การสังเคราะห์และพิสูจน์เอกลักษณ์ของพอลิไวนิลแอลกอฮอล์ที่มีแอลคอกซีคูมารินสายโซ่ยาว

นาย ธีรวัฒ ต้นสวรรค์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SYNTHESIS AND CHARACTERIZATION OF POLY(VINYL ALCOHOL) CONTAINING LONG-CHAIN ALKOXY COUMARINS

Mr. Theerawat Tonsawan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	SYNTHESIS AND CHARACTERIZATION OF POLY(VINYL ALCOHOL) CONTAINING LONG-CHAIN ALKOXY COUMARINS
By	Mr. Theerawat Tonsawan
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Supawan Tantayanon, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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ในงานวิจัยนี้ใช้คูมาริน 2 ชนิด ได้แก่ 5,7-ไดไฮดรอกซี-4-เมทิลคูมารินซึ่งสังเคราะห์ด้วยปฏิกิริยาเพคมาน และ 6,7-ไดไฮดรอกซี-4-เมทิลคูมารินซึ่งสามารถซื้อได้ คูมารินแต่ละชนิดถูกแอลคิเลตด้วยบิวทิลโบรไมด์ หรือ ออกทิลโบรไมด์ ในแอลคิเลชันแต่ละปฏิกิริยาได้โมโนแอลคอกซีคูมาริน 2 ชนิด และ ไดแอลคอกซีคูมาริน 1 ชนิดสำหรับคูมารินชนิดแรกและได้โมโนแอลคอกซีคูมาริน 1 ชนิด และ ไดแอลคอกซีคูมาริน 1 ชนิดสำหรับคูมารินชนิดที่สอง โมโนแอลคอกซีคูมารินทั้ง 6 ชนิดทำปฏิกิริยาต่อไปกับ1,3-ไดโบรโมโพรเพน พบว่า 7-แอลคอกซี-5-ไฮดรอกซี-4-เมทิลคูมาริน 2 ชนิด และ 5-แอลคอกซี-7-ไฮดรอกซี-4-เมทิลคูมาริน 2 ชนิดสามารถทำปฏิกิริยาให้ได้(3'-โบรโม)โพรพอกซีคูมาริน 4 ชนิด นอกจากนี้ ไดไฮดรอกซี-4-เมทิลคูมารินทั้ง 2 ชนิดได้ทำปฏิกิริยา 1,3-ไดโบรโมโพรเพนเพื่อการเปรียบเทียบ ท้ายที่สุด คูมารินที่มี(3'-โบรโม)โพรพอกซี 7ชนิดได้ทำปฏิกิริยากับพอลิไวนิลแอลกอฮอล์ (พีวีเอ) อย่างไรก็ตาม 6-ไฮดรอกซี-4-เมทิล-7-(3'-โบรโม)โพรพอกซีคูมารินไม่เกิดปฏิกิริยาและ หกผลิตภัณฑ์เท่านั้นที่เกิดปฏิกิริยาหลังจากไดแอไลซิสและฟรีสดรายอิงสารประกอบที่สังเคราะห์ได้ทั้งหมดได้พิสูจน์เอกลักษณ์โดย เอฟทีไออาร์ ^{1}เอ็ช-เอ็นเอ็มอาร์ และ ยูวีสเปกโทรสโกปี ในการทดสอบโฟโทรีซิสต์ พีวีเอที่มีอนุพันธ์คูมาริน 4 ชนิดสามารถให้ลวดลายบนสไลด์แก้วหลังจากฉายแสงและล้างด้วยน้ำร้อน ผลที่ได้แสดงว่า พีวีเอที่มี 7-บิวทอกซี-4-เมทิล-5-(3'-โบรโม)โพรพอกซี- และ 5-บิวทอกซี-4-เมทิล-7-(3'-โบรโม)โพรพอกซีคูมาริน เป็นเนกาทีฟโฟโทรีซิสต์ที่ยอมรับได้

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ธีรวัฒ ต้นสวรรค์

ปีการศึกษา 2553 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

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KEYWORDS : COUMARIN / POLY(VINYL ALCOHOL) / PHOTORESIST

THEERAWAT TONSAWAN: SYNTHESIS AND CHARACTERIZATION OF POLY(VINYL ALCOHOL) CONTAINING LONG-CHAIN ALKOXY COUMARINS. ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., 76 pp.

Two coumarins, 5,7-dihydroxy-4-methylcoumarin and 6,7-dihydroxy-4-methylcoumarin, have been used in this study. The former was synthesized via the Pechmann reaction, while the latter is commercially available. Each of them was alkylated with butyl bromide or octyl bromide. In each alkylation, two monoalkoxy- and one dialkoxycoumarins were obtained for the first coumarin, and one monoalkoxy- and one dialkoxycoumarin were yielded for the second coumarin. Each of six monoalkoxy coumarins was further alkylated with 1,3-dibromopropane. It was found that two 7-alkoxy-5-hydroxy-4-methylcoumarins and two 5-alkoxy-7-hydroxy-4-methylcoumarins could react to yield four (3′-bromo)propoxycoumarins. In addition, two parent dihydroxy-4-methylcoumarins were also reacted with 1,3-dibromopropane for comparison. Finally, seven (3′-bromo)propoxycoumarins were reacted with poly(vinyl alcohol) (PVA). However, 6-hydroxy-4-methyl-7-(3'-bromo)coumarin did not reacted and only six products were obtained after dialysis and freez-drying. All synthesized compounds were characterized by FTIR, ^{1}H-NMR and UV spectroscopy. In the photoresist testing, four out of six polymersgave patterns on glass slides after irradiation and developing in hot water. The results revealed that two PVA containing 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin and PVA containing 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin were the most acceptable negative photoresist.

Field of Study : Petrochemistry and Polymer Science Student's Signature Theerawat Tonsawan

Academic Year: 2010 Advisor's Signature

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Finally, I would like to express my gratitude to my family for their love, encouragement and great support throughout my study.

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

°C	: Degree Celsius
h	: Hour
LCD	: Liquid crystalline display
l	: Liter
μ	: Micro
MEMS	: Microelectromechanical systems
ml	: Milliliter
PVA	: Poly(vinyl alcohol)
RAFT	: Reversible addition fragmentation chain transfer

CHAPTER I

INTRODUCTION

1.1 Introduction

Photopolymers with photocrosslinkable groups have been paid much attention for a few decades because of a variety of applications in the field of microlithography, printing materials, liquid crystalline display (LCD) and non-linear optical materials [1-2]. Photopolymers are imaging compositions based on polymers, oligomers, and monomers which can be selectively polymerized or crosslinked upon exposure by light radiation such as ultra-violet light. For final use, they are made into different forms including film/sheet, liquid, and solution which find outlets in printing plates, imaging, stereolithography and photoresists. A popular use of photopolymers is as photoresists which are used to make integrated circuits, flat panel displays, printed circuits, chemically milled parts, microelectromechanical systems (MEMS).

In photoresist application, photosensitive polymers are required to have α, β-unsaturated carbonyl groups or unsaturated double-bond either in the backbone or in pendant position. Generally, photoresists are classified into two groups, positive resists and negative resists. If the irradiated portions of substrate become soluble to the photoresist developer and unexposed area is insoluble to the photoresist developer, these polymers are addressed as negative photoresists. In positive resists, the photochemistry brings about an enhancement of the solubility or of dissolution rate and it is the irradiated areas that are removed by the developer.

In fact, there are a number of commercially available photosensitive polymers. However, they cannot fulfill industrial requirements. For instance, commercially negative resists based on diazo salts and oxides, diazo formaldehyde resins, cinnamate polyesters and chalcone polymers have been used extensively, nevertheless, these resists are not inherently benign and often contain toxic starting materials, intermediates, and products. Some were coated by volatile organic solvents, such as, 1-methyl-2-propyl acetate, that could generate green house gases to the environment.

Therefore, the need for environmentally friendly photoresists, especially completely water-soluble, are strongly desired.

Coumarins were used in this research because they have α, β-unsaturated carbonyl groups. Poly(vinyl alcohol) was used for support material because it is a water-soluble which can be able to form as good film. This research will prepare poly(vinyl alcohol) containing coumarin derivatives to study solubility and negative resists application.

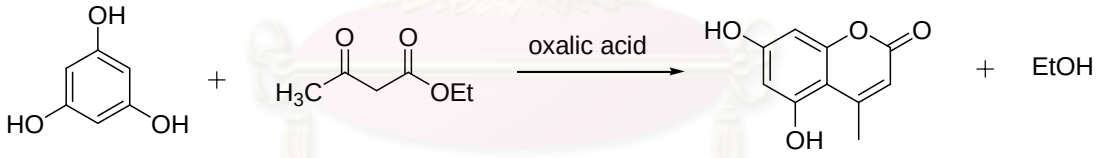
1.2 Objectives of the research work

This study aims to synthesis of negative resists and investigate solubility and photoresist process.

1.3 Scope of the research work

1. Synthesis of 5,7-dihydroxy-4-methylcoumarin

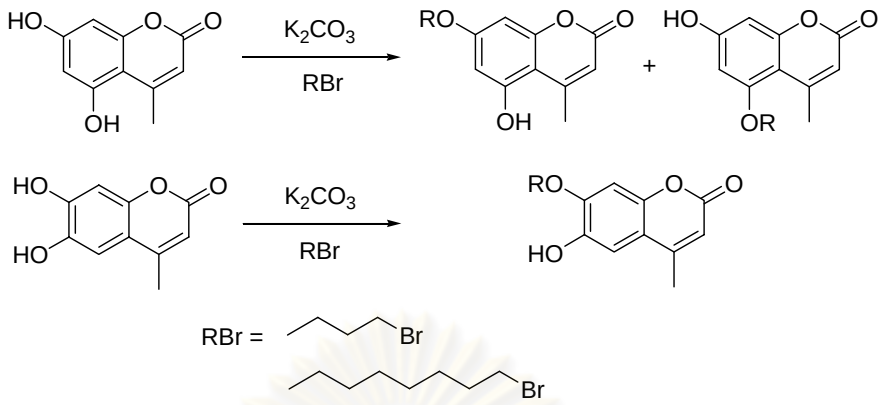
The synthesis will be performed via Pechman reaction but acceptable method using oxalic acid liquid as acid catalyst will be used.



Scheme 1 The synthesis of 5,7-dihydroxy-4-methylcoumarin

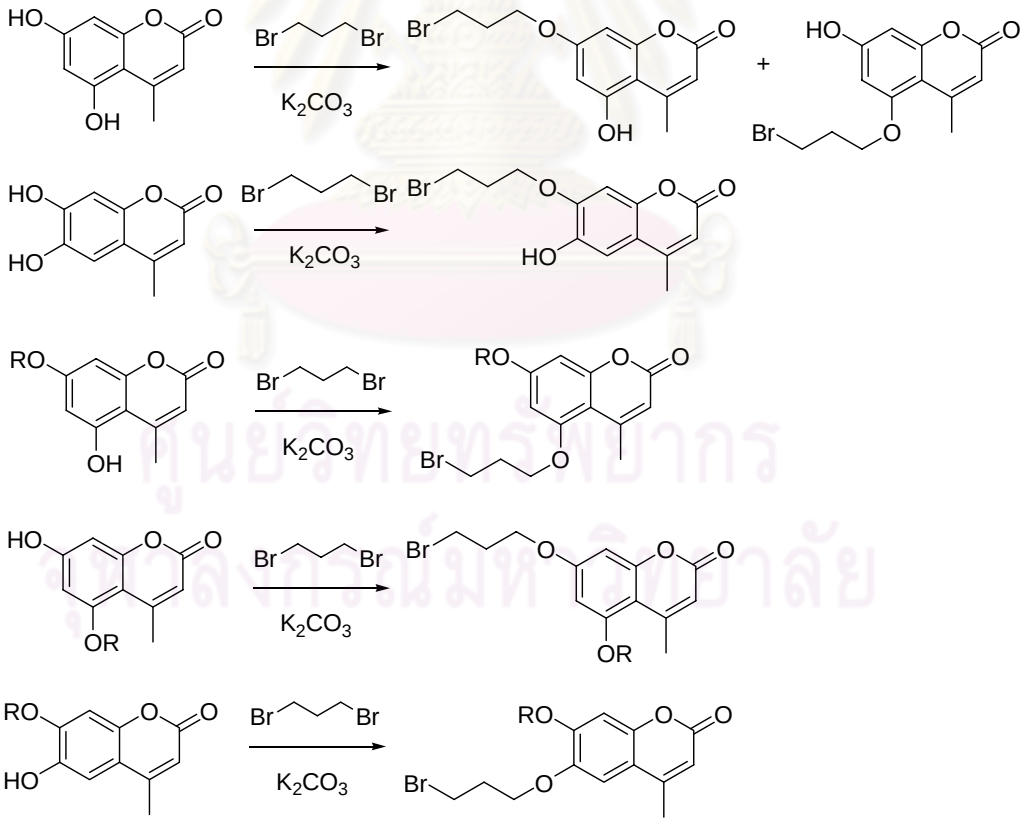
2. Synthesis of monoalkoxy-4-methylcoumarin

The synthesis will be performed via substitution reaction with octhyl bromide and butyl bromide using potassium carbonate as base.



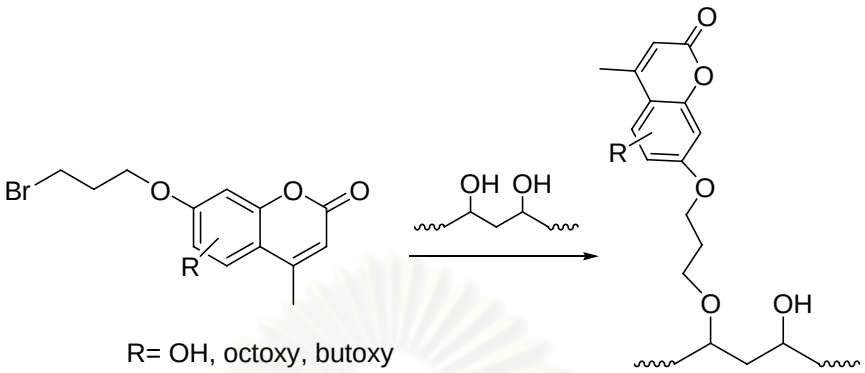
Scheme 2 The synthesis of monoalkoxycoumarin compounds

3. Alkylation of 5,7-dihyrdroxy-4-methylcoumarin, 6,7-dihydroxy-4-methylcoumarin, and monoalkoxy-4-methylcoumarin with 1,3-dibromopropane. Ether linkages will be constructed as Scheme 3 shown below.



Scheme 3 Treament of coumarin derivatives with 1,3-dibromopropane

4. Synthesis of poly(vinyl alcohol) containing coumarin or alkoxy coumarins



Scheme 4 Preparation of poly(vinyl alcohol) containing coumarins

5. Study solubility and negative photoresist application

CHAPTER II

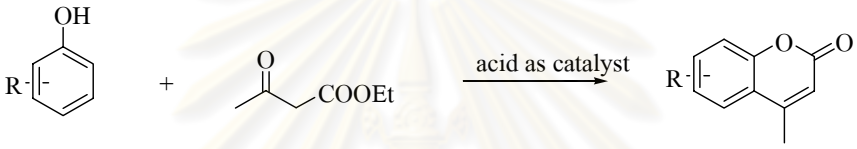
THEORY AND LITERATURE REVIEWS

2.1 Coumarins

Coumarin (2H-1-benzopyran-2-one) and its derivatives are well known heterocycles containing oxygen which are widely used in drugs and dyes. Recently, they have been paid much attention for their fluorescent properties and physiological activities because of their high photostability and quantum yield of photoluminescence and variable emission wavelength continuously throughout the visible spectrum. The dimerization of coumarin and its derivatives would produce various different signals on UV-visible, fluorescent, NMR and mass spectra [3]. Reports found in the literature for coumarin polymers are of great interest. Coumarin-photo-cross-linkable side chain liquid crystalline polymer (SCLP) was reported to have electro-optical properties and ability to induce structure that can be useful in manufacturing information storage devices and nonlinear optical devices [4-6]. Polymeric and oligomeric coumarins were prepared for photomemory and photoactive surface application [7-8]. Tian's group reported oligomeric coumarin derivatives by linking coumarins to cyclic tetrasiloxanes that their substitution at the 3 position of coumarin group displayed mesomorphic properties [9]. A wide range of polymers containing coumarin moieties such as polyamide, polyester, hyperbranched and fully aromatic has received much interest in publishing and patenting for the use as electroluminescent devices [10-11]. It was also found that certain polymers prepared from coumarinyl-oxy ethyl methacrylate could form liquid crystal orientation layers. The photo-cross-linking of the polypeptides containing coumarins were studied as the potentially biodegradable crosslinked materials. At present, many researchers still continue to synthesize new and useful photosensitive coumarin-based polymers and investigate their potential application.

