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PETROLEUM MARKERS DERIVED FROM CARDANOL



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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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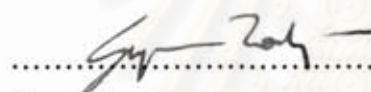
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อ. ที่ปรึกษา: รศ. ดร. อมร เพชรสม; 117 หน้า.

ได้พัฒนาสารทำเครื่องหมายชนิดใหม่และวิธีการตรวจวัดที่ง่าย รวดเร็วและมีประสิทธิภาพสำหรับใช้ติดตามน้ำมันปิโตรเลียม สารทำเครื่องหมายสำหรับน้ำมันปิโตรเลียมนี้เตรียมจากคาร์ดานอลและแบ่งได้ 2 กลุ่ม กลุ่มแรกประกอบด้วยสารทำเครื่องหมายประเภทเอโซซึ่งสังเคราะห์โดยปฏิกิริยากู่ควบของ 2-ไนโตรคาร์ดานอลกับแอนิทีนและอนุพันธ์ สารทำเครื่องหมายประเภทเอโซนี้มีสมบัติการละลายในน้ำมันดีเซลและเบนซินดีและไม่ให้สีที่สามารถเห็นได้ในน้ำมันเชื้อเพลิงดังกล่าวที่ระดับความเข้มข้น 5 ส่วนในล้านส่วน สารทำเครื่องหมายนี้จะให้สีเด่นชัดเมื่อทำปฏิกิริยากับรีเอเจนต์ที่เหมาะสม เกิดเป็นของผสมเนื้อเดียวกันที่คงตัวซึ่งสามารถนำมาวิเคราะห์เชิงคุณภาพและปริมาณสารทำเครื่องหมายได้ด้วยเครื่องสเปกโตรโฟโตมิเตอร์ รีเอเจนต์ดังกล่าวมีเบนซิลไตรเมทิลแอมโมเนียมไฮดรอกไซด์เมทานอลและ 1-เฮกซานอล เป็นองค์ประกอบ กลุ่มที่สองคือสารทำเครื่องหมายประเภทเรืองแสงซึ่งเป็นอนุพันธ์คูมาริน เตรียมได้โดยปฏิกิริยากอนเดนเซชันของคาร์ดานอลกับเอทิลอะซีโตอะซีเทต สารทำเครื่องหมายเรืองแสงนี้ถูกนำมาเติมลงในน้ำมันดีเซลและเบนซินที่ระดับความเข้มข้น 100 ส่วนในล้านส่วน สารทำเครื่องหมายเรืองแสงนี้รวมตัวได้ดีกับน้ำมันเชื้อเพลิงดังกล่าวเช่นเดียวกับสารทำเครื่องหมายประเภทเอโซ เทคนิคฟลูออเรสเซนซ์สเปกโตรสโกปีถูกนำมาใช้วิเคราะห์เชิงคุณภาพและปริมาณสารทำเครื่องหมายด้วยเครื่องสเปกโตรฟลูออโรมิเตอร์ สเปกตรัมฟลูออเรสเซนซ์ของน้ำมันดีเซลที่มีสารทำเครื่องหมายนี้แสดงพีคของสารทำเครื่องหมายที่ความยาวคลื่น 312 นาโนเมตร เมื่อถูกกระตุ้นด้วยแสงอุลตราไวโอเลตที่มีความยาวคลื่น 267 นาโนเมตร ส่วนสเปกตรัมฟลูออเรสเซนซ์ของน้ำมันเบนซินที่มีสารทำเครื่องหมายนี้แสดงพีคของสารทำเครื่องหมายที่ความยาวคลื่น 333 นาโนเมตร ภายใต้แสงอุลตราไวโอเลตที่มีความยาวคลื่น 300 นาโนเมตร สำหรับสารทำเครื่องหมายทั้งสองกลุ่มนั้น การทดสอบสมบัติทางกายภาพด้วยวิธีการตามเอเอสทีเอ็มซีให้เห็นว่าสมบัติทางกายภาพของน้ำมันเชื้อเพลิงที่เติมสารทำเครื่องหมายไม่แตกต่างจากน้ำมันเชื้อเพลิงที่ไม่ได้เติมสารทำเครื่องหมาย นอกจากนี้ ได้ศึกษาความคงตัวของสารทำเครื่องหมายในน้ำมันเชื้อเพลิงและพบว่าสารทำเครื่องหมายคงตัวในระยะเวลาอย่างน้อย 3 เดือน

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ลายมือชื่อนิสิต.....สุกัญญา เข็ญมวรรณท์กุล.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....อมร เพชรสม.....

4573845623: MAJOR PETROCHEMISTRY

KEYWORD: AZO MARKERS/ FLUORESCENT MARKER/ CARDANOL

SUKANYA JIAMWORANUNKUL: PETROLEUM MARKERS DERIVED FROM CARDANOL. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., 117 pp.

Novel markers and simple, rapid, and sensitive detection methods of the markers were developed for use in tagging petroleum fuels. The petroleum markers were derived from cardanol and fell into two categories. The first comprised a number of the azo markers synthesized by the coupling reaction of 2-nitrocardanol with aniline and its derivatives. The azo markers had good solubility in diesel fuel and gasoline and were regarded as silent markers that no color was observable in the fuel oils at a commonly used level (5 ppm). On the other hand, the markers provided clearly visible colors when reacting with the appropriate developing reagent, resulting in stable homogeneous mixtures readily applied for the qualitative and quantitative determinations of the markers in the fuel oils with a vis spectrophotometer. The developing reagent consisted of benzyltrimethylammonium hydroxide, methanol, and 1-hexanol. The second was the fluorescent marker, the coumarin derivative prepared by the condensation reaction of cardanol with ethyl acetoacetate. The fluorescent marker was added into diesel fuel and gasoline at 100 ppm. Like the azo markers, the fluorescent marker had high compatibility with the fuel oils. Fluorescence spectroscopic technique was used to perform both qualitative and quantitative measurements of the marker using a spectrofluorometer. The fluorescence spectrum of the marked diesel fuel exhibited an emission peak attributed to the marker appearing at 312 nm when excited with the ultraviolet radiation having the wavelength of 267 nm. Additionally, the fluorescence spectrum of the tagged gasoline presented an emission band belonging to the marker occurring at 333 nm under the ultraviolet light at 300 nm. For both synthetic markers, the ASTM tests indicated that the physical properties of the marked fuel oils were similar to those of the unmarked fuel oils. Furthermore, the stability of the markers in the marked fuel oils was studied and found that the markers were stable over a period of at least 3 months.

Field of study.....Petrochemistry.....

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Advisor's signature.....*Amorn Petsom*.....

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LIST OF ABBREVIATIONS

API	American Petroleum Institute
δ	chemical shift
cm^{-1}	unit of wavenumber
$^{\circ}\text{C}$	degree Celsius
<i>d</i>	doublet
$^{\circ}\text{F}$	degree Fahrenheit
FT-IR	fourier-transform infrared spectroscopy
Fig	Figure
g	gram (s)
Hz	hertz
hr (s)	hour (s)
<i>J</i>	coupling constant
kPa	kiloPascal
l	liter
MS	mass spectroscopy
<i>m</i>	multiplet
nm	nanometers
mg	milligram
mins	minutes
ml	milliliter (s)
λ_{max}	maximum wavelength
NMR	nuclear magnetic resonance spectroscopy
ppm	parts per million
<i>s</i>	singlet
<i>t</i>	triplet
v	volume
vis	visible
w	weight

CHAPTER I

INTRODUCTION

Nowadays, fuel oils have many kinds and are consumed for various applications. Fuel oils are sometimes mixed for the purpose of adulterating a higher priced or highly taxed product with a lower priced or low taxed material. It is well known that various fuel oils can be tagged by petroleum markers for identification purposes to provide means to distinguish them from seemingly identical products for a number of reasons including to identify various grades of fuel oils, to differentiate similar fuel oils taxed at different rates and to distinguish manufacturers' brands. For example, some petroleum markers are used to discriminate premium grade gasoline from regular grade gasoline or aviation fuel from motor gasoline. In addition, petroleum markers are required by government regulation to monitor the tax classification of fuel oils. Petroleum markers have been proposed including radioactive substances, fluorescent substances and a variety of lightly colored or virtually colorless compounds which react with selected reagents to provide intensely colored derivatives. However, radioactive markers have not gained wide acceptance due to the necessity for special equipment and handling measures to prevent harmful physiological disturbances to personnel. Quinizarin, diphenylamine and some fluorescent markers [1] such as umbelliferone have poor fuel solubility. Regarding the color developable markers including anthraquinones [2-3] like substituted 1,4-dihydroxyanthraquinones, azo compounds [4-11] such as derivatives of phenylazophenol and phenylazonaphthol, isobenzofuranones [12] and 2-naphthylamine derivatives [13], the detection of such markers normally requires marker extraction with a suitable extractant which is time-consuming to perform and limits the efficiency of the quantitative determination of the markers.

With the growing drive to prevent and examine the fraudulent adulteration and tax evasion, more practical markers and improved detection methods are needed. It is therefore of interest to find additional useful markers and methods to detect the markers for identifying fuel oils.

1.1 Objectives of this research

The objectives of this research are to prepare novel petroleum markers having high solubility and stability in fuel oils and to develop simple, quick, and reliable methods to detect the markers qualitatively and quantitatively.

In this work, two types of silent petroleum markers, azo and fluorescent markers will be synthesized from cardanol which has long nonpolar aliphatic side chains to improve their fuel solubility. The application of the synthetic markers will be focused on diesel fuel and gasoline which are most widely used in Thailand. Cardanol utilized in this study is obtained from cashew nut shell liquid which is an agricultural byproduct of the cashew nut manufacturing and commercially available in the southern part of Thailand.



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CHAPTER II

THEORETICAL

2.1 Color of organic compounds [14-15]

Organic compounds can be excited electronically by electromagnetic radiation. When an electronic transition is in the visible range (about 400-750 nm), a compound will appear as colored. The electronic absorption is generally $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition and involves extended π -electronic system. When light passes through and is reflected by a colored substance, a characteristic portion of mixed wavelengths is absorbed. The color observed is not the color absorbed, but its complement which is reflected. For example, pentacene absorbs at 575 nm in the yellow portion of the visible spectrum and reflects the other wavelengths rendering in blue which is the complement of yellow. The colors perceived for different wavelengths of light are summarized in Table 2.1.

Table 2.1 Relation between absorption and colors

Wavelength absorbed (nm)	Color absorbed	Complementary color
400-430	Violet	Green-yellow
430-480	Blue	Yellow
480-490	Green-blue	Orange
490-510	Blue-green	Red
510-530	Green	Purple
530-570	Yellow-green	Violet
570-580	Yellow	Blue
580-600	Orange	Green-blue
600-680	Red	Blue-green
680-750	Purple	Green

2.2 Azo compounds [16-24]

Azo compounds generally have a molecular formula of the form $R-N=N-R'$, in which R and R' can be either aliphatic or aromatic. The $N=N$ group called an azo or a diimide functional group is linked to sp^2 -hybridized carbon atoms and stabilized by making it part of an extended delocalized system.

Aliphatic azo compounds are rather unstable. At an elevated temperature or by irradiation, two carbon-nitrogen (R-N) bonds are cleaved simultaneously with the loss of nitrogen gas to generate carbon-centered radicals. Owing to this process, some aliphatic azo compounds are utilized as radical inhibitors. Azobisisobutyronitrile (AIBN) is a typical one and widely used in industrial processes and in laboratory experiments.

Aromatic azo compounds are usually stable and have vivid colors because the $N=N$ linkage brings the two aromatic rings into conjugation, giving an extended system of delocalized π electrons and allowing strong absorption of light in the visible region. They, because of their intense colors and because they can be synthesized from relatively inexpensive compounds, are used extensively as dyes. The colors of these dyes are due to the absorption of light in certain parts of the visible spectrum by the extended, delocalized system of π -electrons in the dye molecules. With various substituents on the two aromatic rings, an enormous range of possible dyes is available.

Orange II, a dye introduced in 1876, is made from 2-naphtol.

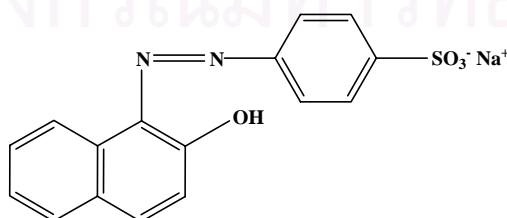


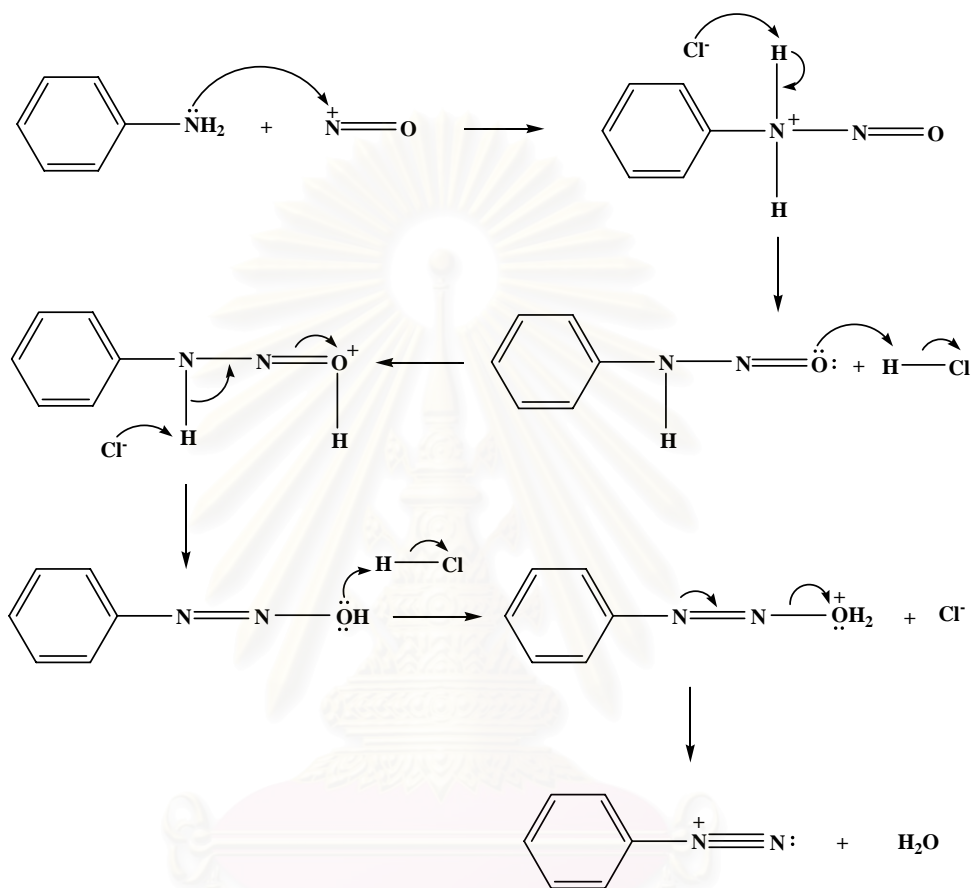
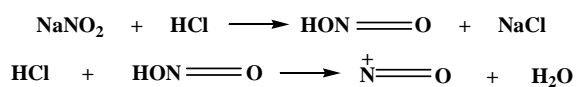
Fig. 2.1 Chemical structure of orange II

Groups such as hydroxyl and amino groups attached to the azo bond can modify the colors of azo compounds. Hydroxyl and amino groups, especially if they are ortho or para to the azo bond, intensify the colors of azo compounds. Each of these compounds, *p*-hydroxyazobenzene and *p*-dimethylaminoazobenzene absorbs at a longer wavelength than azobenzene itself does and in each case the molar absorptivity is also higher. In addition, azo compounds in which an electron-donating group on one of the aromatic rings is conjugated with an electron-withdrawing group on the other ring have especially deep colors. A good example is the azobenzene in which a nitro group is substituted on one ring para to the azo linkage and a dimethylamino group is substituted on the other ring para to the azo linkage.

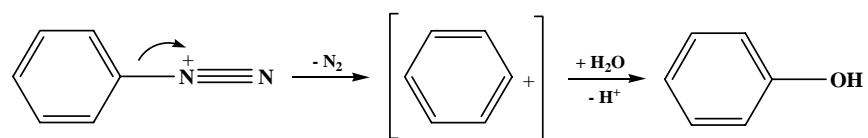
Aromatic azo compounds can be prepared by azo coupling the primary components, diazotized aromatic amines with the secondary components, aromatic compounds containing strongly activating substituent groups such as aromatic amines and phenols. There are two reactions involved in the synthesis of azo compounds.

1. Diazotization

The preparation of aryl diazonium ions is carried out by the nitrous acid diazotization of arylamines in either aqueous solutions or mixtures of water and organic solvents. Nitrous acid is generated by the addition of a solution of sodium nitrite to the suspension of the amine salt in excess mineral acid usually hydrochloric acid or sulfuric acid. The mechanism of this reaction consists of many steps shown below. It begins with the nucleophilic attack of the amine on the nitrosonium ion followed by the loss of a proton; the amine is converted to *N*-nitrosamine. Subsequently, a series of three proton transfer reactions occurs and leads to the loss of water and finally the formation of the diazonium ion.

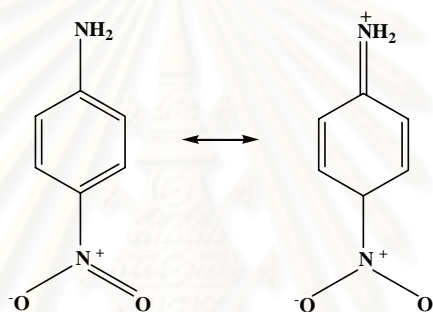


The proper condition of acidity is required to stabilize the diazonium salt and hence to minimize secondary reactions, e.g. the interaction of some of the diazonium salt with unchanged amine to form a diazoamino compound. Additionally, the reaction mixture must be kept very cold during the process; otherwise, the diazonium salt may be partially hydrolyzed to the corresponding phenol.



Moreover, most diazonium salts are unstable at room temperature. Therefore, the reaction is carried out and the solution is used immediately. The stability of diazonium salts varies greatly with the structure of the molecules. For instance, *p*-nitrobenzenediazonium chloride is considerably more stable than benzenediazonium chloride.

Aromatic amines substituted in the nucleus with electron-attracting groups are less easy to diazotize because the nucleophilicity of the amino-nitrogen is reduced by the partial withdrawal of the unshared electron-pair into the nucleus.

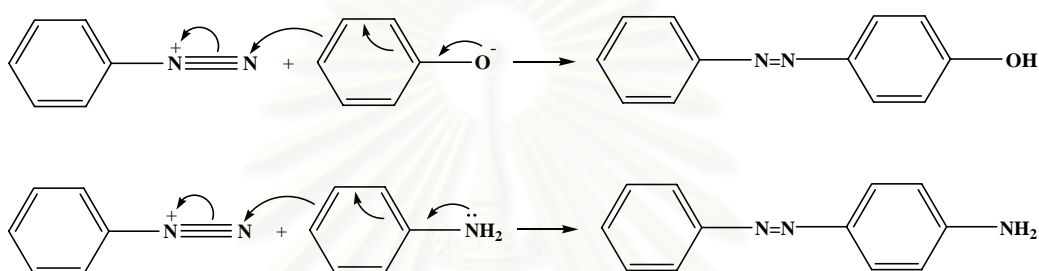


Some aromatic amines, such as nitroanilines, react rather slowly at low temperatures but since the diazonium compounds formed are somewhat more stable, the diazotization may be conducted at room temperature when the reaction proceeds more rapidly.

2. Azo coupling reaction

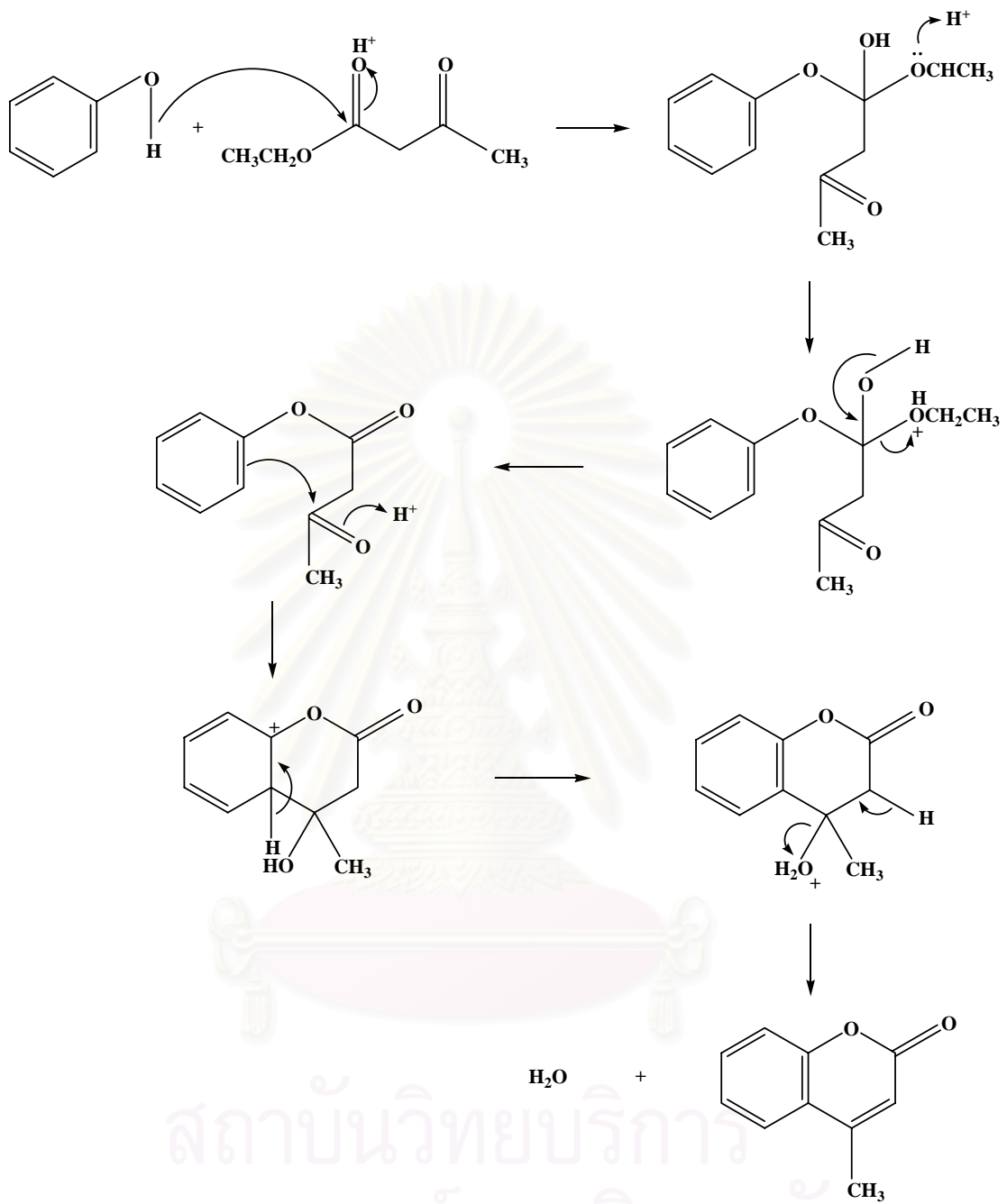
Azo coupling reaction is typical electrophilic aromatic substitution in which the positive charged diazonium ion is the electrophile that reacts with the electron-rich ring of an aromatic phenol or amine in the presence of sodium hydroxide or sodium acetate, respectively. In general, the coupling reaction is carried out in a mild alkaline solution for an aromatic phenol and in a mild acidic solution for an aromatic amine. Furthermore, the coupling medium of the reaction must be adjusted to the right degree of alkalinity and acidity by the addition of the proper amount of sodium hydroxide and sodium acetate.

The coupling usually takes place at the position of the greatest electron availability to introduce the azo group to the para position of the hydroxyl or amino group of an aromatic phenol or amine, or the ortho position if the para position is occupied. If all para and ortho positions are occupied, no coupling takes place. Electron withdrawing groups on the aromatic ring of the diazonium ion facilitate the substitution reaction. The reaction also occurs at the para position, although the ortho attack can take place if the para position is blocked.



2.3 Coumarins [25-42]

Coumarins are six membered lactones or cyclic esters possessing a 2H-1-benzopyran-2-one nucleus. In 1820, coumarin was first isolated from the seeds of *Coumarona odorata* Aubl. Coumarins are found in a variety of plants, microorganisms, and animals or produced synthetically in the laboratory. Coumarins can be synthesized by several routes including Knoevenagel reaction, Pechmann reaction, Perkin reaction, Reformatsky reaction, and Wittig reaction. Among these reactions, Pechmann reaction is the most widely applied method for the preparation of coumarins since it proceeds from very simple starting materials. Pechmann reaction involves the condensation of a phenol with a β -ketoester in the presence of an acidic condensing agent. Various acidic condensing agents employed in Pechmann reaction include sulfuric acid, aluminium chloride, phosphorus pentoxide, and trifluoroacetic acid. Concentrated sulfuric acid is generally used as the condensing agent for simple monohydric phenols and β -ketoesters. The mechanism of the condensation illustrated below involves three reactions: hydroxyalkylation, transesterification and dehydration, which occur concomitantly, condensing the two reactants to form the coumarin heterocycle.



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Coumarins have attracted great interest due to their structures and chemical reactions. Coumarins are employed as precursors for several chemicals. For example, they are used for the preparation of perfumes, soaps, cosmetics, flavorings, insecticides and used in the synthesis of drugs especially anticancer. Coumarins are also utilized widely as anticoagulants, antioxidants, agrochemicals, fragrances, pharmaceuticals, rodenticides, therapeutic agents, fluorescent dyes, fluorescent brighteners, luminescent probes, optical bleaching agents, photographic sensitizers and triplet sensitizers.

2.4 Petroleum markers [3, 11, 43]

Petroleum markers are defined as substances that can be used to tag petroleum products and subsequently detected by performing simple chemical or physical tests on the marked petroleum products. Petroleum markers which have been employed include radioactive substances, fluorescent substances, furfural, quinizarin, diphenylamine, azo compounds and naphthol derivatives. Desirable markers for petroleum products should satisfy the following properties:

1. Are entirely foreign to petroleum products.
2. Have good solubility in compatible solvents and petroleum liquids and can be supplied as concentrated solutions in the solvents.
3. Have a high diffusion index to permit uniform detection throughout tagged petroleum products.
4. Have insolubility in water to prevent the markers from being leached out of tagged petroleum products into the water phase often found in product storage tanks.
5. Are difficult to be removed from marked petroleum products.
6. Are not obscured by natural components of petroleum hydrocarbons.
7. Are stable over the anticipated storage life of marked petroleum products.
8. Are useful at low concentration levels.
9. Can be detected both qualitatively and quantitatively in a quick and simple specific test.
10. Have no effect on the appearance and quality of tagged petroleum products.
11. Have identities which can be confirmed by laboratory methods.

2.5 Ultraviolet-visible spectroscopy [22, 44-46]

Ultraviolet-visible spectroscopy involves the absorption of ultraviolet-visible light (200-800 nm) by a molecule causing the promotion of an electron from a ground electronic state to an excited electronic state. Ultraviolet-visible radiation is absorbed by π electrons and in some cases, by unshared electron pairs in organic compounds. There are several types of electronic transitions available to a molecule including:

$\sigma \rightarrow \sigma^*$ (alkanes)

$\sigma \rightarrow \pi^*$ (carbonyl compounds)

$\pi \rightarrow \pi^*$ (alkenes, alkynes, azo compounds, and carbonyl compounds)

$n \rightarrow \sigma^*$ (halogen, nitrogen, oxygen, and sulfur compounds)

$n \rightarrow \pi^*$ (carbonyl compounds)

However, not all transitions are possible and observed. Some electronic transitions are forbidden by certain selection rules. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is the lowest energy transition. Most electronic transitions of organic compounds are based on the transitions of n or π electrons to the π^* excited state.

In practice, an ultraviolet-visible spectrum is recorded by irradiating a sample with ultraviolet-visible light of continuously changing wavelength. When a wavelength corresponds to the energy level required to excite an electron to a higher level, energy is absorbed. This absorption is detected and displayed on a chart that plots wavelength versus percent radiation absorbed.

Different molecules absorb the radiation in different wavelengths. An absorption operation will show a number of absorption bands corresponding to structural features within a molecule called chromophores which contain valence electrons of low excitation energy. Typical examples of chromophores are C=C, C=N, C=O, N=N, N=O, etc. Some other groups called auxochromes affect the spectral regions of the strong absorption of chromophores. Typical examples of auxochromes are NH₂, OH, CH₃, OCH₃, Cl, etc. Auxochromes have lone pairs of electrons that can

be delocalized along with the delocalized electrons of chromophores. The effects of auxochromes to the absorption of chromophores include:

1. Bathochromic shift (red shift), the shift of absorption to a longer wavelength
2. Hypsochromic shift (blue shift), the shift of absorption to a shorter wavelength

In general, if an auxochrome is attached to a carbon-carbon bond, a bathochromic effect will be observed and if to the double bond where n electrons are available such as a carbonyl group, a hypsochromic effect results.

The wavelength at which the maximum absorption band occurs in the ultraviolet-visible region is generally referred to as the λ_{max} of the sample. The smaller the HOMO-LUMO gap, the longer the wavelength of the absorption. When ultraviolet-visible spectroscopy is used to determine chemical structure, the λ_{max} value is the most important aspect of a spectrum. The structural feature of a compound that is most significant in determining the λ_{max} is the number of consecutive conjugated double or triple bonds. If a compound has enough double bonds in conjugation, its λ_{max} value will be large enough to fall within the visible region and thereby the compound will appear colored. However, other factors are involved in determining the λ_{max} of an organic compound such as substituents.

The exact amount of the light absorbed is expressed as the sample's extinction coefficient (molar absorptivity), ϵ defined by the equation:

$$\epsilon = A/Cl$$

Where A = Absorbance

C = Concentration (mol/l)

l = Sample path length (cm)

The extinction coefficient is a physical constant, characteristic of a particular substance and thus characteristic of the particular π electron system of a molecule. Each absorption in a spectrum has a unique extinction coefficient that depends on wavelength, solvent, and temperature. The extinction coefficient generally becomes greater as conjugation increases. The larger is the extinction coefficient, the greater is

the light absorption at a given concentration and path length. The quantitative relationship of absorbance (the intensity of a band) to concentration is expressed by Beer-Lambert equation:

$$A = \log I_0/I = \epsilon Cl$$

Where I_0 = Intensity of incident light

I = Intensity of light transmitted through the sample

2.6 Fluorescence spectroscopy [47-48]

Fluorescence is the phenomenon in which the light absorption of a given wavelength by a fluorescent molecule is followed by the light emission at longer wavelengths. The distribution of wavelength-dependent intensity that causes fluorescence is known as the fluorescence excitation spectrum, and the distribution of wavelength-dependent intensity of the emitted energy is known as the fluorescence emission spectrum. The phenomenon is derived from the electromagnetic nature of light, the details of molecular structure especially molecular electronic structure and the nature of the environment of the molecule. The principles of electron transfer are depicted by Jablonski diagram.

