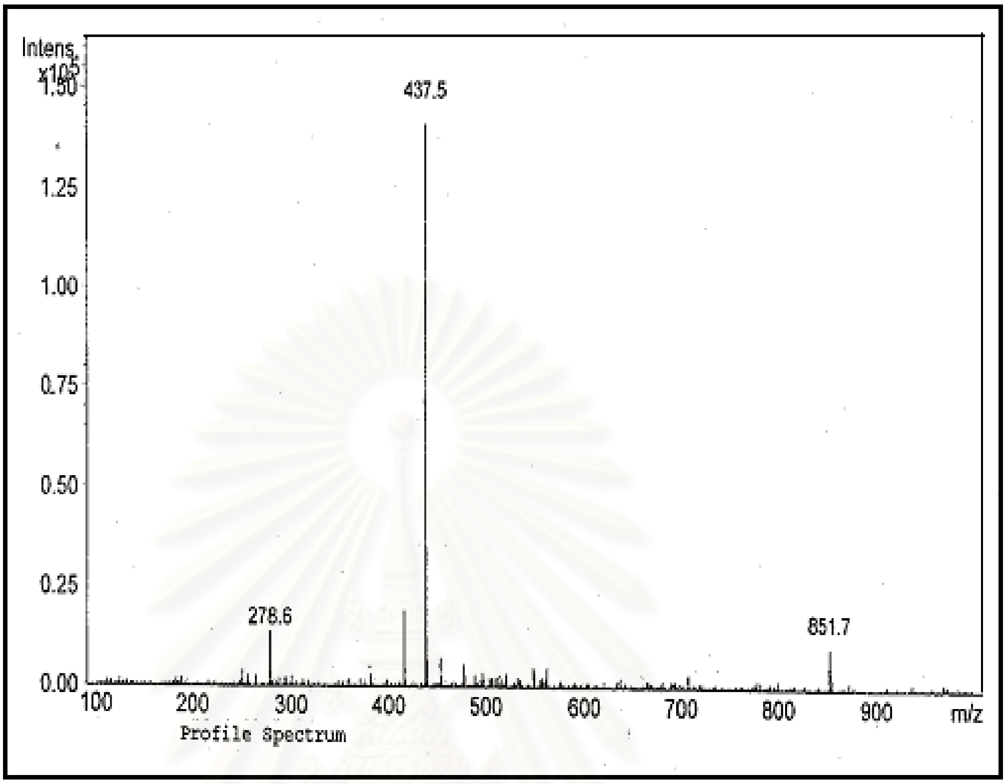

Figure 4.27 The Mass spectrum of compound **4** $[M+Na]^+$

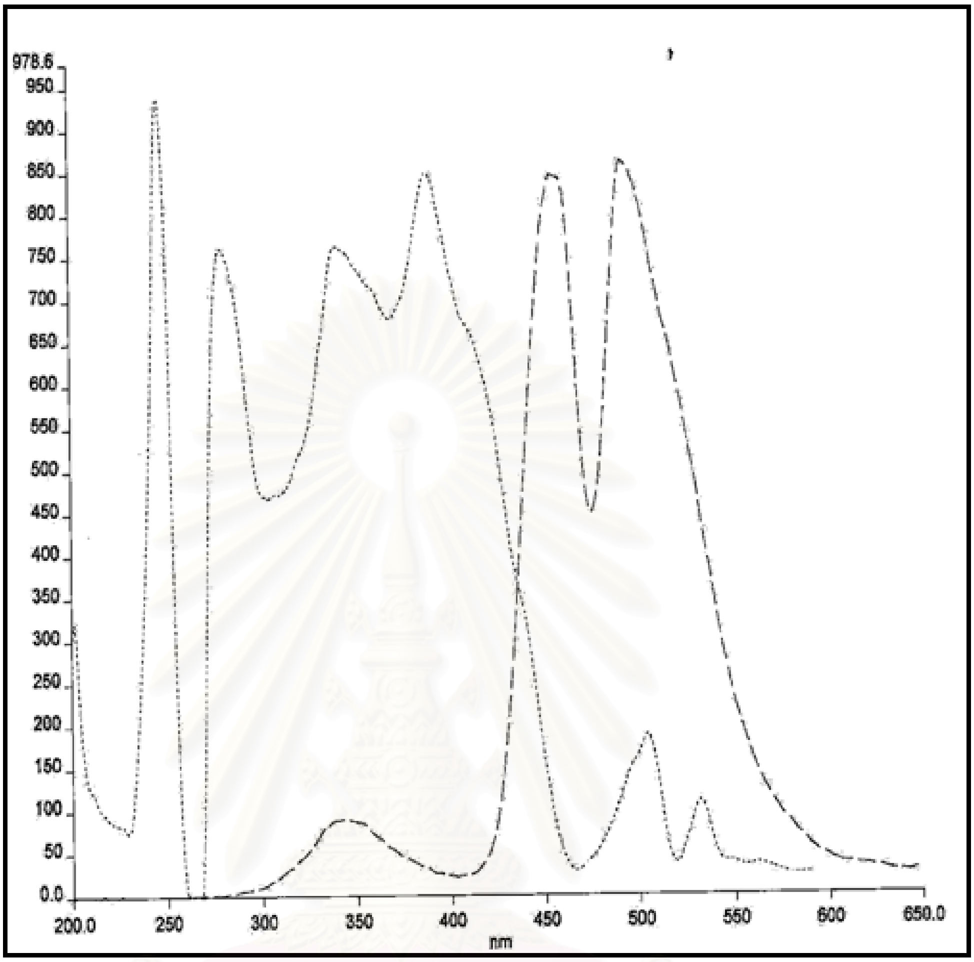

Figure 4.28 The excitation wavelength (λ_{ex} = 246 nm) and emission wavelength (λ_{em} = 491 nm) of barakol in dichloromethane

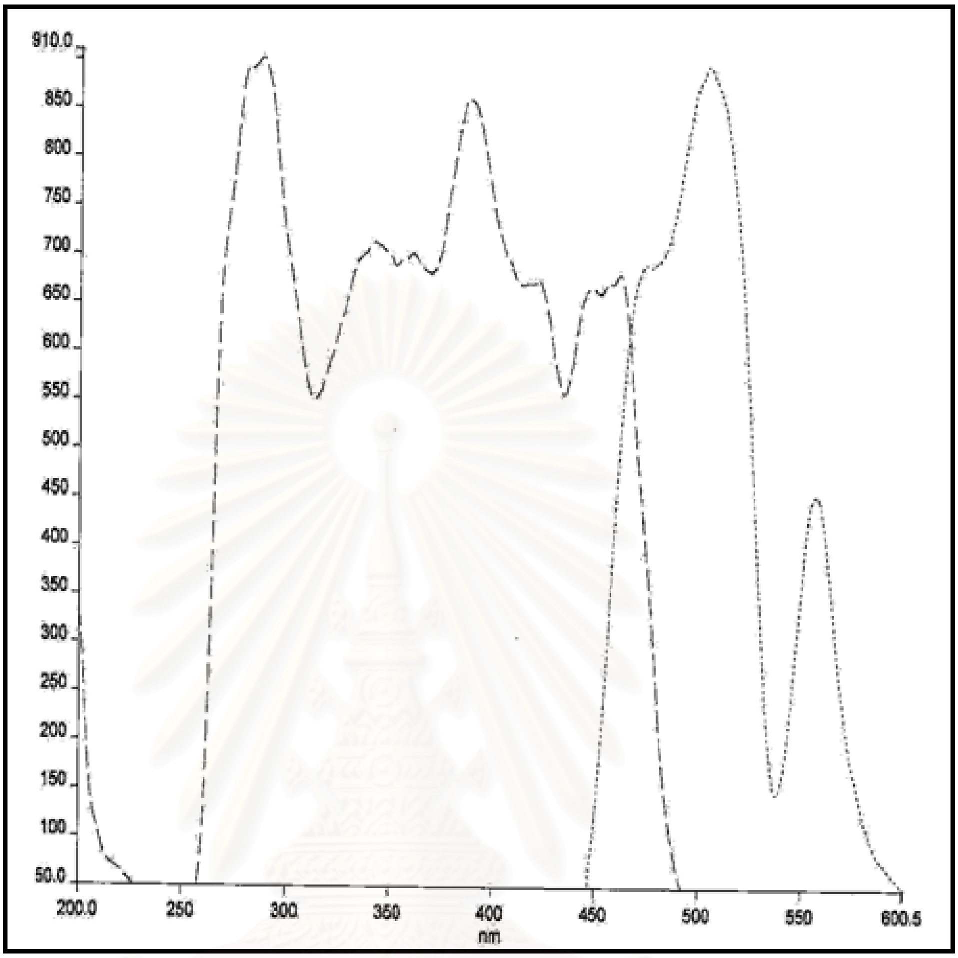

Figure 4.29 The excitation wavelength (λ_{ex} = 285 nm) and emission wavelength (λ_{em} = 504 nm) of barakol in ethyl acetate