2.1.1 Synthesis of coumarins

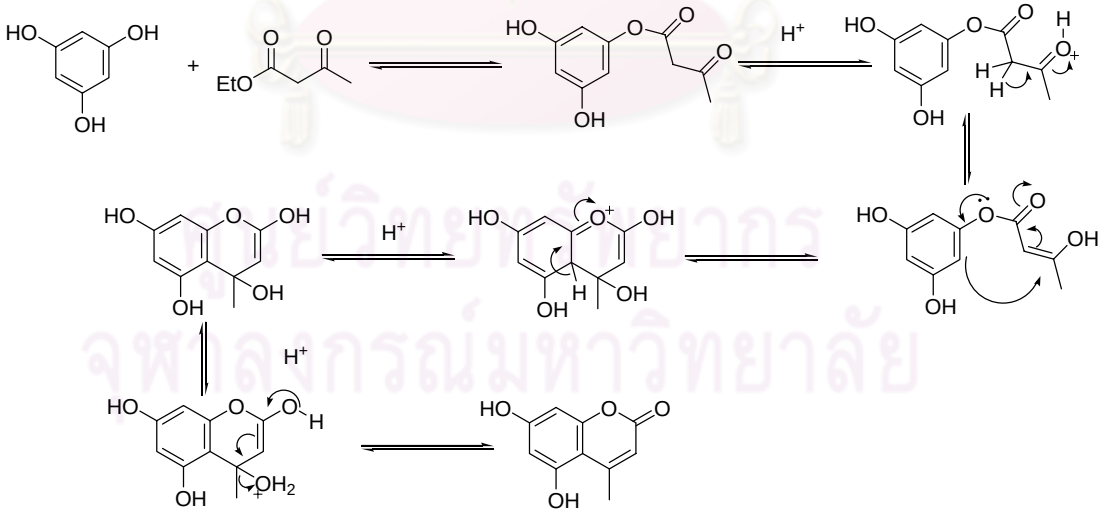
Several methods were used for synthesis of coumarin namely Pechmann, Perkin, Knoevenagel, Reformatsky, and Wittig reactions. Nevertheless, the Pechmann reaction is used for the synthesis of coumarins because of reaction condition and good yields. Several acid catalysts are applied for the Pechmann reaction such as sulfuric acid. However, these acid catalysts have drawback like use of excess catalyst (sulfuric acid: 10 equiv.), unwanted side-product,and longer reaction time, The acid catalyst used in the Pechmann reaction is oxalic acid under solvent-free reaction condition [12].



Scheme 5 Pechmann reaction of phenols

2.1.2 Pechmann condensation mechanism

Coumarins can be formed via Pechmann condensation. Phenols reacted β-keto ester to give aryl ester. Finally, cyclization generate the coumarin.



Scheme 6 Mechanism of Pechmann reaction

A Michael addition leads to the formation of the coumarin. This addition is followed by rearomatisation. Finally, acid-induced elimination of water gives the product.

2.2 S_N2 reaction

2.2.1. The rate of S_N2 reaction

Carbon-bromide bond causes alkyl bromides to undergo substitution reaction. The rate of a nucleophilic substitution depends on the concentrations of both reagents. If the concentration of alkyl bromide or nucleophile in the reaction is doubled, the rate of the substitution reaction will be doubles. If the concentrations of both reactants are doubled, the rate of the reaction will be quadruples [13].

$$RBr + {}^{-}OH \longrightarrow ROH + Br^{-}$$

Scheme 7 Substitution between alkyl bromide and hydroxide

The relationship between the rate of a reaction and the concentration of the reactants can be written as a rate law showed below.

Rate = k[alkyl bromide] [nucleophile]

The rate of this reaction depends on the concentration of two reagents.

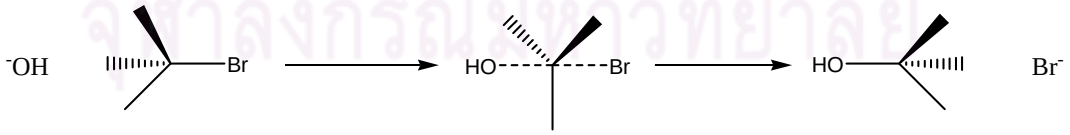
2.2.2. The mechanism of S_N2 reaction

the mechanism for an S_N2 reaction is a concerted reaction, which takes place in a single step. The nucleophile attacks the carbon bearing the leaving group and displaces the leaving group.

Relative reactivities of alkyl halides in an S_N2 reaction

Methyl halide > 1 alkyl halide > 2 alkyl halide > 3 alkyl halide

While the nucleophile approaches the backside of the carbon of methyl bromide, the carbon-hydrogen begins to move away from the nucleophile.



Scheme 8 Inversion of configuration of S_N2 reaction

The carbon is penta coordinate when the nucleophile is closer to the carbon and the bromide moves away from it. Finally, the bond between the carbon and the nucleophile is formed and the bond between the carbon and bromide is broken.

2.2.3. The effect of the solvent on nucleophilicity

When a nucleophile is placed in a protic solvent, the ion is solvated. The solvent arrange themselve to point partially positive charged toward the negative charge molecule. This interaction is called an ion-dipole interaction. The nucleophile would increase reactivity in a non polar solvent because there are no ion-dipole interactions between the ion and the solvent. However, ions are insoluble in non polar solvents. They can dissolve in aprotic polar solvents such as dimethyl formamide (DMF), dimethylsulfoxide (DMSO).

2.3 Poly(vinyl alcohol) (PVA)

Poly(vinyl alcohol) is a commercial polymer. It has good solubility, film forming, and miscibility properties. In addition, it can be modified due to OH functional groups in the backbone [14].

2.4 Negative photoresist

Negative resist behave in the opposite positive resist. When it exposures to the UV light, the negative resist becomes crosslinkable. Therefore, the negative resist remains on the surface. The solvent developer removes only the unexposed substrate. Figure 1 indicated the pattern generated from the negative resist [15].

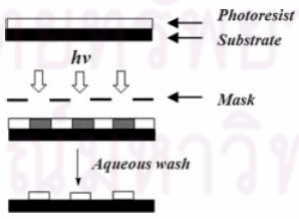


Figure 1 Negative photoresist process [15]

2.5 Literature review

In 2004, Trenor et al. [16] used sunlight to irradiate coumarin that dissolved in alcohol. The result of coumarin after irradiated was increasing the melting point higher than the original one. They studied four different structure of dimer irradiated from coumarin at different reaction condition. These are four possible dimer forms from UV irradiated of coumarin. These dimers were formed via [2π+2π] cycloaddition reaction to form cyclobutane ring. The result of these coumarins had only three products:the syn head-to-head dimer, the anti head-to-head, and the syn head-to-tail dimer. At the high concentration, coumarin reacted with ground-state and formed syn head-to-head dimer. At the low concentration, the anti head-to-head was formed.

In 2006, Barberis et al. [17] reported the two new poly(fluorenediylvinylene)s (CV and CF) with coumarin moieties. These polymers could be dissolved in organic solvent such as tetrahydrofuran. Thin film of CV and CF expressed the maximum photoluminescence emission intensity at 475 nm and 585 nm, respectively. Both of them showed the interesting optical properties.

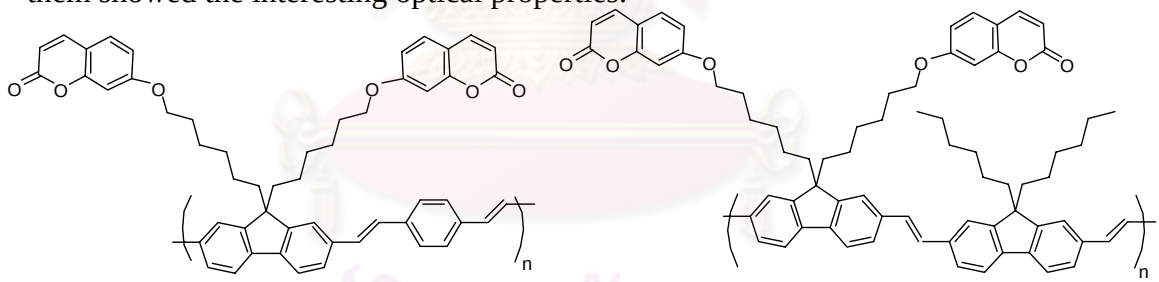


Figure 2 The chemical structure of poly(fluorenediylvinylene)s (CV and CF)

In 2006, Trakhtenberg et al [18] reported water-soluble photopolymers can be useful environmentally benign negative photoresists. This water-soluble polystyrene copolymer, vinylbenzylthymine-vinylphenylsulfonate (VBT-VPS) can be coated on several substrates including plastics such as polyethylterephthalate. The cross-linking and immobilization of the photoresists has been derived from a simple photochemical transformation that occurs in nature (2 + 2 photodimerization of thymine).

In 2007, Feng et al. [19] demonstrated the novel fluorescence poly(7-(4-(acryloyloxy)butoxy)coumarin) which was prepared via the reversible addition fragmentation chain transfer (RAFT) polymerization. The coumarin units exhibiting

in this polymer could undergo [2+2] cycloaddition reaction under UV irradiation in tetrahydrofuran. It was found that the maximum UV-visible absorption of polymer at 322 nm decreased after irradiation under UV light due to the disruption of aromaticity of the coumarin.

In 2007, Wang et al [14] reported the success of synthesizing a new kind of water soluble poly(vinyl alcohol) containing 4-methyl-7-(2,3-epoxypropoxy)coumarin (PVA-MEC). The film forming ability of this polymer is as good as poly(vinyl alcohol). In addition, PVA-MEC exhibited the excellent linear relation between relative fluorescence intensity and temperature in the range of 0-60 ^{o}C and its highest intensity of fluorescence was shown at mass concentration of 4.0% at 382 nm.

Accordingly, this research study is focused on the search of a new kind of polymeric material bearing coumarin moiety. Two different linkages between polymer backbone and coumarin moietys, ether and carbon-carbon linkages will be investigated. The synthesized polymers will sequentially be explored for their optical property in the application of photoresist.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Reagents

1. Oxalic acid (CARLO ERBA) was used as received.
2. Phloroglucinol (SIGMA-ALDRICH) was used as received.
3. Ethyl acetoacetate (ALDRICH) was used as received.
4. Potassium carbonate (CARLO ERBA) was used as received.
5. Octyl bromide (MERCK) was distilled prior to use.
6. Butyl bromide (SIGMA-ALDRICH) was distilled prior to use.
7. 6,7-Dihydroxy-4-methylcoumarin (SIGMA) was used as received.
8. 1,3-Dibromopropane (SIGMA-ALDRICH) was used as received.
9. Poly(vinyl alcohol) 70,000-100,000 (SIGMA) was used as received.
10. Sodium ethoxide (ALDRICH) was used as received.
11. Magnesium sulfate anhydrous (CARLO ERBA) was used as received.
12. Silica gel, 70-230 mesh, 60 A^o (MERCK) was used as received.
13. Hydrochloric acid (CARLO ERBA) was used as received.
14. Sodium chloride (PROGOLF) was used as received.

3.1.2 Solvents

1. Ethanol (commercial) was distilled prior to use.
2. N, N-Dimethylformamide (CARLO ERBA) was used as received.
3. Ethyl acetatate (ZEN POINT) was distilled prior to use.
4. Hexane (ZEN POINT) was distilled prior to use.
5. Acetone (commercial) was distilled prior to use.
6. Chloroform (LAB-SCAN) was used as received.
7. Dimethylsulfoxide (CARLO ERBA) was used as received.
8. Chloroform-*d* (MERCK) was used as received.
9. Dimethylsulfoxide-d_6 (WILMAD LABGLASS) was used as received.

10. Dichlromethane (commercial) was distilled prior to use.

3.2Instruments and equipments

3.2.1 Nuclear magnetic resonance (NMR) spectrometer

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtaine in deuterated chloroform ($CDCl_3$) or deuterated sulfoxide (DMSO-d_6) using a Bruker® AVANCE 400 MHz NMR spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual protonated solvent signal as a reference.

3.2.2 Infrared spectrometer

ATR-IR spectra were obtained by a Nicolet 6700 FTIR spectrometer.

3.2.3 Mass spectrometer

The HRMS (ESI) mass spectra were recorded from Bruker microTOF LC mass spectrometer.

3.2.4 UV-visible spectrophotometer

UV Absorption spectra were obtained by a HP 8453 UV/VIS spectrometer.

3.2.5 Melting point

Melting points were obtained by a Melt-Temp.

3.3 Synthesis of 5,7-dihydroxy-4-methylcoumarin [12]

Phloroglucinol (1.98 g, 15.7 mmol) and ethyl acetoacetate (2.00 ml, 15.7 mmol) were added to around round bottom flask to reflux with oxalic acid (0.34 g, 2.7 mol). The mixture was stirred for 2 hour. The mixture was cooled to room temperature and poured in cold water to stir. The precipitated product was filtered by vacuum filtration, washed with water and dried. The product was crystallized from ethanol.

Yield 73%, yellow solid, m.p. 284-286 ^{o}C, ^{1}H-NMR (400 MHz, DMSO-d6) δ 10.51 (s, 1H, -O**H**), 10.30 (s, 1H, -O**H**), 6.23 (s, 1H, Ar-**H**), 6.14 (s, 1H, Ar-**H**), 5.82 (s, 1H, =C**H**), 2.48 (s, 3H, -C**H**$_3$), ATR-FTIR (neat) 3414, 1662, 1616, 1576, mass (ES/MS): m/z: 215.0062 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 324 nm.

3.4 Alkyltion reaction with alkyl bromides [20]

3.4.1 Synthesis of 5,7-dibutoxy-4-methylcoumarin, 7-butoxy-5-hydroxy-4-methylcoumarin, and 5-butoxy-7-hydroxy-4-methylcoumarin

5,7-Dihydroxy-4-methylcoumarin (0.89 g, 4.6 mmol) was combined with butyl bromide (0.50 mL, 4.7 mmol) and potassium carbonate (0.64 g, 4.6 mmol) in 10 mL dimethylformamide. The mixture was refluxed and stirred for 12 hours. Then 10 mL of 2M hydrochloric acid was added to the reaction. The reaction was then extracted with ethylacetate, and washed with water two times. The crude product was separated by column chromatography using 2:8 ethylacetate:hexane as eluent to obtain 3 different products.

5,7-Dibutoxy-4-methylcoumarin:Yield 17%, white solid, m.p. 69-70 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H, Ar-**H**), 6.27 (s, 1H, Ar-**H**), 5.93 (s, 1H, =C**H**), 3.98 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 2.54 (s, 3H, -C**H**$_3$), 1.79 (m, 4H, -2C**H**$_2$), 1.50 (m, 4H, 2C**H**$_2$), 0.98 (t, *J* = 5 Hz, 6H, -2C**H**$_3$), ATR-FTIR (neat) 2956, 1703, mass (ES/MS): m/z: 327.1440 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 326 nm.

7-Butoxy-5-hydroxy-4-methylcoumarin:Yield 2%, white solid, m.p. 167-169 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$-DMSO-d6) δ 7.04 (s, 1H, O**H**), 6.32 (s, 1H, Ar-**H**), 6.22 (s, 1H, Ar-**H**), 5.89 (s, 1H, =C**H**), 3.88 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.54 (s, 3H, -C**H**$_3$), 1.70 (m, 2H, -C**H**$_2$), 1.41 (m, 2H, C**H**$_2$), 0.90 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 3159,2951 1677, mass (ES/MS): m/z: 271.0871 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 322 nm.