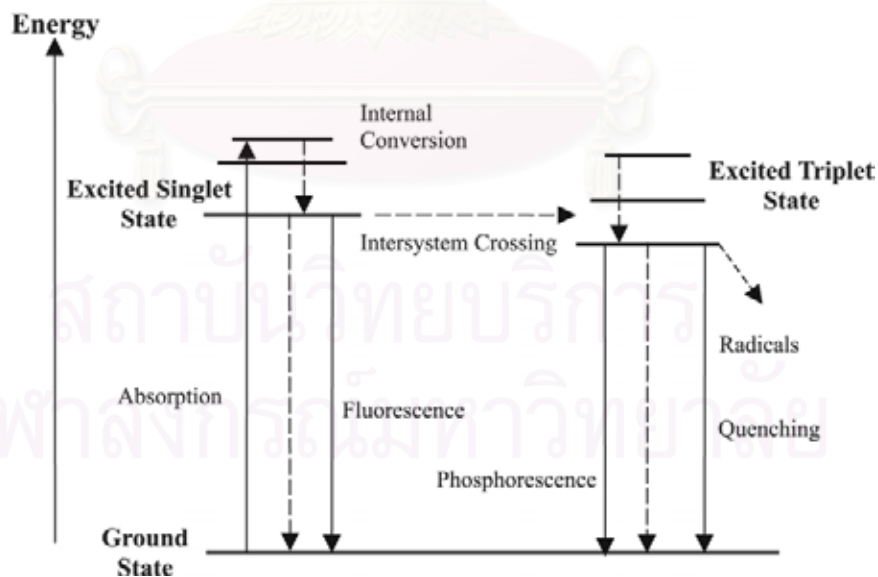


Fig. 2.2 Jablonski diagram

When molecules are irradiated with a monochromatic light source of an appropriate frequency, they can undergo excitation from the ground electronic state to any of several vibrational levels of the excited electronic state. However, the excess vibrational energy is immediately lost as a consequence of collisions between the molecules of the excited species and those of solvent; the result is an energy transfer and a minuscule increase in the temperature of the solvent leading the molecules to the lowest vibrational level of the excited electronic state. This vibrational relaxation process is so efficient that the average lifetime of a vibrationally excited molecule is 10^{-12} second or less, a period significantly shorter than the average lifetime of an excited electronic state. Since the lowest vibrational level of the excited electronic state is also unstable, the molecules can directly return to the ground electronic state with the emission of light and hence fluorescence spectrum is observed in longer wavelength. For the majority of fluorescent compounds, the radiation is produced by either an $n \rightarrow \pi^*$ or a $\pi \rightarrow \pi^*$ transition depending upon which of these is the less energetic. The most intense and useful fluorescence is found in compounds containing aromatic functional groups with low-energy $\pi \rightarrow \pi^*$ transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double-bond structures may also exhibit fluorescence, but the number of these is small compared with the number in the aromatic systems. Because fluorescence originates from the lowest excited state and terminates in the ground state, the effect upon the positions of the fluorescence bands of the size of aromatic system is qualitatively similar to that upon the position of the lowest frequency absorption band. Increasing the size of aromatic system results in the lower frequency of fluorescence because the energy gap between the ground and excited states is compressed as the degree of the conjugation in an aromatic molecule increases.

Substitutions on aromatic rings can cause shifts in the wavelength of absorption maxima and corresponding changes in fluorescence peaks. Aromatic rings containing single substituents such as amino and hydroxyl groups (excited state electron donors) or a carbonyl group (an excited state charge acceptor or a vacant orbital donor) are more extensively conjugated in their lowest excited states than in their ground states. The stabilization of the excited states by exocyclic conjugation, relative to the ground states, results in the longer wavelengths of absorption and

fluorescence relative to unsubstituted aromatic compounds. Furthermore, substitutions frequently affect quantum efficiency; some of these effects are shown by the data for benzene derivatives in Table 2.2.

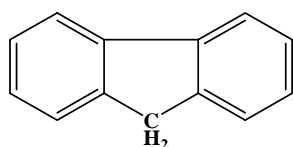
Table 2.2 Effect of substitution on the fluorescence of benzene and derivatives

Compound	Wavelength of fluorescence (nm)	Relative intensity of fluorescence
Benzene	270-310	10
Toluene	270-320	17
Propylbenzene	270-320	17
Fluorobenzene	270-320	10
Chlorobenzene	275-345	7
Bromobenzene	290-380	5
Iodobenzene	-	0
Phenol	285-365	18
Phenolate ion	310-400	10
Anisole	285-345	20
Aniline	310-405	20
Anilinium ion	-	0
Benzoic acid	310-390	3
Benzonitrile	280-360	20
Nitrobenzene	-	0

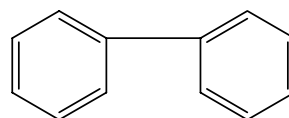
The quantum efficiency is also affected by several factors including:

1. Effect of structure rigidity

Empirically, fluorescence is particularly favored in molecules that possess rigid structures. For example, the quantum efficiencies of fluorene and biphenyl are nearly 1.0 and 0.2, respectively under similar conditions of measurement. The difference in behavior appears to be largely a result of the increased rigidity furnished by the bridging methylene group in fluorene.



Fluorene



Biphenyl

Fig. 2.3 Chemical structures of fluorene and biphenyl

2. Effect of temperature

The quantum efficiency of fluorescence in most molecules decreases with increasing temperature because the increased frequency of collisions at elevated temperatures improves the probability for the deactivation by external conversion.

3. Effect of solvent

A decrease in solvent viscosity increases external conversion and leads to decreased quantum efficiency. The fluorescence of a molecule is also decreased by solvents containing heavy atoms or other solutes with such atoms in their structures such as carbon tetrabromide and ethyl iodide due to orbital spin interactions resulting in an increase in the rate of triplet formation and a corresponding decrease in fluorescence.

4. Effect of pH

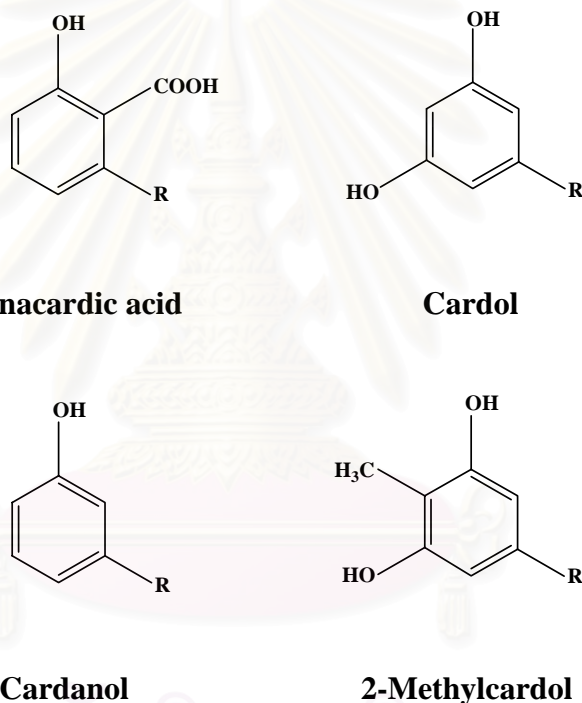
The fluorescence of an aromatic compound with acidic or basic ring substituents is usually pH-dependent. Both wavelength and emission intensity of fluorescence are likely to be different for the ionized and nonionized forms of the compound. Phenol and phenolate, for instance, exhibit fluorescence in the ranges of 283-365 nm and 310-400 nm and their corresponding relative intensities are 18 and 10, respectively.

With nitrogen heterocyclics, the lowest-energy electronic transition is believed to involve an $n \rightarrow \pi^*$ system that rapidly converts to the triplet state and prevents fluorescence. The simple heterocyclics, like pyridine, furan, thiophene, and pyrrole do not exhibit fluorescence; on the other hand, fused-ring structures ordinarily do. The lifetime of an excited state is shorter in such structures; fluorescence is thus observed for the compounds such as quinoline, isoquinoline, and indole. In addition, the fusion

of benzene rings to a heterocyclic nucleus, however, results in an increase in the molar absorptivity of the absorption peak.

2.7 Cashew nut shell liquid [49-51]

Cashew nut shell liquid (CNSL) is natural oil with bitter taste and dark brownish color. CNSL is obtained from the spongy layer between the inner and the outer shell of the cashew nut, *Anacardium occidentale* either by extraction in a solvent or in hot oil. CNSL consists of a mixture of phenolic compounds namely anacardic acid, cardol, cardanol and 2-methylcardol.



Where $R = -(CH_2)_{14}CH_3$

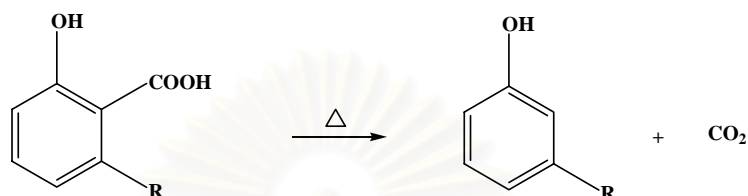
$-(CH_2)_7CH=CH(CH_2)_5CH_3$

$-(CH_2)_7CH=CHCH_2CH=CH(CH_2)_2CH_3$

$-(CH_2)_7CH=CHCH_2CH=CHCH_2CH=CH_2$

Fig. 2.4 Chemical structures of anacardic acid, cardol, cardanol and 2-methylcardol

Typical solvent-extracted CNSL contains anacardic acid (60-65 %), cardol (15-20 %), cardanol (10 %) and traces of 2-methylcardol. In technical CNSL, the heating process leads to the decarboxylation of anacardic acid to form cardanol. The composition of the technical CNSL is mainly cardanol (60-65%), cardol (15-20 %), polymeric materials (10 %) and traces of 2-methylcardol.



CNSL has been used in many industries. CNSL by itself is useful in insecticidal, fungicidal, anti-termite and medicinal applications. In addition, it can be utilized as a starting material for organic syntheses and an alternative source of phenolic compounds. Resins derived from CNSL are widely employed in the field of friction materials, automobiles, adhesives, laminates, surface coating and rubber compounding. The most attractive consideration for CNSL use can be its low cost, abundant availability and chemically reactive nature.

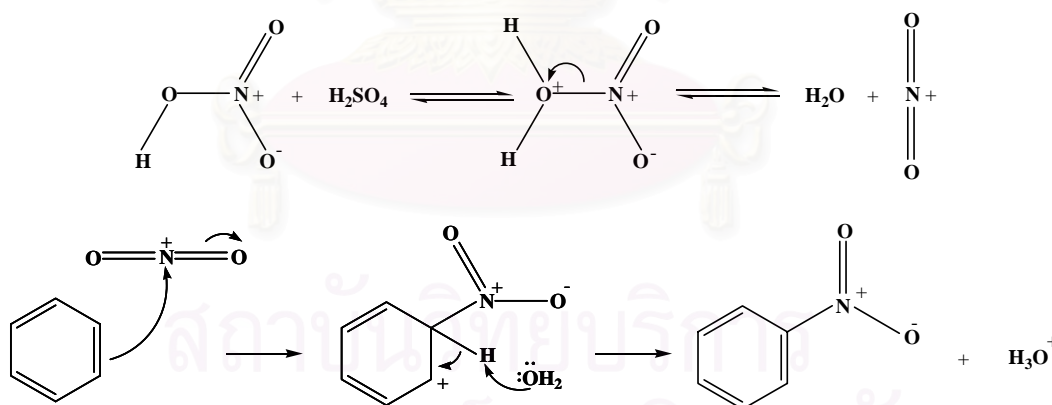
2.8 Cardanol [49-51]

Cardanol (Fig. 2.4) is a yellow liquid which can be obtained by the vacuum distillation of cashew nut shell liquid. Chemically, it represents an interesting reactive substance thanks to the double bonds in its alkyl chains and phenolic character which can be used as a substitute for petroleum-based phenols.

Cardanol is already utilized in various applications including fine chemicals and intermediates, additives for lubricants and diesel fuel, flame retardants, antioxidants, stabilizers, insulating materials, adhesives, surface active agents and polymers.

2.9 Nitration [23, 44, 52-53]

The most commonly employed method for bonding nitrogen to an aromatic system is nitration. The nitration of an aromatic compound may be carried out in many ways involving different concentrations of nitric acid (fuming, concentrated, etc.), different solvents (none, glacial acetic acid, concentrated sulfuric acid, etc.), and varying temperatures. The most common solvent is sulfuric acid, since it promotes the reaction by increasing the amount of the nitronium ion, NO_2^+ which is the effective nitrating agent and by absorbing the water formed during the nitration process. If it is desired to introduce only one nitro group in the ring, mild temperatures (about 0-60 °C) are usually used. More strenuous conditions may bring about the introduction of several nitro groups. The mechanism of the nitration is represented below. The nitronium ion is generated from nitric acid by the protonation and loss of water. The highly reactive nitronium ion can attack the aromatic compound to form the σ bond to the carbon in the rate-determining step of the electrophilic aromatic substitution. The deprotonation of the resonance-stabilized cation restores aromaticity to the ring, yielding nitrobenzene.



In aromatic nitration, when a group is attached to an aromatic ring, there are two effects:

1. A substituent affects the reactivity of the aromatic ring. Some substituents activate the ring, making it more reactive than benzene, and some deactivate the ring, making it less reactive. For instance, a hydroxyl substituent makes the ring 1000 times

more reactive than benzene, while a nitro substituent makes the ring more than 10 million times less reactive.

2. A substituent also affects the orientation of the reaction. The three possible disubstituted products, ortho, meta, and para, are usually not formed in equal amounts. Instead, the nature of the substituent already present on the ring determines the position of the second substitution. Table 2.3 lists the experimental results for the nitration of some substituted rings and shows that some groups direct substitution primarily to the ortho and para positions, while other groups direct substitution primarily to the meta position.

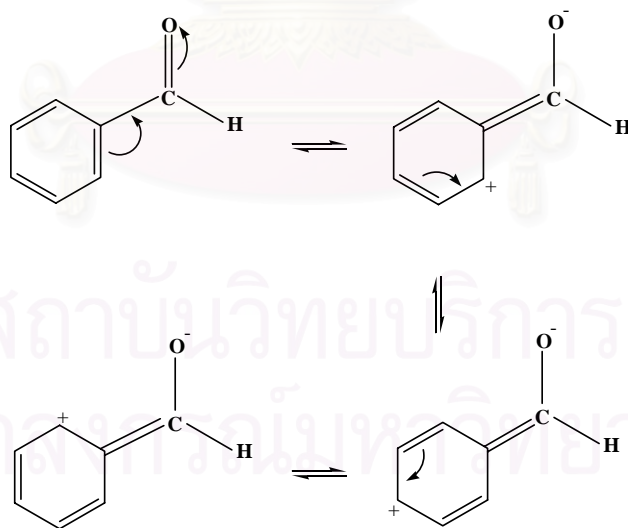
Table 2.3 Experimental results for the nitration of some substituted rings

Substituent	Product (%)		
	Ortho	Meta	Para
Meta-directing deactivators			
-N ⁺ (CH ₃) ₃	2	87	11
-NO ₂	7	91	2
-COOH	22	76	2
-CN	17	81	2
-CO ₂ CH ₂ CH ₃	28	66	6
-COCH ₃	26	72	2
-CHO	19	72	9
Ortho- and para-directing deactivators			
-F	13	1	86
-Cl	35	1	64
-Br	43	1	56
-I	45	1	54
Ortho- and para-directing activators			
-CH ₃	63	3	34
-OH	50	0	50
-NHCOCH ₃	19	2	79

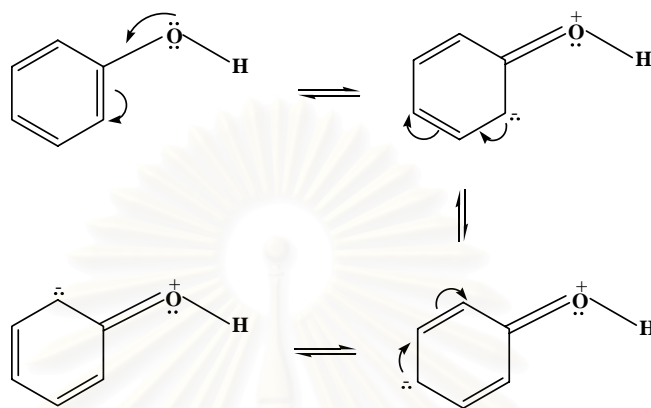
Additionally, the directing effects of the groups correlate with their reactivities. All meta-directing groups are strongly deactivating, and most ortho- and para-directing groups are activating. The halogens are unique in being ortho- and para-directing but weakly deactivating. Moreover, the reactivity and orientation are controlled by an interplay of inductive and resonance effects.

An inductive effect is the withdrawal or donation of electrons through a σ bond due to electronegativity. For instance, halogen, carbonyl, cyano, and nitro groups inductively withdraw electrons through the σ bond linking the substituents to an aromatic ring. Alkyl groups, on the other hand, inductively donate electrons.

A resonance effect is the withdrawal or donation of electrons through a π bond due to the overlap of a p orbital on a substituent with a p orbital on an aromatic ring. Carbonyl, cyano, and nitro substituents, for example, withdraw electrons from the aromatic ring by resonance. As shown by the following resonance structures for benzaldehyde, π electrons flow from the ring to the substituent, leaving a positive charge in the ring. The effect is greatest at the ortho and para positions.



Conversely, halogen, hydroxyl, alkoxy, and amino substituents donate electrons to the aromatic ring by resonance. As shown by the following resonance structures for phenol, π electrons flow from the substituent to the ring, placing a negative charge in the ring. Again, the effect is greatest at the ortho and para positions.

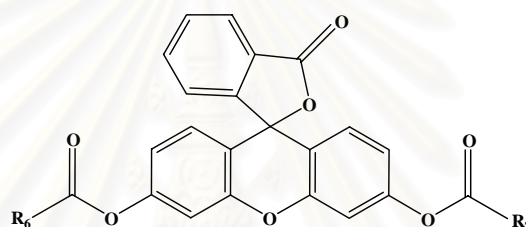
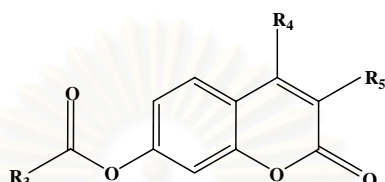
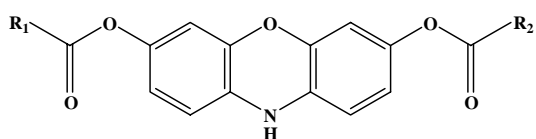


In fact, the inductive effect and resonance effect do not necessarily act in the same direction. Halogen, hydroxyl, alkoxy, and amino substituents, for example, have electron-withdrawing inductive effects because of the electronegativity of the -X, -O, and -N atoms bonded to the aromatic ring but have electron-donating resonance effects because of the lone-pair electrons on those same -X, -O, and -N atoms.

Because the common feature of all deactivating groups is that they withdraw electrons from the ring, thereby destabilizing the carbocation intermediate and causing it to form more slowly. Carbonyl, cyano, and nitro groups are deactivating owing to both electron-withdrawing resonance and inductive effects. Halogens are deactivating because their stronger electron-withdrawing inductive effect outweighs their weaker electron-donating resonance effect. On the other hand, hydroxyl, alkoxy, and amino groups are activating because their stronger electron-donating resonance effect outweighs their weaker electron-withdrawing inductive effect. Alkyl groups are also activating due to their electron-donating inductive effect. Consequently, they stabilize the carbocation intermediate and causing it to form faster. The effect is greatest at the ortho and para positions.

2.10 Literature reviews

Park. *et al.* [54] developed the markers having the general formula:



Wherein R_1 , R_2 , and R_3 which were the same or different, were C_4 - C_{18} alkyl groups.

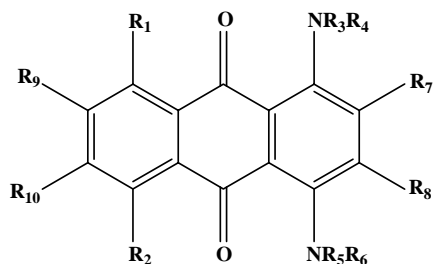
R_4 was a hydrogen atom, methyl group or trifluoromethyl group.

R_5 was a hydrogen atom, halogen atom or cyano group.

R_6 and R_7 , which were the same or different, were C_{19} - C_{24} alkyl groups.

The markers were the ester derivatives of fluorescent materials including resorufin, coumarin, and fluorescein. They were used in petroleum products such as gasoline, liquefied natural gas, diesel fuel, kerosene and heavy oil at 0.01-30 ppm. They could be detected by measuring the fluorescence generated from the selective hydrolysis of an ester moiety under enzymatic action. The dyed petroleum products were added with the aqueous solutions of the appropriate ester-decomposable enzyme. Then the resultant aqueous solution layers were irradiated with light of specific wavelengths. Most lights fluoresced from the aqueous solutions were visible lights. For instance, resorufin, coumarin and fluorescein derivatives released red, blue, and green lights, respectively.

Ho. *et al.* [55] prepared the markers having the general formula:



Wherein R_1 and R_2 were hydrogen, hydroxy, or amino groups.

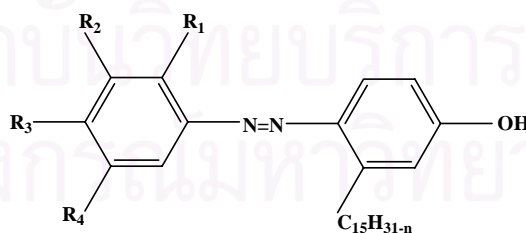
R_3 and R_5 were alkyl, aryl, heteroalkyl or heterocyclic groups.

R_4 and R_6 were hydrogen and alkyl groups.

R_7 , R_8 , R_9 and R_{10} were cyano and nitro or hydrogen groups, provided that at least two of them were cyano or nitro groups.

The substituted anthraquinone marker dyes were added to tag petroleum products such as lubricating oil, gasoline, diesel fuel, kerosene, jet fuel and heating oil. They had absorption maxima in the range from 690 nm to 1000 nm. For example, 1,4,5-tri(4-*n*-butylphenylamino)anthraquinone, obtained from the reaction of 1,4,5-trichloroanthraquinone and 4-*n*-butylaniline, had the maximum absorption band at the wavelength of 675 nm in toluene.

Suwanprasop. *et al.* [4] synthesized the petroleum marker dyes having the general formula:



Wherein R_1 was a hydrogen, chloro, methyl, methoxy, or nitro group.

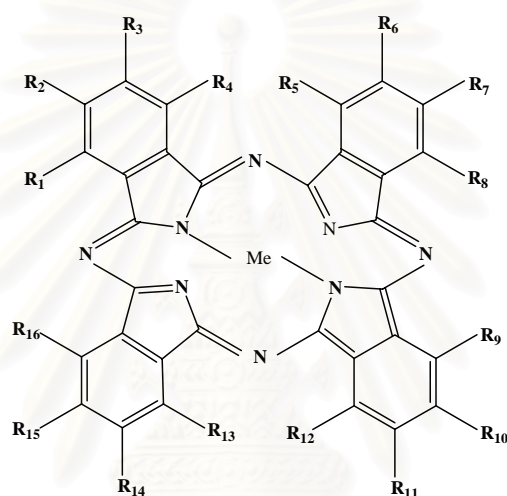
R_2 and R_3 were hydrogen, chloro, methyl, or nitro groups.

R_4 was a hydrogen or nitro group.

$n = 0, 2, 4, 6$

The marker dyes were prepared by the coupling reaction of cardanol with aniline and its derivatives. They were used to tag high-speed diesel fuel and gasoline at the level of 5 ppm. They provided invisible color in the fuel oils while giving visible colors by the extraction with 50 % (v/v) 1,2-diaminoethane in the solution containing ethane-1,2-diol and methanol (1:1, v/v). In addition, the marker dye contents in the fuel oils could be simply quantified with a vis spectrophotometer.

Meyer. *et al.* [56] developed the markers having the general formula:

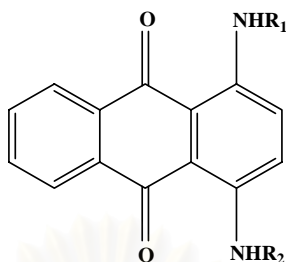


Wherein Me was twice hydrogen, twice lithium, magnesium, zinc, copper, nickel, VO, TiO, AlCl, AlOH, AlOCOCH₃, AlOCOCF₃, SiCl₂ or Si(OH)₂.

At least four of the radicals R₁ to R₁₆ were each independently of the others a five- or six-membered saturated nitrogen-containing heterocyclic radical which was bonded to the phthalocyanine structure via a ring nitrogen atom and which could additionally contain hetero atoms and any remaining radicals R₁ to R₁₆ were each hydrogen, halogen, hydroxysulfonyl or C₁-C₄-dialkylsulfamoyl.

The phthalocyanine markers were used to mark petroleum liquids especially mineral oil. They generally had their absorption maxima within the range from 600 to 1200 nm and fluoresced in the range from 620 to 1200 nm.

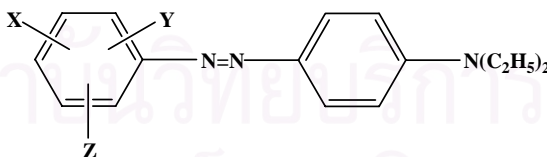
Pauls. *et al.* [57] developed the markers having the general formula:



Wherein R_1 and R_2 , independently from one another, were each hydrogen or C_1 - C_{12} alkyl group where the alkyl group might be interrupted by from 1 to 4 oxygen atoms or substituted with a phenyl or substituted phenyl group.

The markers were employed for tagging various liquid petroleum hydrocarbons such as crude oil, lubricating oil, gasoline, diesel fuel, kerosene, jet fuel and heating oil. They were detected by exposing the marked products to the visible light from a suitable light source having the wavelengths over their characteristic absorption region. They had their maximum absorption at the wavelengths generally from about 500 nm to 700 nm.

Friswell. *et al.* [6] prepared the markers having the general formula:

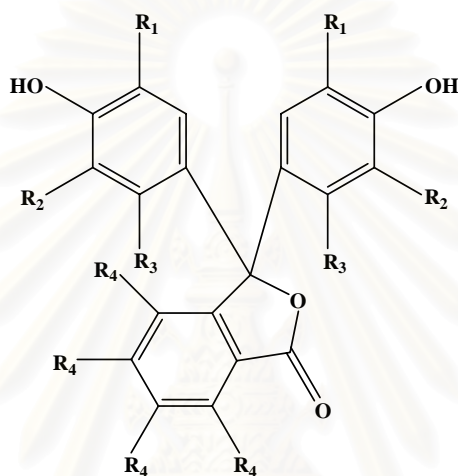


Wherein X and Y were the same or different and selected from hydrogen, halogen, methyl, ethyl, isopropyl, butyl, methoxy, or nitro groups.

Z was a hydrogen or an amino group.

The markers were synthesized by coupling diazotized aniline or substituted anilines with *N,N*-diethylaniline. Each marker could be detected by extracting it from the tagged petroleum with a suitable acidic aqueous solution. Upon the extraction, it underwent a chromophoric reaction, giving an identifiable color.

Smith. *et al.* [12] prepared the petroleum markers having the general formula:



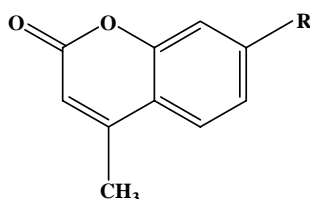
Wherein R₁ was a C₁-C₈ alkyl or alkoxy group.

R₂ and R₃ were hydrogen, alkyl or alkoxy groups.

R₄ was any combination of bromine, chlorine or hydrogen.

The petroleum markers were synthesized by the condensation of phthalic acid or its anhydride with 2-alkylphenol. The presence of each marker in the petroleum product was detected by using an appropriate basic reagent to convert it to an intensely colored dianion. Thymolphthalein in premium gasoline, for example, gave a strong blue color when extracting the marked gasoline with the 10 % solution of tetrabutylammonium hydroxide in ethylene glycol mono-*n*-propyl ether. The marker quantity could be measured by spectrophotometry at the wavelength of its maximum absorbance.

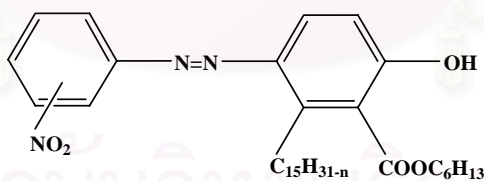
Friswell. *et al.* [1] prepared the silent fluorescent markers having the general formula:



Wherein R was a linear or branched C₁-C₁₈ alkylcarboxy radical.

The markers were synthesized from the esterification between appropriate linear or branched C₁-C₁₈ alkylcarboxylic acids or acid halides and 7-hydroxy-4-methylcoumarin. 7-hydroxy-4-methylcoumarin was attained by the condensation of resorcinol with ethyl acetoacetate employing Amberlyst 15 as catalyst. The markers were used for tagging petroleum products at the levels of 0.25 to 100 ppm. They could be detected in the marked products by the extraction with an alkaline aqueous solution. Fluorescence was obtained when testing the extracts under the ultraviolet light at suitable wavelengths.

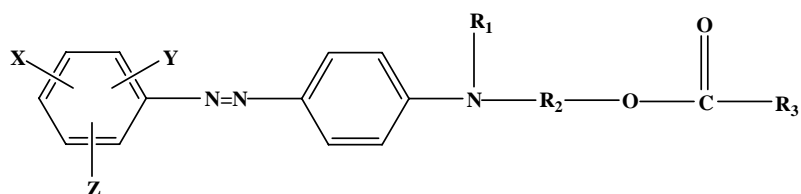
Silapakampeerapab. [58] developed the marker dyes having the general formula:



Wherein n = 0, 2, 4, 6

The marker dyes were prepared by coupling the ester of cashew nut shell extract with nitroanilines. The ester of cashew nut shell extract was obtained from the esterification reaction between cashew nut shell extract and 1-hexanol. The dyes were added to petroleum fuel oils such as gasoline and high-speed diesel at 25 and 15 ppm, respectively. The dye detection was performed by extracting the marked products with the 2 % potassium hydroxide solution in ethylene glycol, giving clearly defined colors in the extracted phases.

Friswell. [59] prepared the petroleum markers having the general formula:



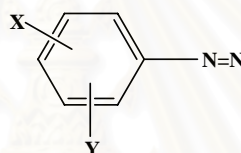
Wherein R₁ was a C₁-C₃ alkyl group.

R₂ was a C₁-C₃ alkylene group.

R₃ was a C₁ or C₂ alkyl group.

X and Y were selected from hydrogen, halogen, methyl, ethyl, and methoxy groups.

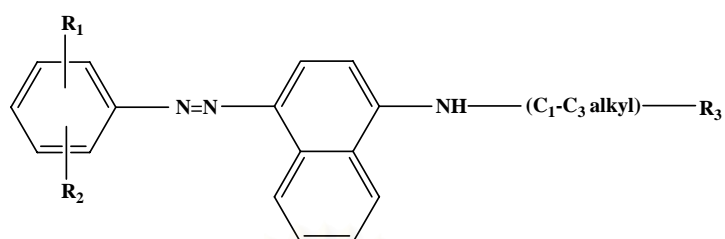
Z was hydrogen or



Wherein X and Y were as defined above.

The markers were prepared in a two-phase system consisting of an acidic aqueous phase and a solvent phase. The resulting markers could be utilized to tag petroleum products at various concentration levels from 0.25 to 100 ppm. The dyed petroleum products were extracted with the strongly acidic solutions of appropriate acids like hydrochloric acid, phosphoric acid, formic acid, acetic acid and propionic acid, giving strong colors in the aqueous extracted phases. During the extraction, the markers underwent the chromophoric reaction with the acids and produced different colors depending on their substituent groups.

Friswell. *et al.* [8] prepared the petroleum markers having the general formula:

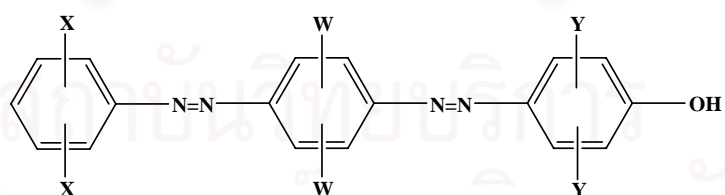


Wherein R_1 and R_2 were selected from hydrogen, halogen, methyl, ethyl, methoxy, cyano, and nitro groups.

R_3 was a methyl, methoxy, or morpholino group.

The markers were synthesized by the azo coupling reaction of substituted anilines to alpha-naphthylamines. Each marker was generally colorless or had a pale yellow color in petroleum products; however it had a rich color in a suitable acidic aqueous solution because it converted to the corresponding amine salt. For instance, in kerosene the marker prepared by coupling the diazonium salt of *o*-anisidine with methoxypropyl-alpha-naphthylamine, produced a magenta extract when extracted with the 10 % hydrochloric acid solution.

Halissy. [11] prepared the petroleum markers having the general formula:



Wherein W s were selected from hydrogen and $O-(C_1-C_3 \text{ alkyl})$ groups, provided that at least one W was an $O-(C_1-C_3 \text{ alkyl})$ group.

X s and Y s were selected from hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fused aryl, substituted fused aryl, alkoxy, halogen, cyano, and nitro groups.

The markers were synthesized by the azo coupling of substituted anilines with phenols such as 2,6-di-sec-butylphenol. They were generally pale red, but they were not readily observable to the naked eyes at the end use levels of 0.25-100 ppm in petroleum products. They could be detected by extracting the tagged petroleum products with alkali aqueous solutions. For example, when the kerosene marked with 2,6-di-sec-butyl-4-(2',5'-dimethoxy-4'-phenylazo)-phenylazophenol (10 ppm) was extracted with the 2.5 % sodium hydroxide solution, a deep blue color was obtained.