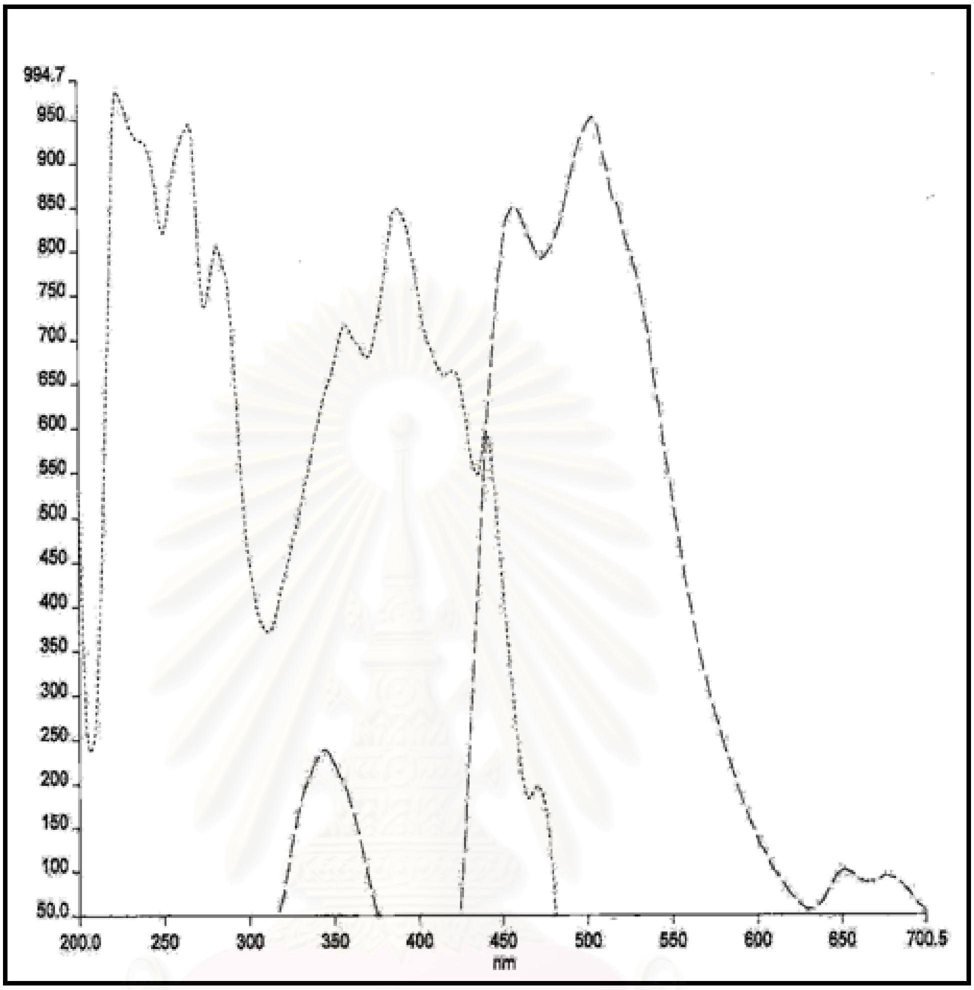

Figure 4.30 The excitation wavelength (λ_{ex} = 222 nm) and emission wavelength (λ_{em} = 505 nm) of barakol in methanol

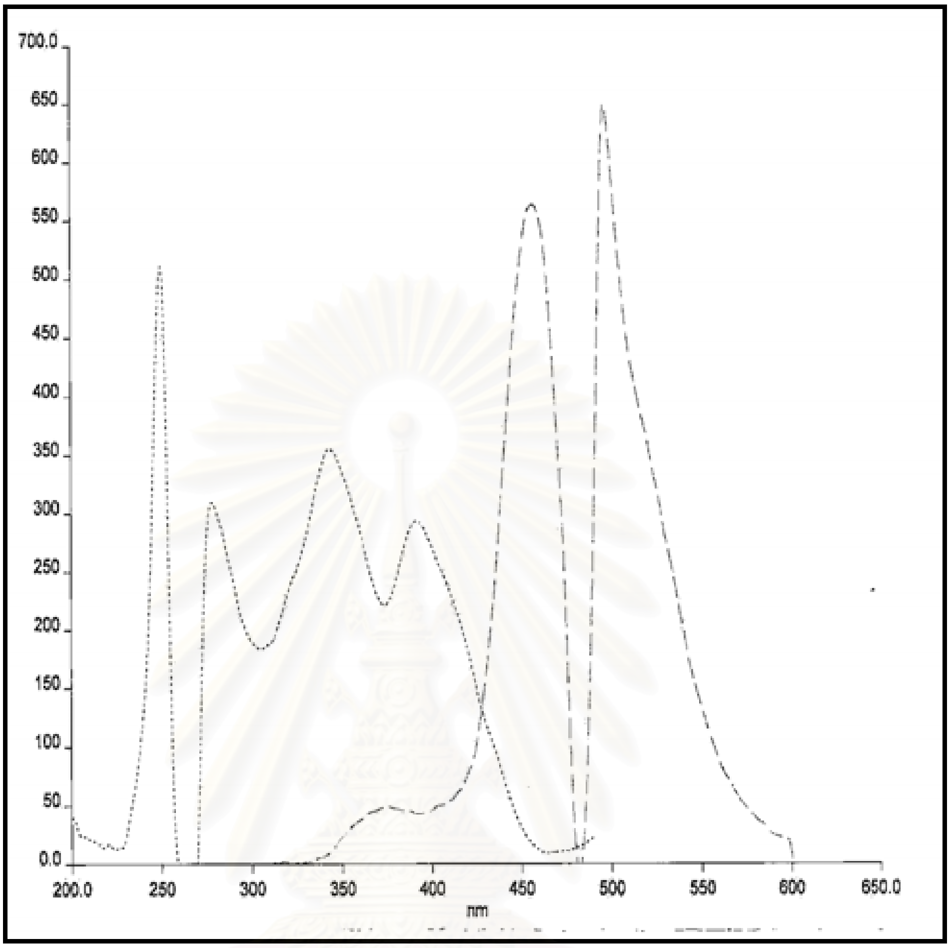

Figure 4.31 The excitation wavelength (λ_{ex} = 250 nm) and emission wavelength (λ_{em} = 498 nm) of compound **a** in dichloromethane

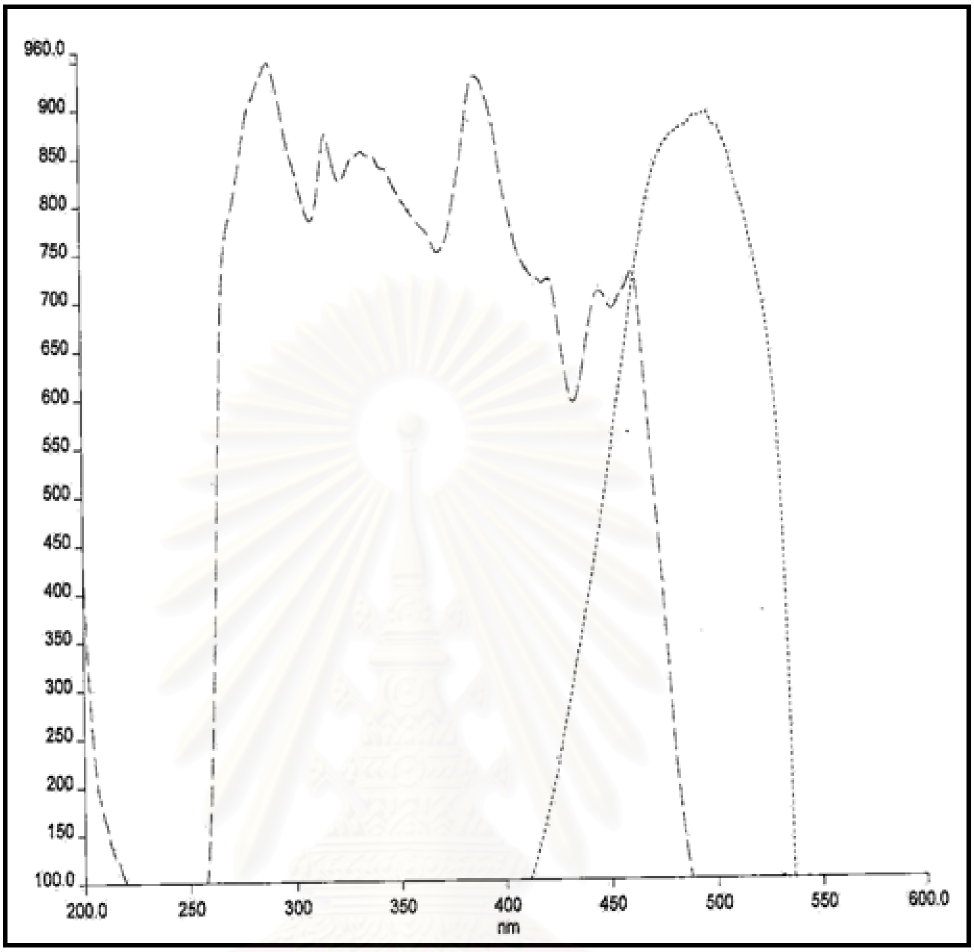

Figure 4.32 The excitation wavelength ($\lambda_{ex} = 282$ nm) and emission wavelength ($\lambda_{em} = 492$ nm) of compound **a** in ethly acetate