5-Butoxy-7-hydroxy-4-methylcoumarin:Yield 5%, white solid, m.p. 185-187 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$-DMSO-d6) δ 9.70 (s, 1H, O**H**), 6.18 (s, 1H, Ar-**H**), 6.05 (s, 1H, Ar-**H**), 5.63 (s, 1H, =C**H**), 3.80 (t, *J* = 8 Hz, 2H, -C**H**$_2$), 2.32 (s, 3H, -C**H**$_3$), 1.62 (m, 2H, -C**H**$_2$), 1.32 (m, 2H, C**H**$_2$), 0.79 (t, *J* = 6 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 3296,2935, 1678, mass (ES/MS): m/z: 271.0821 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 326 nm.

3.4.2 Synthesis of 5,7-dioctoxy-4-methylcoumarin, 5-hydroxy -4-methyl-7-octoxycoumarin and 7-hydroxy-4-methyl-5-octoxycoumarin

Following the same procedure as section 3.4.1 using 5,7-dihydroxy-4-methylcoumarin (0.56 g, 2.9 mmol), octyl bromide (0.50 mL, 2.9 mmol), and potassium carbonate (0.41 g, 3.0 mmol), 3 different products were obtained.

5,7-Dioctoxy-4-methylcoumarin:Yield 13%, white solid, m.p. 48-50 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H, Ar-**H**), 6.27 (s, 1H, Ar-**H**), 5.94 (s, 1H, =C**H**), 3.98 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 2.55 (s, 3H, -C**H**$_3$), 1.82 (m, 4H, -2C**H**$_2$), 1.45 (m, 4H, 2C**H**$_2$), 1.29 (m,16H, 2C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.89 (t, *J* = 6 Hz, 6H, -2C**H**$_3$), ATR-FTIR (neat) 2915, 1713, mass (ES/MS): m/z: 439.2478 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 322 nm.

5-Hydroxy-4-methyl-7-octoxycoumarin:Yield 14%, white solid, m.p. 154-156 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$-DMSO-d6) δ 9.62 (s, 1H, O**H**), 6.41 (s, 1H, Ar-**H**), 6.34 (s, 1H, Ar-**H**), 5.98 (s, 1H, =C**H**), 3.96 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.63 (s, 3H, -C**H**$_3$), 1.78 (m, 2H, -C**H**$_2$), 1.44 (m, 2H, C**H**$_2$), 1.30 (m, 8H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.90 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 3088,2915, 1667, mass (ES/MS): m/z: 327.1284 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 323 nm.

7-Hydroxy-4-methyl-5-octoxycoumarin:Yield 15%, white solid, m.p. 158-160 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$-DMSO-d6) δ 9.68 (s, 1H, O**H**), 6.32 (s, 1H, Ar-**H**), 6.16 (s, 1H, Ar-**H**), 5.76 (s, 1H, =C**H**), 3.87 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.44 (s, 3H, -C**H**$_3$), 1.73 (m, 2H, -C**H**$_2$), 1.36 (m, 2H, C**H**$_2$), 1.19 (m, 8H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.80 (t, *J* = 6 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 3338,2920, 1678, mass (ES/MS): m/z: 327.1304 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 322 nm.

3.4.3 Synthesis of 6,7-dibutoxy-4-methylcoumarin and 7-butoxy-6-hydroxy-4-methylcoumarin

Following the same procedure as section 3.4.1 using 6,7-dihydroxy-4-methylcoumarin (0.89 g, 4.6 mmol), butyl bromide (0.50 mL, 4.7 mmol), and potassium carbonate (0.64 g, 4.6 mmol), 2 different products were obtained.

6,7-Dibutoxy-4-methylcoumarin:Yield 9%, yellow solid, m.p. 76-78 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H, Ar-**H**), 6.81 (s, 1H, Ar-**H**), 6.14 (s, 1H,

=C**H**), 4.04 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 2.38 (s, 3H, -C**H**$_3$), 1.84 (m, 4H, -2C**H**$_2$), 1.53 (m, 4H, 2C**H**$_2$), 0.99 (t, *J* = 7 Hz, 6H, -2C**H**$_3$), ATR-FTIR (neat) 2925, 1708, mass (ES/MS): m/z: 327.1419 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 343 nm.

7-Butoxy-6-hydroxy-4-methylcoumarin:Yield 24%, yellow solid, m.p. 157-159 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$-DMSO-d6) δ 7.08 (s, 1H, Ar-**H**), 6.79 (s, 1H, Ar-**H**), 6.15 (s, 1H, =C**H**), 5.71 (s, 1H, O**H**), 4.10 (t, *J* = 7 Hz, 2H, -C**H**$_2$), 2.35 (s, 3H, -C**H**$_3$), 1.84 (m, 2H, -C**H**$_2$), 1.52 (m, 2H, C**H**$_2$), 0.99 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 3175, 2956, 1667, mass (ES/MS): m/z: 271.8080 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 345 nm.

3.4.4 Synthesis of 6,7-dioctoxy-4-methylcoumarin and 6-hydroxy-7-octoxy-4-methylcoumarin

Following the same procedure as section 3.4.1 using 6,7-dihydroxy-4-methylcoumarin (0.58 g, 3.0 mmol), octyl bromide (0.50 mL, 2.90 mmol) and potassium carbonate (0.41 g, 3.0 mmol), 2 different products were obtained.

6,7-Dioctoxy-4-methylcoumarin:Yield 17%, yellow solid, m.p. 57-58 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H, Ar-**H**), 6.74 (s, 1H, Ar-**H**), 6.06 (s, 1H, =C**H**), 3.96 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 2.31 (s, 3H, -C**H**$_3$), 1.78 (m, 4H, -2C**H**$_2$), 1.42 (m, 4H, 2C**H**$_2$), 1.22 (m,16H, 2C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.82 (t, *J* = 7 Hz, 6H, -2C**H**$_3$), ATR-FTIR (neat) 2915, 1739, mass (ES/MS): m/z: 439.2546 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 343 nm.

6-Hydroxy-4-methyl-7-octoxycoumarin:Yield 39%, white solid, m.p. 116-118 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$-DMSO-d6) δ 7.11 (s, 1H, Ar-**H**), 6.82 (s, 1H, Ar-**H**), 6.18 (s, 1H, =C**H**), 5.70 (s, 1H, O**H**), 4.12 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.38 (s, 3H, -C**H**$_3$), 1.88 (m, 2H, -C**H**$_2$), 1.49 (m, 2H, C**H**$_2$), 1.31 (m, 8H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.99 (t, *J* = 6 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 3287, 2915, 1683, mass (ES/MS): m/z: 327 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 346 nm.

3.5 Alkylation reaction with 1,3-dibromopropane

3.5.1 Synthesis of 5,7-di(3′-bromo)propoxy-4-methylcoumarin, 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin and 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

5,7-Dihydroxycoumarin (0.38 g, 2.0 mmol) was combined with 1,3-dibromobutane (0.20 mL, 2.0 mmol) and sodium ethoxide (0.132 g, 2.0 mmol) in 5 mL dimethylsulfoxide. The mixture was refluxed and stirred for 20 hours. Then 10 mL of 2M hydrochloric acid was added to the reaction. The reaction was then extracted with ethylacetate, and washed with water two times. The crude product was separated by column chromatography using 2:8 ethylacetate:hexane as eluent to obtain 3 different products

5,7-Di(3′-bromo)propoxy-4-methylcoumarin:Yield 8%, yellow solid, m.p. 74-76 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.46 (s, 1H, Ar-**H**), 6.33 (s, 1H, Ar-**H**), 5.97 (s, 1H, =C**H**), 4.16 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 3.60 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 2.53 (s, 3H, -C**H**$_3$), 2.40 (p, 4H, 2C**H**$_2$), ATR-FTIR (neat) 2925, 1708, mass (ES/MS): m/z: 434.760 [obtained M]$^+$, UV-Vis (EtOH) λ_{max} 321 nm.

5-Hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin:Yield 3%, white solid, m.p. 174-176 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H, O**H**), 6.40 (s, 1H, Ar-**H**), 6.24 (s, 1H, Ar-**H**), 5.82 (s, 1H, =C**H**), 4.10 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.53 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.45 (s, 3H, -C**H**$_3$), 2.32 (p, 2H, C**H**$_2$), ATR-FTIR (neat) 3159, 1662, mass (ES/MS): m/z: 336.2378 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 321 nm.

7-Hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin:Yield 5%, white solid, m.p. 188-190 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H, O**H**), 6.98 (s, 1H, Ar-**H**), 6.72 (s, 1H, Ar-**H**), 6.03 (s, 1H, =C**H**), 4.11 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.58 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.50 (s, 3H, -C**H**$_3$), 2.32 (p, 2H, C**H**$_2$), ATR-FTIR (neat) 3287,2945, 1662, mass (ES/MS): m/z: 336.9739 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 325 nm.

3.5.2 Synthesis of 6,7-di(3′-bromo)propoxy-4-methylcoumarin and 6-hydroxy -4-methyl-7-(3′-bromo)propoxycoumarin

Following the same procedure as section 3.5.1 using 6,7-dihydroxy-4-methylcoumarin (0.19 g, 1.0 mmol), 1,3-dibromopropane (0.1 mL, 1.0 mmol), and sodium ethoxide (0.07 g, 1.0 mmol), 2 different products were obtained.

6,7-Di(3′-bromo)propoxy-4-methylcoumarin:Yield 8%, yellow solid, m.p. 79-80 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H, Ar-**H**), 6.86 (s, 1H, Ar-**H**), 6.17 (s, 1H, =C**H**), 4.19 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 3.64 (t, *J* = 6 Hz, 4H, -2C**H**$_2$), 2.40 (s, 3H, -C**H**$_3$), 2.36 (p, 4H, 2C**H**$_2$), ATR-FTIR (neat) 2956, 1723, mass (ES/MS): m/z: 434.715 [obtained M]$^+$, UV-Vis (EtOH) λ_{max} 331 nm.

6-Hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin:Yield 7%, white solid, m.p. 164-166 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H, Ar-**H**), 6.85 (s, 1H, Ar-**H**), 6.17 (s, 1H, =C**H**), 5.53 (s, 1H, O**H**), 4.29 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.59 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.39 (p, 2H, C**H**$_2$), 2.36 (s, 3H, -C**H**$_3$), ATR-FTIR (neat) 3200, 2930,1688, mass (ES/MS): m/z: 336.9736 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 345 nm.

3.5.3 Synthesis of 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

Following the same procedure as section 3.5.1 using 7-butoxy-5-hydroxy-4-methylcoumarin (0.06 g, 0.2 mmol), 1,3-dibromopropane (0.02 mL, 0.2 mmol), and sodium ethoxide (0.02 g, 0.2 mmol), 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin was obtained.

7-Butoxy-4-methyl-5-(3′-bromo)propoxycoumarin:Yield 44%, white solid, m.p. 71-73 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.43 (s, 1H, Ar-**H**), 6.28 (s, 1H, Ar-**H**), 5.96 (s, 1H, =C**H**), 4.14 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.99 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.60 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.55 (s, 3H, -C**H**$_3$), 2.33 (p, 2H, C**H**$_2$), 1.83 (m, 2H, -C**H**$_2$), 1.54 (m, 2H, C**H**$_2$), 0.99 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 2951,1731, mass (ES/MS): m/z: 370.642 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 322 nm.

3.5.4 Synthesis of 5-butoxy-4-methyl -7-(3′-bromo)propoxycoumarin

Following the same procedure as section 3.5.1 using 5-butoxy-7-hydroxy-4-methylcoumarin (0.15 g, 0.6 mmol), 1,3-dibromopropane (0.06 mL, 0.6 mmol), and sodium ethoxide (0.04 g, 0.6 mmol), 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin was obtained.

5-Butoxy-4-methyl-5-(3′-bromo)propoxycoumarin:Yield 64%, white solid, m.p. 83-84 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H, Ar-**H**), 6.25 (s, 1H, Ar-**H**), 5.88 (s, 1H, =C**H**), 4.10 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.93 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.53 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.47 (s, 3H, -C**H**$_3$), 2.33 (p, 2H, C**H**$_2$), 1.72 (m, 2H, -C**H**$_2$), 1.44 (m, 2H, C**H**$_2$), 0.92 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 2956,1708, mass (ES/MS): m/z: 340.671 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 322 nm.

3.5.5 Synthesis of 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

Following the same procedure as section 3.4.1 using 5-hydroxy-4-methyl-7-octyoxycoumarin (0.08 g, 0.26 mmol), 1,3-dibromopropane (0.04 mL, 0.39 mmol), and potassium carbonate (0.027 g, 0.19 mmol), 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin was obtained.

4-Methyl-7-octoxy-5-(3′-bromo)propoxycoumarin:Yield 35%, white solid, m.p. 42-43 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H, Ar-**H**), 6.21 (s, 1H, Ar-**H**), 5.89 (s, 1H, =C**H**), 4.08 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.92 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.53 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.49 (s, 3H, -C**H**$_3$), 2.27 (p, 2H, C**H**$_2$), 1.78 (m, 2H, -C**H**$_2$), 1.41 (m, 2H, C**H**$_2$), 1.22 (m, 8H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.82 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 2919,1718, mass (ES/MS): m/z: 449.1061 [obtained M+Na]$^+$, UV-Vis (EtOH) λ_{max} 322 nm.

3.5.6 Synthesis of 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin

Following the same procedure as section 3.4.1 using 7-hydroxy-4-methyl-5-octoxycoumarin (0.11 g, 0.4 mmol), 1,3-dibromopropane (0.04 mL, 0.4 mmol), and potassium carbonate (0.05 g, 0.4 mmol), 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin was obtained.

4-Methyl-5-octoxy-7-(3′-bromo)propoxycoumarin:Yield 38%, white solid, m.p. 47-48 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H, Ar-**H**), 6.25 (s, 1H, Ar-**H**), 5.89 (s, 1H, =C**H**), 4.10 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.92 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 3.53 (t, *J* = 6 Hz, 2H, -C**H**$_2$), 2.47 (s, 3H, -C**H**$_3$), 2.32 (p, 2H, C**H**$_2$), 1.73 (m, 2H, -C**H**$_2$), 1.39 (m, 2H, C**H**$_2$), 1.39 (m, 8H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$), 0.89 (t, *J* = 7 Hz, 3H, -C**H**$_3$), ATR-FTIR (neat) 2924,1713, mass (ES/MS): m/z: 449.1056 [obtained M+Na]$^{+}$, UV-Vis (EtOH) λ_{max} 323 nm.

3.6 Procedure for preparation of poly(vinyl alcohol) containing coumarins [14]

1 mole of repeating unit poly(vinyl alcohol) (PVA) and 10 %mole sodium ethoxide was added to DMSO. This mixture was heated to 80 °C with continuous magnetic stirring until a clear solution was obtained. Then, 2%mol coumarin dissolved in dimethylsulfoxide was added by dropwise and stirred for 2 h at room temperature. The yellow solution was allowed to dialysis against water. The water was changed 5 times. Dialysis solution was dried by freeze-dry process

3.6.1 PVA containing 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

Procedure was followed employing PVA 0.20 g (4.8 mmol), sodium ethoxide 0.03 g (0.5 mmol and 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin 0.03 g (0.1 mmol) to give PVA containing 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin as white solide. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.30 (s, 1H, Ar-**H**), 6.23 (s, 1H, Ar-**H**), 5.89 (s, 1H, =C**H**), 4.90-1.00 (-CH_2-CH-OH of PVA backbone), UV-Vis (EtOH) λ_{max} 323 nm.

3.6.2 PVA containing 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

Procedure was followed employing PVA 0.07 g (1.6 mmol), sodium ethoxide 0.01 g (0.2 mmol and 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin 0.01g (31.9 μmol) to give PVA containing 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin as white solide. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.29 (s, 1H, Ar-**H**), 6.26 (s, 1H, Ar-**H**), 5.88 (s, 1H, =C**H**), 4.90-1.00 (-CH_2-CH-OH of PVA backbone), UV-Vis (EtOH) λ_{max} 325 nm.