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CHAPTER III

EXPERIMENTAL SECTION

3.1 Instrument

The infrared spectra were recorded on a Nicolet (Impact410) FT-IR spectrophotometer. The ^{13}C NMR and ^1H NMR spectra at 400 MHz were obtained with a Varian spectrometer. The mass spectra were recorded on a Micromass Quattro micro mass spectrometer. The vis spectra and the quantities of the markers in diesel fuel and gasoline were measured using a Spectronic 21 (Milton Roy Company). The fluorescence spectra were obtained with a Perkin Elmer LS50 luminescence spectrophotometer. The kinetic viscosities of the dyed and undyed diesel fuels were measured in a Cannon viscometer. The flash points (Pensky-Martens) of the dyed and undyed diesel fuels were measured using an ISL (PMFP93) flash-point analyzer. The pour points of the dyed and undyed diesel fuels were recorded on an ISL (CPP92) pour-point analyzer. The sulfur contents of the dyed and undyed diesel fuels were determined employing an Outokumpu (X-MET820) X-ray diffraction spectrometer. The distillations of the dyed and undyed diesel fuels were performed with a Herzog (MP626) distillation apparatus and the distillations of the dyed and undyed gasoline were measured in an ISL (AD865G) distillation apparatus. The octane numbers of the dyed and undyed gasoline were recorded on a CFR research octane number analyzer. The Reid vapor pressures of the dyed and undyed gasoline were obtained with a Grabner Reid vapor pressure analyzer. The gravities of the marked and unmarked fuel oils were obtained with an Anpontaar density meter. The total acidities of the marked and unmarked fuel oils were evaluated with a Mettler Toledo titrator. Also, the colors of the marked and unmarked fuel oils were observed with a Lovibond (PFX990/P) petrochemical tintometer.

3.2 Materials

Cashew nut shells were attained from the cashew nut factory in Phuket, Thailand. They were extracted with hexane and the extract was evaporated to dryness to yield cashew nut shell liquid. Cardanol was obtained by the reduced pressure distillation of cashew nut shell liquid yielding a yellow liquid. Other reagents for preparing and detecting petroleum markers were purchased from Fluka and Merck chemical companies. Additionally, all solvents were purified prior to use by standard methodology except for those which were reagent grade.

3.3 Petroleum azo markers

3.3.1 Syntheses

3.3.1.1 2-Nitrocardanol

Concentrated sulfuric acid (20.0 ml, 0.36 mole) was added in portions to concentrated nitric acid (18.0 ml, 0.26 mole) while the mixture was vigorously stirred and its temperature was kept at 2 °C. The solution of cardanol (30 g) in methylene chloride (30 ml) was added dropwise into the above mixed acids. The resulting mixture was continually stirred for 1 hr. The methylene chloride layer was washed with cold water and evaporated to dryness. 2-Nitrocardanol was purified by the silica gel column chromatography with the hexane-ethyl acetate eluent. 2-Nitrocardanol was confirmed by the analyses of FT-IR, MS, ¹H and ¹³C NMR spectral data.

3.3.1.2 Diazonium salts

3.3.1.2.1 Aniline diazonium salt

Aniline (0.56 g, 0.006 mole) was added to the mixture of concentrated hydrochloric acid (1.5 ml) and distilled water (1.5 ml). The mixture was vigorously stirred while being cooled to 2 °C and the solution of sodium nitrite (0.41 g, 0.006 mole) in distilled water (10 ml) was added dropwise into the mixture. The resulting solution of aniline diazonium salt was kept at 2 °C before coupling with 2-nitrocardanol.

3.3.1.2.2 4-Methylaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 4-methylaniline (0.64 g, 0.006 mole) instead of aniline. The solution of 4-methylaniline diazonium salt was obtained.

3.3.1.2.3 4-Bromoaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 4-bromoaniline (1.03 g, 0.006 mole) instead of aniline. The solution of 4-bromoaniline diazonium salt was obtained.

3.3.1.2.4 2-Nitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 2-nitroaniline (0.83 g, 0.006 mole) instead of aniline. The solution of 2-nitroaniline diazonium salt was obtained.

3.3.1.2.5 4-Nitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 4-nitroaniline (0.83 g, 0.006 mole) instead of aniline. The solution of 4-nitroaniline diazonium salt was obtained.

3.3.1.2.6 2-Chloro-4-nitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 2-chloro-4-nitroaniline (1.04 g, 0.006 mole) instead of aniline. The solution of 2-chloro-4-nitroaniline diazonium salt was obtained.

3.3.1.2.7 2-Chloro-5-nitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 2-chloro-5-nitroaniline (1.04 g, 0.006 mole) instead of aniline. The solution of 2-chloro-5-nitroaniline diazonium salt was obtained.

3.3.1.2.8 4-Chloro-3-nitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 4-chloro-3-nitroaniline (1.04 g, 0.006 mole) instead of aniline. The solution of 4-chloro-3-nitroaniline diazonium salt was obtained.

3.3.1.2.9 2,4-Dinitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 2,4-dinitroaniline (1.10 g, 0.006 mole) instead of aniline. The solution of 2,4-dinitroaniline diazonium salt was obtained.

3.3.1.2.10 2-Methoxy-4-nitroaniline diazonium salt

The diazotization was performed in the similar manner to the procedure of 3.3.1.2.1 but exercising 2-methoxy-4-nitroaniline (1.09 g, 0.006 mole) instead of aniline. The solution of 2-methoxy-4-nitroaniline diazonium salt was obtained.

3.3.1.3 2-Nitro-5-*n*-alkylphenolate ion

Potassium hydroxide (0.34 g, 0.006 mole) was dissolved in methanol (10 ml) and the solution was cooled to 2 °C. With continuous stirring, 2-nitrocardanol (1.73 g) was added into the solution to give reddish-orange oil.

3.3.1.4 Azo markers

3.3.1.4.1 4-(Phenylazo)-2-nitrocardanol

The solution of the aniline diazonium salt was added dropwise into the 2-nitro-5-*n*-alkylphenolate ion solution. The reaction mixture was left stirring at 2 °C for 30 mins. The marker product was extracted with methylene chloride and the extract was washed with cold water and evaporated to dryness. 4-(Phenylazo)-2-nitrocardanol was purified by the silica gel column chromatography using the hexane-ethyl acetate eluent.

3.3.1.4.2 4-(4-Methylphenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 4-methylaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.3 4-(4-Bromophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 4-bromoaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.4 4-(2-Nitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 2-nitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.5 4-(4-Nitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 4-nitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.6 4-(2-Chloro-4-nitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 2-chloro-4-nitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.7 4-(2-Chloro-5-nitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 2-chloro-5-nitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.8 4-(4-Chloro-3-nitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 4-chloro-3-nitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.9 4-(2,4-Dinitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 2,4-dinitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.1.4.10 4-(2-Methoxy-4-nitrophenylazo)-2-nitrocardanol

The procedure in 3.3.1.4.1 was repeated except that the 2-methoxy-4-nitroaniline diazonium salt was utilized instead of the aniline diazonium salt.

3.3.2 Characterization of azo markers

All azo markers were individually characterized by the spectroscopic techniques, FT-IR, MS, ^1H and ^{13}C NMR.

3.3.3 Preparation of 1000 ppm stock marker solutions

The stock solution of each marker in diesel fuel or gasoline was prepared by dissolving each marker (0.025 g) with diesel fuel or gasoline and making up to 25 ml in a volumetric flask.

3.3.4 Preparation of 5 ppm marked diesel fuel and gasoline

Each 1000 ppm stock marker solution (0.125 ml) was pipetted into a 25 ml volumetric flask and made up to the volume with diesel fuel or gasoline.

3.3.5 Detection of azo markers in diesel fuel

The developing reagent used consisted of benzyltrimethylammonium hydroxide, methanol and 1-hexanol in the ratio of 1: 1.5: 4.5 (v/v/v).

Each marked diesel fuel (5 ml) was pipetted into a 10-ml screw cap vial. Then, the developing reagent (2.8 ml) was added into the vial, capped and shaken for 10 seconds. Each resulting homogeneous mixture was recorded the maximum absorption in the visible region (350-750 nm) using a vis spectrophotometer.

3.3.6 Detection of azo markers in gasoline

The developing reagent utilized consisted of benzyltrimethylammonium hydroxide, methanol and 1-hexanol in the ratio of 1: 1.5: 2 (v/v/v).

Each marked gasoline (5 ml) was pipetted into a 10-ml screw cap vial. Then, the developing reagent (1.8 ml) was added into the vial, capped and shaken for 10 seconds. Each resulting homogeneous mixture was recorded the maximum absorption in the visible region (350-750 nm) using a vis spectrophotometer.

3.3.7 Quantitative determination of azo markers in diesel fuel

The developing reagent used comprised benzyltrimethylammonium hydroxide, methanol and 1-hexanol in the ratio of 1: 1.5: 4.5 (v/v/v). The quantitative determination of the azo markers in diesel fuel could be made by ultraviolet-visible spectroscopic technique using calibration curve method.

3.3.7.1 Calibration curve of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol

The standard calibration curve of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol was plotted at the marker concentrations, 0, 2, 4, and 6 ppm. The diesel fuel marked with 2, 4, and 6 ppm of the marker was prepared by pipetting the 1000 ppm stock solution of the marker 0.05, 0.10, and 0.15 ml into 25 ml volumetric flasks respectively and making up to the volume with diesel fuel.

The dyed diesel fuel (5 ml) of each marker concentration and the developing reagent (2.8 ml) were added into a 10-ml screw cap vial, capped and shaken for 10 seconds. The absorbance at its maximum absorption wavelength was measured. The calibration curve was plotted between the measured absorbance values and the concentrations of the marker.

3.3.7.2 Calibration curve of 4-(2,4-dinitrophenylazo)-2-nitrocardanol

The procedure of 3.3.7.1 was accomplished by using 4-(2,4-dinitro phenylazo)-2-nitrocardanol instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the standard calibration curve was plotted at the marker concentrations, 0, 2, 4, 6, and 8 ppm.

3.3.7.3 Calibration curve of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol

The procedure of 3.3.7.1 was accomplished by using 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the standard calibration curve was plotted at the marker concentrations, 0, 2, 4, 6, and 8 ppm.

3.3.8 Quantitative determination of azo markers in gasoline

The developing reagent used comprised benzyltrimethylammonium hydroxide, methanol and 1-hexanol in the ratio of 1: 1.5: 2 (v/v/v). The quantitative determination of the azo markers in gasoline could be made by ultraviolet-visible spectroscopic technique using calibration curve method.

3.3.8.1 Calibration curve of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol

The standard calibration curve of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol was plotted at the marker concentrations, 0, 2, 4, and 6 ppm. The gasoline marked with 2, 4, and 6 ppm of the marker was prepared by pipetting the 1000 ppm stock solution of the marker 0.05, 0.10, and 0.15 ml into 25 ml volumetric flasks respectively and making up to the volume with gasoline.

The dyed gasoline (5 ml) of each marker concentration and the developing reagent (1.8 ml) were added into a 10-ml screw cap vial, capped and shaken for 10 seconds. The absorbance at its maximum absorption wavelength was measured. The calibration curve was plotted between the measured absorbance values and the concentrations of the marker.

3.3.8.2 Calibration curve of 4-(2,4-dinitrophenylazo)-2-nitrocardanol

The procedure of 3.3.8.1 was accomplished by employing 4-(2,4-dinitrophenylazo)-2-nitrocardanol instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the standard calibration curve was plotted at the marker concentrations, 0, 2, 4, 6, and 8 ppm.

3.3.8.3 Calibration curve of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol

The procedure of 3.3.8.1 was accomplished by employing 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the standard calibration curve was plotted at the marker concentrations, 0, 2, 4, 6, and 8 ppm.

3.3.9 Effect of azo markers on the general physical properties of diesel fuel

The study of the effect of the azo markers on the general physical properties of the dyed diesel fuel was conducted employing 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (5 ppm) as a marker model. The general physical properties of the undyed and dyed diesel fuels were determined according to the ASTM testing methods in Table 3.1.

Table 3.1 ASTM testing methods of unmarked and marked diesel fuels

Physical property	Test method (ASTM)
API gravity at 60 °F	D 4052
Specific gravity at 15.6/15.6 °C	D 4052
Calculated cetane index	D 976
Kinematic viscosity at 40 °C (mm ² /s)	D 445
Pour point (°C)	D 97
Flash point (°C)	D 93
Sulfur content % (w/w)	D 4294
Copper strip corrosion (3 hrs, 50 °C)	D 130
Distillation	D 86
Total acid number (mg of KOH/g)	D 664
Color	D 1500

3.3.10 Effect of azo markers on the general physical properties of gasoline

The study of the effect of the azo markers on the general physical properties of the dyed gasoline was conducted employing 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (5 ppm) as a marker model. The general physical properties of the undyed and dyed gasoline were determined according to the ASTM testing methods in Table 3.2.

Table 3.2 ASTM testing methods of unmarked and marked gasoline

Physical property	Test method (ASTM)
API gravity at 60 °F	D 4052
Specific gravity at 15.6/15.6 °C	D 4052
Research octane number	D 2699
Reid vapor pressure at 37.8 °C (kPa)	D 5159
Copper strip corrosion (3 hrs, 50 °C)	D 130
Distillation	D 86
Total acid number (mg of KOH/g)	D 664
Color	D 1500

3.3.11 Stability of azo markers in diesel fuel

4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol, 4-(2,4-dinitrophenylazo)-2-nitrocardanol, and 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol were used as marker models at 5 ppm. The developing reagent utilized consisted of benzyltrimethylammonium hydroxide, methanol and 1-hexanol in the ratio of 1: 1.5: 4.5 (v/v/v).

3.3.11.1 4-(2-Chloro-4-nitrophenylazo)-2-nitrocardanol

The quantity of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol was determined monthly for 3 months by the following procedure. The dyed diesel fuel (5 ml) and the developing reagent (2.8 ml) were added to a 10 ml screw cap vial, capped, and shaken for 10 seconds. The obtained mixture was measured the vis absorption at its maximum wavelength. The determination of the marker quantity in the fuel oil was performed by comparing its absorbance with the calibration curve from 3.3.7.1.

3.3.11.2 4-(2,4-Dinitrophenylazo)-2-nitrocardanol

The procedure of 3.3.11.1 was conducted except that 4-(2,4-dinitrophenylazo)-2-nitrocardanol was used instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the calibration curve from 3.3.7.2 was applied.

3.3.11.3 4-(2-Methoxy-4-nitrophenylazo)-2-nitrocardanol

The procedure of 3.3.11.1 was conducted except that 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol was used instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the calibration curve from 3.3.7.3 was applied.

3.3.12 Stability of azo markers in gasoline

4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol, 4-(2,4-dinitrophenylazo)-2-nitrocardanol, and 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol were used as marker models at 5 ppm. The developing reagent utilized consisted of benzyltrimethylammonium hydroxide, methanol and 1-hexanol in the ratio of 1: 1.5: 2 (v/v/v).

3.3.12.1 4-(2-Chloro-4-nitrophenylazo)-2-nitrocardanol

The quantity of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol was determined monthly for 3 months by the following procedure. The dyed gasoline (5 ml) and the developing reagent (1.8 ml) were added to a 10 ml screw cap vial, capped, and shaken for 10 seconds. The obtained mixture was measured the vis absorption at its maximum wavelength. The determination of the marker quantity in the fuel oil was performed by comparing its absorbance with the calibration curve from 3.3.8.1.

3.3.12.2 4-(2,4-Dinitrophenylazo)-2-nitrocardanol

The procedure of 3.3.12.1 was carried out except that 4-(2,4-dinitrophenylazo)-2-nitrocardanol was used instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the calibration curve from 3.3.8.2 was applied.

3.3.12.3 4-(2-Methoxy-4-nitrophenylazo)-2-nitrocardanol

The procedure of 3.3.12.1 was carried out except that 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol was used instead of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol and the calibration curve from 3.3.8.3 was applied.

3.4 Petroleum fluorescent marker

3.4.1 Synthesis of fluorescent marker

The fluorescent marker, 7-alkyl-4-methylcoumarin was prepared by the following procedure. The mixture of cardanol (21 g), ethyl acetoacetate (18.3 g, 0.14 mole), concentrated sulfuric acid (3 ml) and toluene (25 ml) was heated under reflux for 6 hrs. Then, the reaction mixture was cooled, washed with cold water and stripped from toluene. 7-Alkyl-4-methylcoumarin was purified by the silica gel column chromatography using hexane-ethyl acetate as eluent.

3.4.2 Characterization of fluorescent marker

The fluorescent marker was confirmed by the analyses of FT-IR, MS, ^1H and ^{13}C NMR spectral data.

3.4.3 Preparation of 1000 ppm stock marker solution

The stock solution of the fluorescent marker in diesel fuel or gasoline was prepared by dissolving the marker (0.025 g) with diesel fuel or gasoline and making up to 25 ml in a volumetric flask.

3.4.4 Preparation of 100 ppm marked diesel fuel and gasoline

Each 1000 ppm stock marker solution (2.5 ml) was pipetted into a 25 ml volumetric flask and made up to the volume with diesel fuel or gasoline.

3.4.5 Detection of fluorescent marker in diesel fuel

The diesel fuel marked with the fluorescent marker (100 ppm) was subjected to the ultraviolet radiation at the wavelength of 267 nm to record the emitted fluorescence spectrum with a spectrofluorometer. The measuring parameters were set as the followings:

1. The wavelength of the excitation monochromator was set at 267 nm.
2. The spectrum bandwidth of the excitation monochromator was set at 10.
3. The spectrum bandwidth of the emission monochromator was set at 10.

3.4.6 Detection of fluorescent marker in gasoline

The gasoline marked with the fluorescent marker (100 ppm) was subjected to the ultraviolet radiation at the wavelength of 300 nm to record the emitted fluorescence spectrum with a spectrofluorometer. The measuring parameters were set as the followings:

1. The wavelength of the excitation monochromator was set at 300 nm.
2. The spectrum bandwidth of the excitation monochromator was set at 10.
3. The spectrum bandwidth of the emission monochromator was set at 10.

3.4.7 Quantitative determination of fluorescent marker in diesel fuel

The quantitative determination of the fluorescent marker in diesel fuel could be made by fluorescence spectroscopic technique using calibration curve method. The standard calibration curve of the fluorescent marker was plotted at the marker concentrations, 0, 40, 80, 120, and 160 ppm. The diesel fuel marked with 40, 80, 120, and 160 ppm of the marker was prepared by pipetting the 1000 ppm stock solution of the marker 1, 2, 3, and 4 ml into 25 ml volumetric flasks respectively and making up to the volume with diesel fuel.

The dyed diesel fuel of each marker concentration was measured the intensity of the fluorescence peak occurring at the wavelength of 312 nm. The calibration curve was plotted between the intensity values and the concentrations of the marker.

3.4.8 Quantitative determination of fluorescent marker in gasoline

The quantitative determination of the fluorescent marker in gasoline could be made by fluorescence spectroscopic technique using calibration curve method. The standard calibration curve of the fluorescent marker was plotted at the marker concentrations, 0, 40, 80, 120, and 160 ppm. The gasoline marked with 40, 80, 120, and 160 ppm of the marker was prepared by pipetting the 1000 ppm stock solution of the marker 1, 2, 3, and 4 ml into 25 ml volumetric flasks respectively and making up to the volume with gasoline.

The dyed gasoline of each marker concentration was measured the intensity of the fluorescence band occurring at the wavelength of 333 nm. The calibration curve was plotted between the intensity values and the concentrations of the marker.

3.4.9 Effect of fluorescent marker on the general physical properties of diesel fuel

The diesel fuel containing the fluorescent marker (100 ppm) was employed to study the effect of the marker on the general physical properties of the dyed fuel. The general physical properties of the undyed and dyed diesel fuels were determined according to the ASTM testing methods in Table 3.3.

Table 3.3 ASTM testing methods of unmarked and marked diesel fuels

Physical property	Test method (ASTM)
API gravity at 60 °F	D 4052
Specific gravity at 15.6/15.6 °C	D 4052
Calculated cetane index	D 976
Kinematic viscosity at 40 °C (mm ² /s)	D 445
Pour point (°C)	D 97
Flash point (°C)	D 93
Sulfur content % (w/w)	D 4294
Copper strip corrosion (3 hrs, 50 °C)	D 130
Distillation	D 86
Total acid number (mg of KOH/g)	D 664
Color	D 1500

3.4.10 Effect of fluorescent marker on the general physical properties of gasoline

The gasoline containing the fluorescent marker (100 ppm) was employed to study the effect of the marker on the general physical properties of the dyed fuel. The general physical properties of the undyed and dyed gasoline were determined according to the ASTM testing methods in Table 3.4.

Table 3.4 ASTM testing methods of unmarked and marked gasoline

Physical property	Test method (ASTM)
API gravity at 60 °F	D 4052
Specific gravity at 15.6/15.6 °C	D 4052
Research octane number	D 2699
Reid vapor pressure at 37.8 °C (kPa)	D 5159
Copper strip corrosion (3 hrs, 50 °C)	D 130
Distillation	D 86
Total acid number (mg of KOH/g)	D 664
Color	D 1500

3.4.11 Stability of fluorescent marker in diesel fuel

The quantity of the fluorescent marker in diesel fuel was determined monthly for 3 months by fluorescence spectroscopic technique using calibration curve method. The dyed diesel fuel was measured the intensity of the fluorescence peak appearing at the wavelength of 312 nm. The marker quantity in the fuel oil was assessed by comparing the emission intensity with the calibration curve from 3.4.7.

3.4.12 Stability of fluorescent marker in gasoline

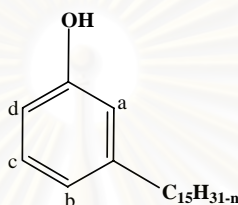
The quantity of the fluorescent marker in gasoline was determined monthly for 3 months by fluorescence spectroscopic technique using calibration curve method. The dyed gasoline was measured the intensity of the fluorescence band appearing at the wavelength of 333 nm. The marker quantity in the fuel oil was assessed by comparing the emission intensity with the calibration curve from 3.4.8.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Cardanol

Cardanol was obtained as a yellow liquid from the reduced pressure distillation of cashew nut shell liquid. The structure and characterization data of cardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of cardanol (Fig. 4.1) showed the absorption peaks at 3354 cm^{-1} (O-H stretching of phenol), 3003 cm^{-1} (=C-H stretching of aromatic), 2925 cm^{-1} and 2852 cm^{-1} (C-H stretching of aliphatic), 1593 cm^{-1} and 1454 cm^{-1} (C=C ring stretching of aromatic), 1348 cm^{-1} (O-H bending of phenol), and 1258 cm^{-1} (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) of cardanol (Fig. 4.2) revealed the signals of the aromatic protons at the positions a, b, c, and d at δ_H 6.70 (*s*), 6.78 (*d*, 7.8 Hz), 7.15 (*t*, 7.8 Hz), and 6.66 (*d*, 7.8 Hz), respectively. The spectrum also demonstrated the signals of the alkyl protons in the side chains at δ_H 5.87 (*m*, $\text{CH}=\text{CH}_2$), 5.43 (*m*, olefinic proton), 5.05 (*m*, $\text{CH}=\text{CH}_2$), 2.85 (*m*, $=\text{CHCH}_2\text{CH}=\text{}$), 2.58 (*t*, 7.8 Hz, ArCH_2), 2.07 (*m*, $=\text{CHCH}_2$), 1.61 (*m*, CH_2), 1.34 (*m*, CH_2), and 0.93 (*m*, CH_3).

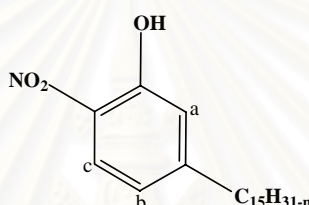
The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of cardanol (Fig. 4.3) exhibited the presence of the oxycarbon in the aromatic ring (C-OH) at δ_C 155.4, the methylene and methyl groups at δ_C 13.8-36.0 and the double bonds in the aromatic ring and side chains at δ_C 112.5-144.9.

The mass spectrum of cardanol (Fig. 4.4) showed the molecular ion peak $[M+H]^+$ at $m/z = 299$.

4.2 Petroleum azo markers

4.2.1 Preparation of 2-nitrocardanol

The starting material of the preparation of 2-nitrocardanol was the naturally occurring substrate, cardanol. Cardanol could be converted to 2-nitrocardanol by the nitration with the mixed acids of concentrated nitric acid and sulfuric acid. 2-Nitrocardanol 80 % (w/w) was obtained as a greenish yellow liquid. The structure and characterization data of 2-nitrocardanol are presented below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 2-nitrocardanol (Fig. 4.5) showed the absorption peaks at 3215 cm^{-1} (O-H stretching of phenol), 3007 cm^{-1} (=C-H stretching of aromatic), 2917 cm^{-1} and 2852 cm^{-1} (C-H stretching of aliphatic), 1622 cm^{-1} and 1479 cm^{-1} (C=C ring stretching of aromatic), 1536 cm^{-1} (N=O asymmetric stretching of NO₂ group), 1332 cm^{-1} (N=O symmetric stretching of NO₂ group), 1270 cm^{-1} (C-O stretching of phenol), and 874 cm^{-1} (C-N stretching vibration of C-N bond).

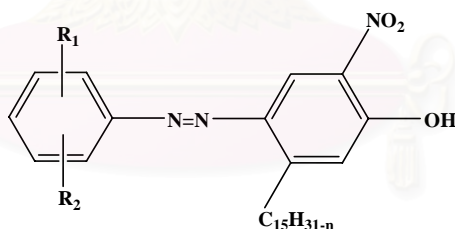
The ¹H-NMR spectrum (CDCl₃) of 2-nitrocardanol (Fig. 4.6) indicated the signals of the aromatic protons at the positions a, b, and c at δ_H 6.93 (*s*), 6.78 (*d*, 8.6 Hz), and 7.98 (*d*, 8.6 Hz). The spectrum also showed the signals of the hydroxyl proton at δ_H 10.63 and alkyl protons in the side chains at δ_H 5.83 (*m*, CH=CH₂), 5.39 (*m*, olefinic proton), 5.01 (*m*, CH=CH₂), 2.81 (*m*, =CHCH₂CH=), 2.54 (*t*, 7.8 Hz, ArCH₂), 2.03 (*m*, =CHCH₂), 1.57 (*m*, CH₂), 1.30 (*m*, CH₂), and 0.89 (*m*, CH₃).

The ^{13}C -NMR spectrum (CDCl_3) of 2-nitrocardanol (Fig. 4.7) exhibited the presence of the oxycarbon in the aromatic ring (C-OH) at δ_C 155.4, the methylene and methyl groups at δ_C 14.1-36.0 and the double bonds in the aromatic ring and side chains at δ_C 114.7-136.8. The spectrum also showed the signal of the aromatic carbon adjacent to the nitro group at 155.2 ppm.

The mass spectrum of 2-nitrocardanol (Fig. 4.8) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 344$ and 346 .

4.2.2 Preparation of azo markers

The azo markers **1-10** were successfully synthesized by coupling 2-nitro-5-*n*-alkylphenolate ion, derived from 2-nitrocardanol, with aniline and its derivatives in the alkali solution. The azo markers bearing various substituents both electron donating groups and electron withdrawing groups were obtained in the yields of 66-82 % (w/w). The general chemical structure of the azo markers is illustrated below. All synthetic markers were miscible with diesel fuel and gasoline and regarded as silent markers that provide no visual indication to interfere the intrinsic colors of the fuel oils.

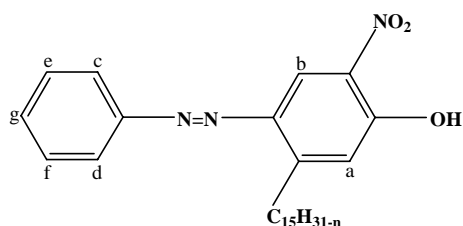


Where R₁ and R₂ are each hydrogen, methyl, bromo, nitro, chloro, or methoxy group.

$$n = 0, 2, 4, 6$$

4.2.2.1 4-(Phenylazo)-2-nitrocardanol

Aniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(phenylazo)-2-nitrocardanol (**1**) 73 % (w/w) which was orange brown. The structure and characterization data of 4-(phenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(phenylazo)-2-nitrocardanol (Fig. 4.9) showed the absorption peaks at 3207 cm^{-1} (O-H stretching of phenol), 3064 cm^{-1} (=C-H stretching of aromatic), 2929 cm^{-1} and 2852 cm^{-1} (C-H stretching of aliphatic), 1622 cm^{-1} and 1475 cm^{-1} (C=C ring stretching of aromatic), 1530 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1307 cm^{-1} (N=O symmetric stretching of NO_2 group), 1274 cm^{-1} (C-O stretching of phenol), and 909 cm^{-1} (C-N stretching vibration of C-N bond).

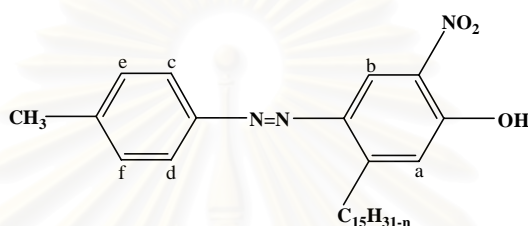
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(phenylazo)-2-nitrocardanol (Fig. 4.10) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.14 (s) and 8.47 (s) , respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at $\delta_H 10.72$. In addition, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at $\delta_H 5.83\text{ (m, CH=CH}_2\text{)}$, $5.39\text{ (m, olefinic proton)}$, $5.01\text{ (m, CH=CH}_2\text{)}$, $3.16\text{ (t, 7.8 Hz, ArCH}_2\text{)}$, $2.79\text{ (m, =CHCH}_2\text{CH=)}$, $2.01\text{ (m, =CHCH}_2\text{)}$, $1.70\text{ (m, CH}_2\text{)}$, $1.32\text{ (m, CH}_2\text{)}$, and $0.88\text{ (m, CH}_3\text{)}$. The spectrum also demonstrated the existence of the benzene ring in the marker at $\delta_H 7.91\text{ (2H, d, 7.0 Hz, positions c and d)}$, $7.54\text{ (2H, t, 7.0 Hz, positions e and f)}$, and $7.49\text{ (t, 7.0 Hz, position g)}$.

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(phenylazo)-2-nitrocardanol (Fig. 4.11) showed the signals of the double bonds in the aromatic rings and side chains at $\delta_C 111.7\text{-}153.8$. The spectrum also revealed the presence of the methylene and methyl groups at $\delta_C 13.8\text{-}36.0$ and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at $\delta_C 156.0$.

The mass spectrum of 4-(phenylazo)-2-nitrocardanol (Fig. 4.12) showed the molecular ion peaks $[M+H]^+$ at $m/z = 448, 450, 452,$ and 454 .

4.2.2.2 4-(4-Methylphenylazo)-2-nitrocardanol

4-Methylaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(4-methylphenylazo)-2-nitrocardanol (**2**) 66 % (w/w) which was reddish brown. The structure and characterization data of 4-(4-methylphenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(4-methylphenylazo)-2-nitrocardanol (Fig. 4.13) revealed the absorption peaks at 3207 cm^{-1} (O-H stretching of phenol), 3072 cm^{-1} (=C-H stretching of aromatic), 2921 cm^{-1} and 2844 cm^{-1} (C-H stretching of aliphatic), 1626 cm^{-1} and 1471 cm^{-1} (C=C ring stretching of aromatic), 1532 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1328 cm^{-1} (N=O symmetric stretching of NO_2 group), 1270 cm^{-1} (C-O stretching of phenol), and 907 cm^{-1} (C-N stretching vibration of C-N bond).

The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(4-methylphenylazo)-2-nitrocardanol (Fig. 4.14) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.04 (s) and 8.38 (s) , respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at $\delta_H 10.64$. In addition, the signals of the alkyl protons adjacent to the aromatic ring of the coupled 2-nitrocardanol were observed at $\delta_H 5.73\text{ (m, CH=CH}_2)$, $5.26\text{ (m, olefinic proton)}$, $4.94\text{ (m, CH=CH}_2)$, $3.07\text{ (t, 7.8 Hz, ArCH}_2)$, $2.73\text{ (m, =CHCH}_2\text{CH=)}$, $1.92\text{ (m, =CHCH}_2)$, $1.62\text{ (m, CH}_2)$, $1.20\text{ (m, CH}_2)$, and $0.78\text{ (m, CH}_3)$. The spectrum also demonstrated the existence of the para-substituted azo benzene ring in the marker at $\delta_H 7.75\text{ (2H, d, 7.8 Hz, positions c and d)}$, and $7.26\text{ (2H, d, 7.8 Hz, positions e and f)}$.