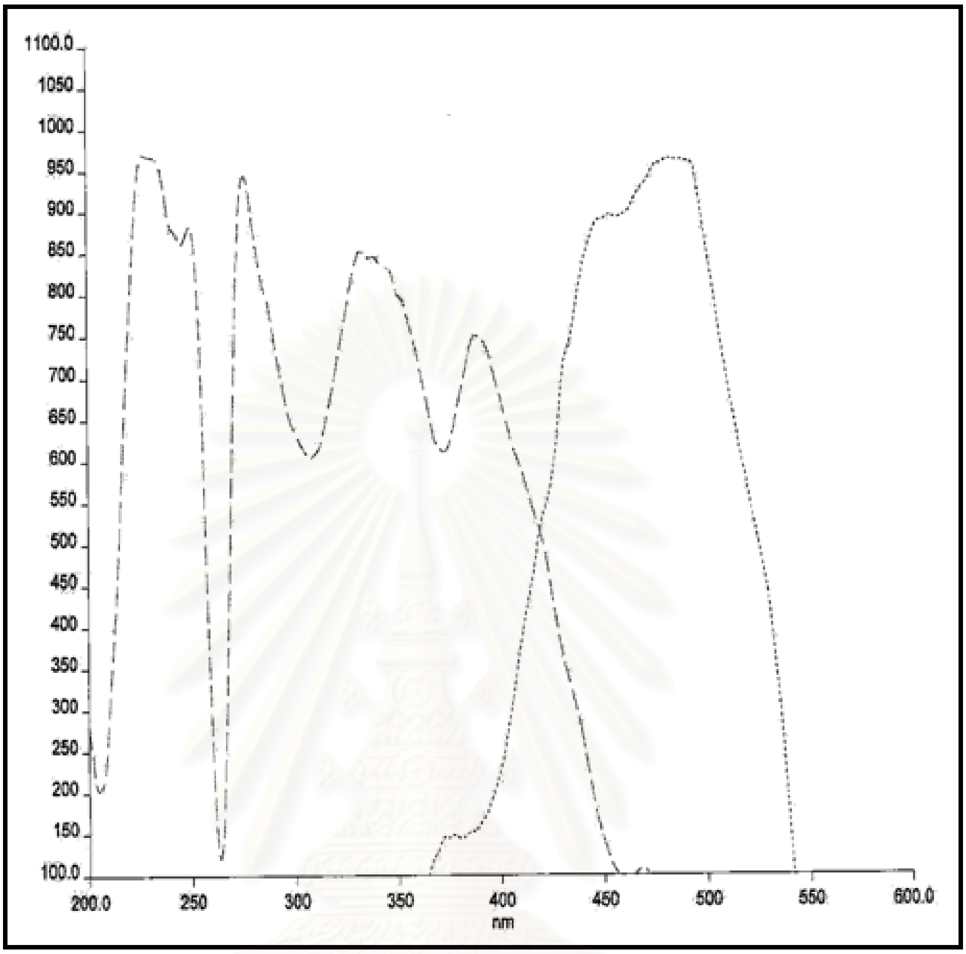

Figure 4.33 The excitation wavelength (λ_{ex} = 225 nm) and emission wavelength (λ_{em} = 495 nm) of compound **a** in methanol

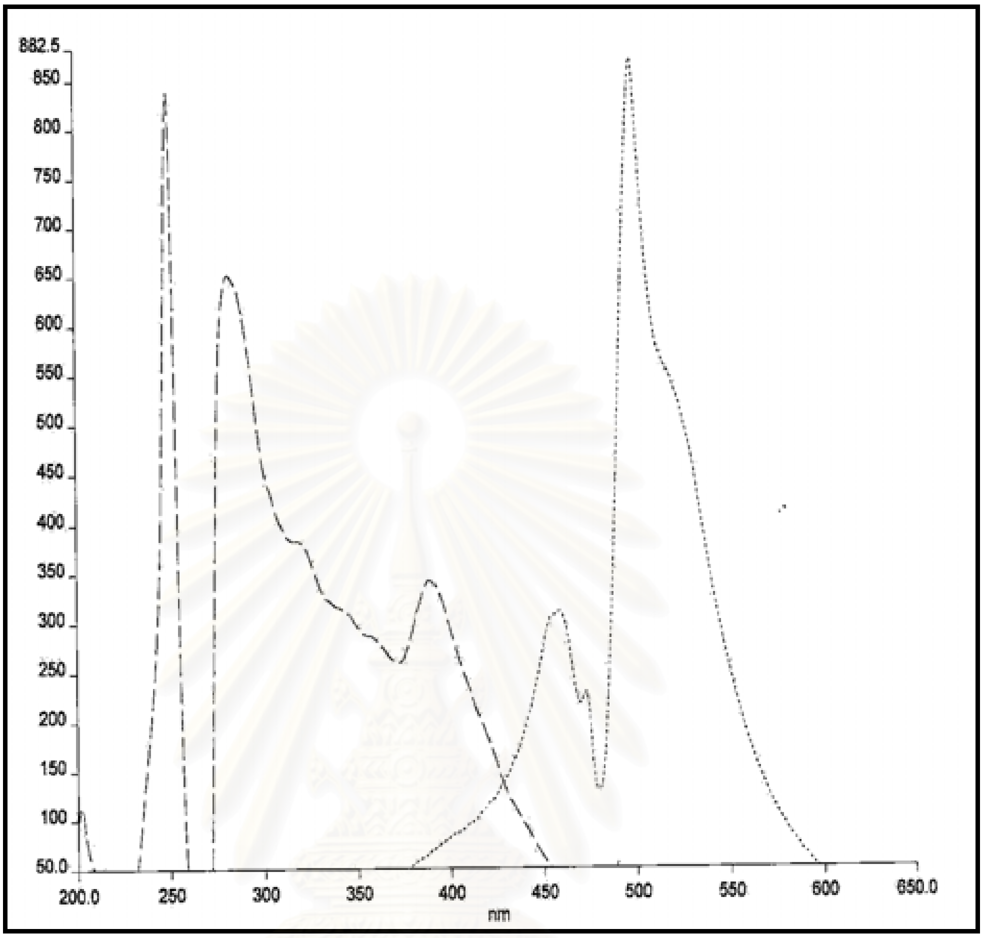

Figure 4.34 The excitation wavelength (λ_{ex} = 250 nm) and emission wavelength (λ_{em} = 500 nm) of compound **1** in dichloromethane

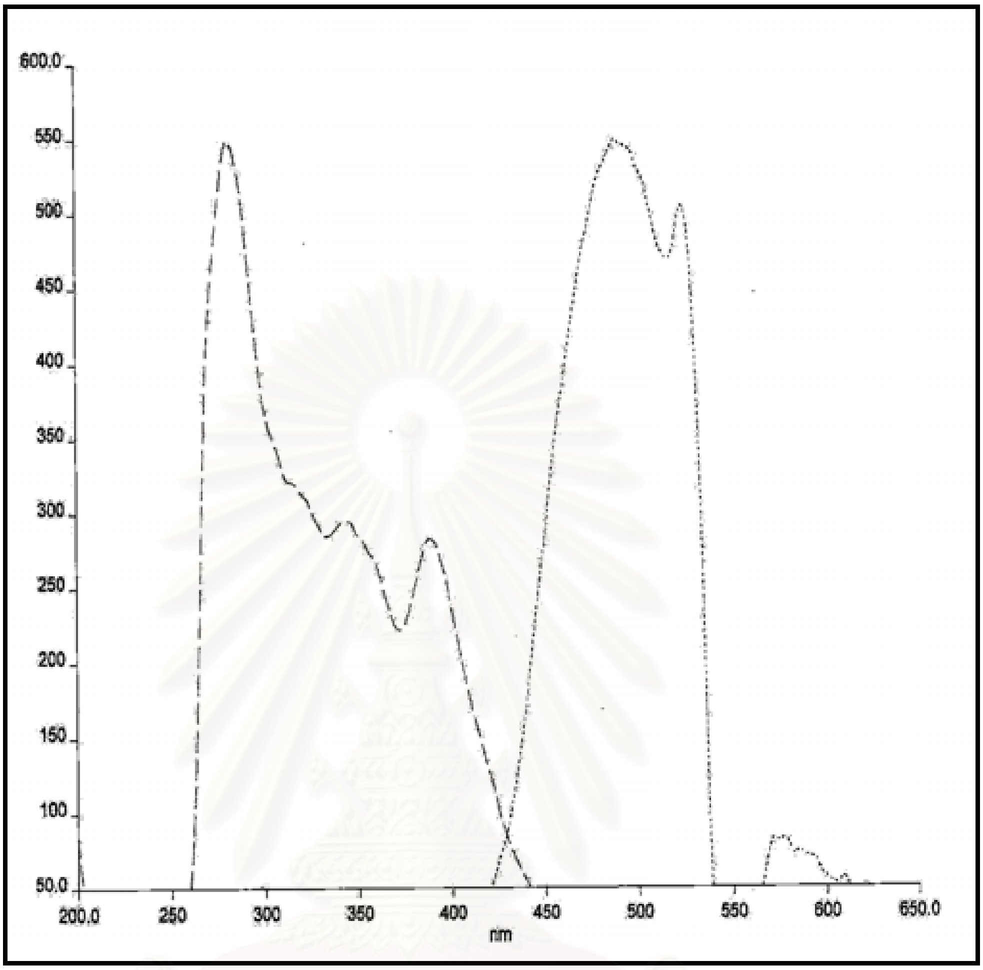

Figure 4.35 The excitation wavelength (λ_{ex} = 281 nm) and emission wavelength (λ_{em} = 492 nm) of compound **1** ethyl acetate