3.6.3 PVA containing 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

Procedure was followed employing PVA 0.20 g (4.5 mmol), sodium ethoxide 0.03 g (0.4 mmol and 7-butoxy-4-methyl -5-(3′-bromo)propoxycoumarin 0.03 g (0.1 mmol) to give PVA containing 7-butoxy-4-methyl -5-(3′-bromo)propoxycoumarin as white solide. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.52 (s, 1H, Ar-**H**), 6.43 (s, 1H, Ar-**H**), 5.97 (s, 1H, =C**H**), 4.90-1.00 (-CH_2-CH-OH of PVA backbone), UV-Vis (EtOH) λ_{max} 323 nm.

3.6.4 PVA containing 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

Procedure was followed employing PVA 0.20g (4.5 mmol), sodium ethoxide 0.03 g (0.4 mmol) and 5-butoxy-4-methyl -7-(3′-bromo)propoxycoumarin 0.03 g (0.1 mmol) to give PVA containing 5-butoxy-4-methyl -7-(3′-bromo)propoxycoumarin as white solide. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.52 (s, 1H, Ar-**H**), 6.46 (s, 1H, Ar-**H**), 5.97 (s, 1H, =C**H**), 4.90-1.00 (-CH_2-CH-OH of PVA backbone), UV-Vis (EtOH) λ_{max} 322 nm.

3.6.5 PVA containing 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

Procedure was followed employing PVA 0.31 g (7.1 mmol), sodium ethoxide 0.05 g (0.7 mmol) and 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin 0.06 g (0.1 mmol) to give PVA containing 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin as white solide. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 1H, Ar-**H**), 6.49 (s, 1H, Ar-**H**), 5.99 (s, 1H, =C**H**), 4.90-1.00 (-CH_2-CH-OH of PVA backbone), UV-Vis (EtOH) λ_{max} 323 nm.

3.6.6 PVA containing 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin

Procedure was followed employing PVA 0.21 g (4.7 mmol), sodium ethoxide 0.03 g (0.5 mmol and 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin 0.04 g (0.09 mmol) to give PVA containing 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin as white solide. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 1H, Ar-**H**), 6.47 (s, 1H, Ar-**H**),

5.99 (s, 1H, =C**H**), 4.90-1.00 (-CH_2-CH-OH of PVA backbone), UV-Vis (EtOH) λ_{max} 322 nm.

3.7 Photoresist test

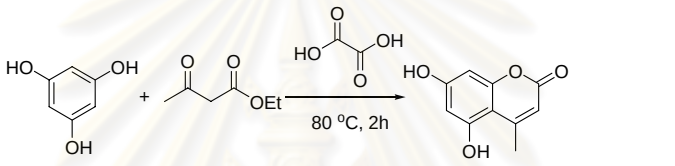
10 % w/v PVA containing coumarins in DMSO were coated onto glass slide. The film was dried in oven at 80 °C for 1 h. Then the film coated on glass slide was irradiated with a I-line UV lamp 365 nm through a patterned mask for 2 minutes. Then the film was immerged in hot water for 2-6 minutes so as to remove the non-cross-linked polymer. The dried UV-exposed films were imaged by microscope instrument.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of 5,7-dihydroxy-4-methylcoumarin

The reaction of phloroglucinol and ethyl acetoacetate was carried out in the presence of 15%mol oxalic acid. After the reaction was completed, the isolation of the product was performed by precipitation from ethanol and water.



5,7-Dihydroxy-4-methylcoumarin

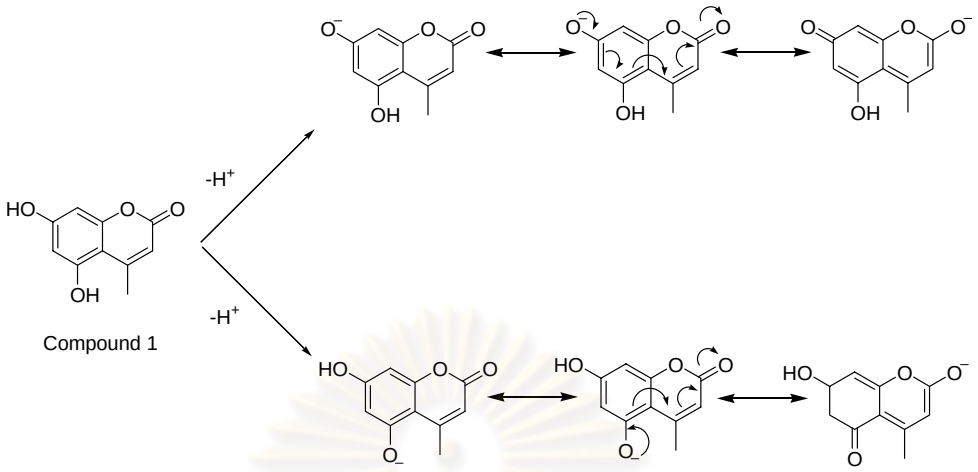
Compound 1

Scheme 9 Pechmann reaction between phloroglucinol and ethyl acetoacetate with oxalic acid as catalyst

Figure A1 revealed the signal of methyl group at δ 2.48 (s,3H). The signal of olefinic proton was detected at δ 5.82 (s,1H). Two signals belonging to aromatic proton were observed at δ 6.23 (s,1H) and 6.14 (s,1H). The signal of two hydroxy protons were observed at 10.51 (s,1H) and 10.30 (s,1H). This ^{1}H NMR spectrum confirmed that the product was 5,7-dihydroxy-4-methylcoumarin (Compound 1) with 73% yield.

4.2 Alkylation of 5,7-dihydroxy-4-methylcoumarin with alkyl bromides

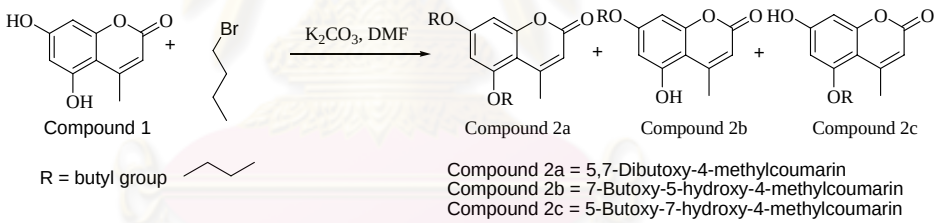
The alkylation of Compound 1 with alkyl bromides was carried out. Considering the nucleophilic substitution of Compound 1, there are two possibilities according to the available hydroxy groups which can be substituted by alkyl bromide. Under basic condition, there two can undergo phenolic anions. Both of anions are stable because of their resonance structures as indicated in Scheme 10.



Scheme 10 Resonance structures of 5,7-dihydroxy-4-methylcoumarin anions

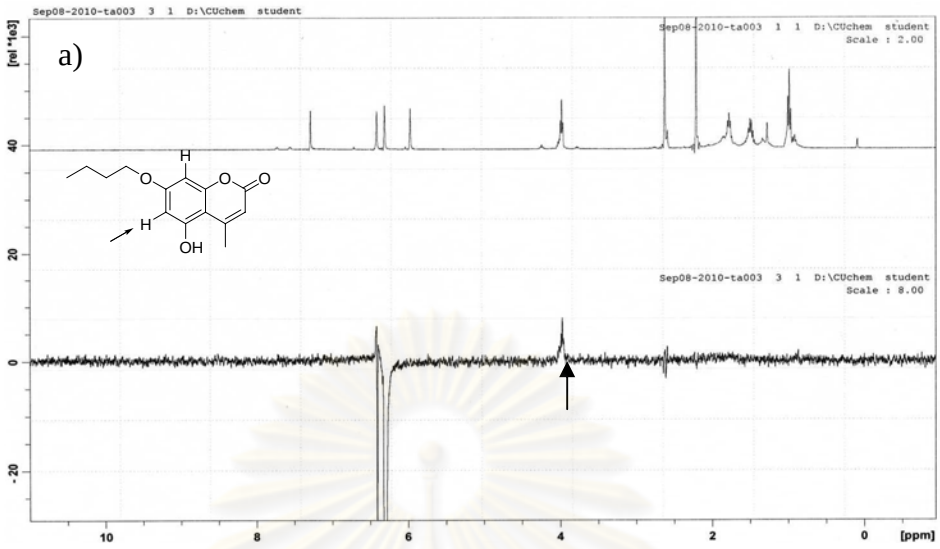
4.2.1 Alkylation of 5,7-dihydroxy-4-methylcoumarin with butyl bromide

When Compound 1 was treated with 1 equivalent butyl bromide, 3 different products were obtained as shown in Scheme 11.

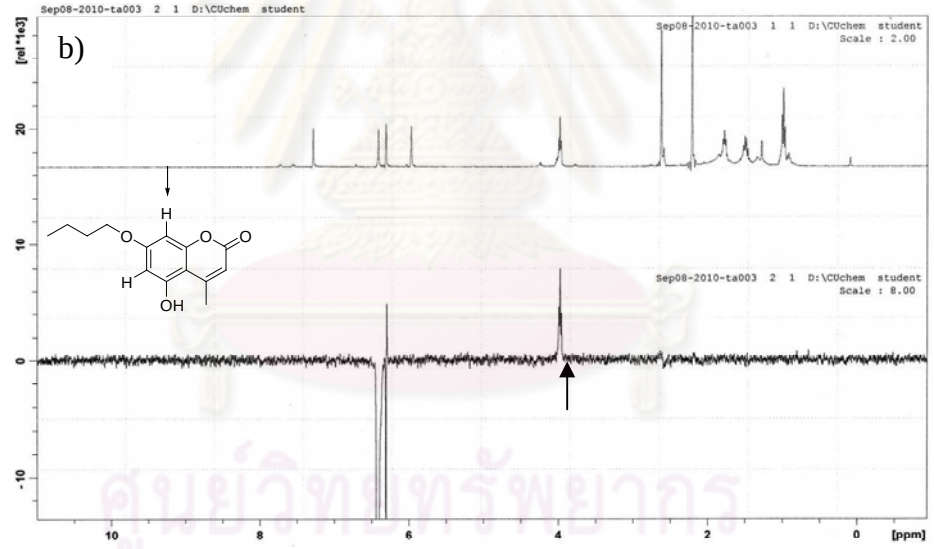


Scheme 11 Alkylation of 5,7-dihydroxy-4-methylcoumarin with butyl bromide

The structures of these three products were elucidated by IR and UV spectra. The IR spectra and UV spectra at 1703 cm^{-1} (Figures B2-B4) and 324 nm (Figures C2-C4) were coumarin characteristic peak. It should be pointed out that TLC and column chromatography showed three types of products occurred in this reaction. Surprisingly, two monoalkoxy coumarins had the same ^{1}H-NMR. The differentiation can be performed by NOE difference technique.

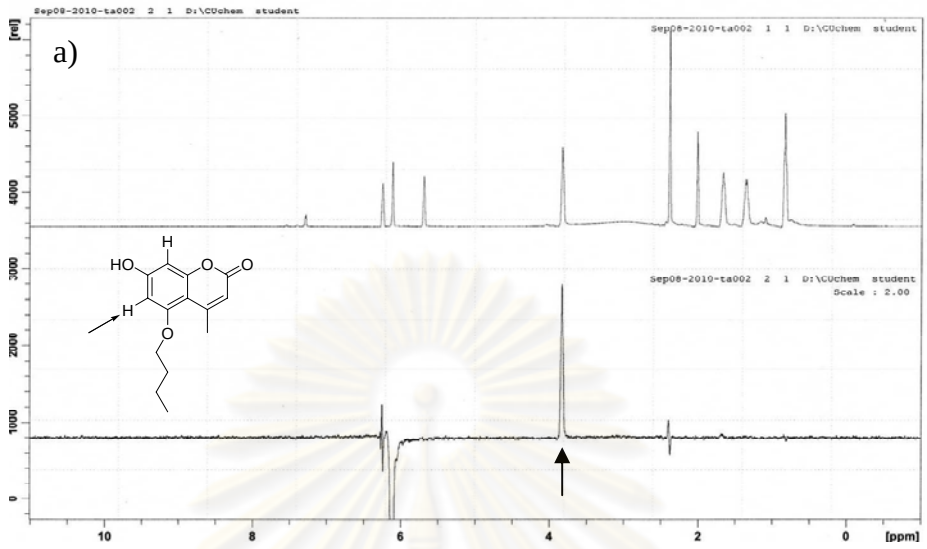


NOE difference spectrum resulting from irradiation of H-6

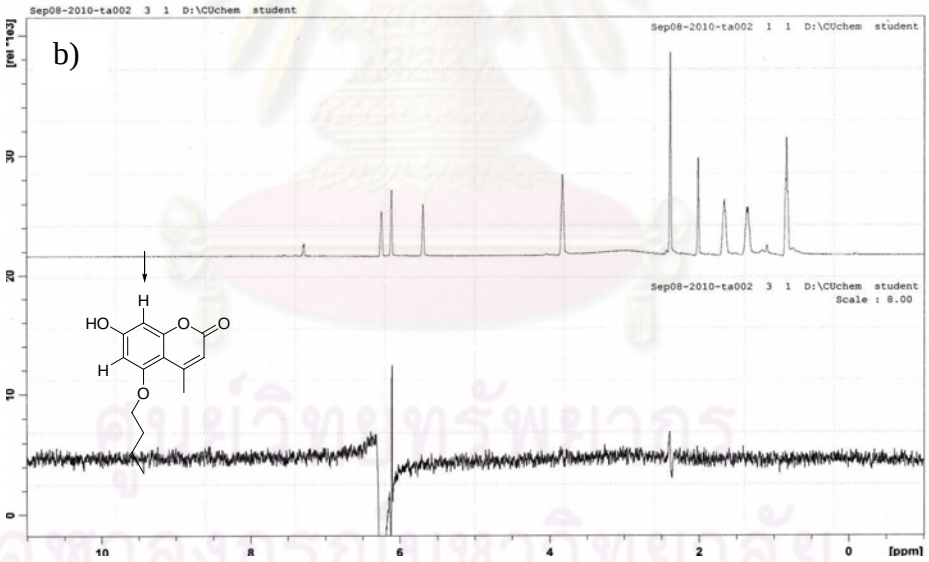


NOE difference spectrum resulting from irradiation of H-8

Figure 3 NOE difference spectrum of 7-butoxy-5-butoxy-4-methylcoumarin



NOE difference spectrum resulting from irradiation of H-6



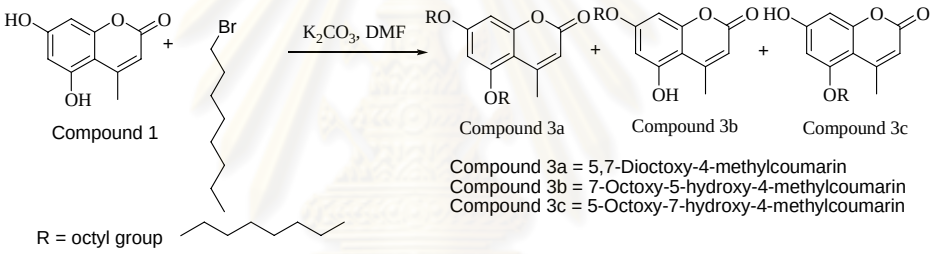
NOE difference spectrum resulting from irradiation of H-8

Figure 4 NOE difference spectrum of 5-butoxy-7-butoxy-4-methylcoumarin

Figure 3 is the 7-butoxy-5-hydroxy-4-methylcoumarin. The significant enhancement of the signal of the -OCH_2- at δ 3.8 was observed upon irradiation of hydrogen-6 and hydrogen-8 as revealed in Figure 3a and b, respectively. In contrast, the irradiation of the hydrogen-8 of Compound 2c did not result in an NOE on -OCH_2- as shown in Figure 4b [21-22]. These two figures are different and can be assigned to be 7-butoxy-5-hydroxy-4-methylcoumarin (Compound 2b) and 5-butoxy-7-hydroxy-4-methylcoumarin (Compound 2c).