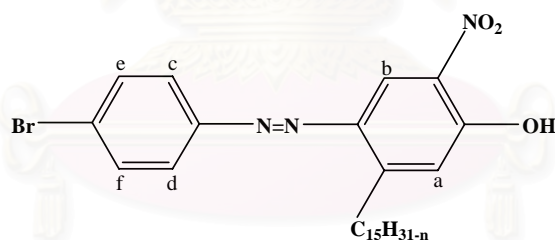
Furthermore, the methyl moiety on the aromatic ring resonanced characteristically at δ_H 2.38.

The ^{13}C -NMR spectrum (CDCl_3) of 4-(4-methylphenylazo)-2-nitrocardanol (Fig. 4.15) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 111.6-155.1. The spectrum also revealed the presence of the methylene and methyl groups at δ_C 14.1-36.0 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_C 155.8.

The mass spectrum of 4-(4-methylphenylazo)-2-nitrocardanol (Fig. 4.16) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 462, 464, 466, \text{ and } 468$.

4.2.2.3 4-(4-Bromophenylazo)-2-nitrocardanol

4-Bromoaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(4-bromophenylazo)-2-nitrocardanol (**3**) 80 % (w/w) which was reddish brown. The structure and characterization data of 4-(4-bromophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(4-bromophenylazo)-2-nitrocardanol (Fig. 4.17) showed the absorption peaks at 3213 cm^{-1} (O-H stretching of phenol), 3009 cm^{-1} (=C-H stretching of aromatic), 2922 cm^{-1} and 2848 cm^{-1} (C-H stretching of aliphatic), 1622 cm^{-1} and 1474 cm^{-1} (C=C ring stretching of aromatic), 1526 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1300 cm^{-1} (N=O symmetric stretching of NO_2 group), 1274 cm^{-1} (C-O stretching of phenol), 1066 cm^{-1} (C-Br stretching vibration of C-Br bond), and 907 cm^{-1} (C-N stretching vibration of C-N bond).

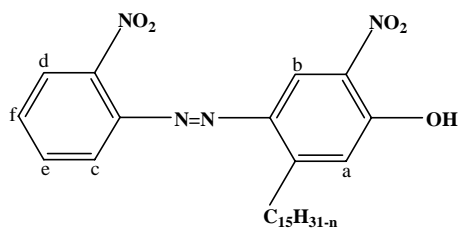
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(4-bromophenylazo)-2-nitrocardanol (Fig. 4.18) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.18 (s) and 8.51 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.78. Additionally, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.86 (m, $\text{CH}=\text{CH}_2$), 5.43 (m, olefinic proton), 5.07 (m, $\text{CH}=\text{CH}_2$), 3.19 (t, 7.8 Hz, ArCH_2), 2.84 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 2.05 (m, $=\text{CHCH}_2$), 1.76 (m, CH_2), 1.40 (m, CH_2), and 0.93 (m, CH_3). The spectrum also demonstrated the existence of the para-substituted azo benzene ring in the marker at δ_H 7.71 (2H, d, 8.6 Hz, positions c and d), and 7.82 (2H, d, 8.6 Hz, positions e and f).

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(4-bromophenylazo)-2-nitrocardanol (Fig. 4.19) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 111.8-153.9. The spectrum also revealed the presence of the methylene and methyl groups at δ_C 14.1-32.6 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_C 156.2.

The mass spectrum of 4-(4-bromophenylazo)-2-nitrocardanol (Fig. 4.20) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 527, 529, 531, \text{ and } 533$.

4.2.2.4 4-(2-Nitrophenylazo)-2-nitrocardanol

2-Nitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(2-nitrophenylazo)-2-nitrocardanol (**4**) 70 % (w/w) which was reddish brown. The structure and characterization data of 4-(2-nitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(2-nitrophenylazo)-2-nitrocardanol (Fig. 4.21) showed the absorption peaks at 3213 cm^{-1} (O-H stretching of phenol), 3000 cm^{-1} (=C-H stretching of aromatic), 2922 cm^{-1} and 2848 cm^{-1} (C-H stretching of aliphatic), 1617 cm^{-1} and 1474 cm^{-1} (C=C ring stretching of aromatic), 1530 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1322 cm^{-1} (N=O symmetric stretching of NO_2 group), 1274 cm^{-1} (C-O stretching of phenol), and 913 cm^{-1} (C-N stretching vibration of C-N bond).

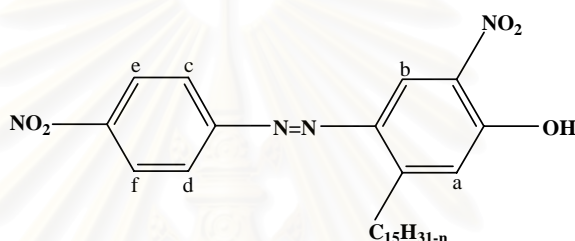
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(2-nitrophenylazo)-2-nitrocardanol (Fig. 4.22) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.08 (s) and 8.37 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.73. Moreover, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.72 (m, $\text{CH}=\text{CH}_2$), 5.29 (m, olefinic proton), 4.92 (m, $\text{CH}=\text{CH}_2$), 3.05 (t, 7.8 Hz, ArCH_2), 2.69 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 1.89 (m, $=\text{CHCH}_2$), 1.61 (m, CH_2), 1.23 (m, CH_2), and 0.81 (m, CH_3). The spectrum also demonstrated the existence of the ortho-substituted azo benzene ring in the marker at δ_H 7.63 (d, 7.8 Hz, position c), 7.86 (d, 7.8 Hz, position d), and 7.55 (2H, m, positions e and f).

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(2-nitrophenylazo)-2-nitrocardanol (Fig. 4.23) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 112.7-155.1. The spectrum also revealed the presence of the methylene and methyl groups at δ_C 14.1-36.0 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_C 156.8.

The mass spectrum of 4-(2-nitrophenylazo)-2-nitrocardanol (Fig. 4.24) showed the molecular ion peak $[M+H]^+$ at $m/z = 495$.

4.2.2.5 4-(4-Nitrophenylazo)-2-nitrocardanol

4-Nitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(4-nitrophenylazo)-2-nitrocardanol (**5**) 82 % (w/w) which was reddish brown. The structure and characterization data of 4-(4-nitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(4-nitrophenylazo)-2-nitrocardanol (Fig. 4.25) showed the absorption peaks at 3235 cm^{-1} (O-H stretching of phenol), 3004 cm^{-1} (=C-H stretching of aromatic), 2922 cm^{-1} and 2852 cm^{-1} (C-H stretching of aliphatic), 1617 cm^{-1} and 1470 cm^{-1} (C=C ring stretching of aromatic), 1526 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1339 cm^{-1} (N=O symmetric stretching of NO_2 group), 1304 cm^{-1} (C-O stretching of phenol), and 865 cm^{-1} (C-N stretching vibration of C-N bond).

The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(4-nitrophenylazo)-2-nitrocardanol (Fig. 4.26) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.17 (s) and 8.53 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.78. Furthermore, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.79 (m, $\text{CH}=\text{CH}_2$), 5.36 (m, olefinic proton), 4.99 (m, $\text{CH}=\text{CH}_2$), 3.18 (t, 7.8 Hz, ArCH_2), 2.76 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 1.99 (m, $=\text{CHCH}_2$), 1.71 (m, CH_2), 1.33 (m, CH_2), and 0.87 (m, CH_3). The spectrum also demonstrated the

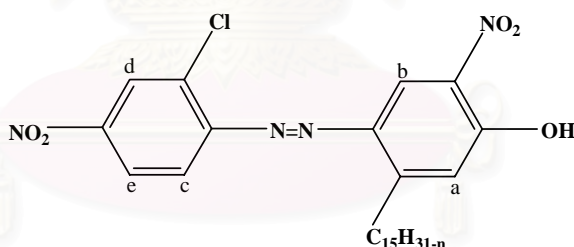
existence of the para-substituted azo benzene ring in the marker at δ_H 8.02 (2H, *d*, 9.4 Hz, positions c and d), and 8.40 (2H, *d*, 9.4 Hz, positions e and f).

The ^{13}C -NMR spectrum (CDCl_3) of 4-(4-nitrophenylazo)-2-nitrocardanol (Fig. 4.27) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 112.0-156.1. The spectrum also revealed the presence of the methylene and methyl groups at δ_C 13.7-32.6 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_C 157.2.

The mass spectrum of 4-(4-nitrophenylazo)-2-nitrocardanol (Fig. 4.28) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 493, 495, 497,$ and 499 .

4.2.2.6 4-(2-Chloro-4-nitrophenylazo)-2-nitrocardanol

2-Chloro-4-nitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (**6**) 78 % (w/w) which was reddish brown. The structure and characterization data of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (Fig. 4.29) showed the absorption peaks at 3225 cm^{-1} (O-H stretching of phenol), 3005 cm^{-1} (=C-H stretching of aromatic), 2925 cm^{-1} and 2849 cm^{-1} (C-H stretching of aliphatic), 1623 cm^{-1} and 1471 cm^{-1} (C=C ring stretching of aromatic), 1527 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1339 cm^{-1} (N=O symmetric stretching of NO_2 group), 1303 cm^{-1} (C-O stretching of phenol), 1047 cm^{-1} (C-Cl stretching vibration of C-Cl bond), and 892 cm^{-1} (C-N stretching vibration of C-N bond).

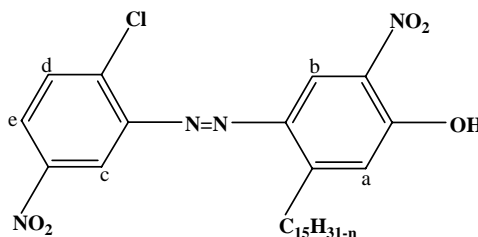
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (Fig. 4.30) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.19 (s) and 8.47 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.80. In addition, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.81 (m, $\text{CH}=\text{CH}_2$), 5.36 (m, olefinic proton), 5.00 (m, $\text{CH}=\text{CH}_2$), 3.19 (t, 7.8 Hz, ArCH_2), 2.76 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 2.01 (m, $=\text{CHCH}_2$), 1.69 (m, CH_2), 1.33 (m, CH_2), and 0.86 (m, CH_3). The spectrum also demonstrated the existence of the benzene ring in the marker at δ_H 7.70 (d, 8.6 Hz, position c), 8.56 (s, position d), and 8.22 (d, 8.6 Hz, position e).

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(2-nitro-4-chlorophenylazo)-2-nitrocardanol (Fig. 4.31) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 112.9-154.8. The spectrum also revealed the presence of the methylene and methyl groups at δ_C 13.7-32.0 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_C 157.2.

The mass spectrum of 4-(2-nitro-4-chlorophenylazo)-2-nitrocardanol (Fig. 4.32) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 527.5$, 529.5, 531.5, and 533.5.

4.2.2.7 4-(2-Chloro-5-nitrophenylazo)-2-nitrocardanol

2-Chloro-5-nitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol (**7**) 75 % (w/w) which was reddish brown. The structure and characterization data of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol (Fig. 4.33) revealed the absorption peaks at 3223 cm^{-1} (O-H stretching of phenol), 2996 cm^{-1} (=C-H stretching of aromatic), 2924 cm^{-1} and 2853 cm^{-1} (C-H stretching of aliphatic), 1621 cm^{-1} and 1470 cm^{-1} (C=C ring stretching of aromatic), 1526 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1347 cm^{-1} (N=O symmetric stretching of NO_2 group), 1299 cm^{-1} (C-O stretching of phenol), 1060 cm^{-1} (C-Cl stretching vibration of C-Cl bond), and 912 (C-N stretching vibration of C-N bond).

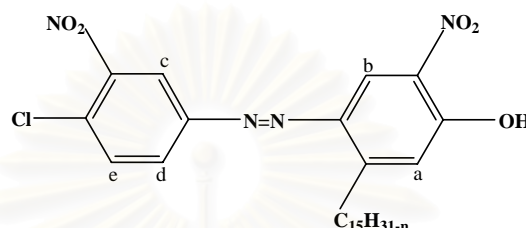
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol (Fig. 4.34) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.17 (s) and 8.44 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.80 . Indeed, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.80 (m, $\text{CH}=\text{CH}_2$), 5.34 (m, olefinic proton), 5.00 (m, $\text{CH}=\text{CH}_2$), 3.20 (t, 7.8 Hz , ArCH_2), 2.75 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 1.97 (m, $=\text{CHCH}_2$), 1.72 (m, CH_2), 1.35 (m, CH_2), and 0.86 (m, CH_3). The spectrum also demonstrated the existence of the benzene ring in the marker at δ_H 8.55 (s, position c), 7.77 (d, 8.6 Hz , position d), and 8.27 (d, 8.6 Hz , position e).

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol (Fig. 4.35) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 112.7 - 154.8 . The spectrum also revealed the presence of the methylene and methyl groups at δ_C 11.4 - 34.2 and the oxycarbon in the couple 2-nitrocardanol (C-OH) at δ_C 157.1 .

The mass spectrum of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol (Fig. 4.36) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 527.5$, 529.5 , 531.5 , and 533.5 .

4.2.2.8 4-(4-Chloro-3-nitrophenylazo)-2-nitrocardanol

4-Chloro-3-nitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol (**8**) 77 % (w/w) which was reddish brown. The structure and characterization data of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol (Fig. 4.37) revealed the absorption peaks at 3230 cm^{-1} (O-H stretching of phenol), 3013 cm^{-1} (=C-H stretching of aromatic), 2921 cm^{-1} and 2852 cm^{-1} (C-H stretching of aliphatic), 1617 cm^{-1} and 1470 cm^{-1} (C=C ring stretching of aromatic), 1535 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1352 cm^{-1} (N=O symmetric stretching of NO_2 group), 1304 cm^{-1} (C-O stretching of phenol), 1048 cm^{-1} (C-Cl stretching vibration of C-Cl bond), and 913 cm^{-1} (C-N stretching vibration of C-N bond).

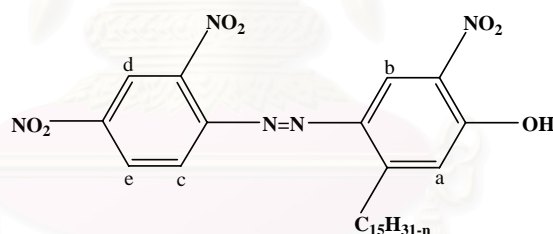
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol (Fig. 4.38) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.16 (s) and 8.36 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.77. In addition, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.81 (m, $\text{CH}=\text{CH}_2$), 5.34 (m, olefinic proton), 4.99 (m, $\text{CH}=\text{CH}_2$), 3.16 (t, 7.8 Hz, ArCH_2), 2.77 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 1.98 (m, $=\text{CHCH}_2$), 1.68 (m, CH_2), 1.31 (m, CH_2), and 0.86 (m, CH_3). The spectrum also demonstrated the existence of the benzene ring in the marker at δ_H 8.51 (s, position c), 8.08 (d, 8.6 Hz, position d), and 7.73 (d, 8.6 Hz, position e).

The ^{13}C -NMR spectrum (CDCl_3) of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol (Fig. 4.39) showed the signals of the double bonds in the aromatic rings and side chains at δ_{C} 110.4-154.5. The spectrum also revealed the presence of the methylene and methyl groups at δ_{C} 14.0-34.3 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_{C} 156.9.

The mass spectrum of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol (Fig. 4.40) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 527.5$, 529.5, 531.5, and 533.5.

4.2.2.9 4-(2,4-Dinitrophenylazo)-2-nitrocardanol

2,4-Dinitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(2,4-dinitrophenylazo)-2-nitrocardanol (**9**) 71 % (w/w) which was reddish brown. The structure and characterization data of 4-(2,4-dinitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(2,4-dinitrophenylazo)-2-nitrocardanol (Fig. 4.41) showed the absorption peaks at 3224 cm^{-1} (O-H stretching of phenol), 3012 cm^{-1} (=C-H stretching of aromatic), 2919 cm^{-1} and 2847 cm^{-1} (C-H stretching of aliphatic), 1617 cm^{-1} and 1473 cm^{-1} (C=C ring stretching of aromatic), 1521 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1340 cm^{-1} (N=O symmetric stretching of NO_2 group), 1296 cm^{-1} (C-O stretching of phenol), and 894 cm^{-1} (C-N stretching vibration of C-N bond).

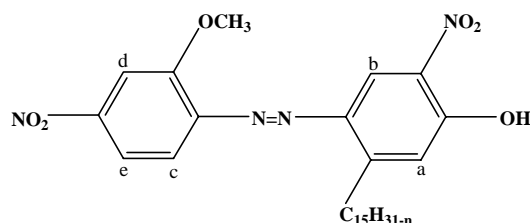
The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(2,4-dinitrophenylazo)-2-nitrocardanol (Fig. 4.42) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.17 (s) and 8.46 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.73. Additionally, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.79 (m, $\text{CH}=\text{CH}_2$), 5.36 (m, olefinic proton), 5.00 (m, $\text{CH}=\text{CH}_2$), 3.19 (t, 7.8 Hz, ArCH_2), 2.71 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 1.99 (m, $=\text{CHCH}_2$), 1.71 (m, CH_2), 1.30 (m, CH_2), and 0.88 (m, CH_3). The spectrum also demonstrated the existence of the benzene ring in the marker at δ_H 7.70 (d, 8.6 Hz, position c), 8.55 (s, position d), and 8.21 (d, 8.6 Hz, position e).

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(2,4-dinitrophenylazo)-2-nitrocardanol (Fig. 4.43) showed the signals of the double bonds in the aromatic rings and side chains at δ_C 112.9-154.8. The spectrum also revealed the presence of the methylene and methyl groups at δ_C 13.7-32.5 and the oxycarbon in the coupled 2-nitrocardanol (C-OH) at δ_C 157.3.

The mass spectrum of 4-(2,4-dinitrophenylazo)-2-nitrocardanol (Fig. 4.44) showed the molecular ion peak $[\text{M}+\text{H}]^+$ at $m/z = 544$.

4.2.2.10 4-(2-Methoxy-4-nitrophenylazo)-2-nitrocardanol

2-Methoxy-4-nitroaniline diazonium salt could be coupled with 2-nitro-5-*n*-alkylphenolate ion yielding 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (**10**) 80 % (w/w) which was reddish brown. The structure and characterization data of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol are shown below.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (Fig. 4.45) revealed the absorption peaks at 3269 cm^{-1} (O-H stretching of phenol), 3003 cm^{-1} (=C-H stretching of aromatic), 2929 cm^{-1} and 2856 cm^{-1} (C-H stretching of aliphatic), 1618 cm^{-1} and 1462 cm^{-1} (C=C ring stretching of aromatic), 1528 cm^{-1} (N=O asymmetric stretching of NO_2 group), 1343 cm^{-1} (N=O symmetric stretching of NO_2 group), 1303 cm^{-1} (C-O stretching of phenol), and 915 (C-N stretching vibration of C-N bond).

The $^1\text{H-NMR}$ spectrum (CDCl_3) of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (Fig. 4.46) revealed the presence of the coupled 2-nitrocardanol in the marker, whose δ_H at the positions a and b were at 7.11 (s) and 8.41 (s), respectively. The hydroxyl proton of the coupled 2-nitrocardanol was assigned at δ_H 10.73 . In addition, the signals of the alkyl protons in the side chains of the coupled 2-nitrocardanol were observed at δ_H 5.77 (m, $\text{CH}=\text{CH}_2$), 5.31 (m, olefinic proton), 4.97 (m, $\text{CH}=\text{CH}_2$), 3.12 (t, 7.8 Hz , ArCH_2), 2.76 (m, $=\text{CHCH}_2\text{CH}=\text{}$), 1.98 (m, $=\text{CHCH}_2$), 1.66 (m, CH_2), 1.32 (m, CH_2), and 0.85 (m, CH_3). The spectrum also demonstrated the existence of the benzene ring in the marker at δ_H 7.59 (d, 8.6 Hz , position c), 7.94 (s, position d), and 7.87 (d, 9.4 Hz , position e). Moreover, the methoxy protons resonanced characteristically at δ_H 4.13 .

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (Fig. 4.47) showed the signals of the double bonds in the aromatic rings and side chains at δ_C $108.0\text{-}154.2$. The spectrum also revealed the presence of the methylene and methyl groups at δ_C $14.0\text{-}32.2$ and the oxycarbon in the

coupled 2-nitrocardanol (C-OH) at δ_C 156.9. Furthermore, the spectrum exhibited the signal at δ_C 56.7 attributed to the methoxy carbon (C-OCH₃).

The mass spectrum of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (Fig. 4.48) showed the molecular ion peak [M+H]⁺ at m/z = 523.

4.2.3 Detection of azo markers in diesel fuel and gasoline

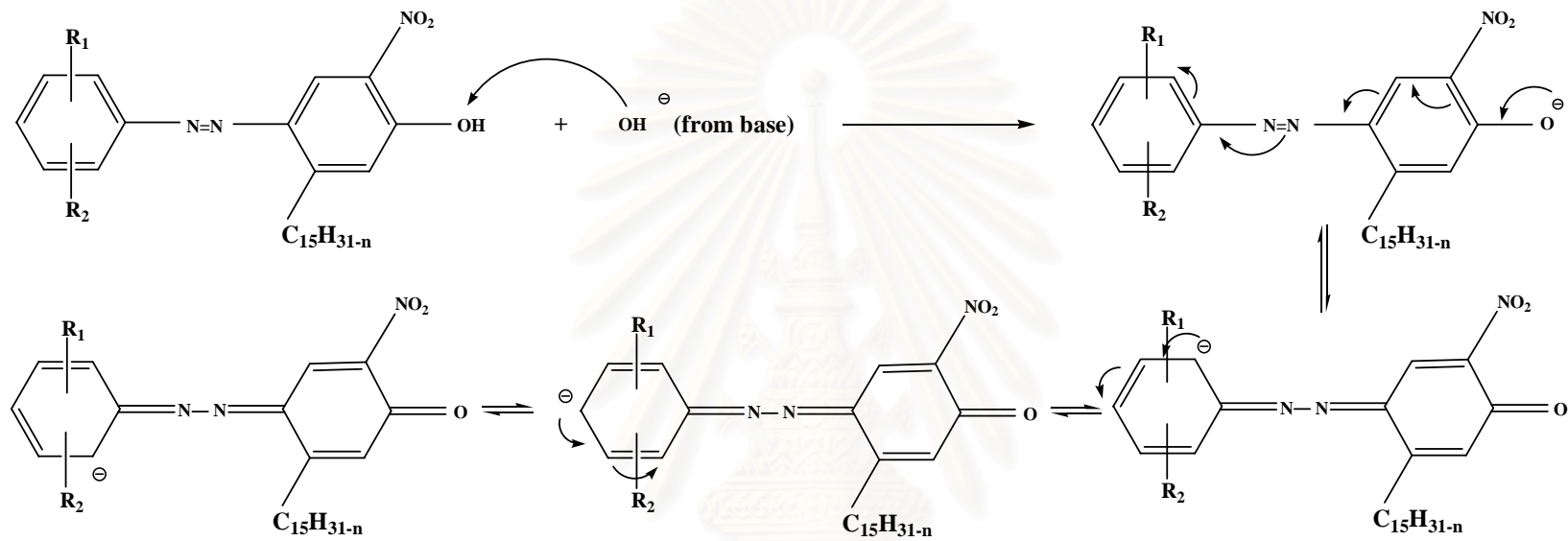
The azo markers were detected by reacting them with a suitable developer to turn to visibly intense colors. Because the markers had acidic character, an appropriate basic developing system was designed. The basic developing system was composed of benzyltrimethylammonium hydroxide, methanol, and 1-hexanol. The developing reagent was well soluble in the marked diesel fuel and gasoline after shaking, giving stable homogeneous mixtures able to be directly measured both qualitatively and quantitatively with a vis spectrophotometer. The reaction mixtures could be examined visually for the qualitative determination of the markers. The visual colors and maximum wavelengths of the mixtures were reported in Table 4.1. It was found that the markers provided distinct colors and different maximum wavelengths. Figure 4.49 illustrated that the colors of the markers arose from the proton transfer reaction of the markers and the base, benzyltrimethylammonium hydroxide. The base underwent the protonation on its oxygen atom resulting in the prompt formation of the anions which were believed to be colored. From this mechanism, the negative charge would appear in the positions ortho and para to the azo group. If the positions ortho and para to the azo group were occupied by electron-withdrawing moieties such as bromo, chloro and nitro groups, the structure was stabilized by a strong inductive effect. Moreover, if the substituent at the position ortho or para to the azo group was a nitro group, the structure was stabilized by both strong inductive effect and strong resonance effect because the nitro functionality could delocalize the negative charge through its structure. From Table 4.1, it was also revealed that the maximum wavelengths varied in different mediums. In the same marker, the maximum wavelength obtained from the marked diesel fuel was shorter than that from the dyed gasoline. In addition, the findings indicated that the colors and maximum wavelengths were influenced not only by the type and position of the substituents and the type of the fuel oils, but also by the number of the substituents

that acted as chromophores or auxochromes including nitro, bromo, chloro, and methoxy groups. Each chromophore or auxochrome caused an intensification of color and a bathochromic shift and thereby the maximum wavelength of the developed color shifted to longer wavelength. This bathochromic shift presumably resulted from the reduction in the energy transition between the excited state and the ground state owing to extended conjugation system. The more the conjugation was extended, the closer the energy levels were spaced and the longer the maximum wavelength was shifted. Among the markers prepared, 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (**6**), 4-(2,4-dinitrophenylazo)-2-nitrocardanol (**9**), and 4-(2-methoxy-4-nitrophenyl azo)-2-nitrocardanol (**10**) therefore gave deep colors and exhibited the maximum wavelengths in the higher portion of the visible region giving the coloration in the range from red to green shades which were more clearly distinguishable as depicted in Figures 4.50-4.53.

By means of the efficient markers and developing reagent, it was very simple to tag the marked fuel oils; the developed colors would become immediately visible to the naked eyes and would constitute the first indication of the markers' presence.

Table 4.1 Visual colors and maximum wavelengths of the azo markers **1-10** in diesel fuel and gasoline

Marker (5 ppm)	Diesel fuel		Gasoline	
	Visual color	λ_{\max} (nm)	Visual color	λ_{\max} (nm)
1	Yellow	456	Yellow	462
2	Yellow	442	Yellow	452
3	Yellow	464	Orange	470
4	Orange	476	Orange	494
5	Orange	496	Red	512
6	Red	528	Blue	600
7	Orange	488	Orange	504
8	Orange	480	Orange	500
9	Red	540	Green	612
10	Red	502	Red	526



Where R_1 and R_2 are each hydrogen, methyl, bromo, nitro, chloro, or methoxy group.

$n = 0, 2, 4, 6$

Fig. 4.49 Proton transfer reaction of the azo markers and base, benzyltrimethylammonium hydroxide

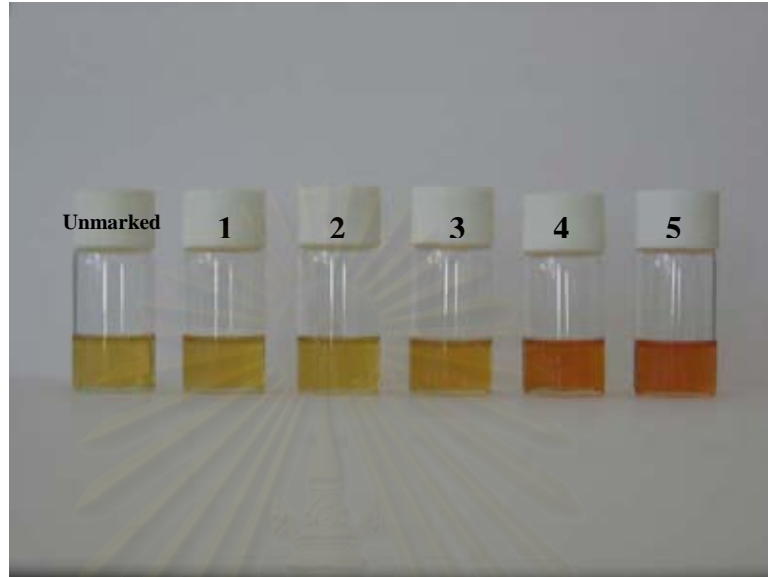


Fig. 4.50 Developed colors of the azo markers **1-5** in diesel fuel

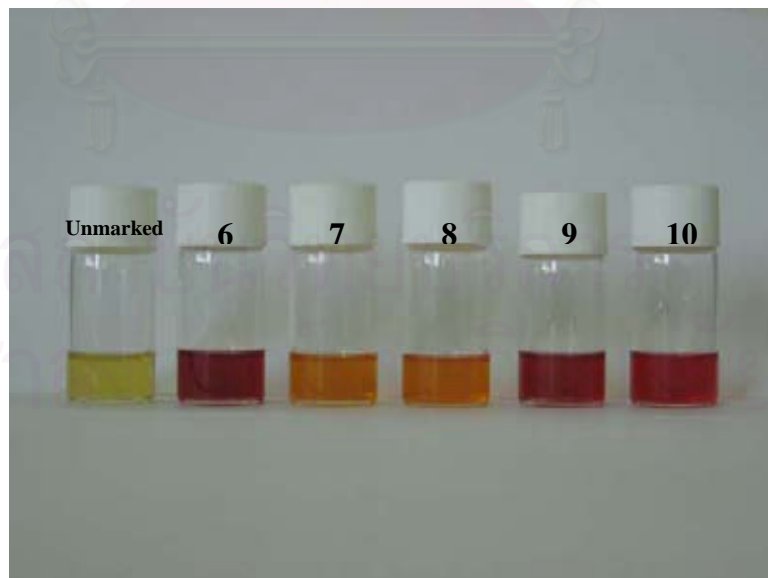


Fig. 4.51 Developed colors of the azo markers **6-10** in diesel fuel

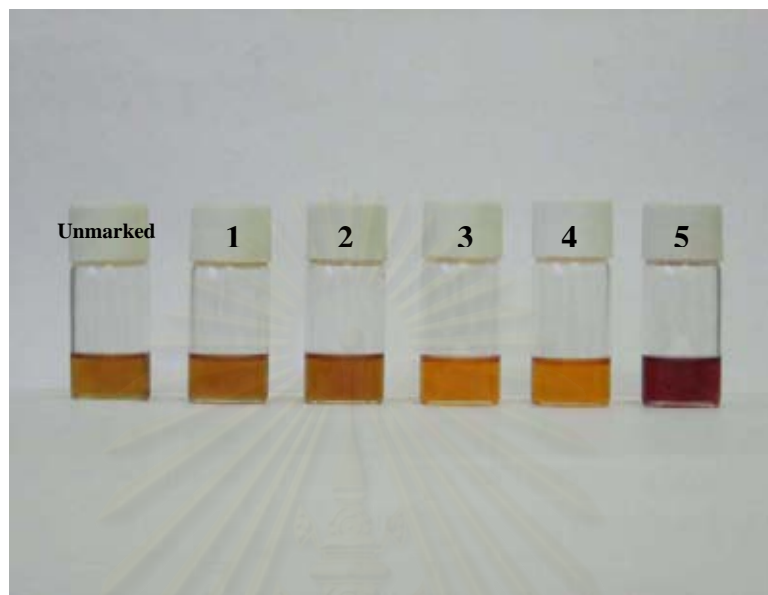


Fig. 4.52 Developed colors of the azo markers **1-5** in gasoline

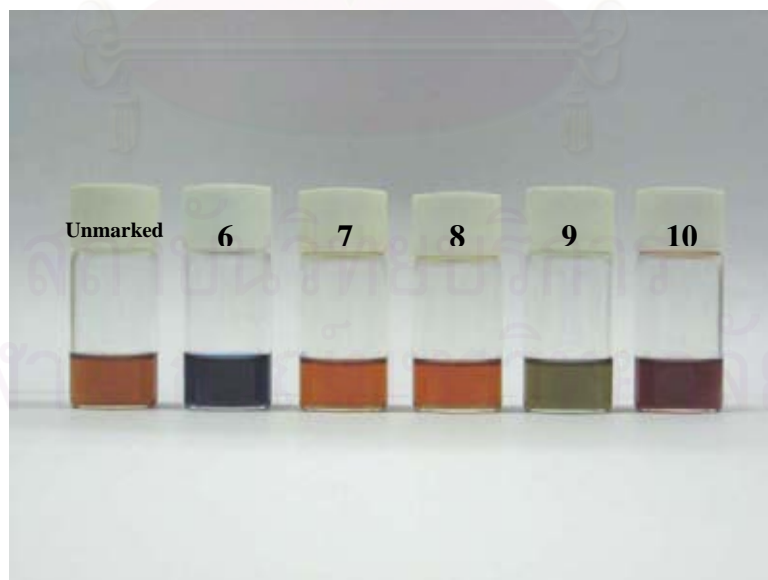


Fig. 4.53 Developed colors of the azo markers **6-10** in gasoline

4.2.4 Quantitative determination of azo markers in diesel fuel and gasoline

The quantitative determination of the useful markers, 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (**6**), 4-(2,4-dinitrophenylazo)-2-nitrocardanol (**9**), and 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (**10**) in diesel fuel and gasoline was carried out by a vis spectrophotometer using calibration curve method. Since the absorbance obtained was directly related to the concentration of the markers in the tagged fuel oils according to Beer's law, the absorbance readings would indicate the exact concentrations of the markers in the fuel oils, inturn revealing if the fuel oils were diluted, blended, or tampered with. This method was very straightforward in measuring the concentration of the markers upon the comparison with standard calibration curves. The calibration curves were plotted between the absorbance values at the maximum absorption wavelengths and the concentrations of the markers in the fuel oils. The standard calibration curves of the markers in the fuel oils are illustrated in Figures 4.54-4.59 and the standard calibration equations of the markers in the fuel oils are shown in Table 4.2 below.