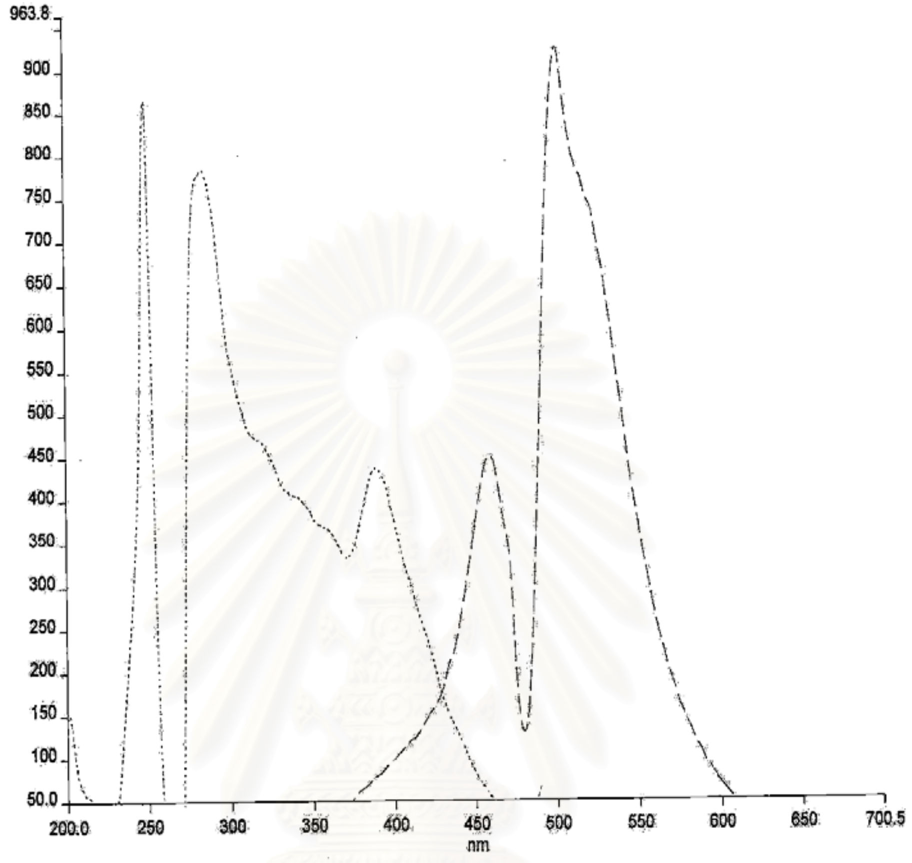

Figure 4.36 The excitation wavelength (λ_{ex} = 250 nm) and emission wavelength (λ_{em} = 500 nm) of compound **2** in dichloromethane

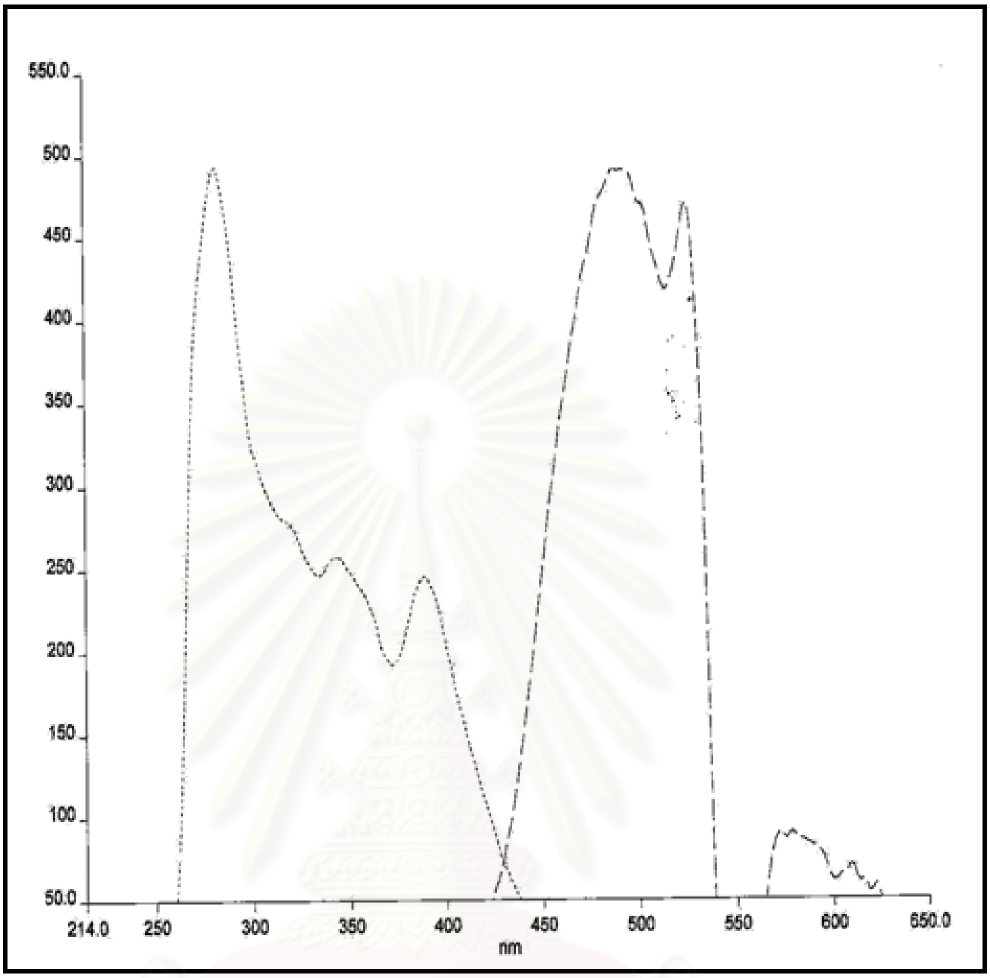

Figure 4.37 The excitation wavelength (λ_{ex} = 250 nm) and emission wavelength (λ_{em} = 250 nm) of compound **2** in ethyl acetate

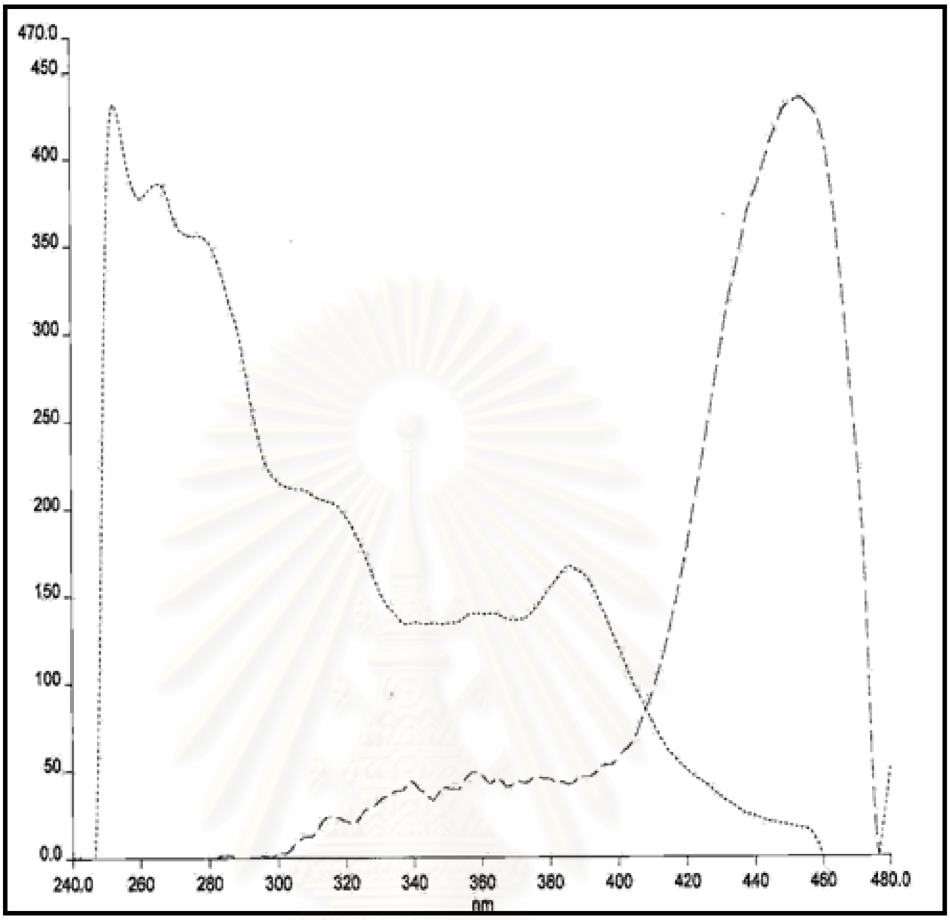

Figure 4.38 The excitation wavelength (λ_{ex} = 252 nm) and emission wavelength (λ_{em} = 455 nm) of compound **3** in hexane