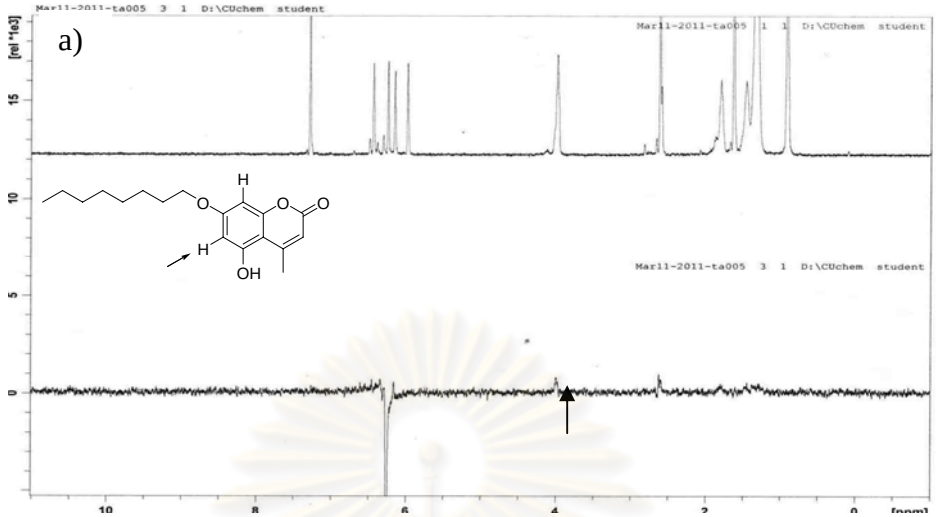
4.2.2 Alkylation of 5,7-dihydroxy-4-methylcoumarin with octyl bromide

When compound 1 was treated with 1 equivalent octyl bromide, 3 different products were obtained as showed in Scheme 12.

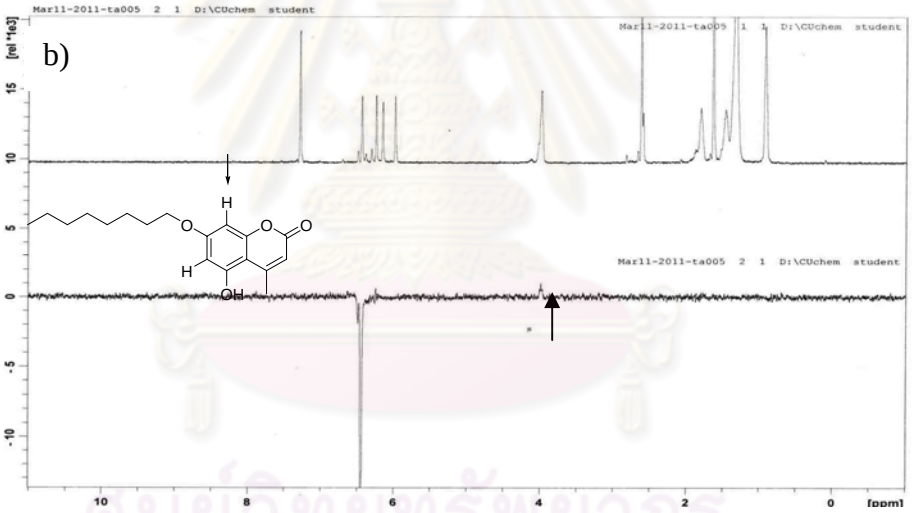


Scheme 12 Alkylation of 5,7-dihydroxy-4-methylcoumarin with octyl bromide

The structures of these three products were elucidated by IR and UV spectra. The IR spectra and UV spectra at 1713 cm^{-1} (Figures B5-B7) and 322 nm (Figures C5-C7) were coumarin characteristic peak. It should be pointed out that TLC and column chromatography showed three types of products occurred in this reaction. Surprisingly, two monoalkoxy coumarins had the same ^{1}H-NMR. The differentiation can be performed by NOE difference technique.

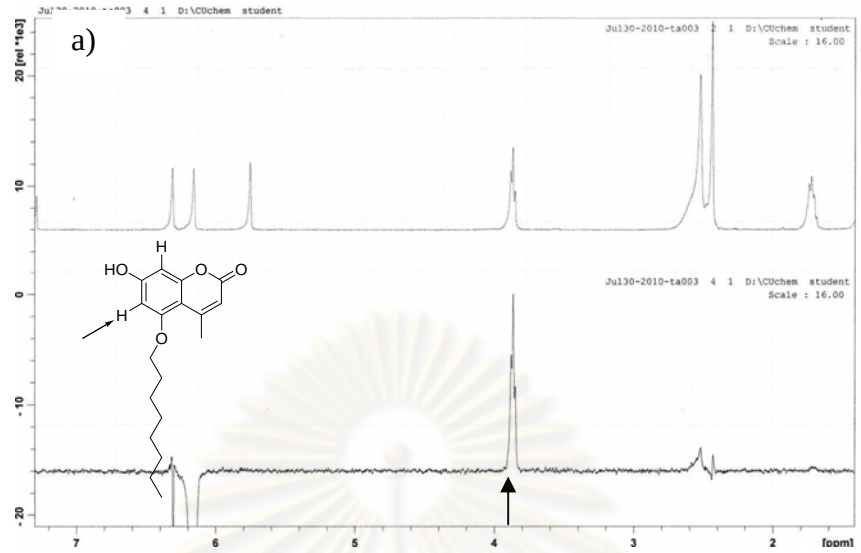


NOE difference spectrum resulting from irradiation of H-6

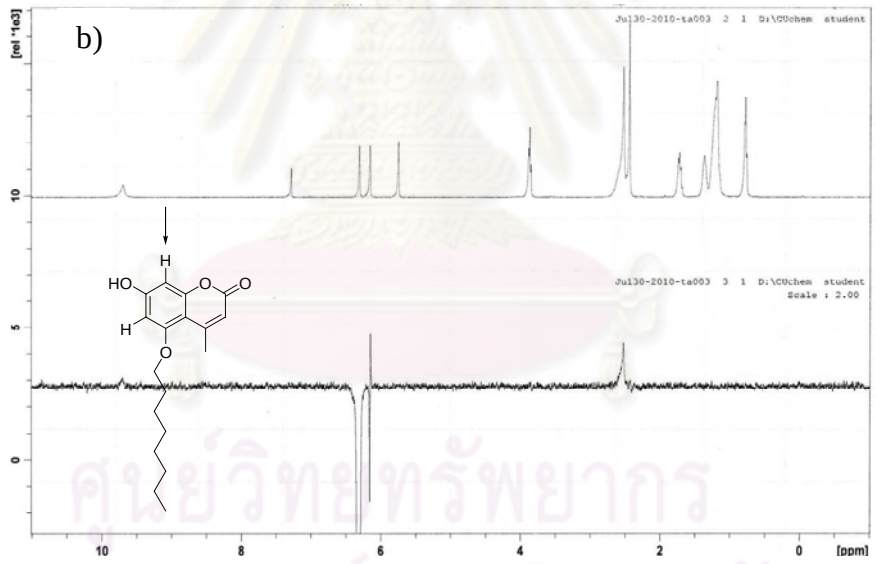


NOE difference spectrum resulting from irradiation of H-8

Figure 5 NOE difference spectrum of 5-hydroxy-4-methyl-7-octoxycoumarin



NOE difference spectrum resulting from irradiation of H-6

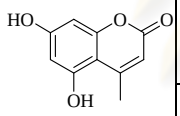
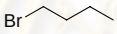
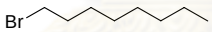


NOE difference spectrum resulting from irradiation of H-8

Figure 6 NOE difference spectrum of 5-hydroxy-4-methyl-7-octoxycoumarin

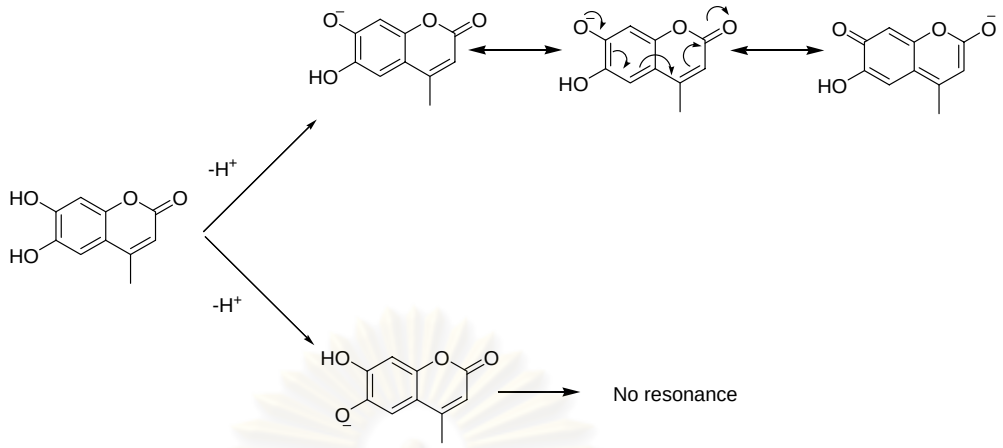
Figure 5 is the 7-octoxy-5-hydroxy-4-methylcoumarin. The significant enhancement of the signal of the -OCH_2- at δ 3.9 was observed upon irradiation of hydrogen-6 and hydrogen-8 as revealed in Figure 5a and b, respectively. In contrast, the irradiation of the hydrogen-8 of Compound 3c did not result in an NOE on -OCH_2- as shown in Figure 6b. These two figures are different and can be assigned to be 7-octoxy-5-hydroxy-4-methylcoumarin (Compound 3b) and 5-octoxy-7-hydroxy-4-methylcoumarin (Compound 3c). In conclusion, the alkylation of 5,7-dihydroxy-4-methylcoumarin with either butyl bromide or octyl bromide afforded two monoalkoxycoumarins and one dialkoxycoumarin as exhibited in Table 1.

Table 1 5,7-Dihydroxy-4-methylcoumarin alkylated with alkyl bromides

coumarin	Alkyl bromides	products	%yields	mp
 compound 1		2a	17	69-70
		2b	2	167-169
		2c	5	185-187
		3a	13	48-50
		3b	14	154-156
		3c	15	158-160

4.3 Alkylation of 6,7-dihydroxy-4-methylcoumarin with alkyl bromides

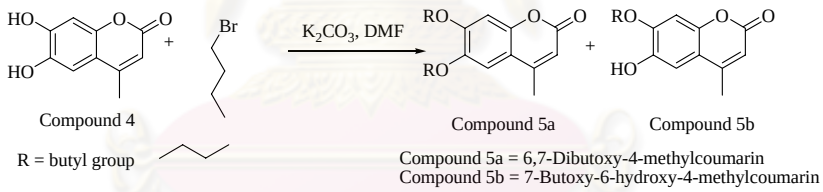
The alkylation of 6,7-dihydroxy-4-methylcoumarin (Compound 4) was carried out. Considering the nucleophilic substitution of Compound 4, two hydroxy groups on Compound 4 is different from Compound 1. There is one factor causing 7-hydroxy of Compound 4 to be much stronger acid than 6-hydroxy of Compound 4. The conjugate base of the 7-hydroxy group is more stable than the conjugate base of the 6-hydroxy group. When 7-hydroxy loses a proton, the electrons are delocalized as shown in Scheme 13. While 6-hydroxy loses a proton, it could not have any resonance form.



Scheme 13 Resonance structure of 6,7-dihydroxy-4-methylcoumarin anions

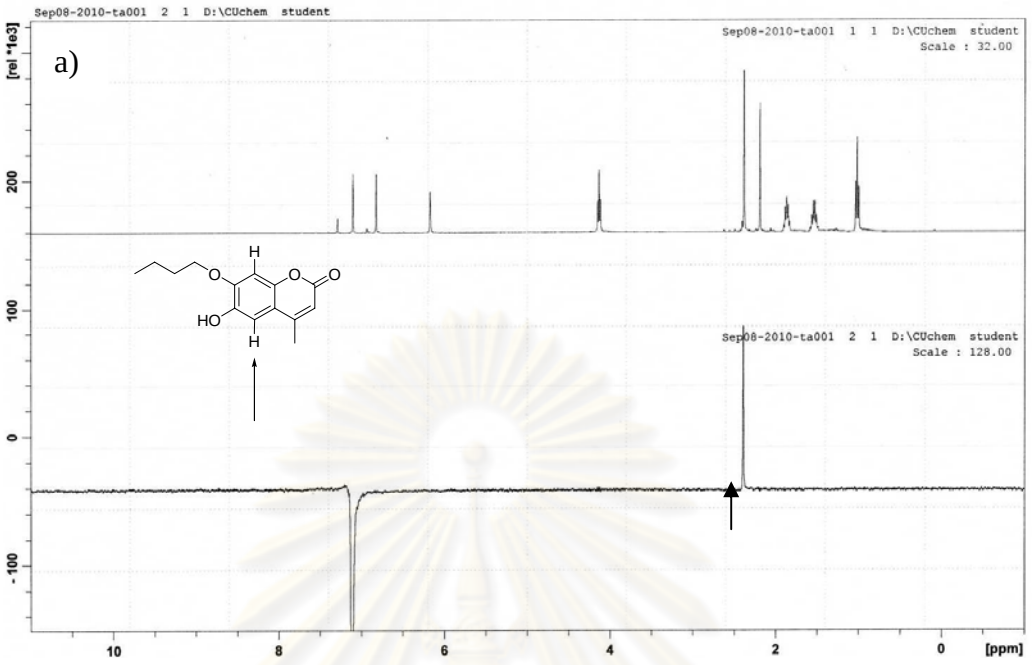
4.3.1 The Alkylation of 6,7-dihydroxy-4-methylcoumarin with butyl bromide

When 6,7-dihydroxy-4-methylcoumarin was treated with 1 equivalent butyl bromide, 2 different products were obtained as shown in Scheme 14

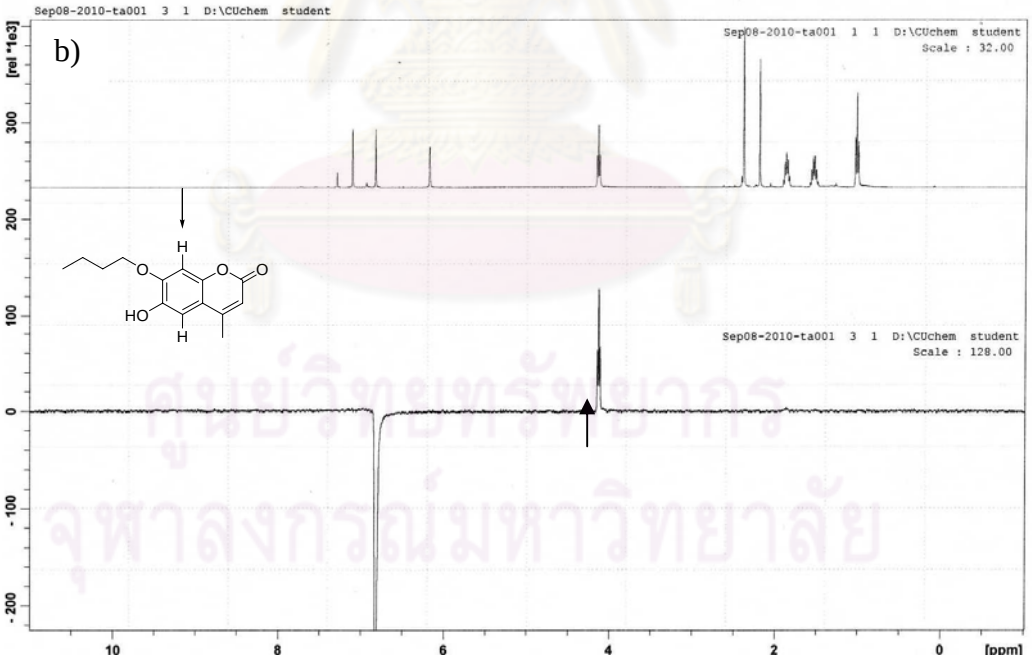


Scheme 14 Alkylation of 6,7-dihydroxy-4-methylcoumarin with butyl bromide

The structures of these two products were elucidated by IR UV. The IR spectra and UV spectra at 1708 cm^{-1} (Figures B8-B9) and 343 nm (Figures C8-C9) were coumarin characteristic peak. It should be pointed out that TLC and column chromatography showed two types of products occurred in this reaction.