Table 4.2 Standard calibration equations and their correlation coefficients for the quantitative determination of the azo markers **6**, **9**, and **10** in diesel fuel and gasoline

Marker	Diesel fuel		Gasoline	
	Calibration equation	r	Calibration equation	r
6	$y = 0.1383x + 0.0065$	0.9996	$y = 0.1533x - 0.0085$	0.9993
9	$y = 0.0220x + 0.0002$	0.9996	$y = 0.0283x - 0.0022$	0.9991
10	$y = 0.0242x - 0.0012$	0.9998	$y = 0.0222x - 0.0004$	0.9993

From Figures 4.54-4.59, it was found that the absorbance values were clearly detectable even at the low marker concentrations and exhibited the variability for the different concentrations. The calibration curves were linear over the marker concentration range of 0-8 ppm commonly used in commercial fuel oils, and the correlation coefficients (r) of the standard calibration equations were closed to 1. Thus, the markers permitted the precisely quantitative determination in the fuel oils.

4.2.5 Effect of azo markers on the general physical properties of diesel fuel and gasoline

4-(2-Chloro-4-nitrophenylazo)-2-nitrocardanol was employed as a marker model. The general physical properties of diesel fuel and gasoline which were undyed and dyed with the marker at 5 ppm were tested by using the ASTM methods. From Tables 4.3 and 4.4, it was revealed that the physical properties of the marked diesel fuel and gasoline were not significantly different from those of the unmarked diesel fuel and gasoline. Both marked and unmarked diesel fuels gave similar gravities, calculated cetane indexes, kinematic viscosities, pour points, flash points, distillation values, copper strip corrosion properties, total acid numbers, and colors. Also, both dyed and undyed gasoline provided similar gravities, research octane numbers, Reid vapor pressures, distillation values, copper strip corrosion properties, total acid numbers, and colors. Consequently, the physical properties of the diesel fuel and gasoline being dyed were unaffected by the model marker; it was therefore possible to assume that the series of the synthetic markers did not affect the physical properties of the fuel oils.

Table 4.3 General physical properties of marked^a and unmarked diesel fuels

Physical property	Method (ASTM) ^b	Marked	Unmarked
API gravity at 60 °F	D 4052	38.83	38.77
Specific gravity at 15.6/15.6 °C	D 4052	0.8307	0.8310
Calculated cetane index	D 976	57.44	57.38
Kinematic viscosity at 40 °C (mm ² /s)	D 445	3.103	3.129
Pour point (°C)	D 97	1.0	1.0
Flash point (°C)	D 93	60.0	60.5
Sulfur content % (w/w)	D 4294	0.0295	0.0320
Copper strip corrosion (3 hrs, 50 °C)	D 130	No.1	No.1
Distillation IBP ^c (°C)	D 86	164.7	166.1
10 % (v/v) Recovery (°C)		208.3	207.7
50 % (v/v) Recovery (°C)		284.8	285.8
90 % (v/v) Recovery (°C)		350.8	352.0
Total acid number (mg of KOH/g)	D 664	0.03	0.01
Color	D 1500	1.0	1.0

^a With 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (5 ppm) ^b American Society for Testing and Materials ^c Initial boiling point

Table 4.4 General physical properties of marked^a and unmarked gasoline

Physical property	Method (ASTM) ^b	Marked	Unmarked
API gravity at 60 °F	D 4052	58.72	58.88
Specific gravity at 15.6/15.6 °C	D 4052	0.7438	0.7432
Research octane number	D 2699	96.2	96.5
Reid vapor pressure at 37.8 °C (kPa)	D 5159	57.5	58.6
Copper strip corrosion (3 hrs, 50 °C)	D 130	No.1	No.1
Distillation	D 86		
IBP ^c (°C)		34.7	36.6
10 % (v/v) Evaporated (°C)		51.8	51.9
50 % (v/v) Evaporated (°C)		81.8	80.5
90 % (v/v) Evaporated (°C)		150.6	149.5
End point (°C)		186.7	187.6
Recovery % (v/v)		97.4	98.2
Residue % (v/v)		1.3	0.9
Total acid number (mg of KOH/g)	D 664	0.0	0.0
Color	D 1500	1.0	1.0

^a With 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (5 ppm) ^b American Society for Testing and Materials ^c Initial boiling point

4.2.6 Stability of azo markers in diesel fuel and gasoline

The stability of the selected azo markers, 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol (**6**), 4-(2,4-dinitrophenylazo)-2-nitrocardanol (**9**), and 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol (**10**) in diesel fuel and gasoline was studied by monitoring the quantity of the markers using ultraviolet-visible spectroscopic technique. The quantity of the markers added into the fuel oils was 5 ppm and determined monthly for 3 months. The determination of the marker contents in the fuel oils was performed by measuring the absorbance values of the marked fuel oils at their maximum absorption bands. The marker concentrations in the fuel oils are summarized in Table 4.5. It was found that there was no significant change in the concentrations of the markers from the initial concentration in both fuel oils so the markers in the fuel oils were disclosed to be unchanged after at least three months' storage. Generally, each batch of the fuel oils is consumed within 3 months after release to the market. Therefore, the markers remained sufficiently stable in the fuel oils over a commercial significant period of time.

Table 4.5 Concentrations of the azo markers **6**, **9**, and **10** in diesel fuel and gasoline over a period of 3 months

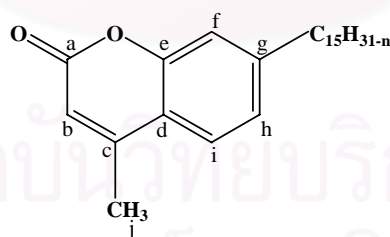
Marker (5 ppm)	Diesel fuel			Gasoline		
	Concentration ^a (ppm)			Concentration ^a (ppm)		
	Month 1	Month 2	Month 3	Month 1	Month 2	Month 3
6	5.02 ± 0.0231	5.03 ± 0.0321	5.05 ± 0.0351	5.05 ± 0.0153	5.07 ± 0.0306	5.08 ± 0.0361
9	5.01 ± 0.0265	5.02 ± 0.0153	5.03 ± 0.0208	5.04 ± 0.0265	5.05 ± 0.0252	5.05 ± 0.0300
10	5.01 ± 0.0253	5.01 ± 0.0265	5.02 ± 0.0153	5.03 ± 0.0173	5.04 ± 0.0252	5.05 ± 0.0321

^a Average ± standard deviation, $n = 3$

4.3 Petroleum fluorescent marker

4.3.1 Preparation of fluorescent marker

The preparation of the fluorescent marker, 7-alkyl-4-methylcoumarin, could be carried out in the one-pot reaction via Pechmann condensation of cardanol with ethyl acetoacetate in the presence of concentrated sulfuric acid. The fluorescent marker was obtained as a light yellow liquid in the yield of 60 % (w/w). The structure and characterization data of the fluorescent marker are represented below. Like the azo markers abovementioned, the fluorescent marker was itself readily soluble in the diesel fuel and gasoline to be marked and regarded as a silent marker that did not impart its visible color to interfere the intrinsic colors of the fuel oils.



Where $n = 0, 2, 4, 6$

The infrared spectrum of 7-alkyl-4-methylcoumarin (Fig. 4.60) showed the absorption peaks at 3072 cm^{-1} ($=\text{C-H}$ stretching of aromatic), 2925 cm^{-1} and 2848 cm^{-1} (C-H stretching of aliphatic), 1728 cm^{-1} (C=O stretching of lactone), 1618 cm^{-1} (C=C stretching of conjugated double bond), 1454 cm^{-1} (C=C ring stretching of aromatic), and 1262 cm^{-1} (C-O stretching of lactone).

The $^1\text{H-NMR}$ spectrum (CDCl_3) of 7-alkyl-4-methylcoumarin (Fig. 4.61) showed the proton signals of the positions b, f, h, i, and j at δ_H 6.17 (*s*), 7.06 (*s*), 7.43 (*d*, 7.8 Hz), 7.05 (*d*, 7.8 Hz), and 2.35 (3H, *s*), respectively. The spectrum also demonstrated the signals of the alkyl protons in the side chains at δ_H 5.70 (*m*, $\text{CH}=\text{CH}_2$), 5.31 (*m*, olefinic proton), 5.08 (*m*, $\text{CH}=\text{CH}_2$), 2.62 (*t*, 7.8 Hz, ArCH_2), 1.93 (*m*, $=\text{CHCH}_2$), 1.54 (*m*, CH_2), 1.21 (*m*, CH_2), and 0.81 (*m*, CH_3).

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) of 7-alkyl-4-methylcoumarin (Fig. 4.62) revealed the presence of the coumarin moiety in the marker, whose δ_C at the positions a, b, c, d, e, f, g, h, and i were at 161.2, 113.9, 152.5, 117.7, 153.6, 116.5, 147.9, 124.3, and 124.7, respectively. The spectrum also exhibited the methylene and methyl groups at δ_C 14.1-35.8 and the double bonds in the side chains in the range of 129.7-130.5 ppm.

The mass spectrum of 7-alkyl-4-methylcoumarin (Fig. 4.63) showed the molecular ion peaks $[\text{M}+\text{H}]^+$ at $m/z = 365, 367, 369, \text{ and } 371$.

4.3.2 Detection of fluorescent marker in diesel fuel and gasoline

The fluorescent marker, 7-alkyl-4-methylcoumarin, was a derivative of coumarin which was a six membered lactone. Due to the lactone skeleton, the marker could produce fluorescence; thus, it was detected instrumentally by measuring the generated fluorescence using a spectrofluorometer. In general, coumarins characteristically fluoresce under the ultraviolet light. The diesel fuel and gasoline marked with the marker were exposed to the ultraviolet radiation to collect the spectral patterns of the fluorescence emission to confirm the marker's presence. In addition, the fluorescence measurement in the ultraviolet region was chosen to avoid strong interference of the background fuel oils occurring in the visible region. Figures 4.64 and 4.66 showed the absorption-emission spectra of the marker in diesel fuel and

gasoline. The absorption-emission spectra of diesel fuel and gasoline were also illustrated in Figures 4.65 and 4.67, respectively. In both cases, it was revealed that the marker employed could fluoresce within the ultraviolet region which had less interference of the background fuel oils than the visible region. Concerning diesel fuel, when the tagged oil was irradiated with the light at the wavelength of 267 nm, it was found that the emission spectrum obtained was differentiable from that of the background diesel fuel giving the characteristic fluorescence band of the marker at 312 nm. Considering gasoline, when the tagged oil was subjected to the light at the wavelength of 300 nm, the characteristic fluorescence peak of the marker was located at 333 nm.

Accordingly, this method afforded by the fluorescent marker could detect the presence of the marker in the fuel oils from its fluorescence spectral signature in the simple and quick manner which did not require any chemical manipulation and marker extraction.

4.3.3 Quantitative determination of fluorescent marker in diesel fuel and gasoline

The quantitative determination of the fluorescent marker, 7-alkyl-4-methylcoumarin in diesel fuel and gasoline was conducted by a spectrofluorometer using calibration curve method. This equipment could be utilized to calculate the concentrations of the marker from its fluorescence emission data by comparing with standard calibration curves to determine whether the fuel oils were adulterated or counterfeited. The standard calibration curves were constructed by plotting the intensity values at its characteristic emission peaks versus the marker concentrations in the fuel oils. The standard calibration curves of the marker in the fuel oils are illustrated in Figures 4.68 and 4.69 and the standard calibration equations of the marker in the fuel oils are shown in Table 4.6 below.

Table 4.6 Standard calibration equations and their correlation coefficients for the quantitative determination of the fluorescent marker in diesel fuel and gasoline

Fuel oil	Calibration equation	r
Diesel fuel	$y = 0.1263x - 0.02$	0.9998
Gasoline	$y = 0.1245x - 0.16$	0.9996

From Figures 4.68 and 4.69, it was disclosed that the marker exhibited the particular fluorescent variation with its varying concentrations in both fuel oils. All calibration curves were linear over the marker concentration range of 0-160 ppm, and the correlation coefficients (r) of the standard calibration equations were closed to 1, thereby providing the true quantitative results of the marker in the fuel oils.

4.3.4 Effect of fluorescent marker on the general physical properties of diesel fuel and gasoline

The general physical properties of the diesel fuel and gasoline which were unmarked and marked with the fluorescent marker, 7-alkyl-4-methylcoumarin, at 100 ppm were tested by using the ASTM methods and compared in order to evaluate the influence of the marker on the properties of the fuel oils. The results in Tables 4.7 and 4.8 revealed that the physical properties of the marked diesel fuel and gasoline did not differ significantly from those of the unmarked diesel fuel and gasoline. Both dyed and undyed diesel fuels gave similar gravities, calculated cetane indexes, kinematic viscosities, pour points, flash points, distillation values, copper strip corrosion properties, total acid numbers, and colors. Also, both dyed and undyed gasoline provided similar gravities, research octane numbers, Reid vapor pressures, distillation values, copper strip corrosion properties, total acid numbers, and colors. As a result, the marker had no effect on the physical properties of the fuel oils being dyed.

Table 4.7 General physical properties of marked^a and unmarked diesel fuels

Physical property	Method (ASTM) ^b	Marked	Unmarked
API gravity at 60 °F	D 4052	38.79	38.77
Specific gravity at 15.6/15.6 °C	D 4052	0.8309	0.8310
Calculated cetane index	D 976	57.41	57.38
Kinematic viscosity at 40 °C (mm ² /s)	D 445	3.101	3.129
Pour point (°C)	D 97	1.0	1.0
Flash point (°C)	D 93	58.0	60.5
Sulfur content % (w/w)	D 4294	0.0319	0.0320
Copper strip corrosion (3 hrs, 50 °C)	D 130	No.1	No.1
Distillation IBP ^c (°C)	D 86	165.4	166.1
10 % (v/v) Recovery (°C)		208.5	207.7
50 % (v/v) Recovery (°C)		286.3	285.8
90 % (v/v) Recovery (°C)		353.1	352.0
Total acid number (mg of KOH/g)	D 664	0.01	0.01
Color	D 1500	1.0	1.0

^a With 7-alkyl-4-methylcoumarin (100 ppm) ^b American Society for Testing and Materials ^c Initial boiling point

Table 4.8 General physical properties of marked^a and unmarked gasoline

Physical property	Method (ASTM) ^b	Marked	Unmarked
API gravity at 60 °F	D 4052	58.89	58.88
Specific gravity at 15.6/15.6 °C	D 4052	0.7430	0.7432
Research octane number	D 2699	96.61	96.50
Reid vapor pressure at 37.8 °C (kPa)	D 5159	58.3	58.6
Copper strip corrosion (3 hrs, 50 °C)	D 130	No.1	No.1
Distillation IBP ^c (°C)	D 86	35.7	36.6
10 % (v/v) Evaporated (°C)		51.7	51.9
50 % (v/v) Evaporated (°C)		81.1	80.5
90 % (v/v) Evaporated (°C)		150.7	149.5
End point (°C)		186.3	187.6
Recovery % (v/v)		98.8	98.2
Residue % (v/v)		1.0	0.9
Total acid number (mg of KOH/g)	D 664	0.0	0.0
Color	D 1500	1.0	1.0

^a With 7-alkyl-4-methylcoumarin (100 ppm) ^b American Society for Testing and Materials ^c Initial boiling point

4.3.5 Stability of fluorescent marker in diesel fuel and gasoline

The stability of the fluorescent marker, 7-alkyl-4-methylcoumarin in diesel fuel and gasoline was studied by monitoring the marker quantity added (100 ppm) for 3 months by use of a spectrofluorometer. The marker concentrations were calculated based on the fluorescence intensities of its characteristic emission bands. From Table 4.9, it was found that the marker concentrations in both diesel fuel and gasoline were not almost different from the original concentration, and in consequence the marker remained dissolved in the fuel oils throughout a period of 3 months. Generally, each batch of the fuel oils is consumed within 3 months after release to the market. Therefore, the marker was stable in the fuel oils for a commercial significant period of time.

Table 4.9 Concentrations of the fluorescent marker in diesel fuel and gasoline over a period of 3 months

Marker (100 ppm)	Concentration ^a (ppm)		
	Month 1	Month 2	Month 3
Diesel fuel	100.06 ± 0.0208	100.04 ± 0.0153	100.05 ± 0.0153
Gasoline	100.05 ± 0.0115	100.03 ± 0.0252	100.08 ± 0.0379

^a Average ± standard deviation, $n = 3$

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

This research was engrossed in the preparation of efficient petroleum markers and their practical applications. Novel silent petroleum markers having sufficient solubility and stability in fuel oils were synthesized from the naturally occurring substrate, cardanol which was inexpensive and had long nonpolar aliphatic side chains to enhance their fuel solubility. Two interesting classes of markers, the azo and fluorescent markers, were successfully achieved. The azo markers were obtained by coupling 2-nitrocardanol with various anilines whereas the fluorescent marker, a coumarin derivative, was attained by condensing cardanol with ethyl acetoacetate. In accord with expectation, the cardanol's side chains played a major role in improving the fuel solubility property of the markers. All synthetic markers were completely soluble in diesel fuel and gasoline to which they were added at effective usable levels.

The azo and fluorescent markers were found to be detected qualitatively and quantitatively with ease by ultraviolet-visible and fluorescence spectroscopic techniques, respectively. In case of the azo markers, the markers' presence in the fuel oils could be confirmed by means of the color development without marker extraction. The markers provided invisible colors in the fuel oils but gave visible colors when only adding the new developing reagent containing benzyltrimethylammonium hydroxide, methanol and 1-hexanol. In addition, the markers showed a pronounced dependence of their developed colors and maximum absorption wavelengths on their substituents. 4-(2-Chloro-4-nitrophenylazo)-2-nitrocardanol, 4-(2,4-dinitrophenylazo)-2-nitrocardanol, and 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol were discovered to be effective in their role as petroleum markers with their long wavelength absorption, rendering in rich colors ranging from red to green which were easily detectable to the naked eyes. Furthermore, the quantitative measurement of the markers could be simply carried out by a vis spectrophotometer with a high degree of accuracy. With regard to the fluorescent marker, 7-alkyl-4-methylcoumarin, it had the silent property in the fuel oils in the same manner with the azo markers. The qualitative and quantitative

assessments of the marker could be accomplished easily with good precision, taking advantages of the ability to identify the fuel oils without any chemical manipulation and marker extraction. The marker detection in the fuel oils was done based on the emission spectra of the marked fuel oils. The spectra revealed the presence of the characteristic fluorescence bands ascribed to the marker at 312 and 333 nm for diesel fuel and gasoline with the excitation at 267 and 300 nm, respectively.

The effect of the azo and fluorescent markers on the general physical properties of the dyed diesel fuel and gasoline was also investigated. The ASTM tests disclosed that the markers did not affect the physical properties of the fuel oils. Moreover, the stability of the markers in the marked fuel oils was studied and found that the markers were stable in the fuel oils over the commercial storage period of three months.

To my best knowledge, the utilization of the azo and fluorescent markers had no report in chemical literatures for tagging fuel oils. Clearly, the outcomes of this work indicated that the synthetic markers were of value as petroleum markers. The markers and detection methods facilitated both qualitative and quantitative determinations and were useful from the practical points of view presenting viable alternatives to fuel identification purposes.

5.2 Suggestion for the further work

Petroleum azo and fluorescent markers having other fascinating substituents such as an amino group are interesting to be prepared and examined for their ability to tag fuel oils. Additionally, marker systems comprising two or more petroleum markers would be another challenging topic to continually study.

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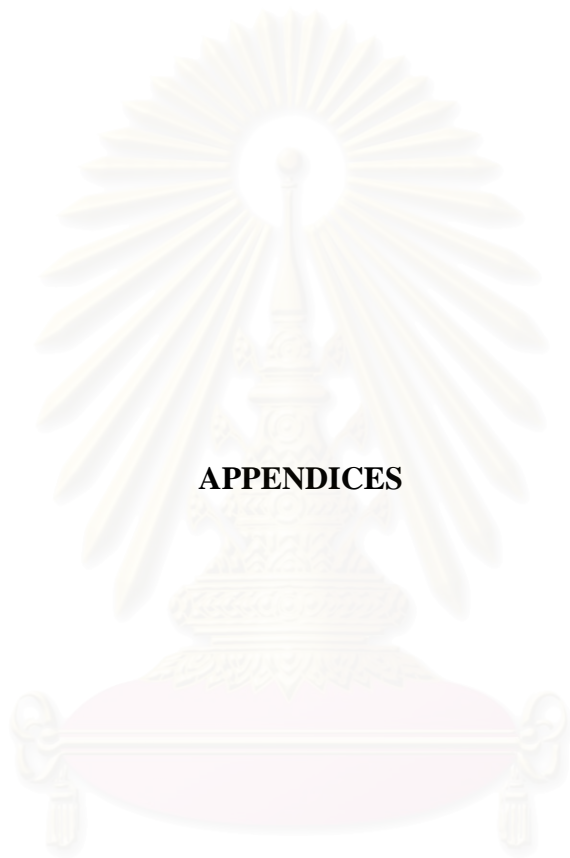
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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