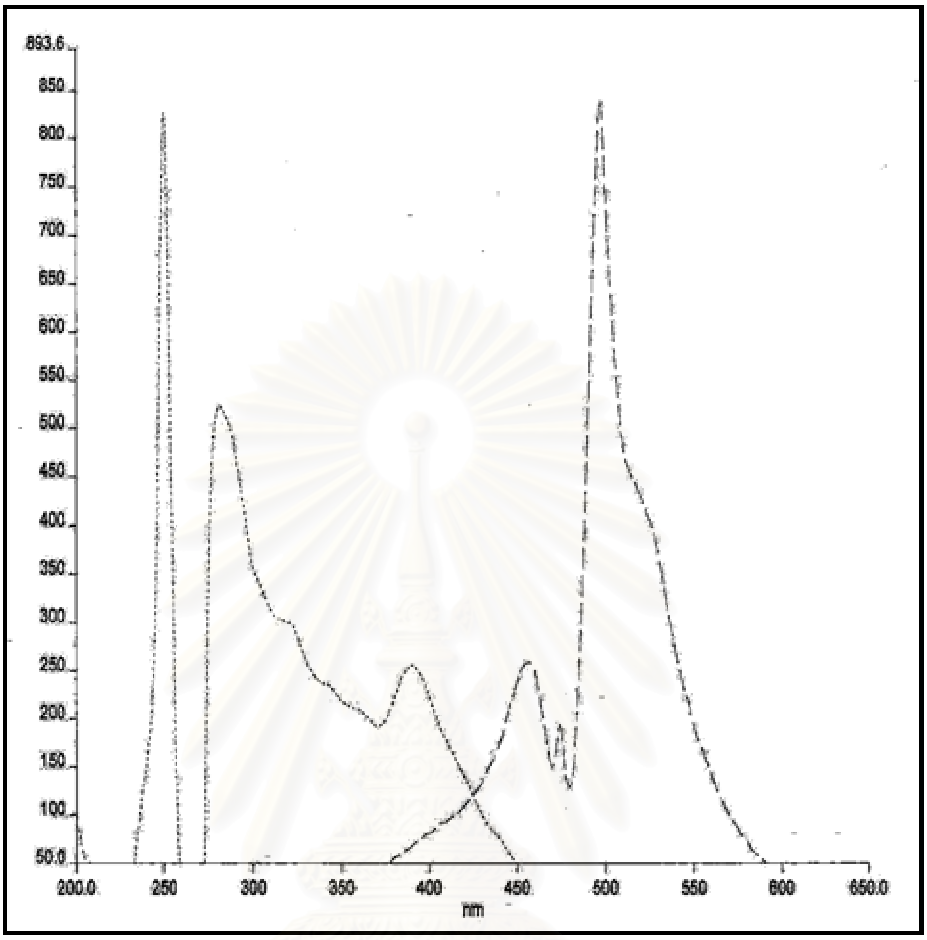

Figure 4.39 The excitation wavelength (λ_{ex} = 250 nm) and emission wavelength (λ_{em} = 500 nm) of compound **3** in dichloromethane

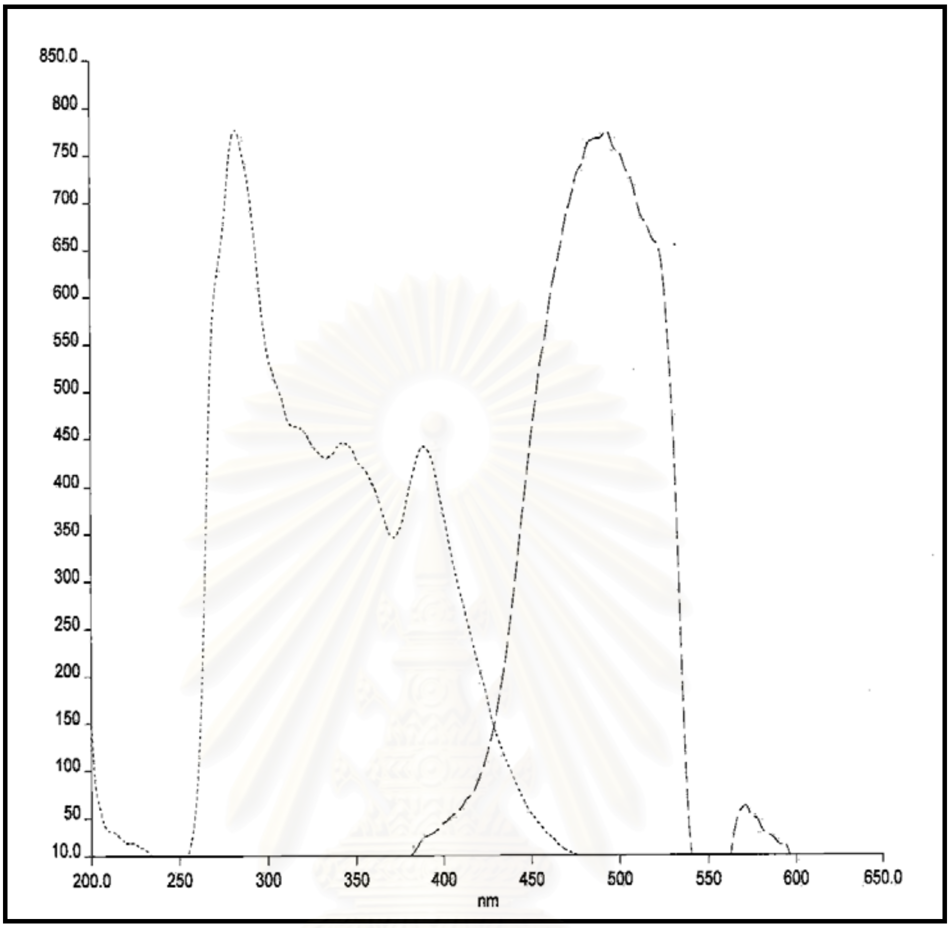

Figure 4.40 The excitation wavelength (λ_{ex} = 281 nm) and emission wavelength (λ_{em} = 492 nm) of compound **3** in ethyl acetate

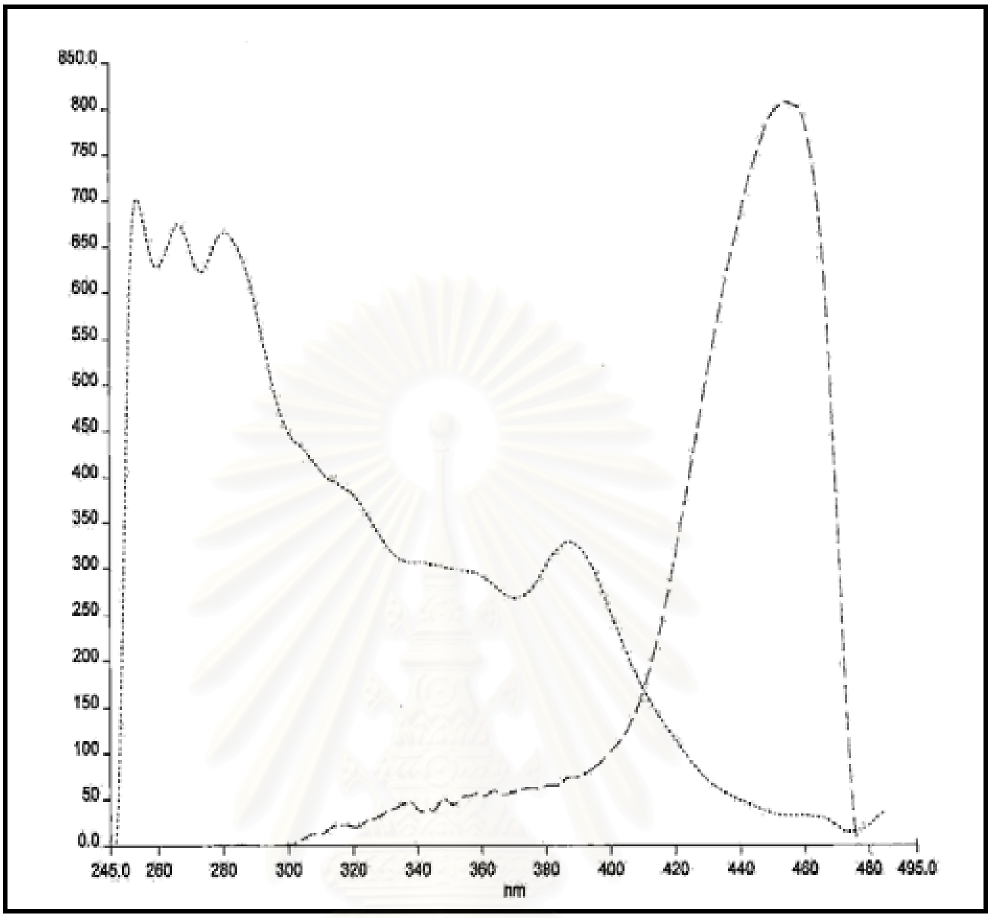

Figure 4.41 The excitation wavelength (λ_{ex} = 252 nm) and emission wavelength (λ_{em} = 455 nm) of compound **4** in hexane