NOE difference spectrum resulting from irradiation of H-5



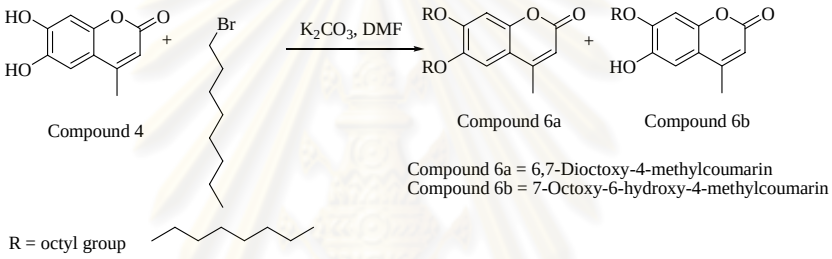
NOE difference spectrum resulting from irradiation of H-8

Figure 7 NOE difference spectrum of 7-butoxy-6-hydroxy-4-methylcoumarin

Figure 7 is the 7-butoxy-6-hydroxy-4-methylcoumarin. The significant enhancement of the signal of the -OCH_2- at δ 3.9 was observed upon irradiation of hydrogen-8 as revealed in Figure 7b. This figure can be assigned to be 7-octoxy-5-hydroxy-4-methylcoumarin (Compound 5b).

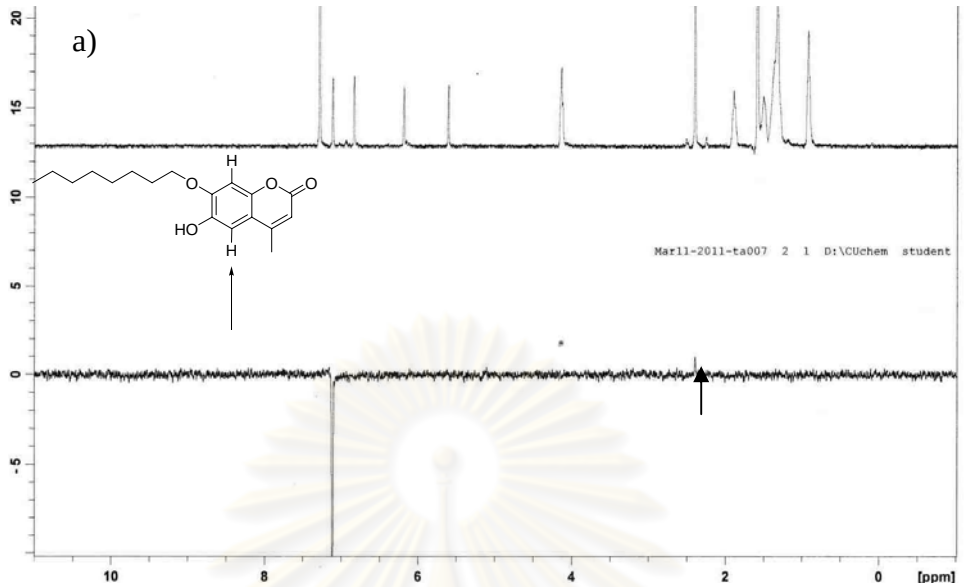
4.3.2 The Alkylation of 6,7-dihydroxy-4-methylcoumarin with octyl bromide

When 6,7-dihydroxy-4-methylcoumarin was treated with 1 equivalent octyl bromide, 2 different products were obtained as shown in Scheme 15.

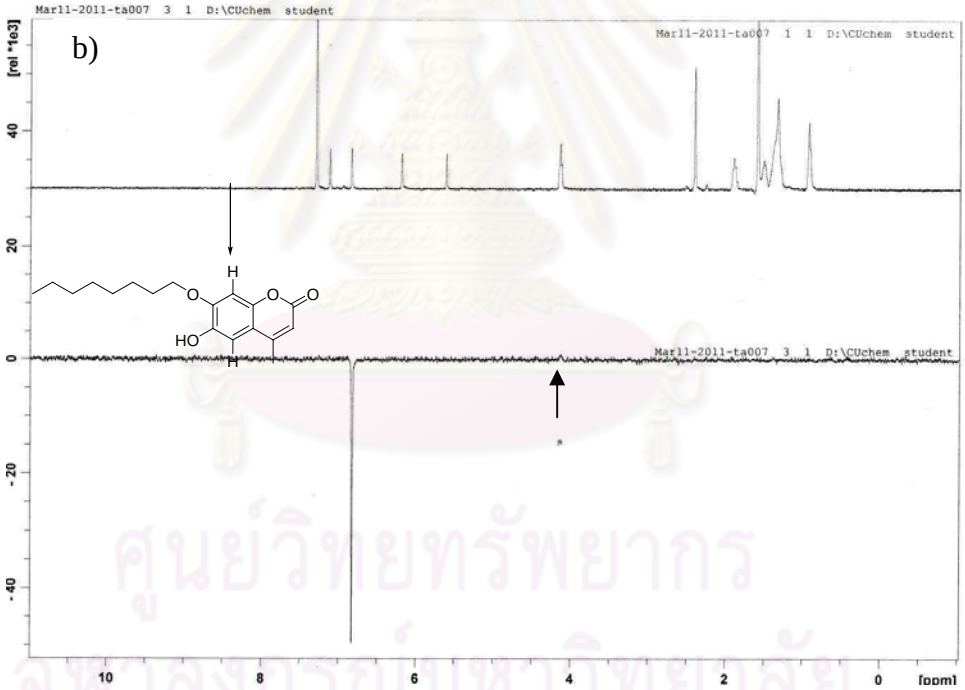


Scheme 15 Alkylation of 6,7-dihydroxy-4-methylcoumarin with octyl bromide

The structures of these two products were elucidated by IR and UV spectra. The IR spectra and UV spectra at 1739 cm^{-1} (Figures B10-B11) and 343 nm (Figures C10-C11) were coumarin characteristic peak. It should be pointed out that TLC and column chromatography showed two types of products occurred in this reaction.



NOE difference spectrum resulting from irradiation of H-5

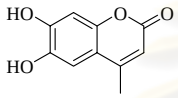
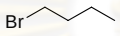
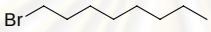


NOE difference spectrum resulting from irradiation of H-8

Figure 8 NOE difference spectrum of 6-hydroxy-4-methyl-7-octoxycoumarin

Figure 8 is the 7-octoxy-6-hydroxy-4-methylcoumarin. The significant enhancement of the signal of the -OCH_2- at δ 4.1 was observed upon irradiation of hydrogen-8 as revealed in Figure 8b. This figure can be assigned to be 5-hydroxy-7-octoxy -4-methylcoumarin (Compound 6b).

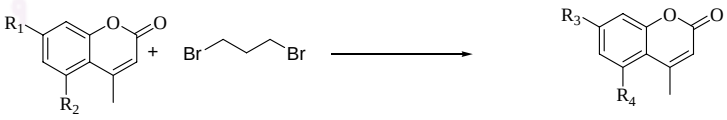
Table 2 6,7-Dihydroxy-4-methylcoumarin alkylated with alkyl bromides

Coumarin	Alkyl bromide	Products	%yields	mp
 Compound 4		5a	9	76-78
		5b	24	157-159
		6a	17	57-58
		6b	39	116-118

4.4 Alkylation with 1,3-dibromopropane

4.4.1 Monoalkoxy-4-methylcoumarins

Compound 2a, 3a, 5a, 6a contain dialkoxy group. Therefore, these compounds could not undergo further alkylation reaction with 1,3-dibromopropane. The coumarin derivatives, Compound 2b, 2c, 3b, 3c, 5b, and 6b, were reacted with 1,3-dibromopropane in order to create the linkage in next step. The reactions of Compound 5b and 6b did not occur, probably due to the steric effect of alkoxy group at position 7. Figures A17-A20 revealed the significant signals of (3′-bromo)propoxy group approximately at δ 4.14 (t, 2H), 3.60 (t, 2H) and, 2.33 (p, 2H). These ^{1}H-NMR spectra confirmed the expected products are Compound 2b, 2c, 3b and 3c as detailed in Table 3.

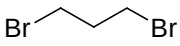


Compound 2b : R_1 =butoxy R_2 = hydroxy
Compound 2c : R_1 = hydroxy R_2 = butoxy
Compound 3b : R_1 = octoxy R_2 = hydroxy
Compound 3c : R_1 = hydroxy R_2 = octoxy

Compound 2'b : R_3 = butoxy R_4 = (3'-bromo)propoxy
Compound 2'c : R_3 = (3'-bromo)propoxy R_4 = butoxy
Compound 3'b : R_3 = octoxy R_4 = (3'-bromo)propoxy
Compound 3'c : R_3 = (3'-bromo)propoxy R_4 = octoxy

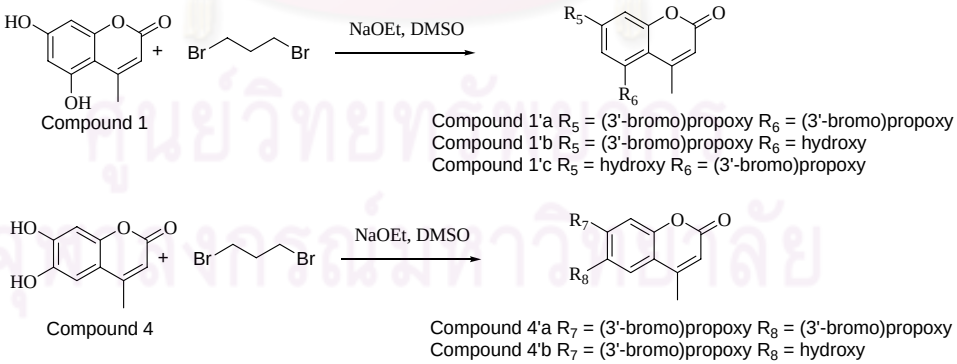
Scheme 16 Alkylation of monoalkoxy-4-methylcoumarin with 1,3-dibromopropane

Table 3 Monoalkoxy-4-methylcoumarin alkylated with 1,3 dibromopropane

1,3-Dibromopropane	Coumarins	Base	Products	%Yields	mp
	2b	NaOEt	2′b	44	71-73
	2c	NaOEt	2′c	64	83-84
	3b	K_2CO_3	3′b	38	42-43
	3c	K_2CO_3	3′c	35	47-48
	5b	NaOEt,K_2CO_3	-	-	-
	6b	NaOEt,K_2CO_3	-	-	-

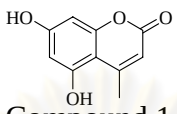
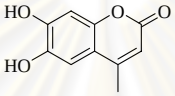
4.4.2 5,7-Dihydroxy-4-methylcoumarin and 6,7-dihydroxy-4-methylcoumarin

In addition, Compound 1 and Compound 4 were separately treated by 1,3-dibromopropane. The reaction of Compound 1 afforded 5,7-di(3′-bromo)propoxy-4-methylcoumarin (Compound 1′a), 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin (Compound 1′b) and 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin (Compound 1′c). For Compound 4, only 6,7-di(3′-bromo)propoxy-4-methylcoumarin (Compound 4′a), 6-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin (Compound 4′b) were obtained. These results can be explained in the same mechanism as described in section 4.2 and 4.3. Table 4 exhibited the yields and melting point of all products.



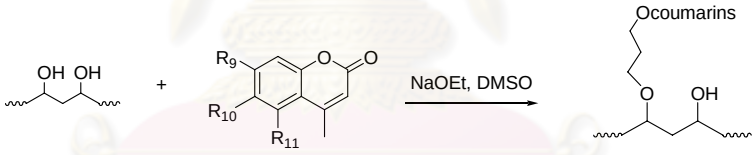
Scheme 17 Alkylation of 5,7-dihydroxy-4-methylcoumarin and 6,7-dihydroxy-4-methylcoumarin with 1,3-dibromopropane

Table 4 5,7-Dihydroxy-4-methylcoumarin and 6,7-dihydroxy-4-methylcoumarin alkylated with 1,3-dibromopropane

1,3-Dibromopropane	Coumarins	products	%yields	mp
Br Br	 Compound 1	1′a	7.9	69-70
		1′b	3.2	167-169
		1′c	4.9	185-187
	 Compound 4	4′a	8.3	48-50
		4′b	6.9	154-156

4.5 Preparation of poly(vinyl alcohol) containing coumarin derivatives

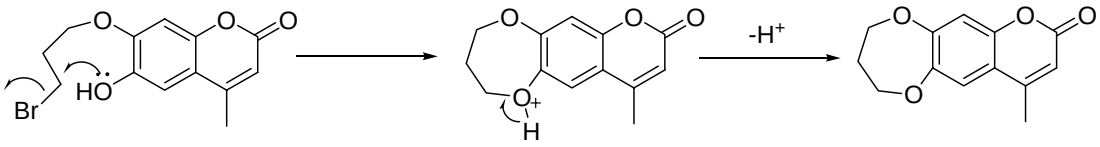
4.5.1 Synthesis and characterization of poly(vinyl alcohol) containing coumarin derivatives



Compound 1'b R_9 =(3'-bromo)propoxy R_{10} = H R_{11} = hydroxy
Compound 1'c R_9 = hydroxy R_{10} = H R_{11} = (3'-bromo)propoxy
Compound 2'b R_9 =butoxy R_{10} = H R_{11} = (3'-bromo)propoxy
Compound 2'c R_9 =(3'-bromo)propoxy R_{10} = H R_{11} = butoxy
Compound 3'b R_9 =octoxy R_{10} = H R_{11} = (3'-bromo)propoxy
Compound 3'c R_9 =(3'-bromo)propoxy R_{10} = H R_{11} = octoxy
Compound 4'b R_9 =(3'-bromo)propoxy R_{10} = hydroxy R_{11} = H

Scheme 18 Synthesis of poly(vinyl alcohol) containing coumarin derivatives

7 coumarin derivatives with (3′-bromo)propoxy group were used in the synthesis of poly(vinyl alcohol) containing coumarin derivatives. The reaction was carried out in the presence of sodium ethoxide for two hours. The isolation of the product was performed by using dialysis tube against water and freeze drying. It was found that the reaction of Compound 4′b could not occur because no additional signal other than signals belonging to PVA in the ^{1}H-NMR spectrum of the material after freeze drying. It is possible that self nucleophilic substitution can occur readily than the reaction with PVA as shown in Scheme 19. The (3′-bromo)propoxy group was at the position 7 which was next to hydroxyl group at position 6.



Scheme 19 Proposed mechanism for side reaction of 6-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

The other 6 coumarin derivatives were reacted with PVA and gave the corresponding products. The presence of coumarin in the product was a set of signals at 6.30 (s,1H), 6.23 (s1H), and 5.89 (s,1H) as shown in Figures A21-A26. These ^{1}H-NMR spectra confirmed that all 6 products are PVA containing coumarin derivatives.

4.5.2 Determination of coumarin content incoperated into PVA

Coumarins have chromophore UV absorption of wavelength at 323 nm as shown in Figure 9.

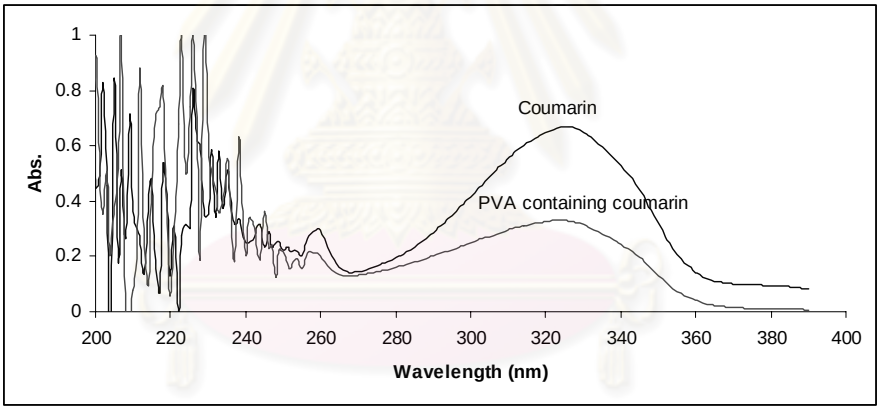


Figure 9 UV spectra of coumarin and PVA containing coumarin

Therefore, the coumarin content in PVA can be determined by UV-visible spectrum. The coumarin content in each product was determined by UV-visible spectroscopy using the calibration curves of 3 coumarins as shown in Figures E1-E3. Table 5 shows the coumarin content incoperated in PVA.