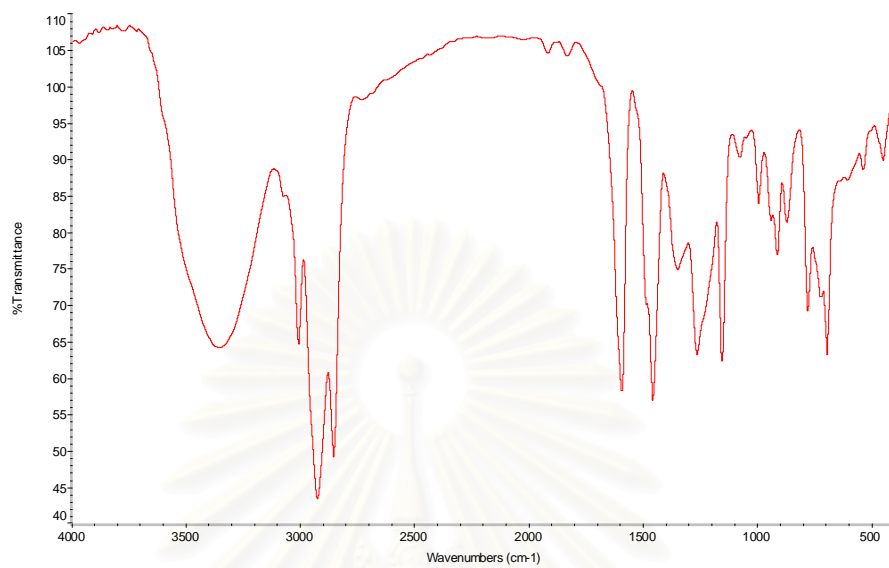


Fig. 4.1 Infrared spectrum of cardanol

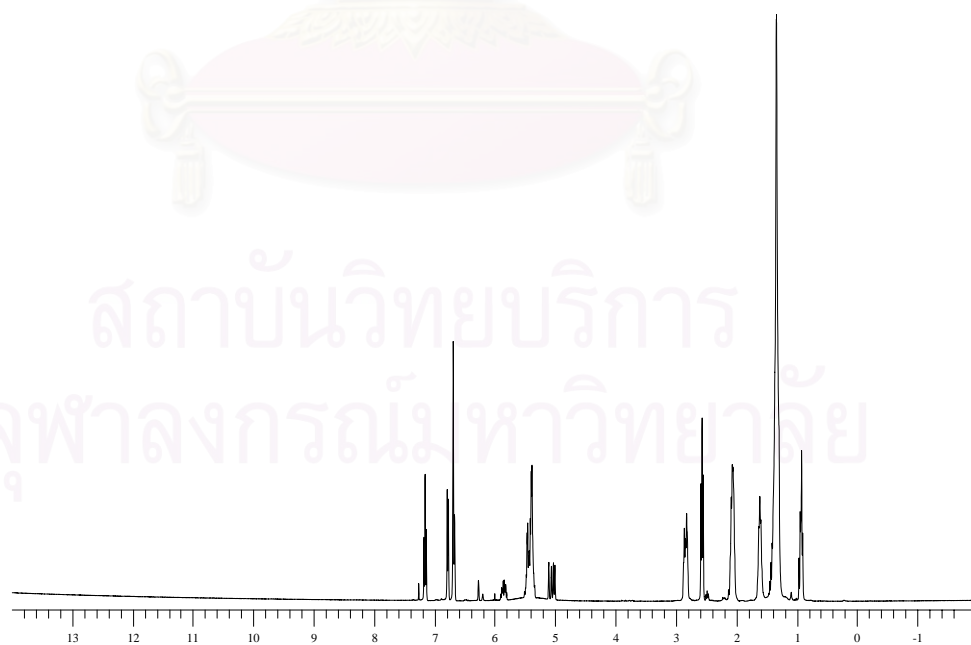


Fig. 4.2 ¹H-NMR spectrum of cardanol

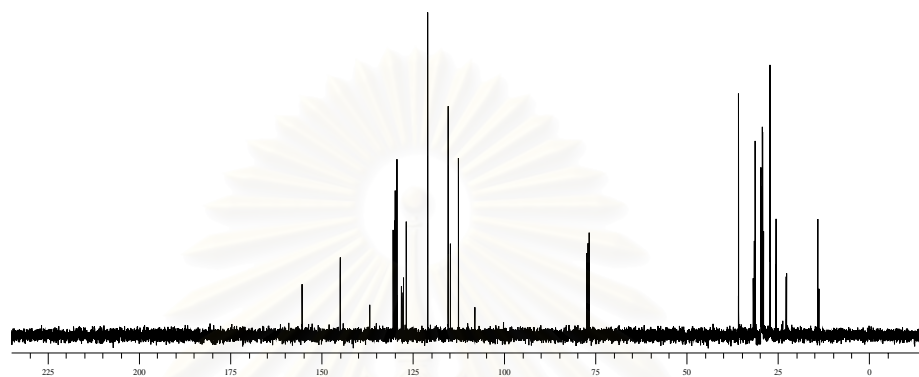


Fig. 4.3 ^{13}C -NMR spectrum of cardanol

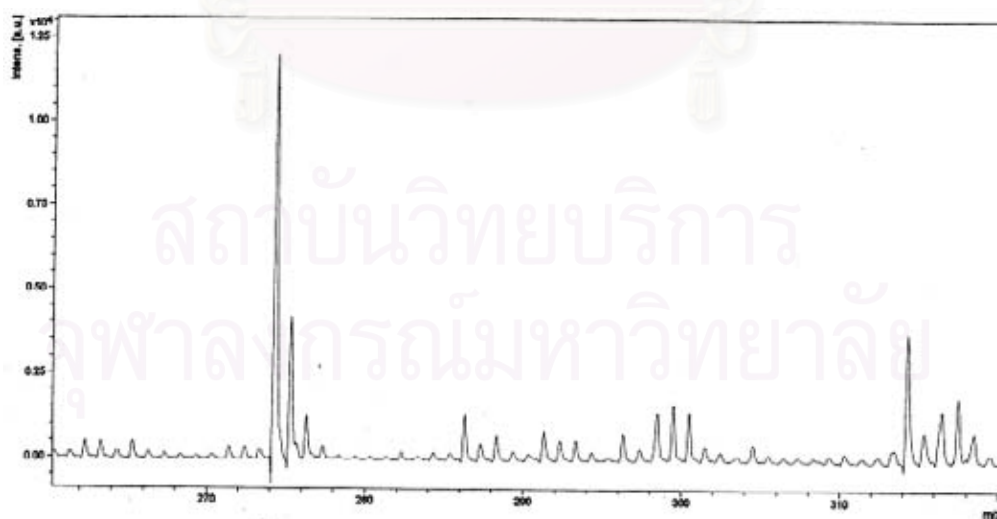


Fig. 4.4 Mass spectrum of cardanol

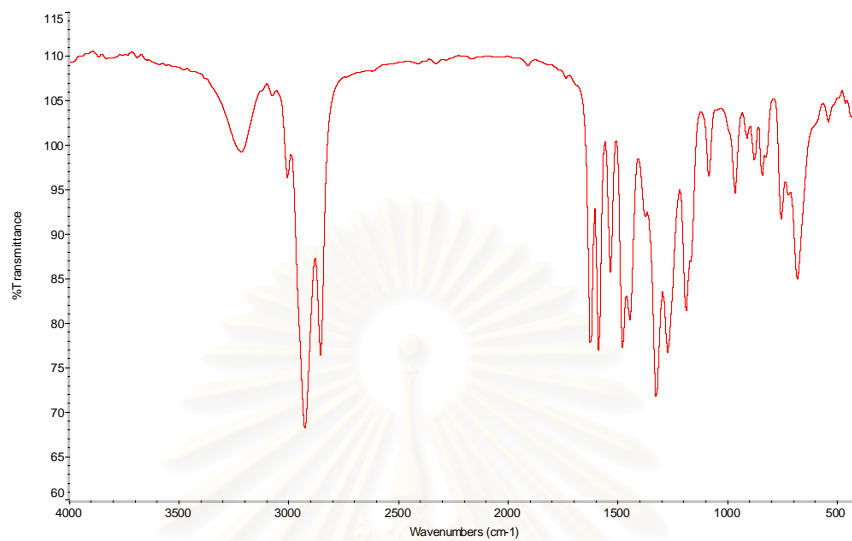


Fig. 4.5 Infrared spectrum of 2-nitrocardanol

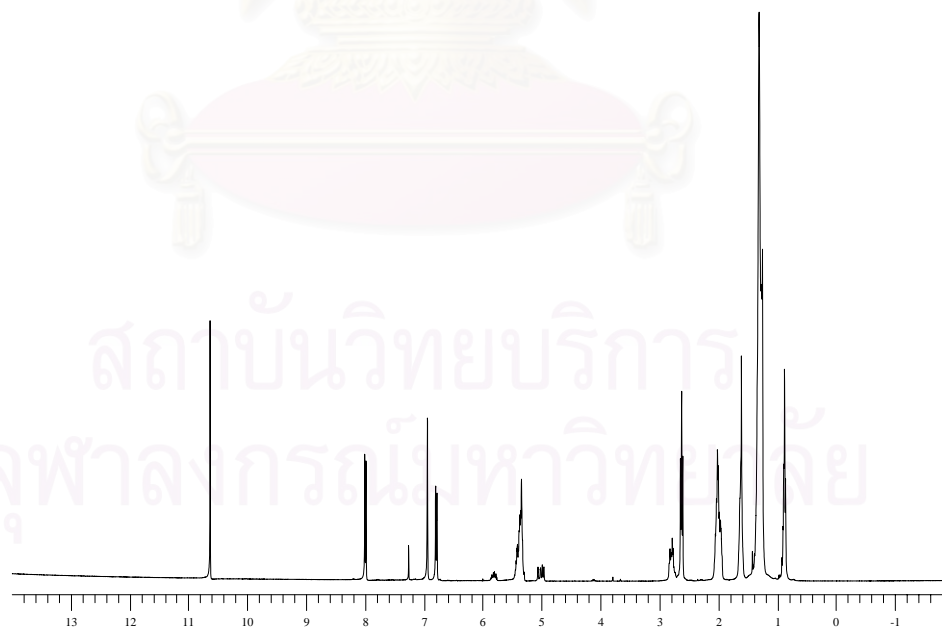


Fig. 4.6 ¹H-NMR spectrum of 2-nitrocardanol

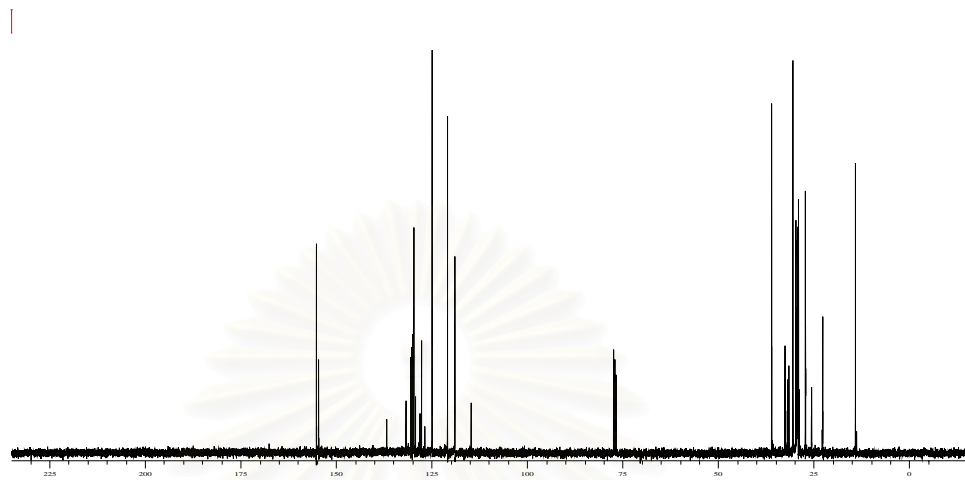


Fig. 4.7 ^{13}C -NMR spectrum of 2-nitrocardanol

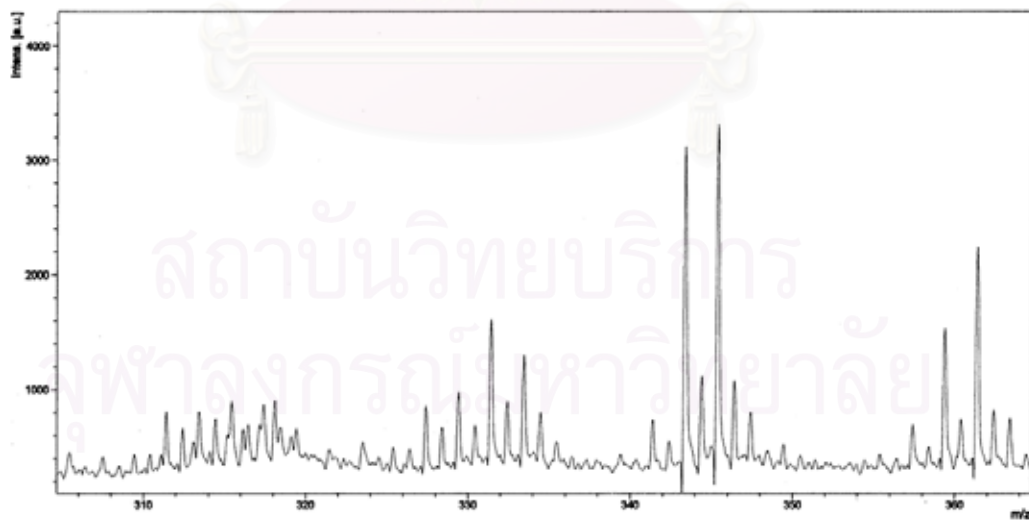


Fig. 4.8 Mass spectrum of 2-nitrocardanol

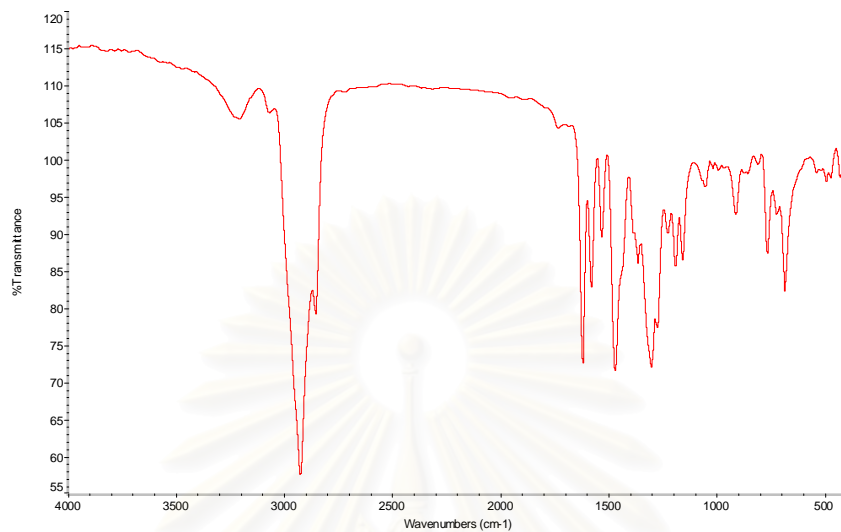


Fig. 4.9 Infrared spectrum of 4-(phenylazo)-2-nitrocardanol

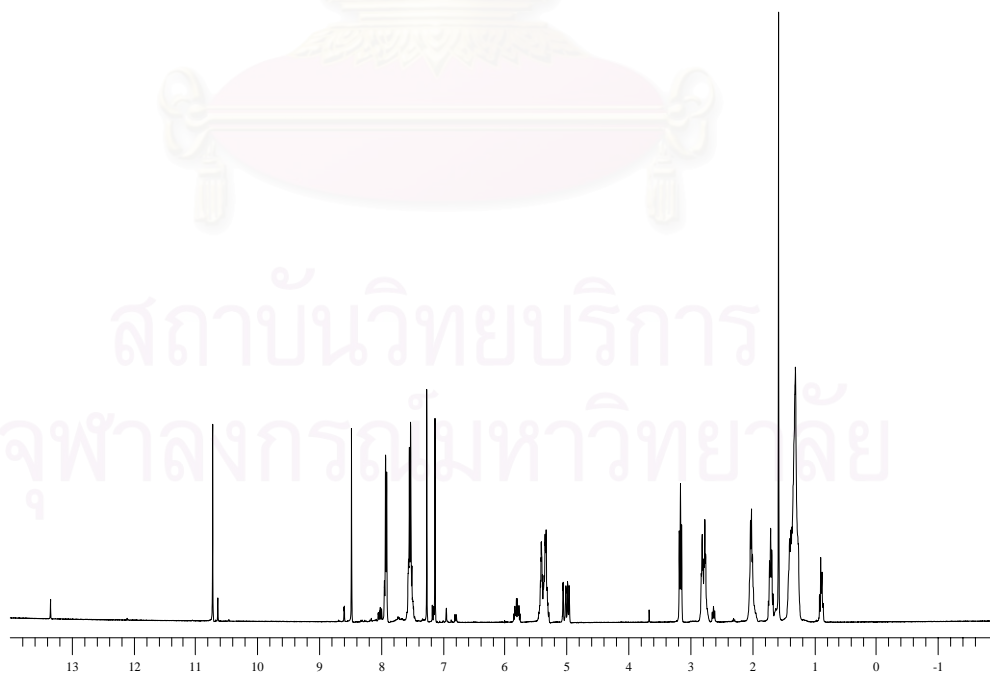


Fig. 4.10 $^1\text{H-NMR}$ spectrum of 4-(phenylazo)-2-nitrocardanol

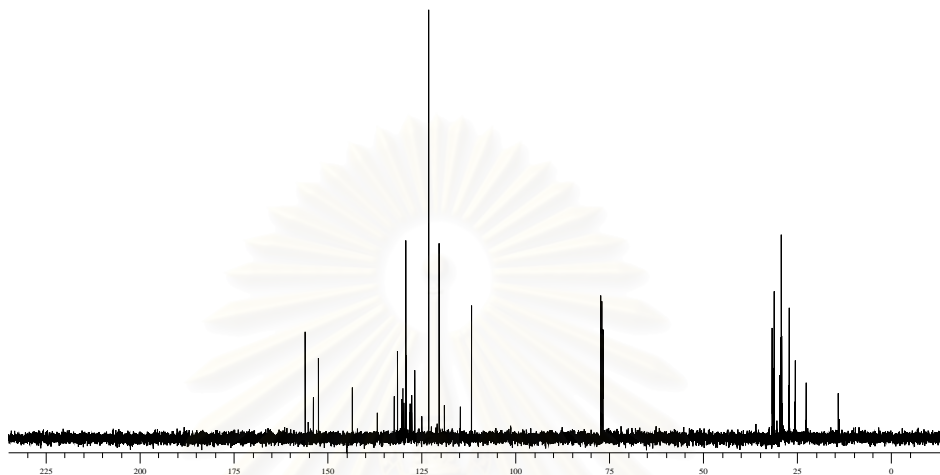


Fig. 4.11 ¹³C-NMR spectrum of 4-(phenylazo)-2-nitrocardanol

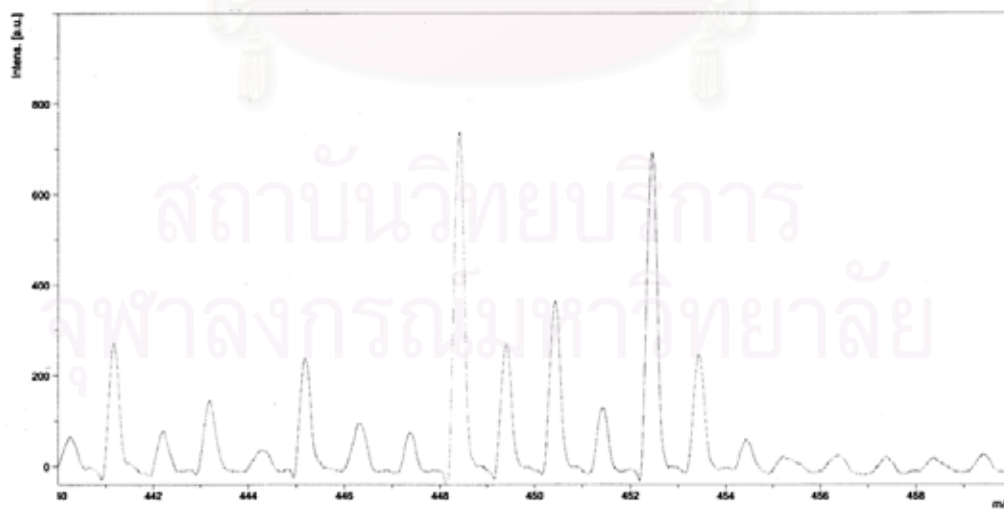


Fig. 4.12 Mass spectrum of 4-(phenylazo)-2-nitrocardanol

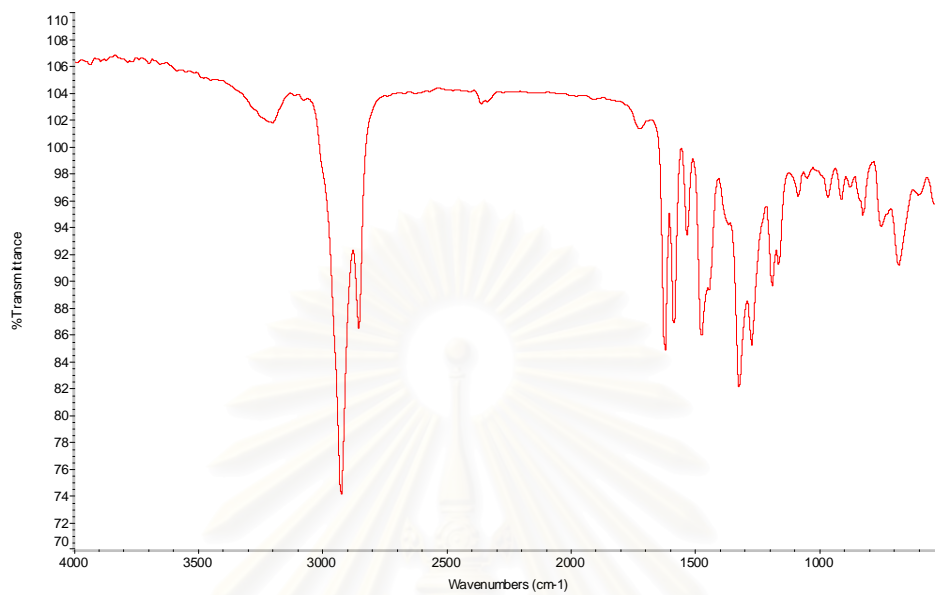


Fig. 4.13 Infrared spectrum of 4-(4-methylphenylazo)-2-nitrocardanol

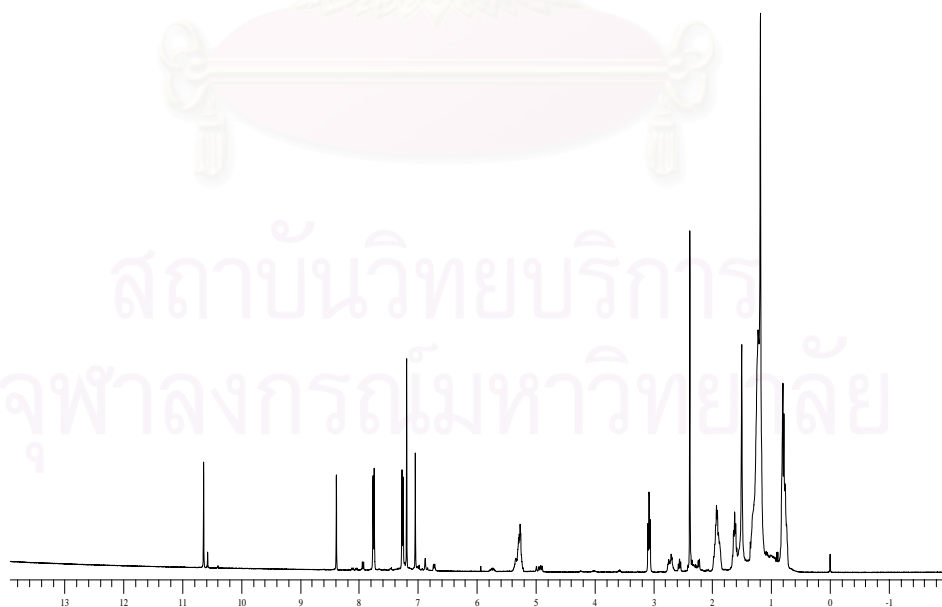


Fig. 4.14 $^1\text{H-NMR}$ spectrum of 4-(4-methylphenylazo)-2-nitrocardanol

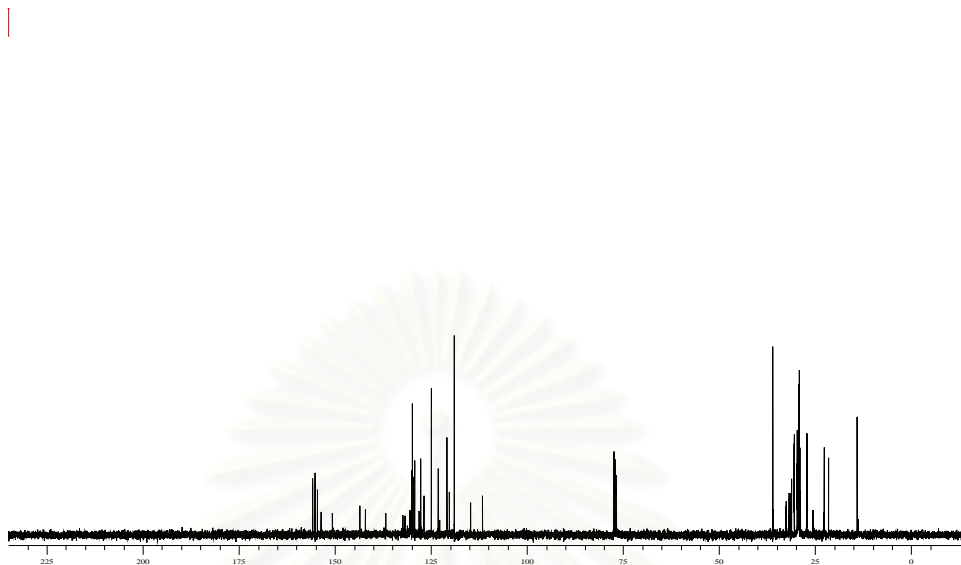


Fig. 4.15 ^{13}C -NMR spectrum of 4-(4-methylphenylazo)-2-nitrocardanol

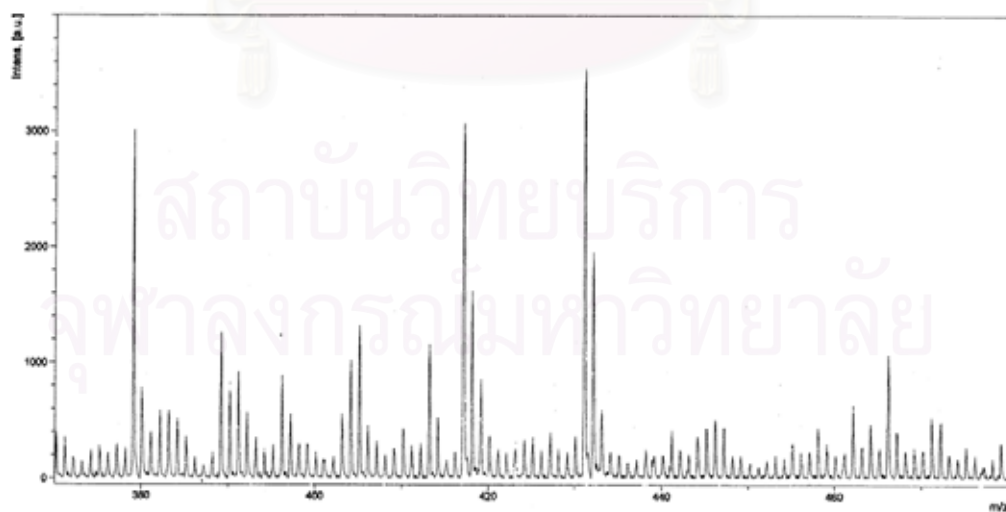


Fig. 4.16 Mass spectrum of 4-(4-methylphenylazo)-2-nitrocardanol

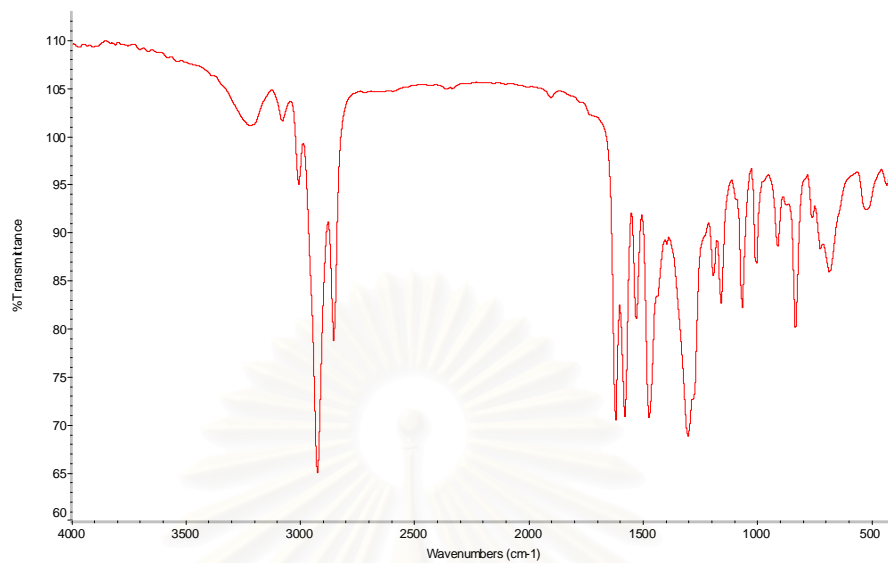


Fig. 4.17 Infrared spectrum of 4-(4-bromophenylazo)-2-nitrocardanol

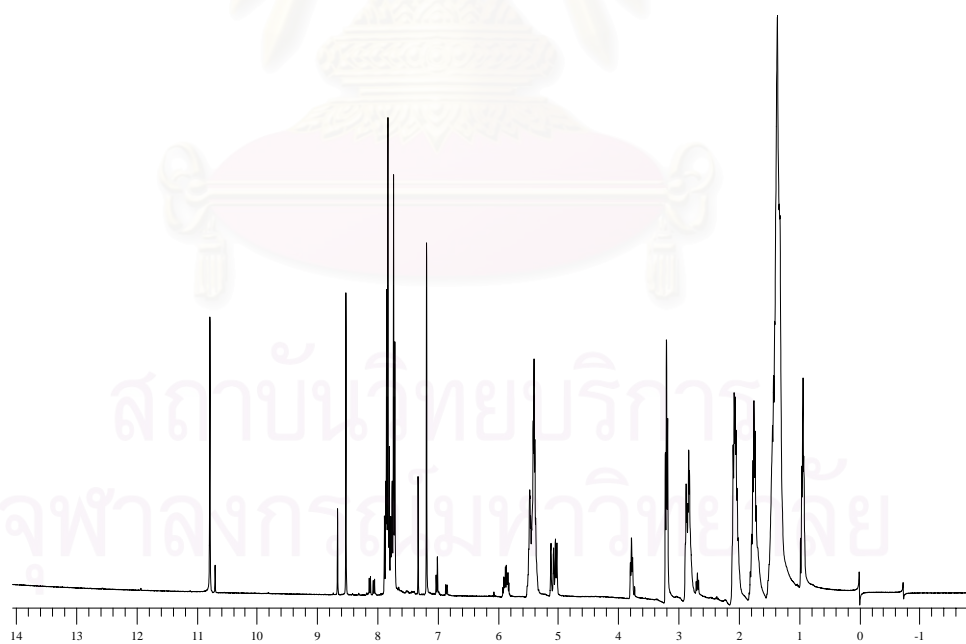


Fig. 4.18 ^1H -NMR spectrum of 4-(4-bromophenylazo)-2-nitrocardanol

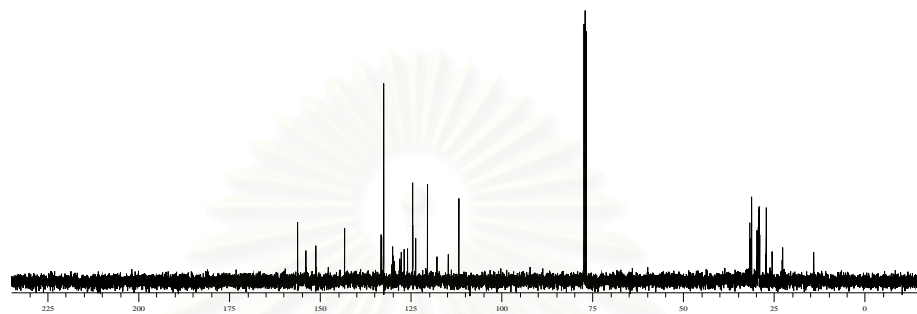


Fig. 4.19 ^{13}C -NMR spectrum of 4-(4-bromophenylazo)-2-nitrocardanol

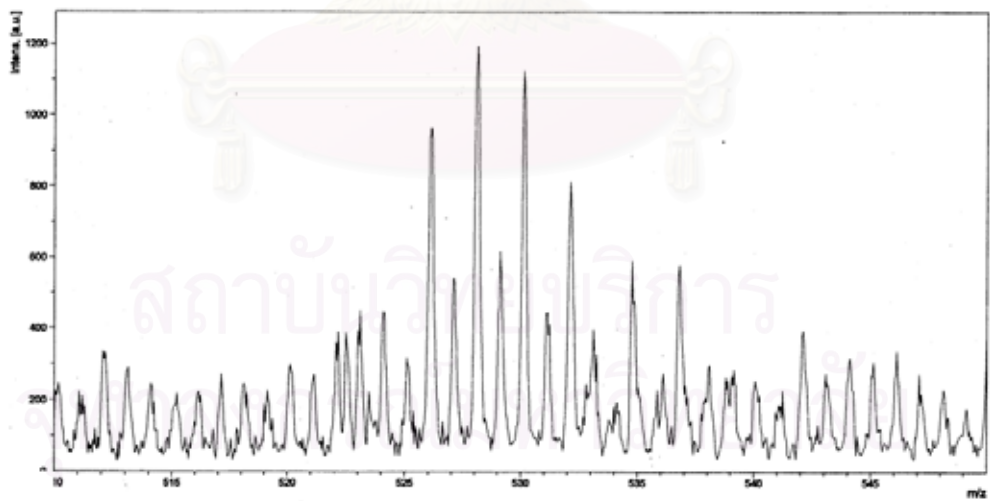


Fig. 4.20 Mass spectrum of 4-(4-bromophenylazo)-2-nitrocardanol

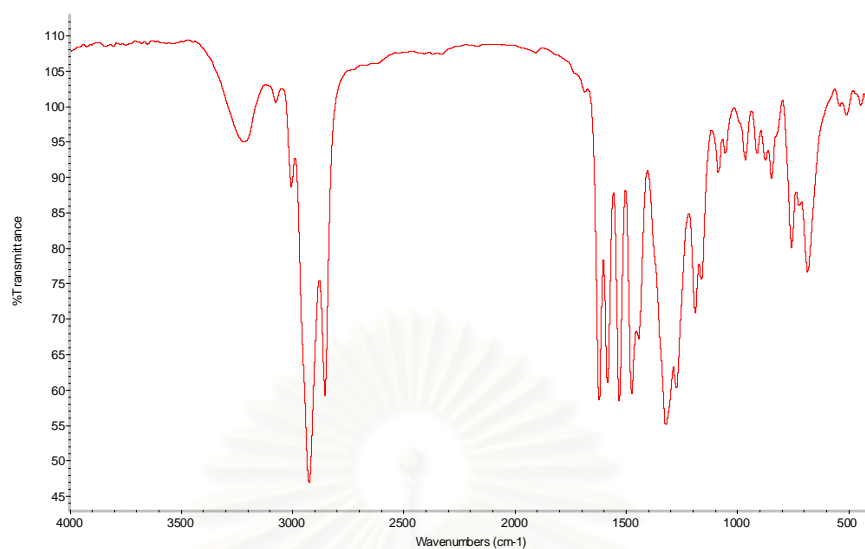


Fig. 4.21 Infrared spectrum of 4-(2-nitrophenylazo)-2-nitrocardanol

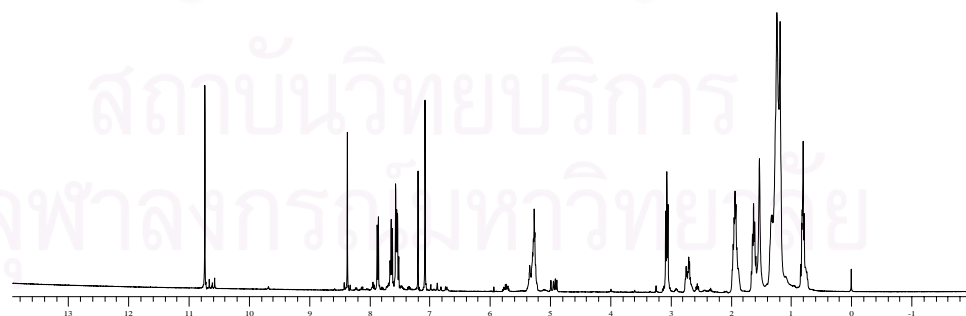


Fig. 4.22 ^1H -NMR spectrum of 4-(2-nitrophenylazo)-2-nitrocardanol

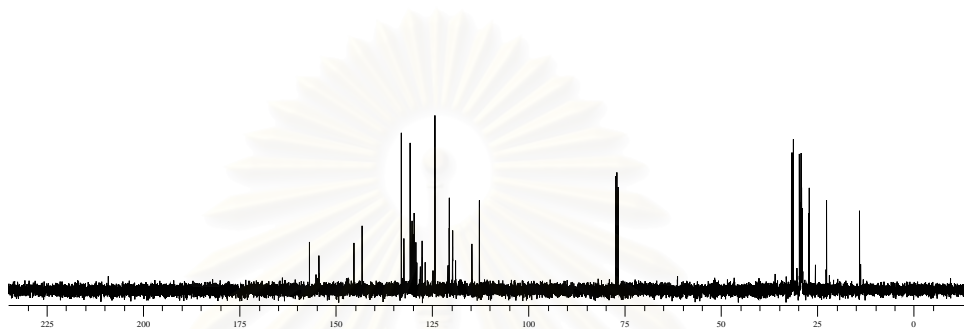


Fig. 4.23 ¹³C-NMR spectrum of 4-(2-nitrophenylazo)-2-nitrocardanol

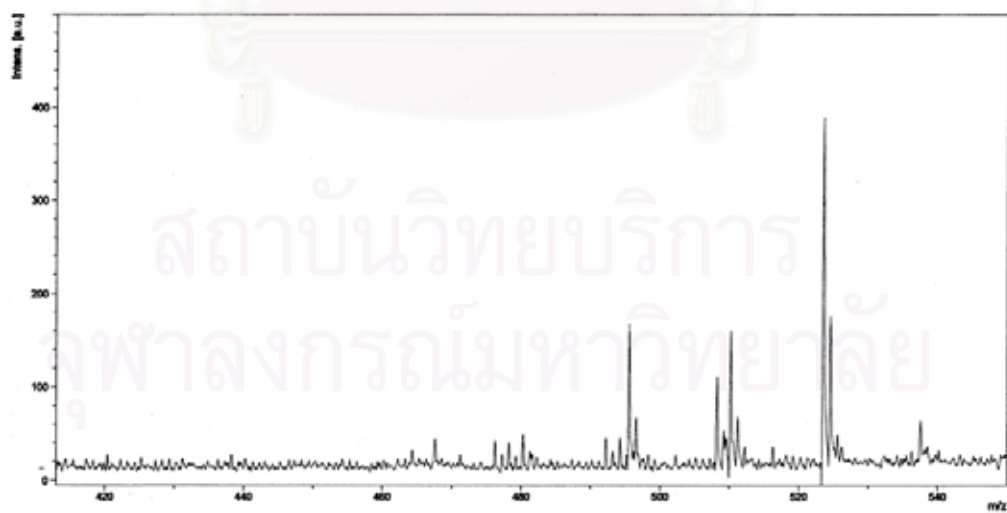


Fig. 4.24 Mass spectrum of 4-(2-nitrophenylazo)-2-nitrocardanol

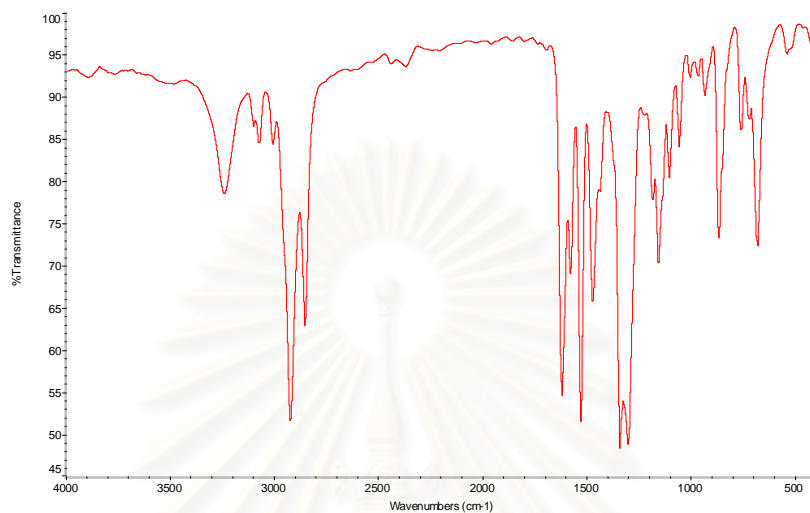