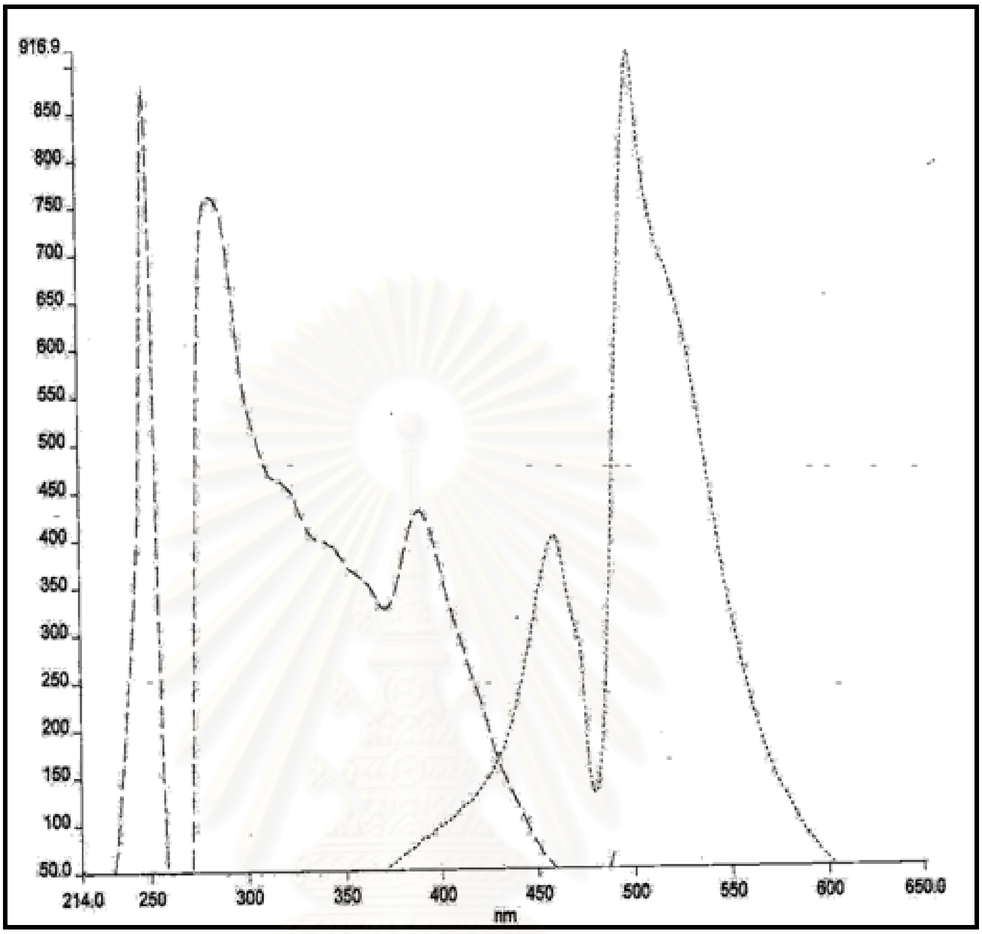

Figure 4.42 The excitation wavelength (λ_{ex} = 250 nm) and emission wavelength (λ_{em} = 500 nm) of compound **4** in dichloromethane

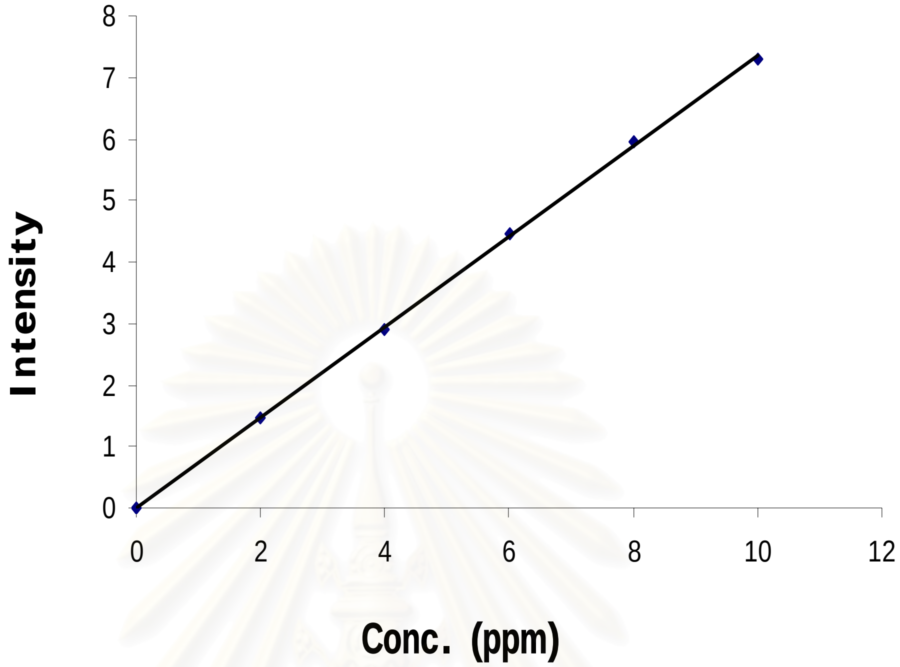

Figure 4.43 The calibration curve for the quantitative determinations of compound **4** in diesel (λ_{ex} = 464 nm and λ_{em} = 612 nm)

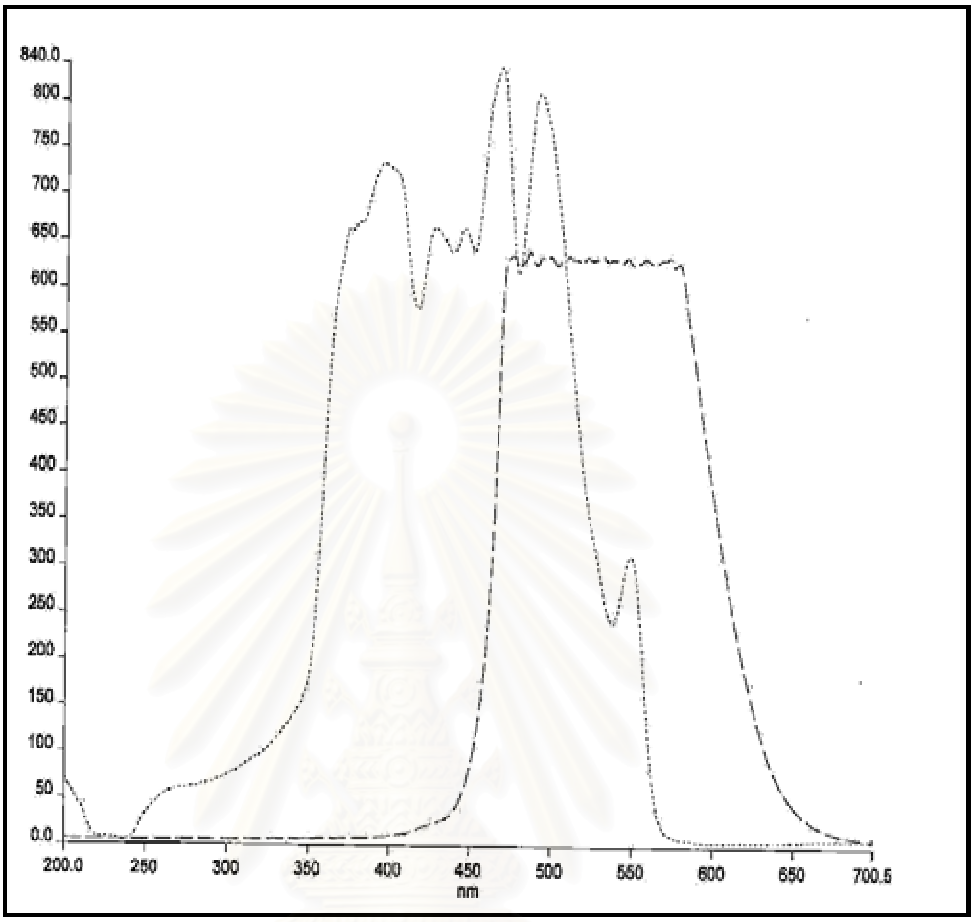

Figure 4.44 The excitation wavelength (λ_{ex} = 464 nm) and emission wavelength (λ_{em} = 612 nm) of diesel