Table 5 Coumarin content in poly(vinyl alcohol)

In feed (%mole)	% mole of coumarin content*
2%mole Compound 1′b	0.235
2%mole Compound 1′c	0.248
2%mole Compound 2′b	0.332
2%mole Compound 2′c	0.314
2%mole Compound 3′b	0.338
2%mole Compound 3′c	0.283

***** % mole of coumarin per repeating PVA unit

4.6 Poly(vinyl alcohol) containing coumarin derivatives as a photoresist

6 PVA containing coumarin derivatives were investigated for being used as photoresist by irradiation through the photoresist mask, as shown in Figure 10, and developing in hot water to observe the patterns.

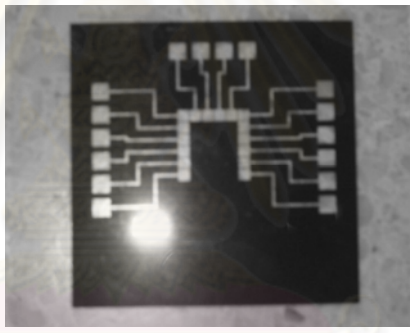
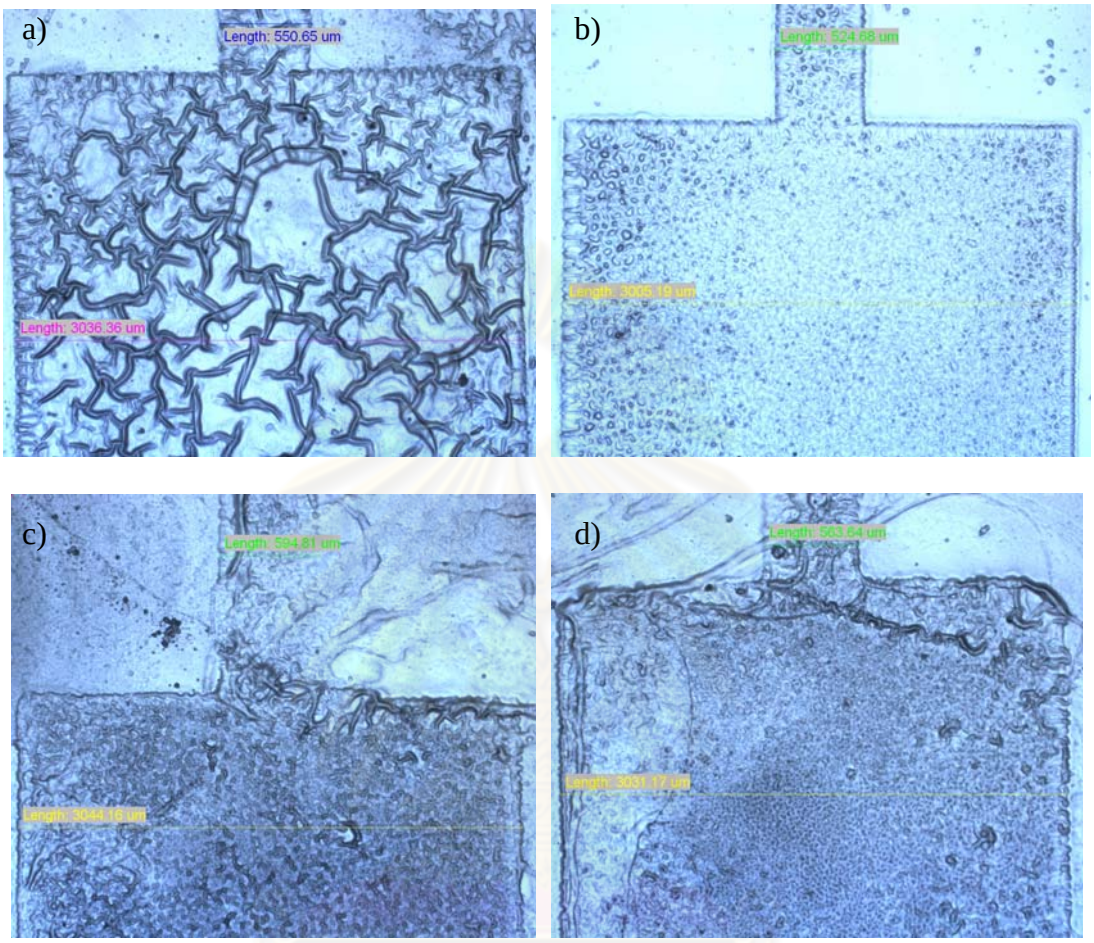


Figure 10 The feature of the photoresist mask

After irradiation with UV light at 365 nm for 2 minutes, all 6 colorless films looked the same. However, in the following step, the development in hot water for 2 minutes, PVA containing 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin and PVA containing 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin were all dissolved while the mask patterns were observed for the other 4 films as shown in Figure 11.



a) PVA containing 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

b) PVA containing 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

c) PVA containing 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

d) PVA containing 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin

Figure 11 Microscope images (x25) of poly(vinyl alcohol) containing alkoxycoumarins after developing in hot water

It can be seen that good patterns of one mask unit were developed from the films of PVA containing 7-butyl-4-methyl-5-(3′-bromo)propoxycoumarin (Figure 11 a) and PVA containing 5-butyl-4-methyl-7-(3′-bromo)propoxycoumarin (Figure 11 b). In case of PVA containing 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin and PVA containing 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin (Figure 11 c and d), both patterns of one mask unit were also observed but longer development of 6 minutes in hot water was required. The explanation could be due to the existence of longer alkoxy substituents, comparing to the previous two types of PVA, caused their poor solubility in hot water. Accordingly, these two polymers could not dissolve readily and then contaminated on the patterns. The results indicated that the alkoxy substituents of coumarin moiety have much influence on the photocrosslinking upon irradiation. This was confirmed by no photodimerization occurred in these two cases. It was probably due to the unavailability of molar volume of these polymers which caused the restricted coumarin mobility upon irradiation.

Accordingly, PVA containing 7-butyl-4-methyl-5-(3′-bromo)propoxycoumarin and PVA containing 5-butyl-4-methyl-7-(3′-bromo)propoxycoumarin could be served as the acceptable negative photoresist.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The synthesis of poly(vinyl alcohol) containing coumarins was focused during the course of this research. In alkylation step, it was founded that hydroxy groups of 6,7-dihydroxy-4-methylcoumarin on aromatic ring have different selectivity. In contrast, 5,7-dihydroxy-4-methylcoumarin, both of hydroxy groups have the same reactivity. In photoresist test, poly(vinyl alcohol) containing 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin and poly(vinyl alcohol) containing 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin have good patterns after developing by hot water because they could be more soluble than poly(vinyl alcohol) containing 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin and poly(vinyl alcohol) containing 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin which have long alkoxy chain. Therefore, there is problem in developing with hot water.

5.2 Recommendations

- 4 poly(vinyl alcohol) containing alkoxycoumarins need to be improved in surface adhesion.

REFERENCES

[1] Sasa, N. and Yamaoka, T. Surface-activated photopolymer microgels. Advanced Materials. 6 (1994):417-421.

[2] Kityk, I.V.; Majchrowski, A.; Ebothe, J. and Sahraoui, B. Nonlinear optical effects in Bi12TiO20 nanocrystallites embedded within a photopolymer matrix. Optics Communications.;236 (2004):123-129.

[3] Gnanaguru, K.; Ramasubbu, N.; Venkatesan, K. and Ramamurthy, V. A study on the photochemical dimerization of coumarins in the solid state. The Journal of Organic Chemistry. 50 (1985):2337-2346.

[4] Obi, M.; Morino, S.y. and Ichimura, K. Factors Affecting Photoalignment of Liquid Crystals Induced by Polymethacrylates with Coumarin Side Chains. Chemistry of Materials. 11 (1999):656-664.

[5] Jackson, P.O.; et al. An Investigation of the Role of Cross-Linking and Photodegradation of Side-Chain Coumarin Polymers in the Photoalignment of Liquid Crystals. Chemistry of Materials. 13 (2001):694-703.

[6] Kawatsuki, N.; Goto, K.; Kawakami, T. and Yamamoto, T. Reversion of Alignment Direction in the Thermally Enhanced Photoorientation of Photo-Cross-Linkable Polymer Liquid Crystal Films. Macromolecules. 35 (2001):706-713.

[7] Li, W.; Lynch, V.; Thompson, H. and Fox, M.A. Self-Assembled Monolayers of 7-(10-Thiodecoxy)coumarin on Gold: Synthesis, Characterization, and Photodimerization. Journal of the American Chemical Society. 119 (1997):7211-7217.

[8] Fang, J.; et al. Synthesis and photodimerization in self-assembled monolayers of 7-(8-trimethoxysilyloctyloxy)coumarin. Journal of Materials Chemistry. 11 (2001):2992-2995.

[9] Tian, Y.; Akiyama, E. and Nagase, Y. Liquid crystalline cyclic tetramethyltetrasiloxanes containing coumarin moieties. Journal of Materials Chemistry. 13 (2003):1253-1258.

[10] Fomine, S.; Delgado, C.; Fomina, L.; Gaviño, R. and Ogawa, T. Polymers from coumarins, 3. Design and synthesis of novel fully aromatic coumarin-containing polyesters. Macromolecular Chemistry and Physics. 198 (1997):3065-3075.

[11] Fomine, S.; Rivera, E.; Fomina, L.; Ortiz, A. and Ogawa, T. Polymers from coumarines: 4. Design and synthesis of novel hyperbranched and comb-like coumarin-containing polymers. Polymer. 39 (1998):3551-3558.

[12] Kokare, N.D.; Sangshetti, J.N. and Shinde, D.B. Oxalic acid catalyzed solvent-free one pot synthesis of coumarins. Chinese Chemical Letters. 18 (2007):1309-1312.

[13] Bruice, P.Y. Organic chemistry. 3rd ed. Upper Saddle River N.J.: Prentice Hall, 2001.

[14] Wang, B.; Guan, X.; Hu, Y. and Su, Z. Preparation and fluorescent properties of poly(vinyl alcohol) bearing coumarin. Polymers for Advanced Technologies. 18 (2007):529-534.

[15] Bianchini, J.R.; Saito, K.; Balin, T.B.; Dua, V. and Warner, J.C. Thymine-based, water-soluble phototerpolymers: Their preparation and synthesis. Journal of Polymer Science Part A: Polymer Chemistry. 45 (2007):1296-1303.

[16] Trenor, S.R.; Shultz, A.R.; Love, B.J. and Long, T.E. Coumarins in Polymers: From Light Harvesting to Photo-Cross-Linkable Tissue Scaffolds. Chemical Reviews. 104 (2004):3059-3078.

[17] Barberis, V.P.; Mikroyannidis, J.A. and Cimrová, V. Coumarin-containing poly(fluorenediylvinylene)s: Synthesis, photophysics, and electroluminescence. Journal of Polymer Science Part A: Polymer Chemistry. 44 (2006):5750-5762.

[18] Trakhtenberg, S.; et al. Spectroscopic and Microscopic Analysis of Photo-cross-linked Vinylbenzylthymine Copolymers for Photoresist Applications. Chemistry of Materials. 18 (2006):2873-2878.

[19] Feng, P.; Zhu, J.; Cheng, Z.P.; Zhang, Z.B. and Zhu, X.L. Reversible addition-fragmentation chain transfer polymerization of 7-(4-(acryloyloxy)butoxy)coumarin. Polymer. 48 (2007):5859-5866.

[20] Brieger, G.; Hachey, D. and Nestrick, T. Convenient O-alkylation of phenols. Journal of Chemical and Engineering Data. 13 (1968):581-582.

[21] Heinisch, G.and Holzer, W. Convenient and rapid determination of the configuration of aldoximes and ketoximes by means of noe difference spectroscopy. Tetrahedron Letters. 31 (1990):3109-3112.

[22] Holzer, W. Spectral and structural assignments with various N-substituted 1,2,4-triazoles: Noe difference spectroscopy as a powerful tool. Tetrahedron. 47 (1991):5471-5480.

[23] Skoog, D.A. Fundamentals of analytical chemistry. 7th ed. Fort Worth : Saunders College Publishing, 1996.