Fig. 4.25 Infrared spectrum of 4-(4-nitrophenylazo)-2-nitrocardanol

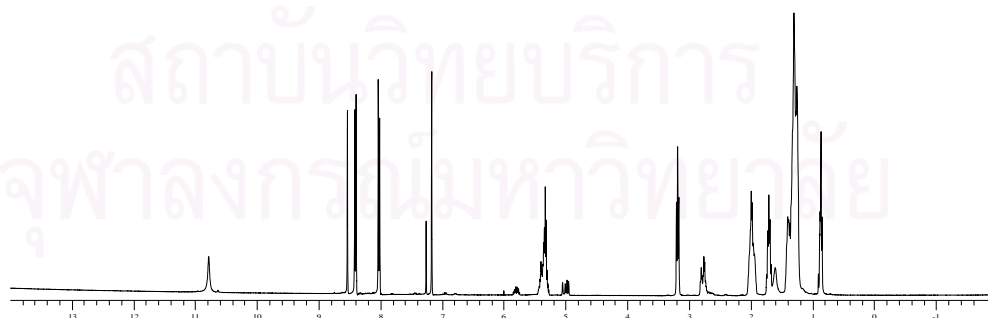


Fig. 4.26 $^1\text{H-NMR}$ spectrum of 4-(4-nitrophenylazo)-2-nitrocardanol

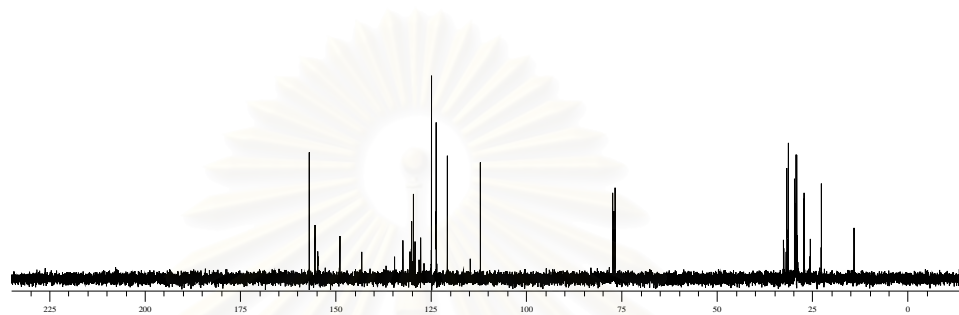


Fig. 4.27 ¹³C-NMR spectrum of 4-(4-nitrophenylazo)-2-nitrocardanol

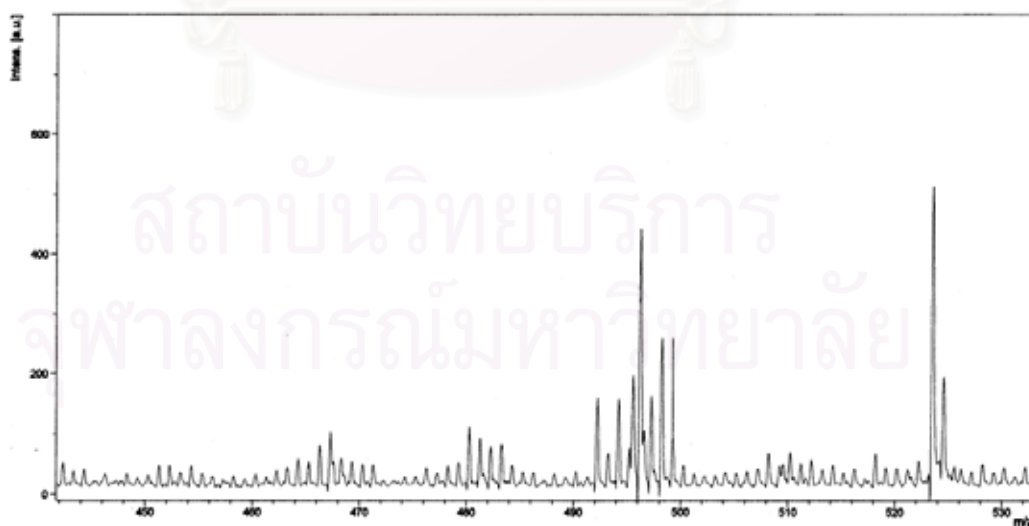


Fig. 4.28 Mass spectrum of 4-(4-nitrophenylazo)-2-nitrocardanol

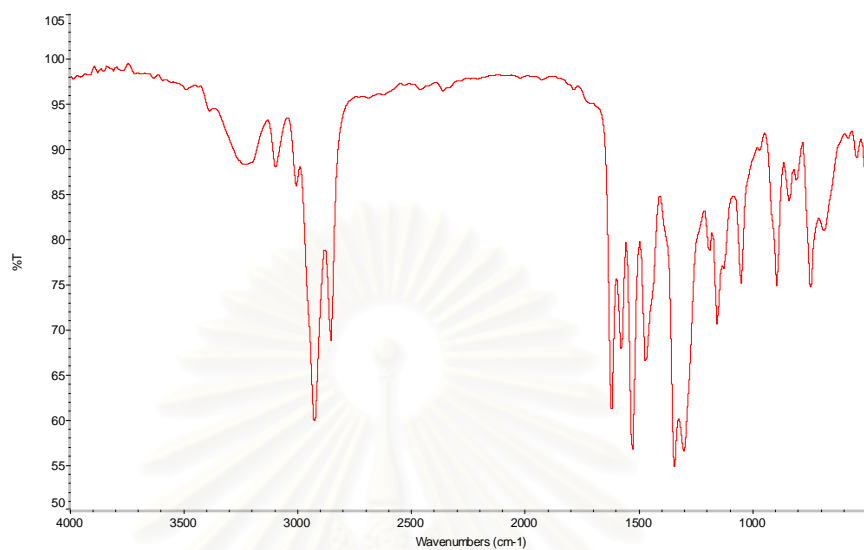


Fig. 4.29 Infrared spectrum of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol

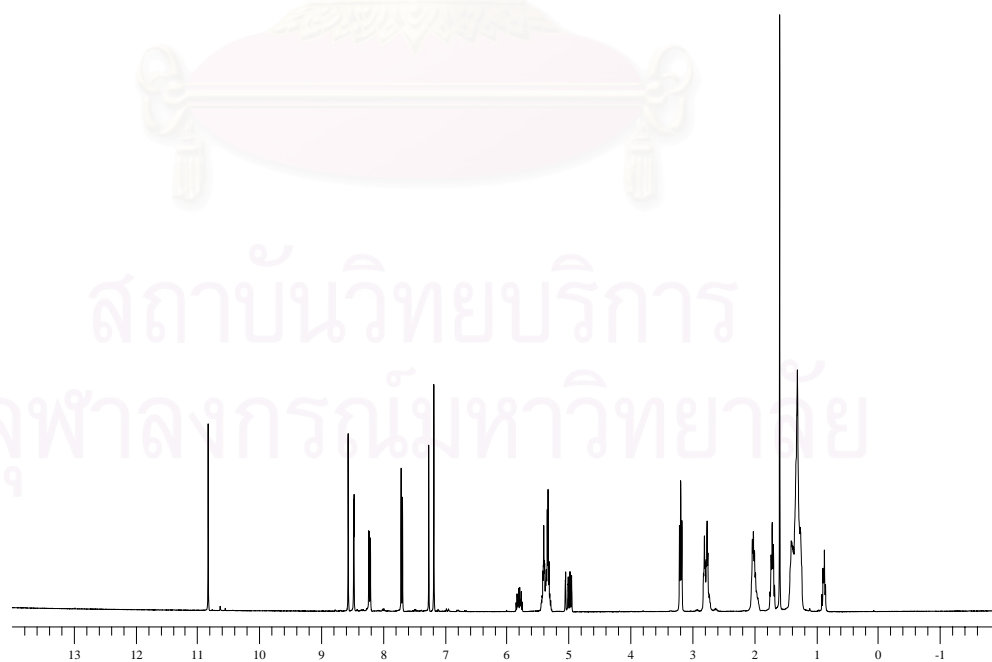


Fig. 4.30 ^1H -NMR spectrum of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol

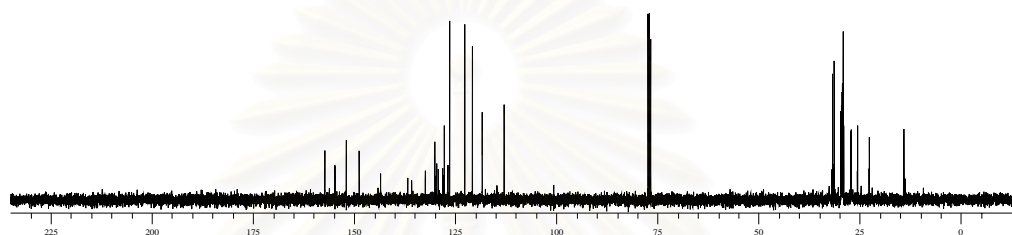


Fig. 4.31 ^{13}C -NMR spectrum of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol

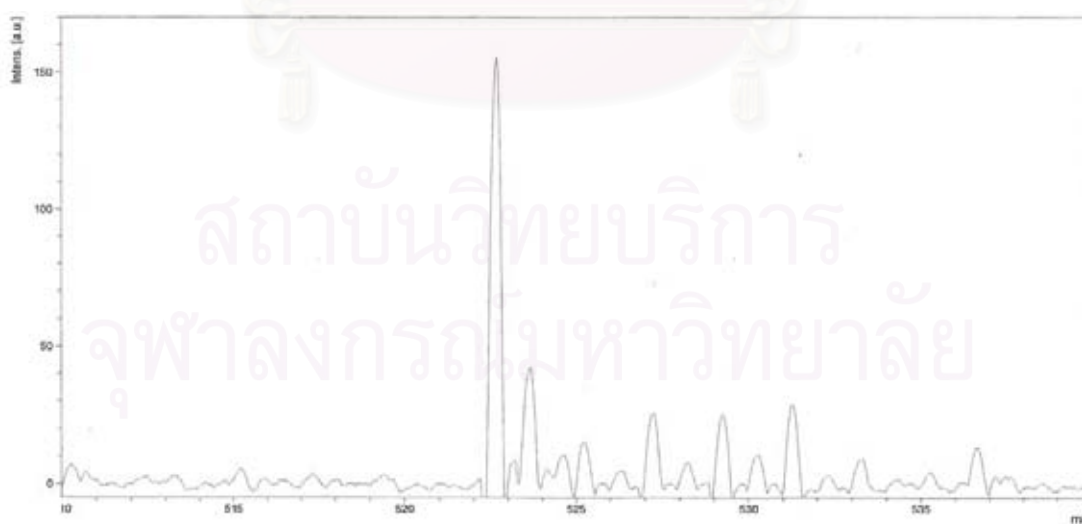


Fig. 4.32 Mass spectrum of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol

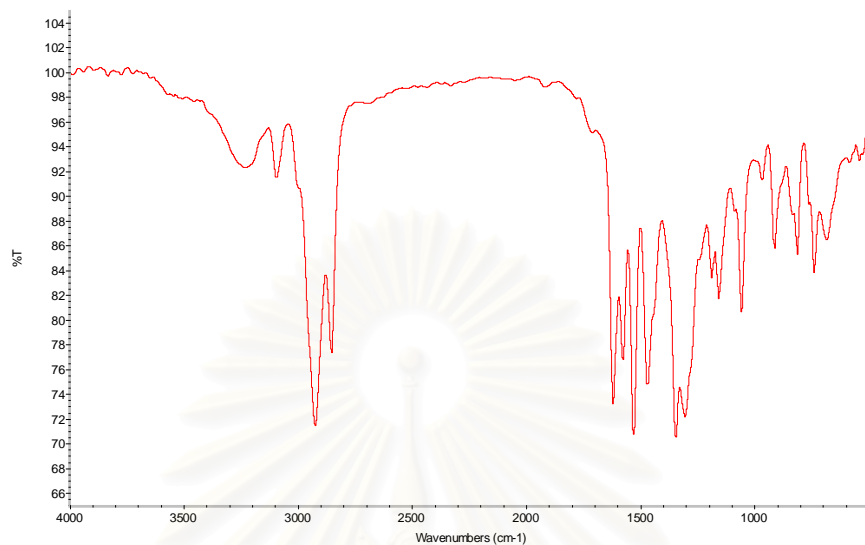


Fig. 4.33 Infrared spectrum of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol

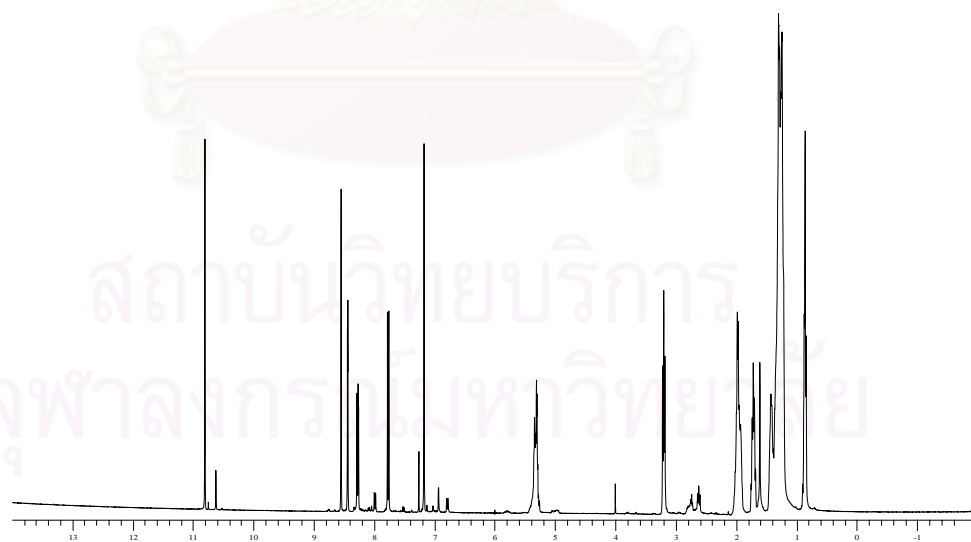


Fig. 4.34 $^1\text{H-NMR}$ spectrum of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol

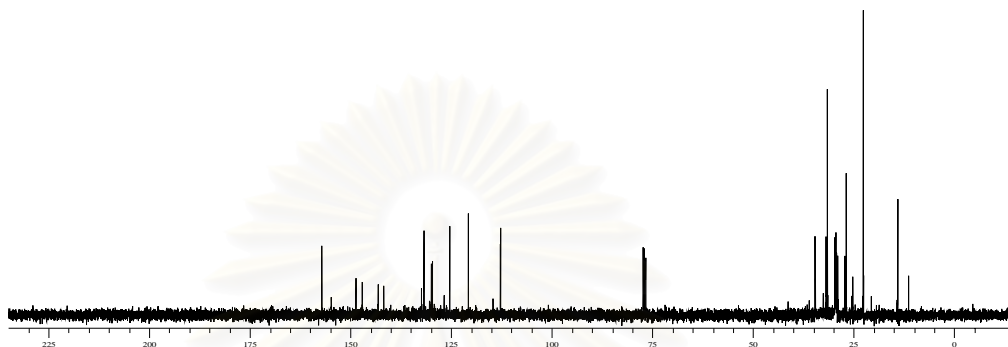


Fig. 4.35 ^{13}C -NMR spectrum of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol

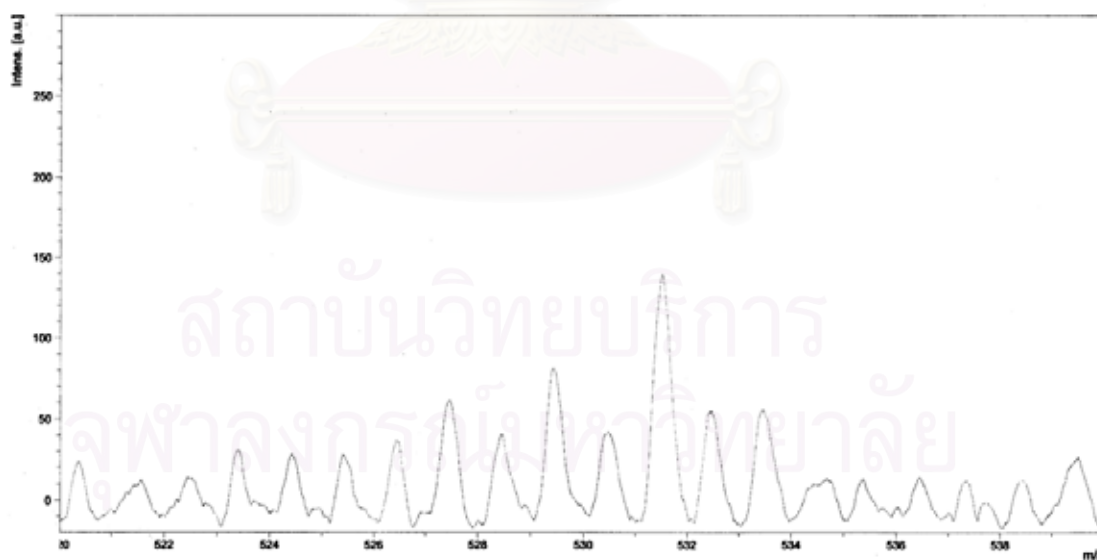


Fig. 4.36 Mass spectrum of 4-(2-chloro-5-nitrophenylazo)-2-nitrocardanol

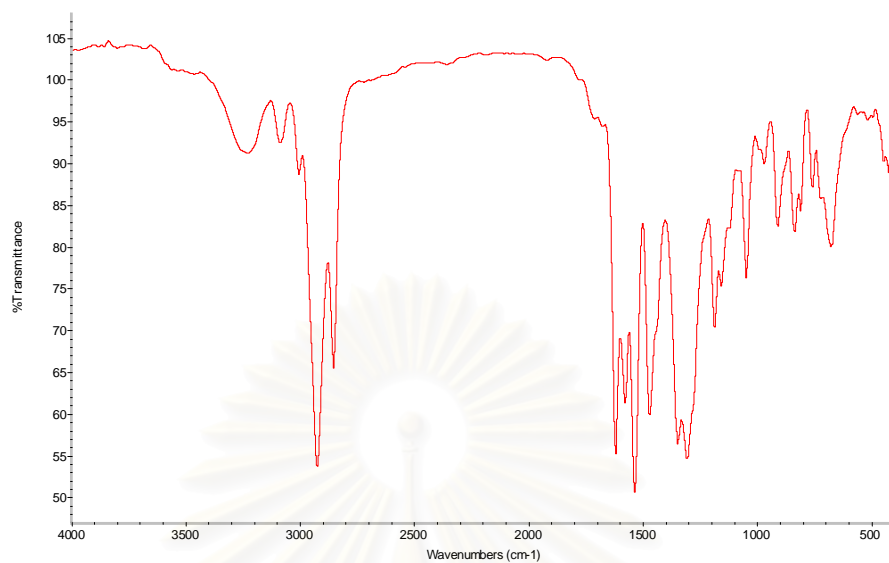


Fig. 4.37 Infrared spectrum of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol

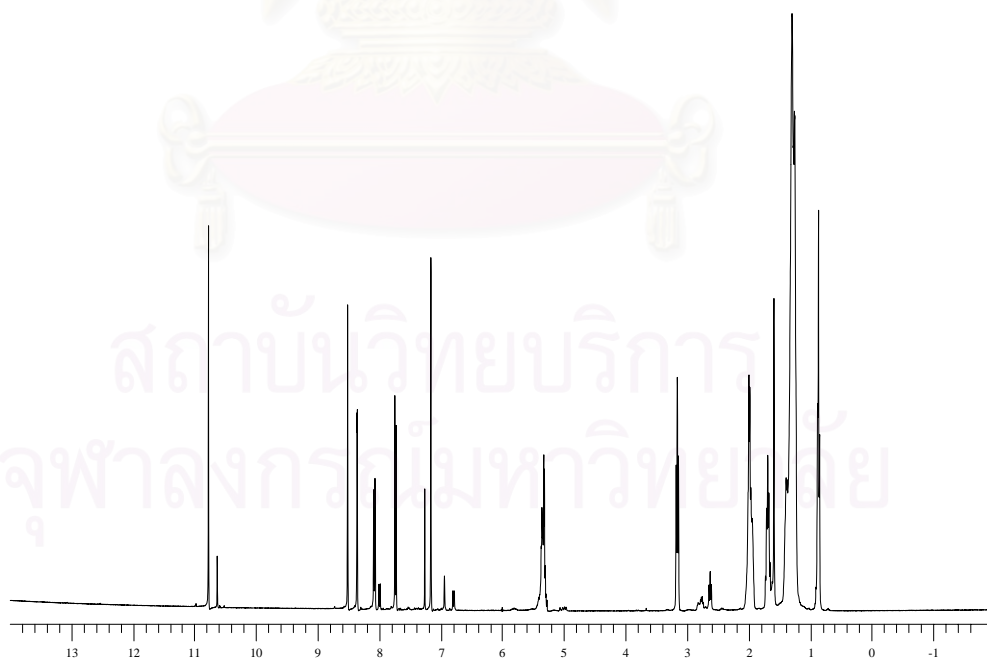


Fig. 4.38 $^1\text{H-NMR}$ spectrum of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol

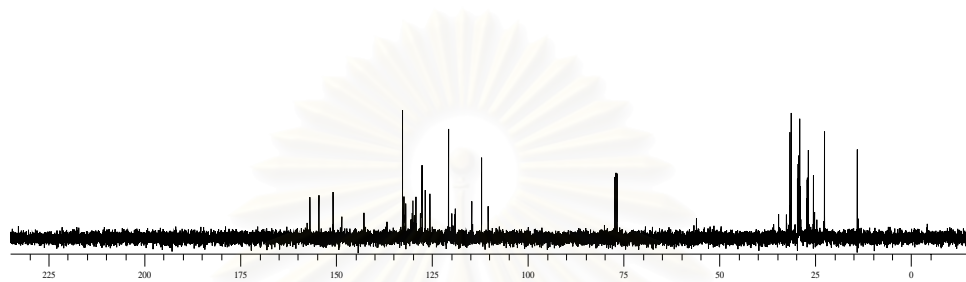


Fig. 4.39 ^{13}C -NMR spectrum of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol

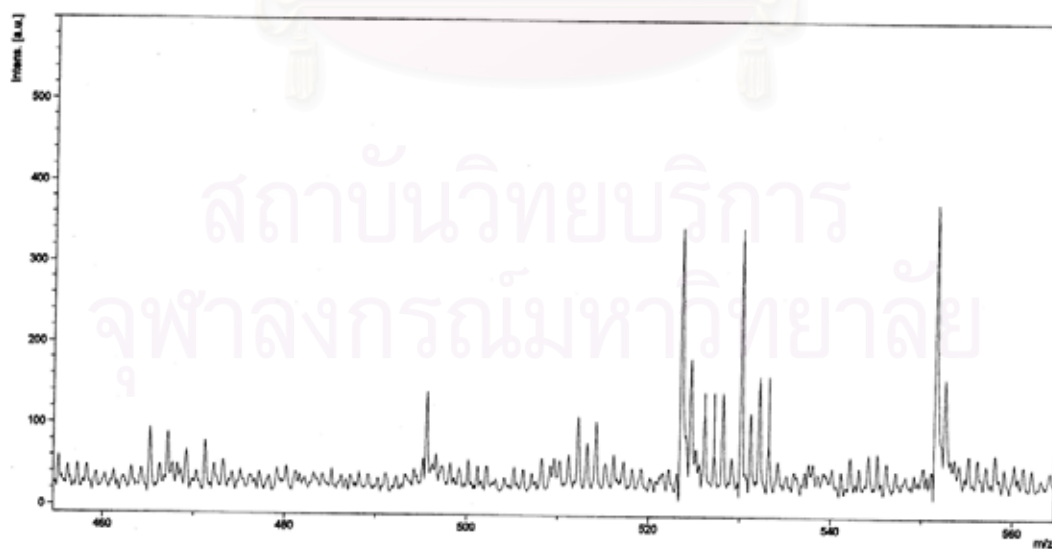


Fig. 4.40 Mass spectrum of 4-(4-chloro-3-nitrophenylazo)-2-nitrocardanol

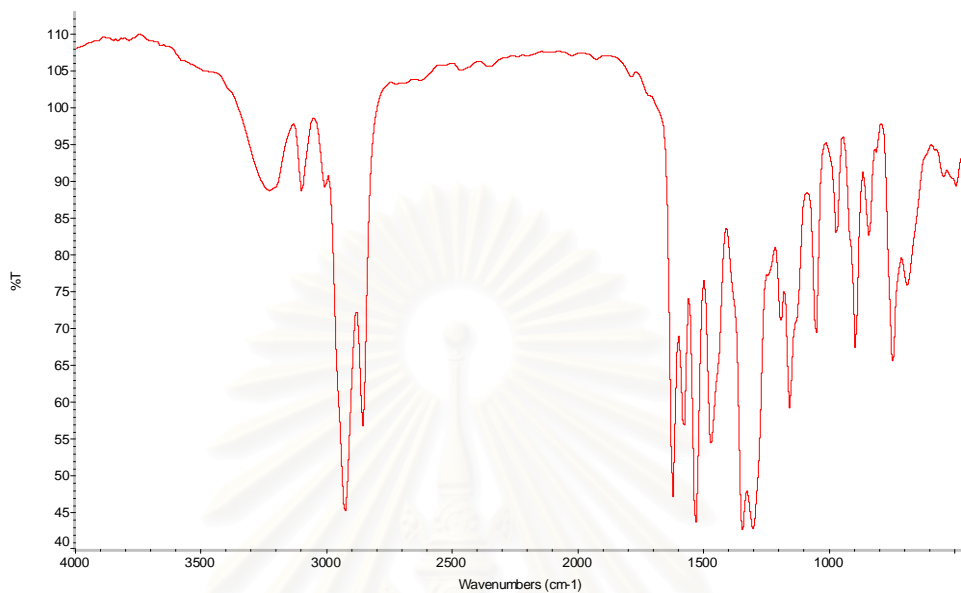


Fig. 4.41 Infrared spectrum of 4-(2,4-dinitrophenylazo)-2-nitrocardanol

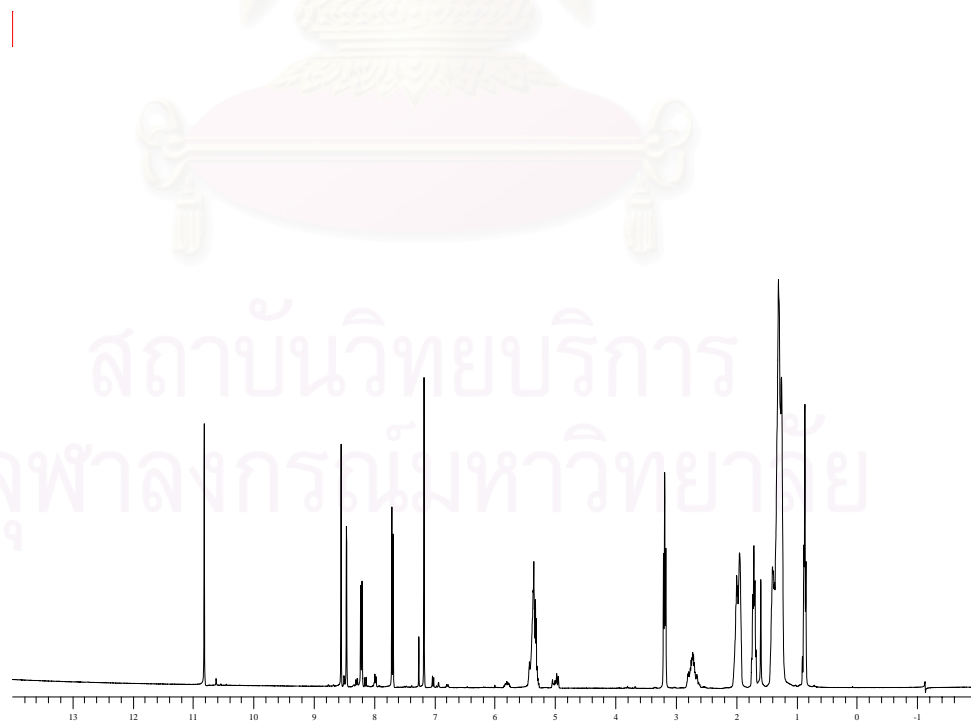


Fig. 4.42 $^1\text{H-NMR}$ spectrum of 4-(2,4-dinitrophenylazo)-2-nitrocardanol

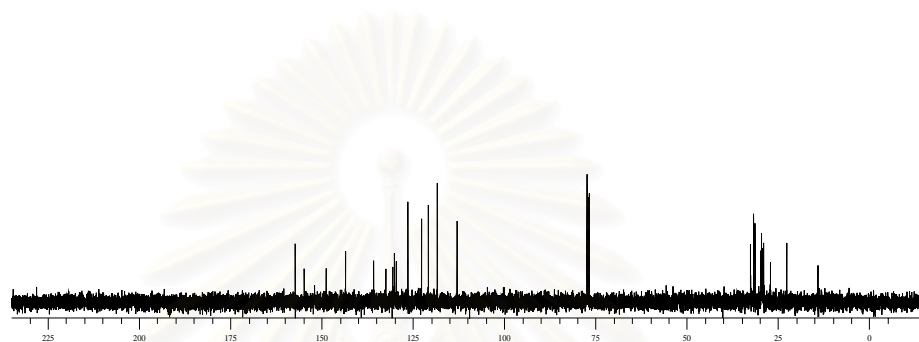


Fig. 4.43 ^{13}C -NMR spectrum of 4-(2,4-dinitrophenylazo)-2-nitrocardanol

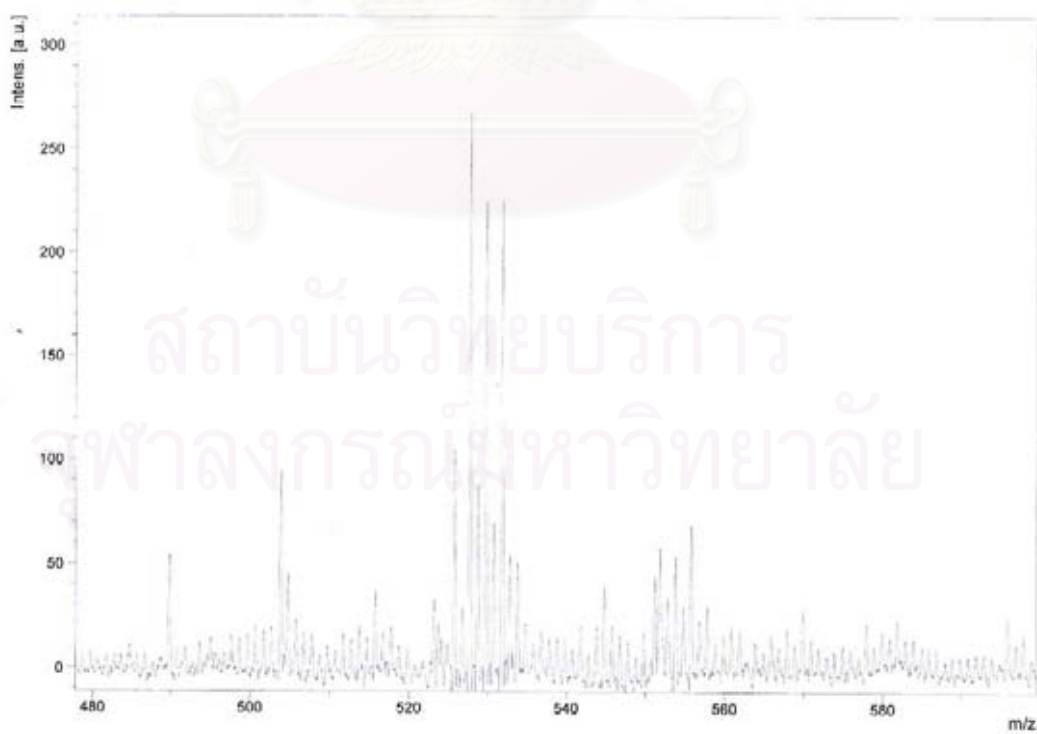


Fig. 4.44 Mass spectrum of 4-(2,4-dinitrophenylazo)-2-nitrocardanol

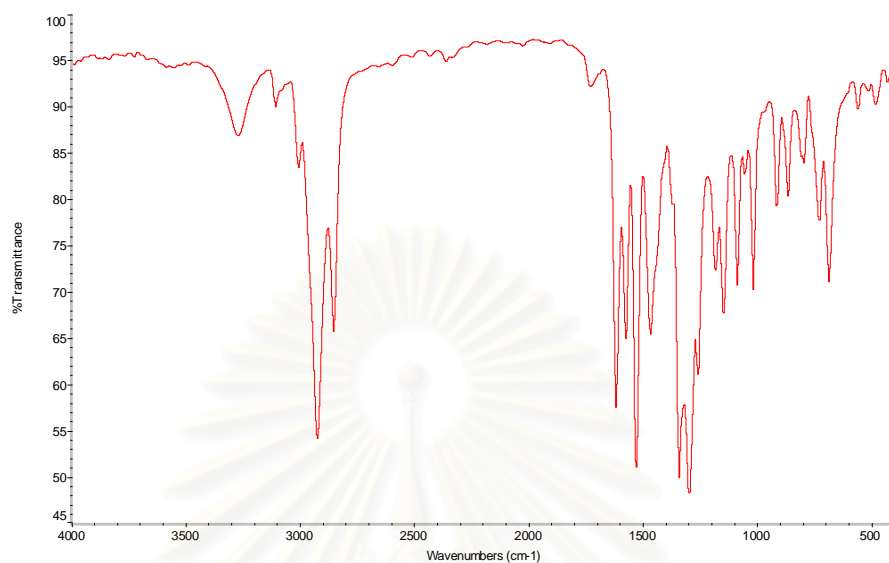


Fig. 4.45 Infrared spectrum of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol

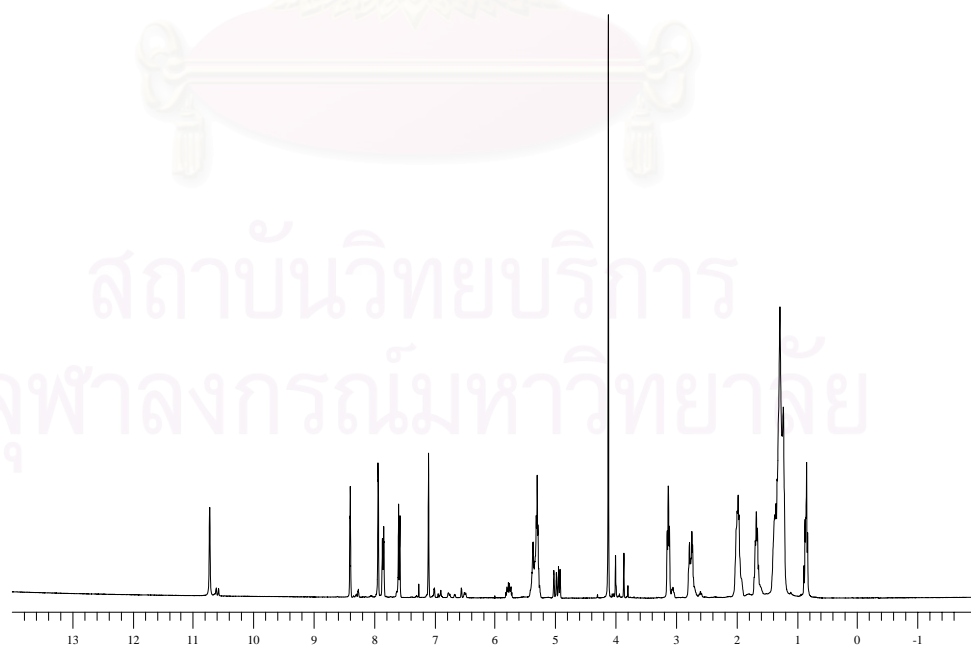


Fig. 4.46 $^1\text{H-NMR}$ spectrum of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol

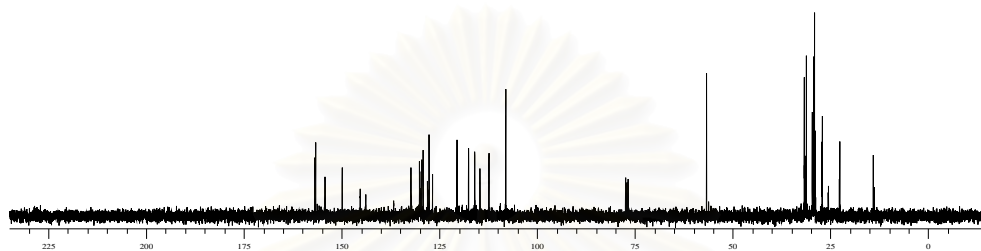


Fig. 4.47 ^{13}C -NMR spectrum of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol

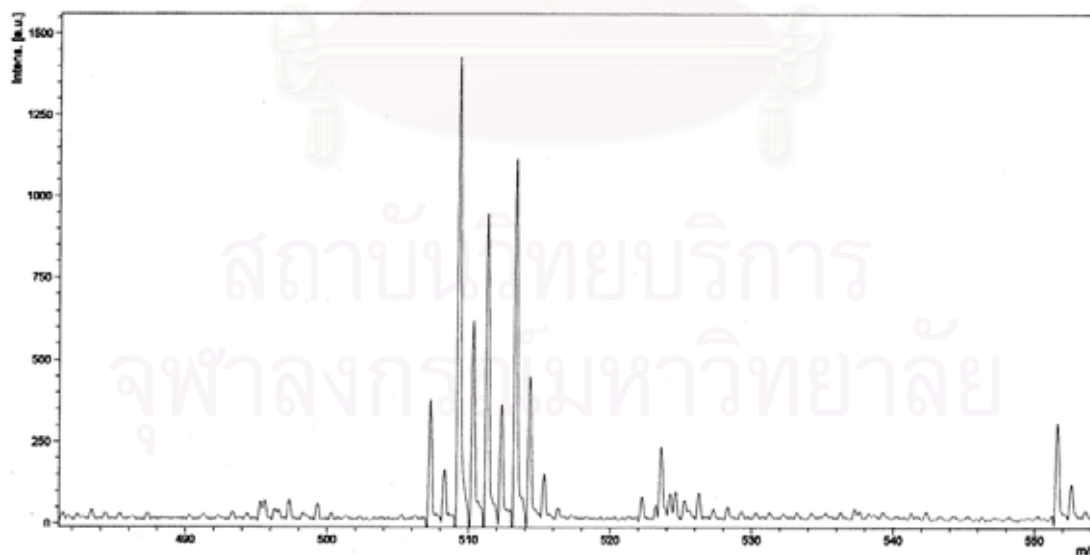


Fig. 4.48 Mass spectrum of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol

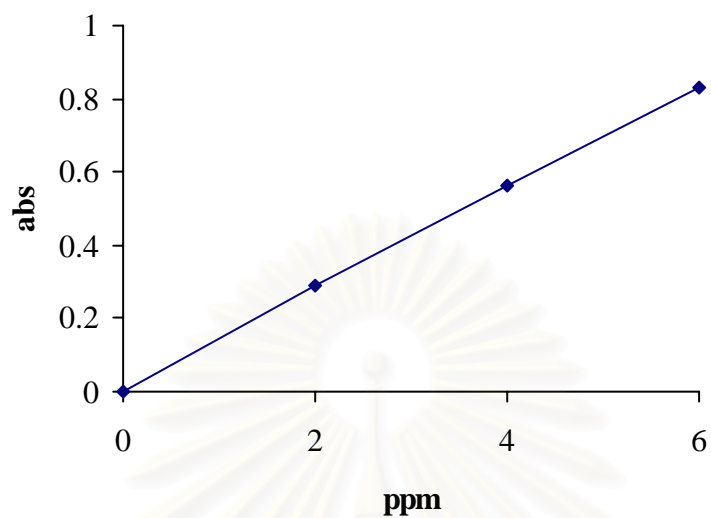


Fig. 4.54 Calibration curve of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol in diesel fuel

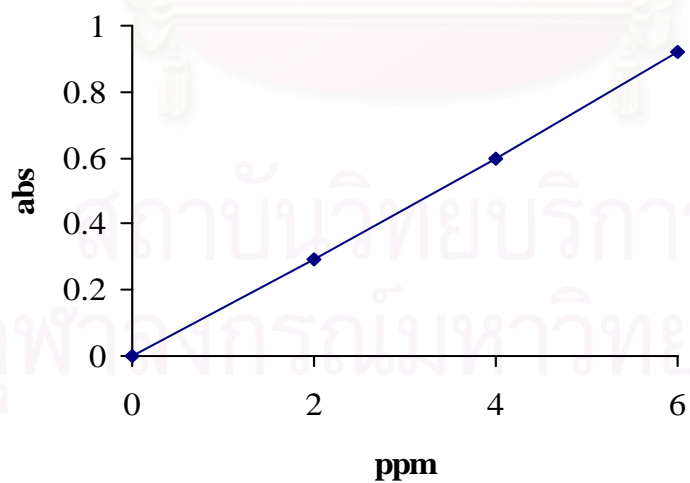


Fig. 4.55 Calibration curve of 4-(2-chloro-4-nitrophenylazo)-2-nitrocardanol in gasoline

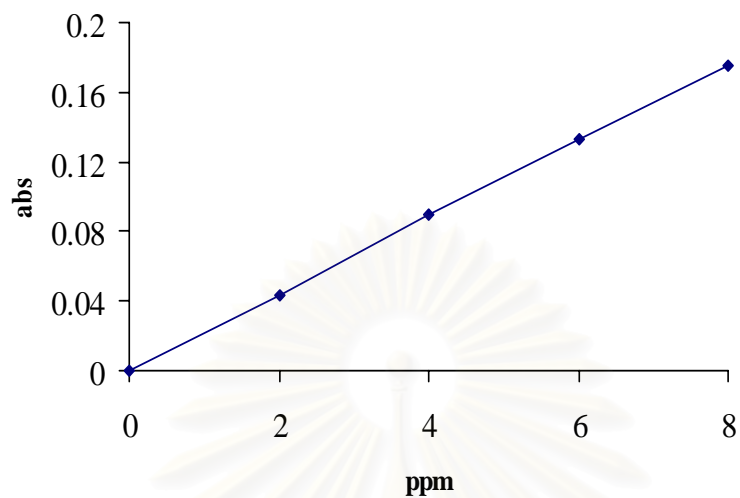


Fig. 4.56 Calibration curve of 4-(2,4-dinitrophenylazo)-2-nitrocardanol in diesel fuel

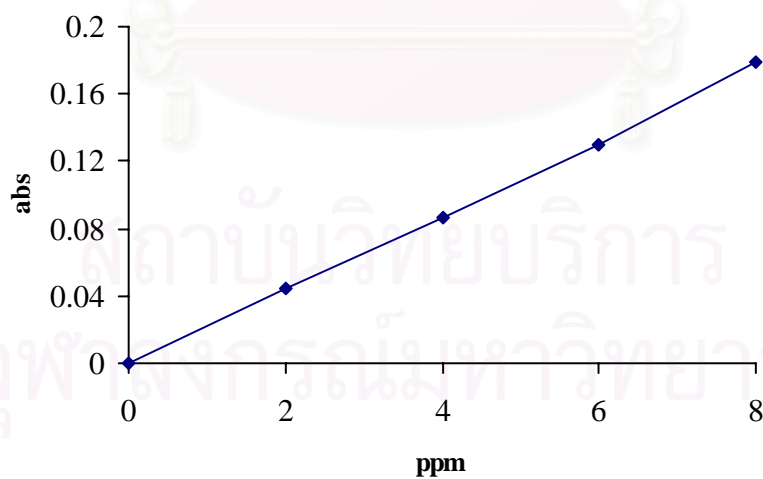


Fig. 4.57 Calibration curve of 4-(2,4-dinitrophenylazo)-2-nitrocardanol in gasoline

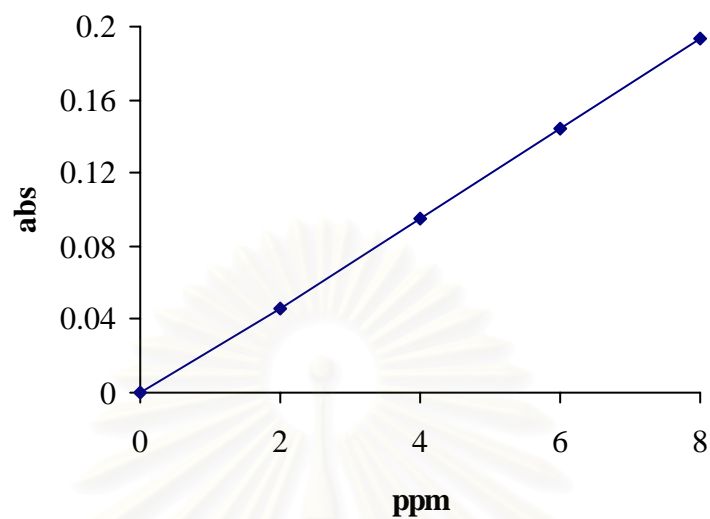


Fig. 4.58 Calibration curve of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol in diesel fuel

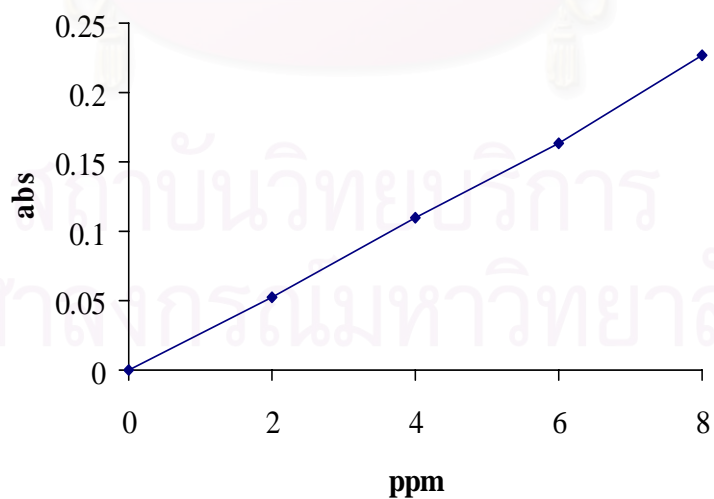


Fig. 4.59 Calibration curve of 4-(2-methoxy-4-nitrophenylazo)-2-nitrocardanol in gasoline

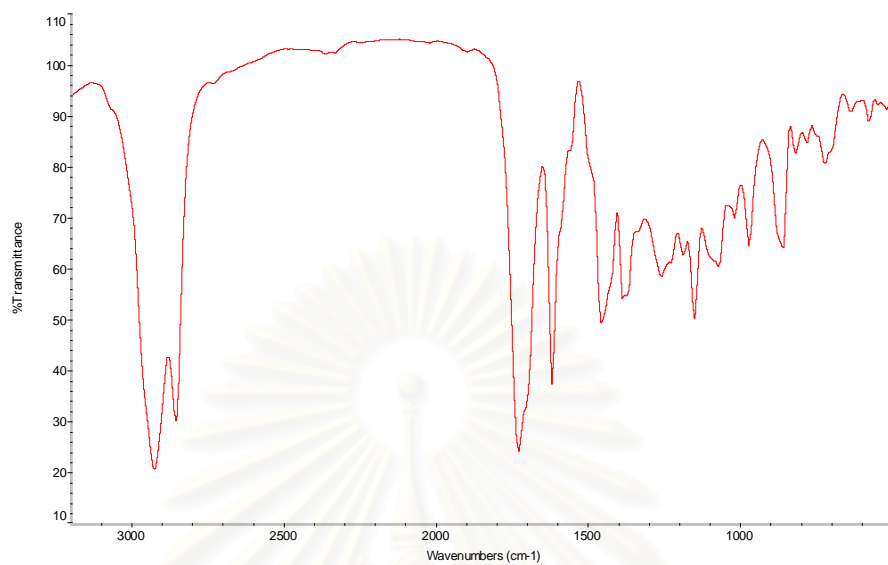


Fig. 4.60 Infrared spectrum of 7-alkyl-4-methylcoumarin

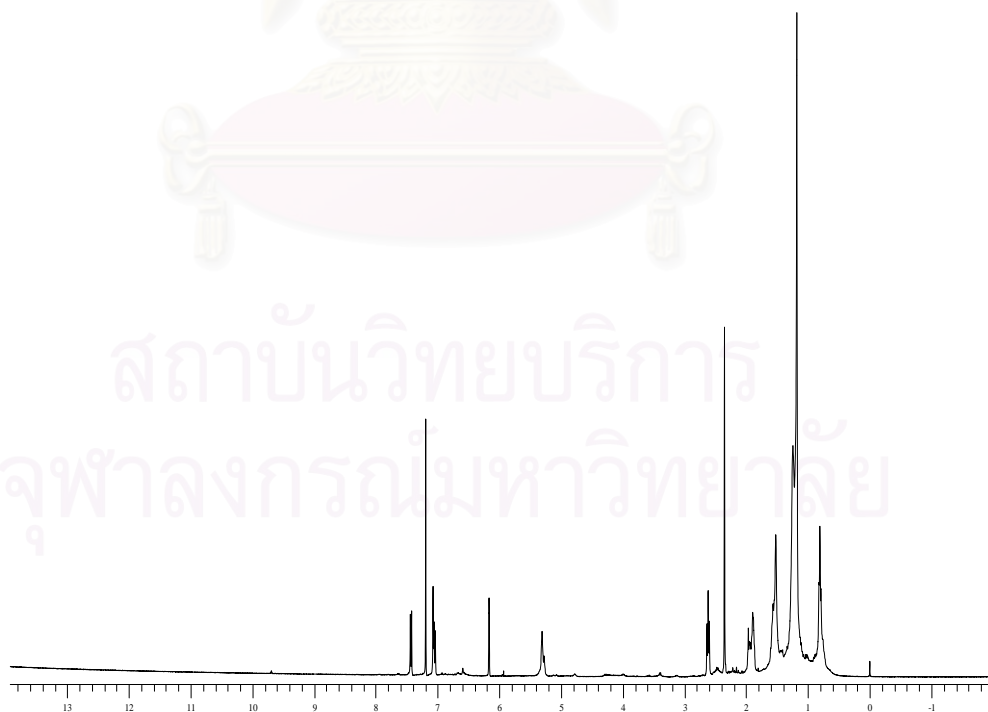


Fig. 4.61 ^1H -NMR spectrum of 7-alkyl-4-methylcoumarin

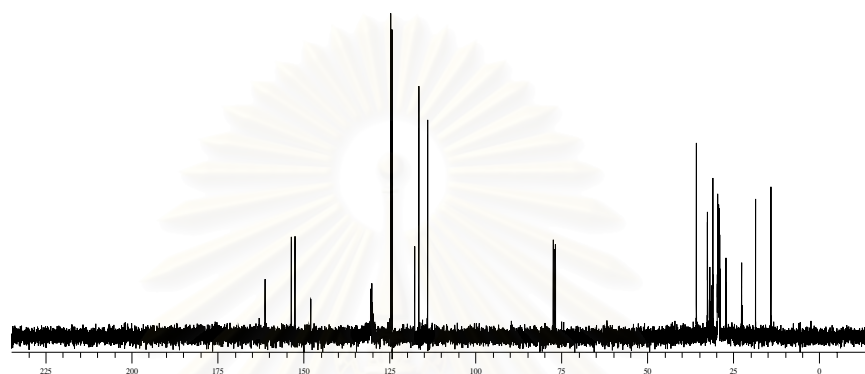


Fig. 4.62 ^{13}C -NMR spectrum of 7-alkyl-4-methylcoumarin

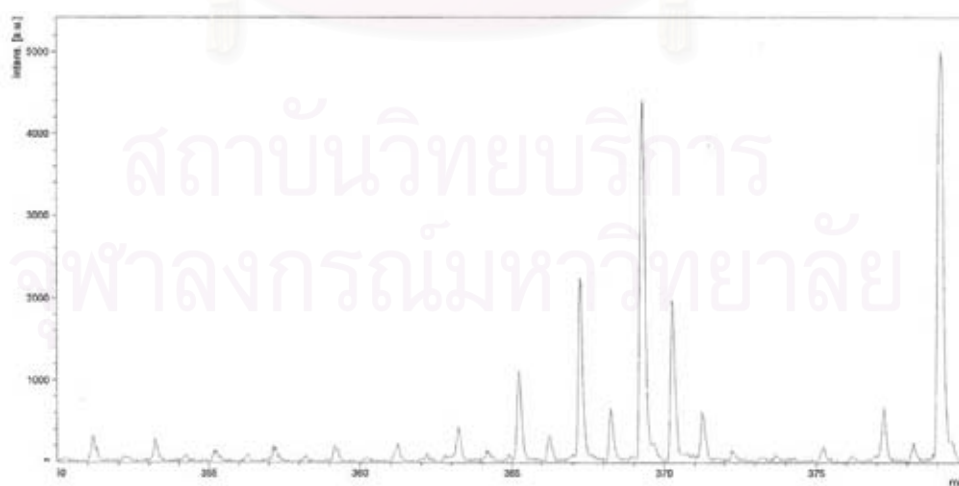


Fig. 4.63 Mass spectrum of 7-alkyl-4-methylcoumarin

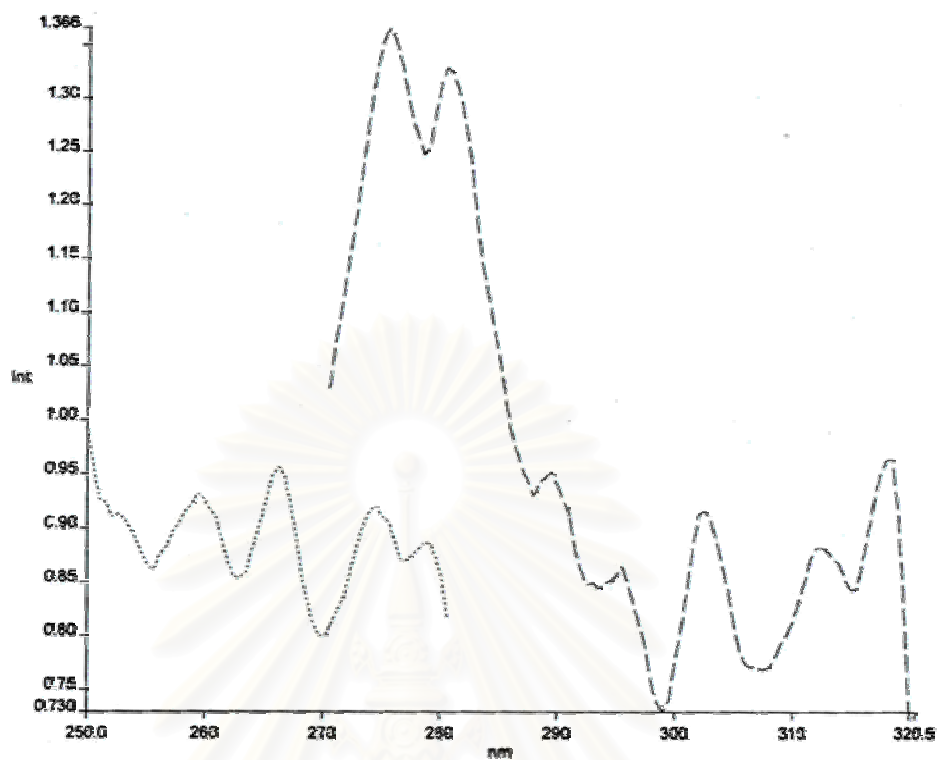


Fig. 4.64 Absorption-emission spectra of 7-alkyl-4-methylcoumarin in diesel fuel

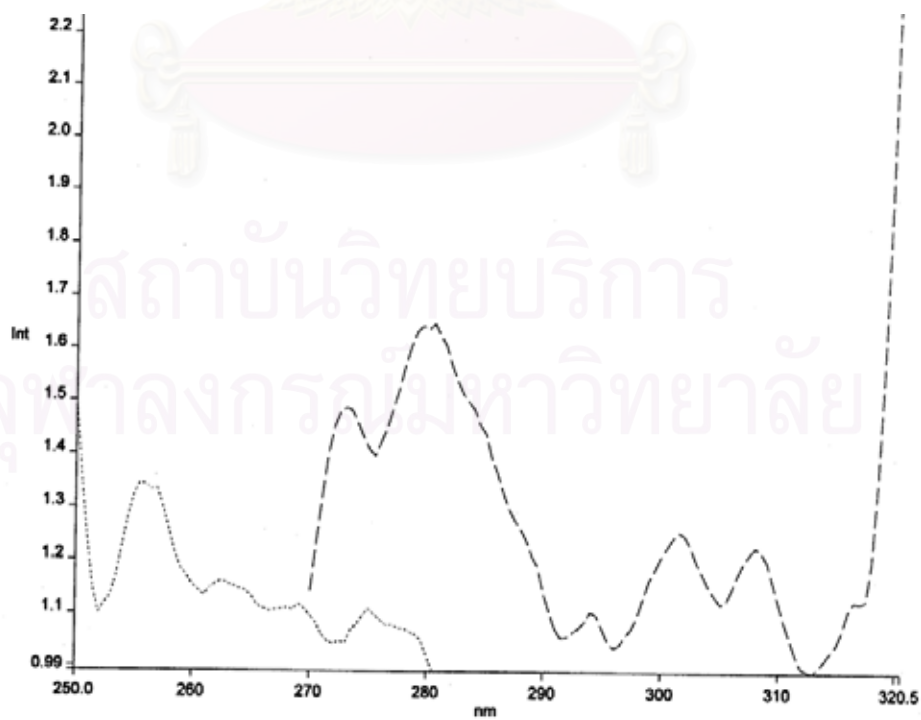


Fig. 4.65 Absorption-emission spectra of diesel fuel

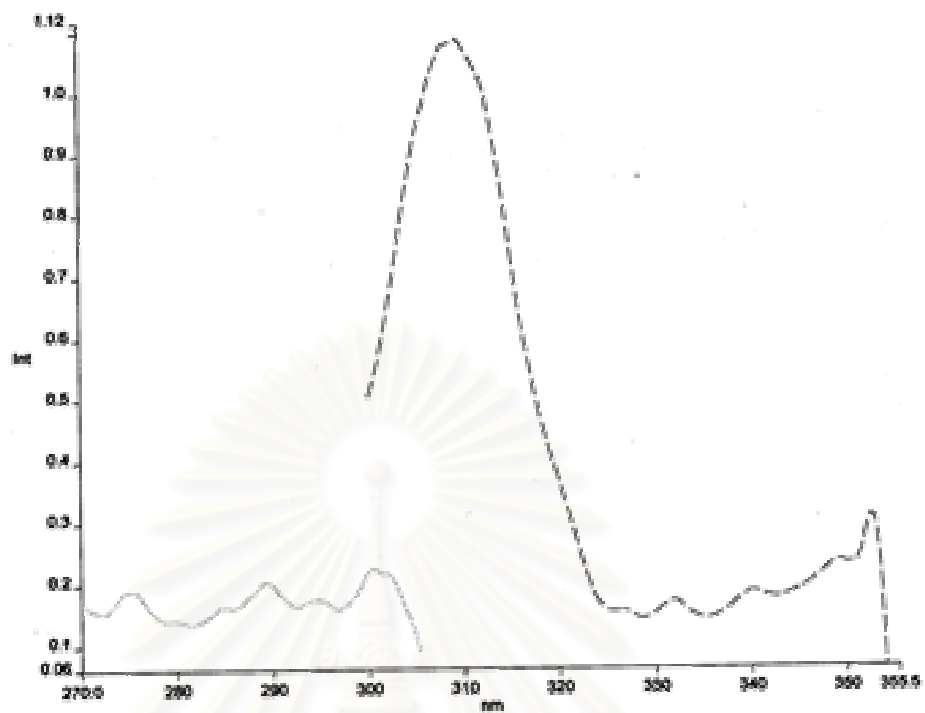


Fig. 4.66 Absorption–emission spectra of 7-alkyl-4-methylcoumarin in gasoline

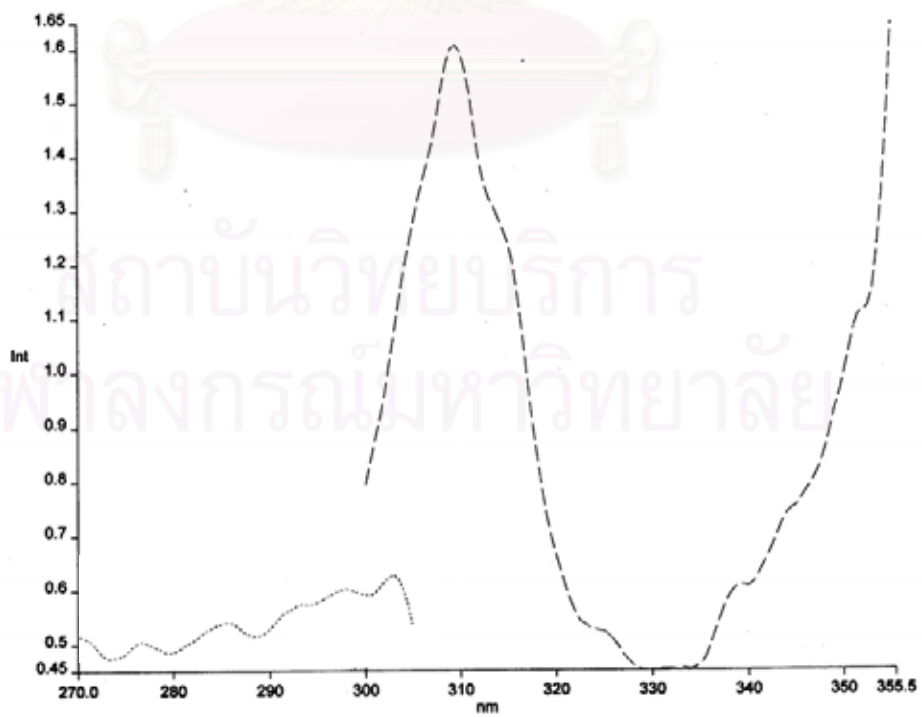


Fig. 4.67 Absorption–emission spectra of gasoline

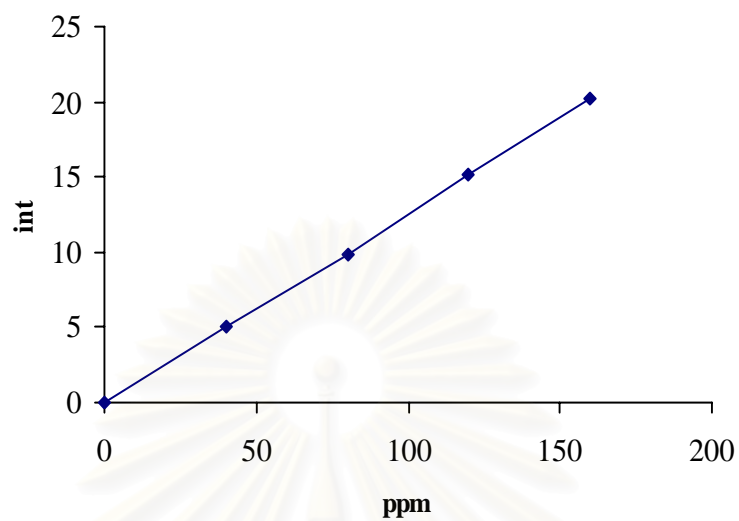


Fig. 4.68 Calibration curve of 7-alkyl-4-methylcoumarin in diesel fuel

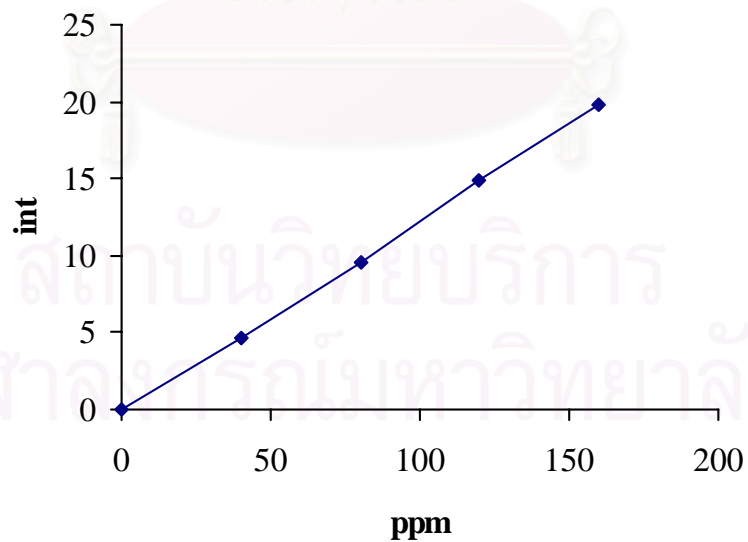


Fig. 4.69 Calibration curve of 7-alkyl-4-methylcoumarin in gasoline

CURRICULUM VITAE

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สถาบันวิทยบริการ
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