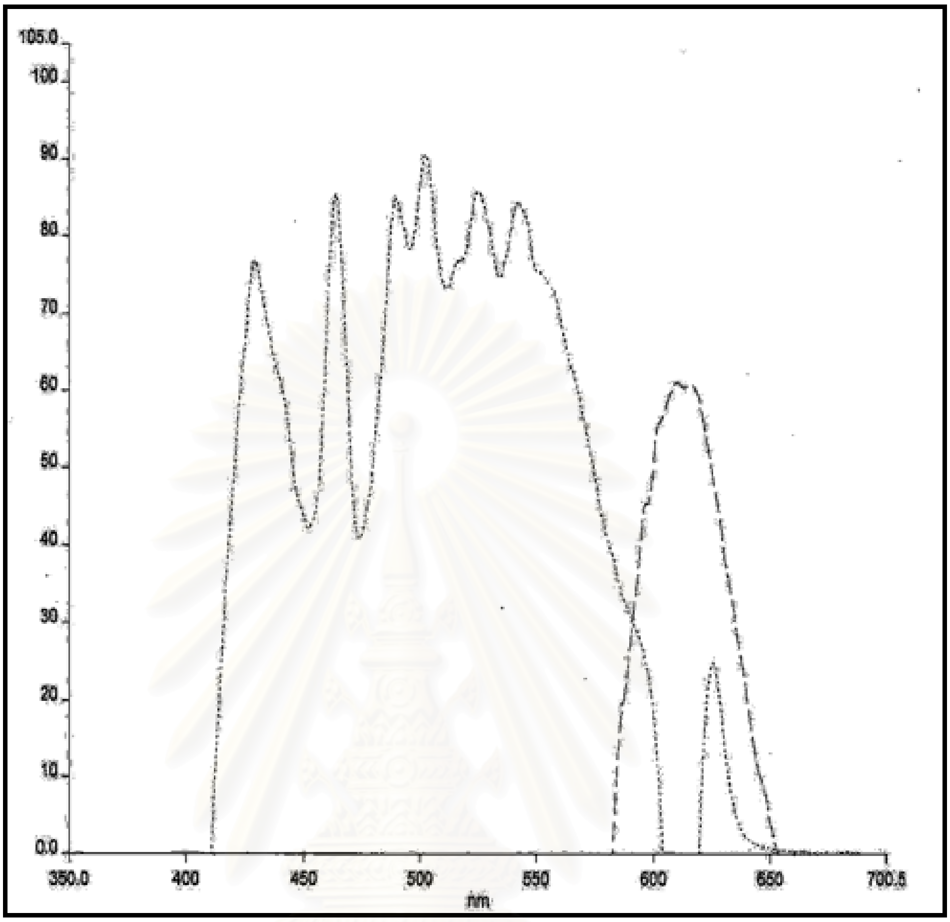

Figure 4.45 The excitation wavelength (λ_{ex} = 464 nm) and emission wavelength (λ_{em} = 612 nm) of compound **4** in diesel

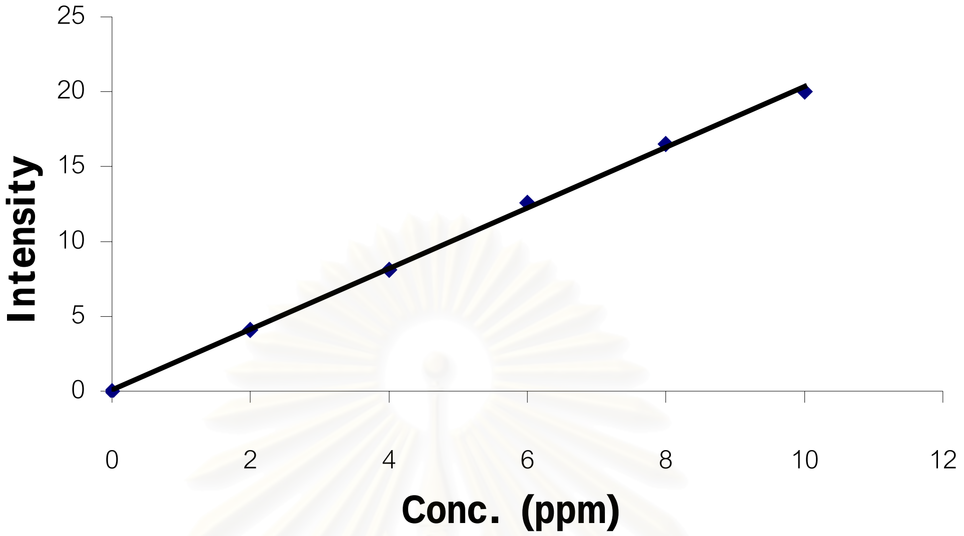

Figure 4.46 The calibration curve for the quantitative determinations of compound **4** solvent (white spirit No.0340) (λ_{ex} = 481 nm and (λ_{em} = 560 nm)

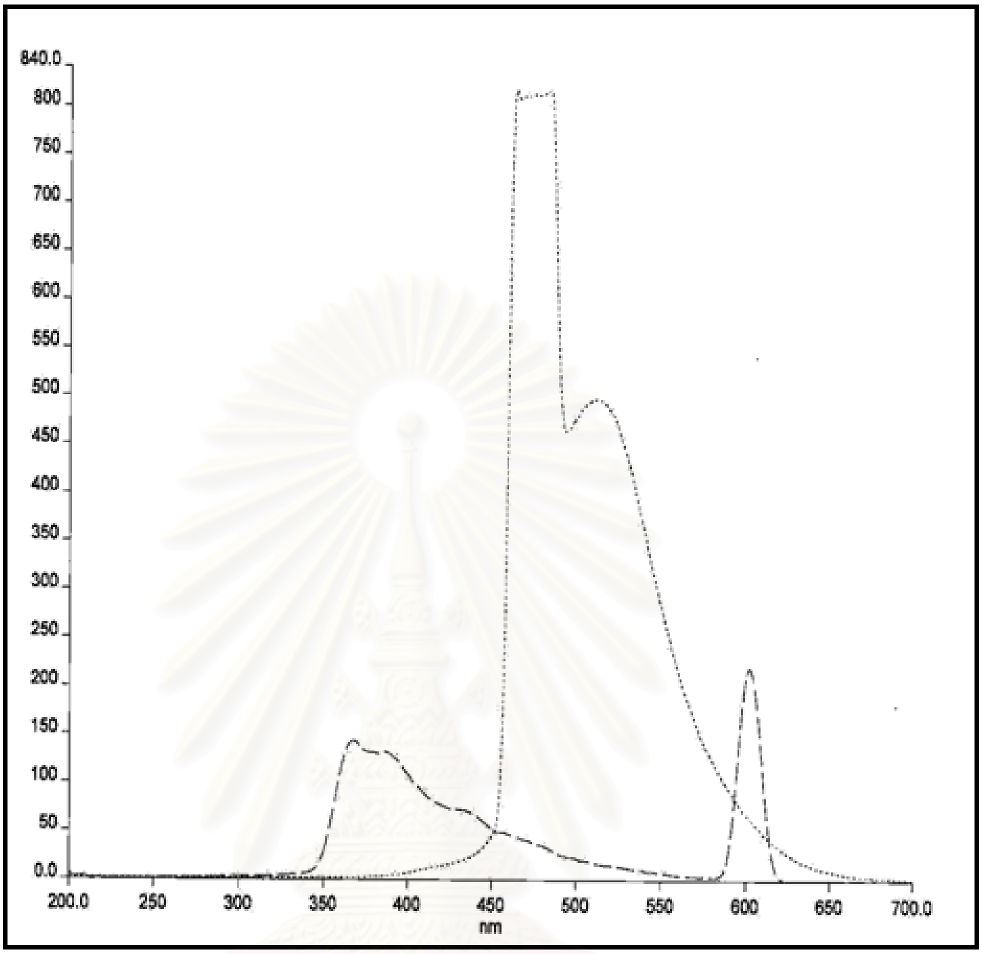

Figure 4.47 The excitation wavelength (λ_{ex} = 481nm) and emission wavelength (λ_{em} = 560 nm) of solvent (white spirit No.0340)

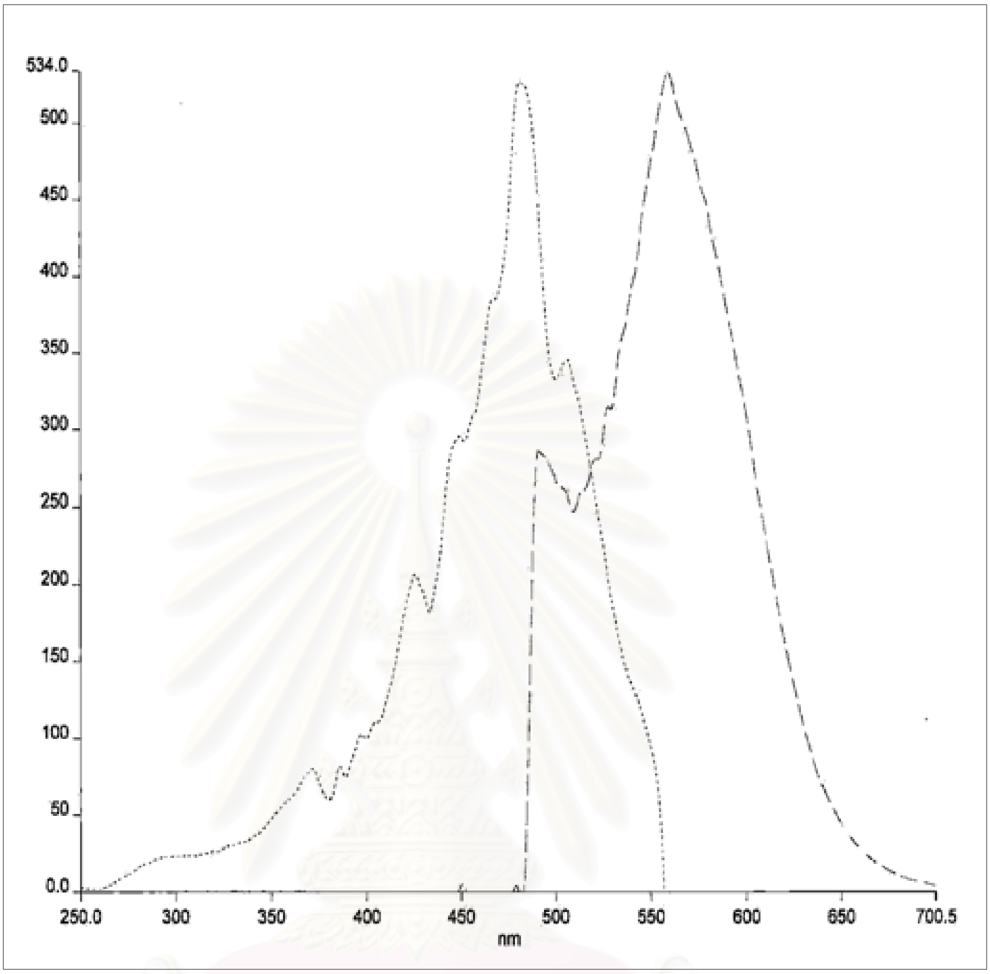

Figure 4.48 The excitation wavelength (λ_{ex} = 481 nm) and emission wavelength (λ_{em} = 560 nm) of compound **4** in solvent (white spirit No.0340)

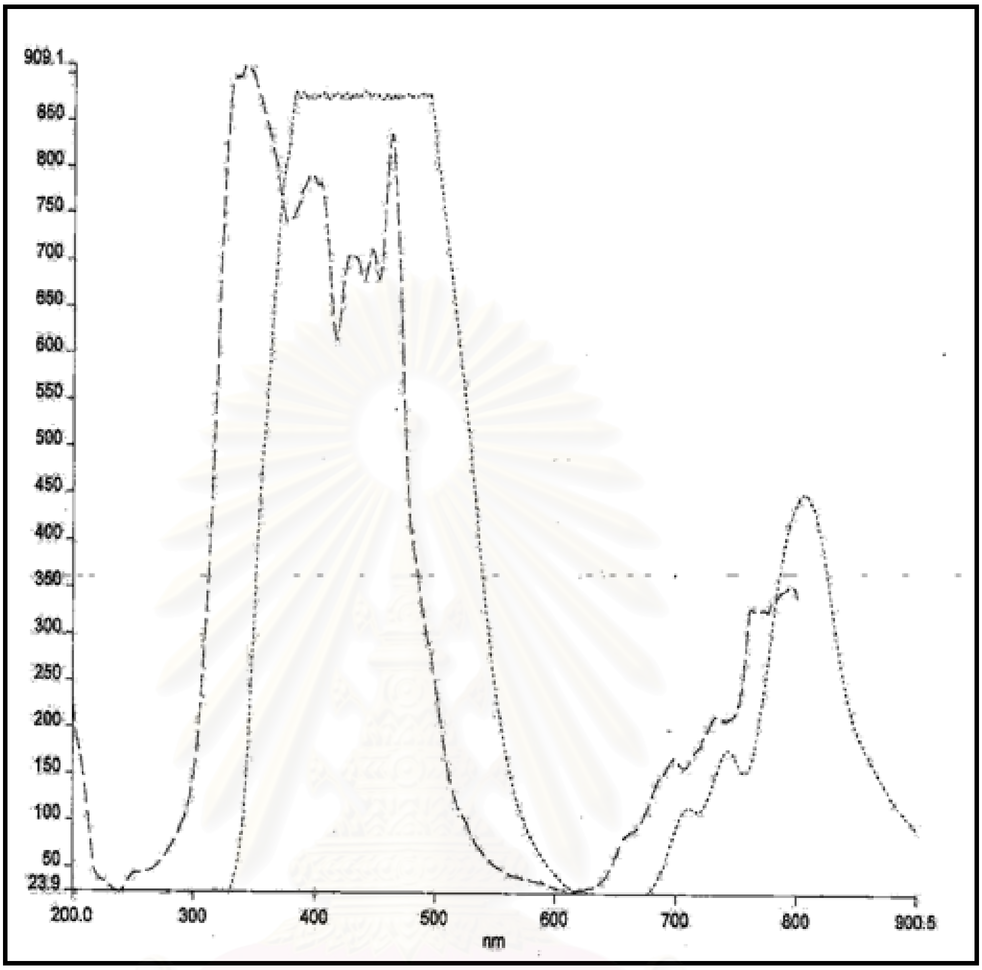

Figure 4.49 The excitation wavelength (λ_{ex} = 396 nm) and emission wavelength (λ_{em} = 570 nm) of gasoline

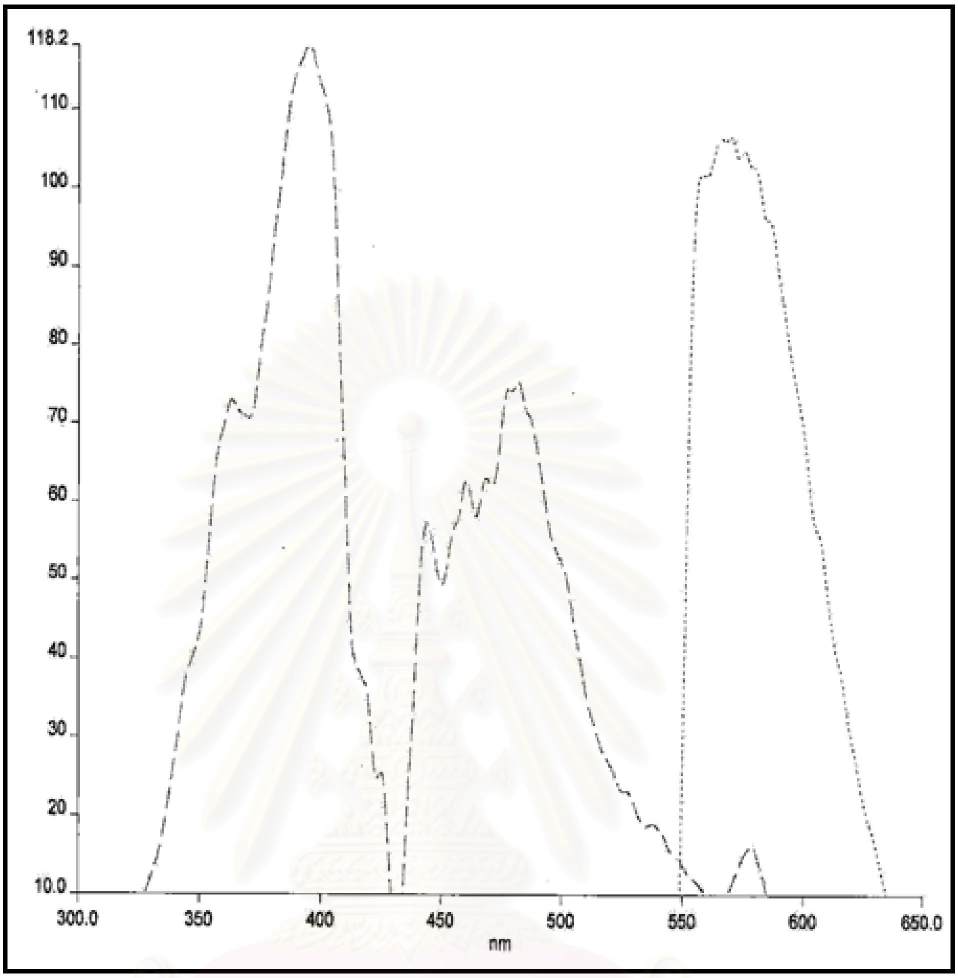

Figure 4.50 The excitation wavelength (λ_{ex} = 396 nm) and emission wavelength (λ_{em} = 570 nm) of compound **4** in gasoline

VITA

Miss Narisara Howhan was born on March 8, 1980 in Kanchanaburi Province, Thailand. She received a Bachelor’s Degree of Science, from Department of Chemistry at Silpakorn University in 2002. In the same year she has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science at Chulalongkorn University and completed her Master Degree of Science in 2005.