APPENDICES

Appendix A

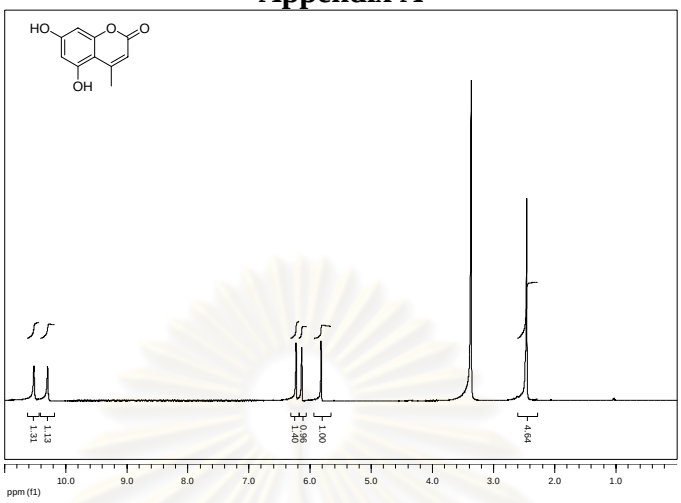


Figure A1 ^{1}H-NMR spectrum of 5,7-dihydroxy-4-methylcoumarin

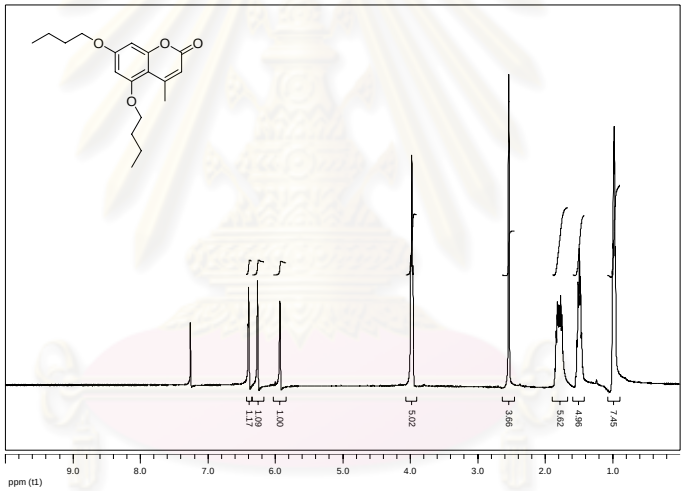


Figure A2 ^{1}H-NMR spectrum of 5,7-dibutoxy-4-methylcoumarin

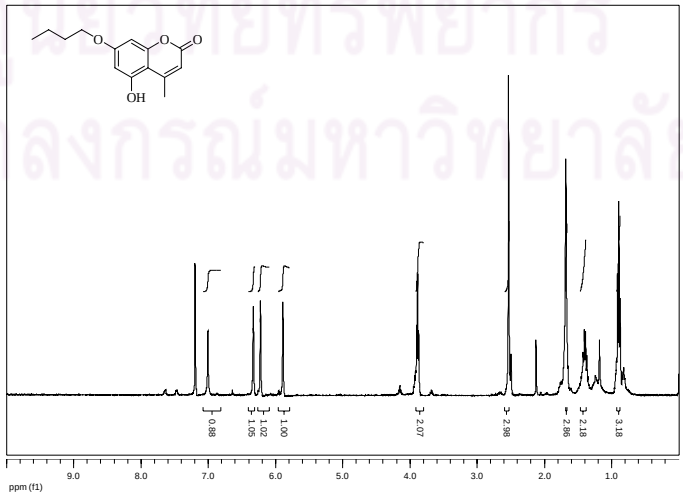


Figure A3 ^{1}H-NMR spectrum of 7-butoxy5-hydroxy-4-methylcoumarin

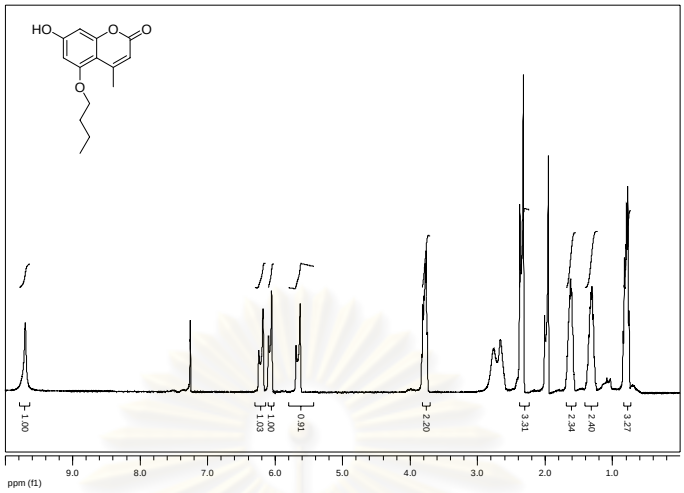


Figure A4 ^{1}H-NMR spectrum of 5-butoxy-7-hydroxy-4-methylcoumarin

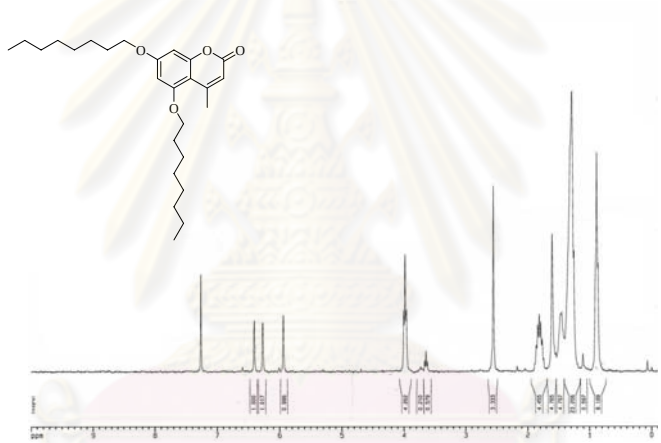


Figure A5 ^{1}H-NMR spectrum of 5,7-dioctoxy-4-methylcoumarin

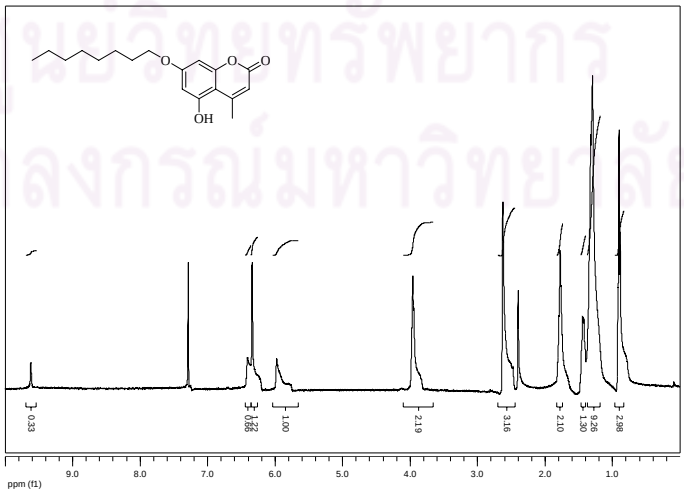


Figure A6 ^{1}H-NMR spectrum of 5-hydroxy-4-methyl-7-octoxycoumarin

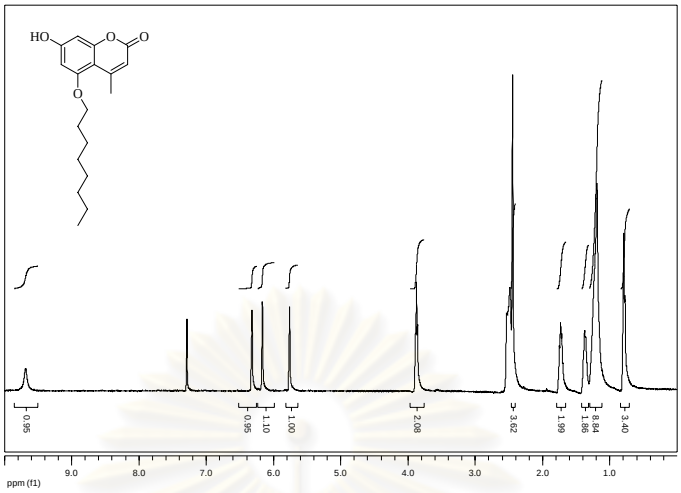


Figure A7 ^{1}H-NMR spectrum of 7-hydroxy-4-methyl-5-octoxycoumarin

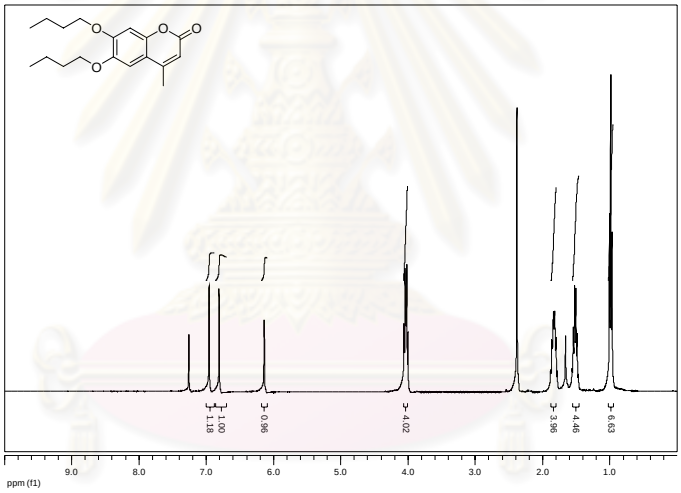


Figure A8 ^{1}H-NMR spectrum of 6,7-dibutoxy-4-methylcoumarin

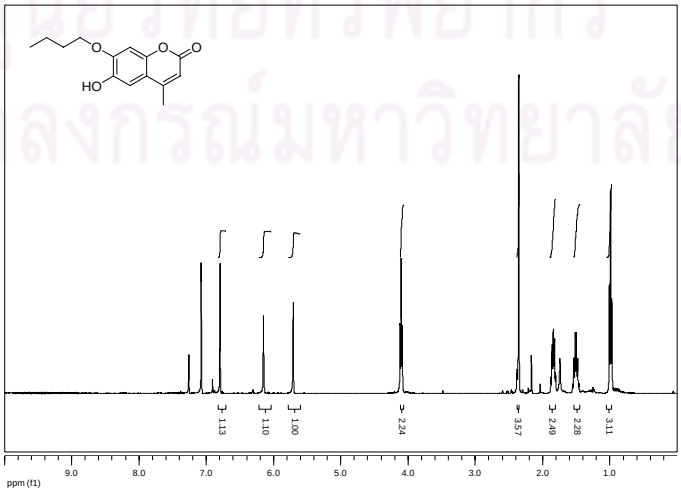


Figure A9 ^{1}H-NMR spectrum of 7-butoxy-6-hydroxy-4-methylcoumarin

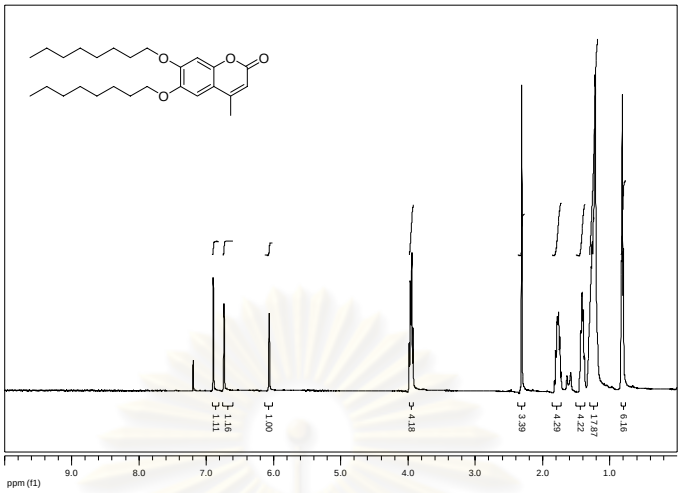


Figure A10 ^{1}H-NMR spectrum of 6,7-dioctoxy-4-methylcoumarin

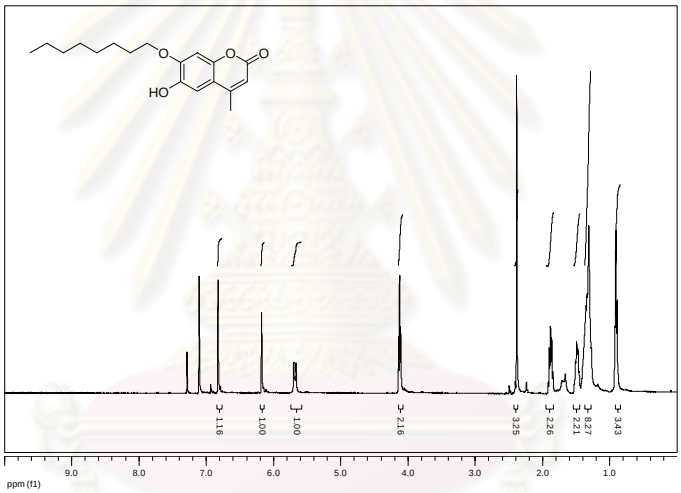


Figure A11 ^{1}H-NMR spectrum of 6-hydroxy-4-methyl-7-octoxycoumarin

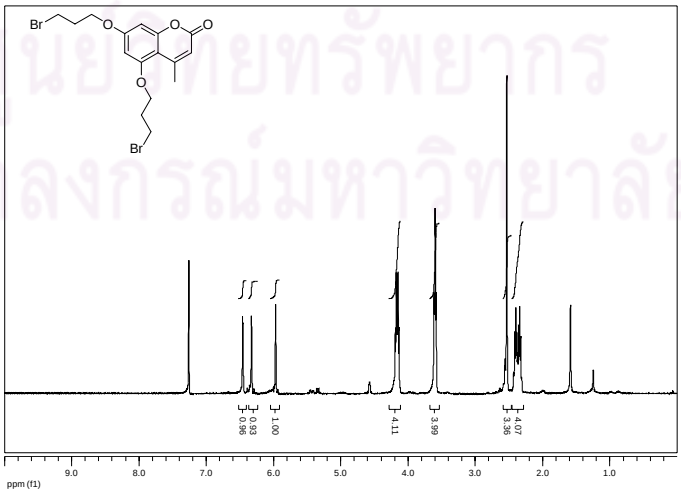


Figure A12 ^{1}H-NMR spectrum of 5,7-di(3′-bromo)propoxy-4-methylcoumarin

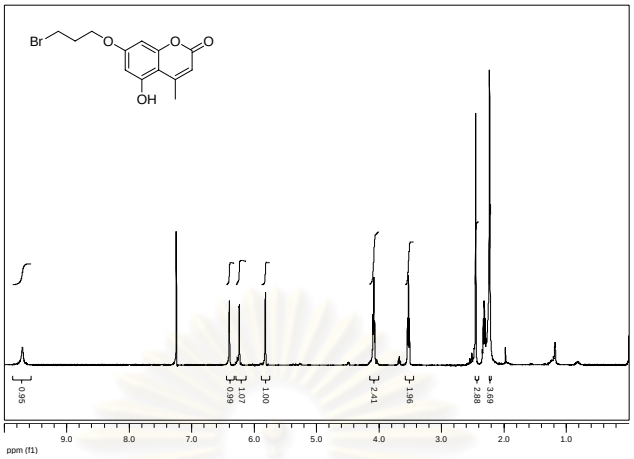


Figure A13 ^{1}H-NMR spectrum of 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

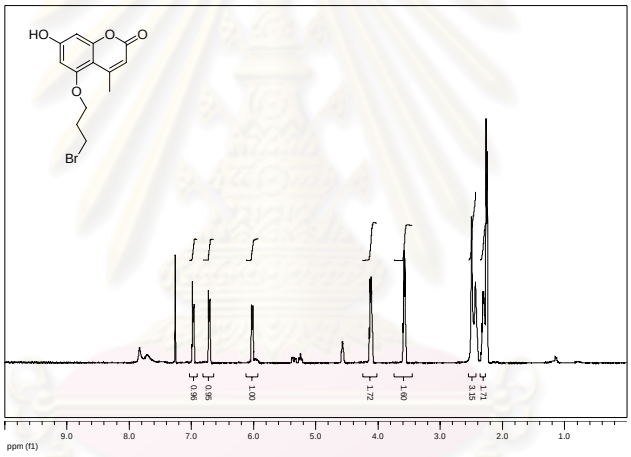


Figure A14 ^{1}H-NMR spectrum of 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

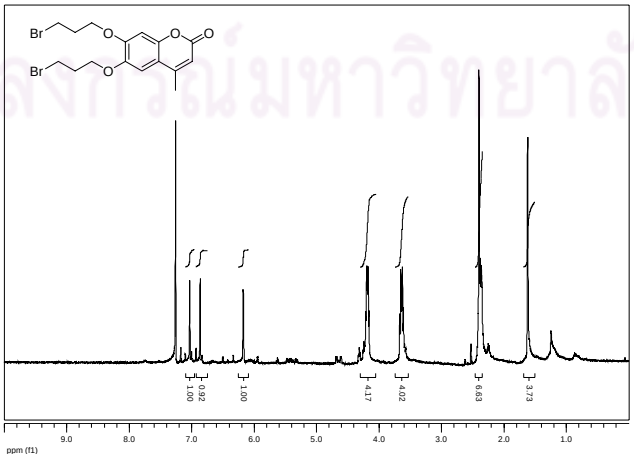


Figure A15 ^{1}H-NMR spectrum of 6,7-di(3′-bromo)propoxy-4-methylcoumarin

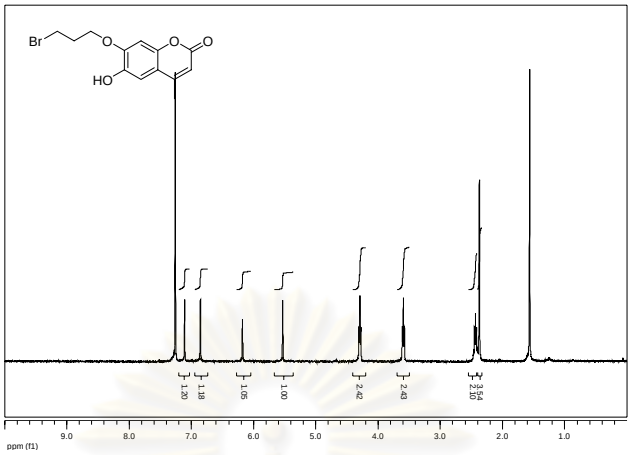


Figure A16 ^{1}H-NMR spectrum of 6-hydroxy-4-methyl-7-(3′-bromo)propoxy coumarin

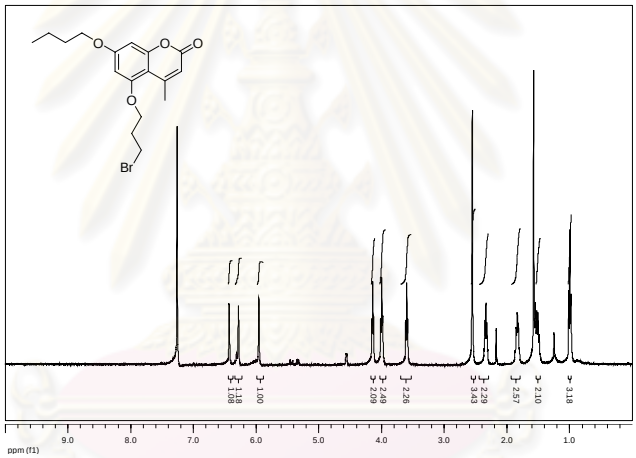


Figure A17 ^{1}H-NMR spectrum of 7-butoxy-4-methyl-5-(3′-bromo)propoxy-coumarin

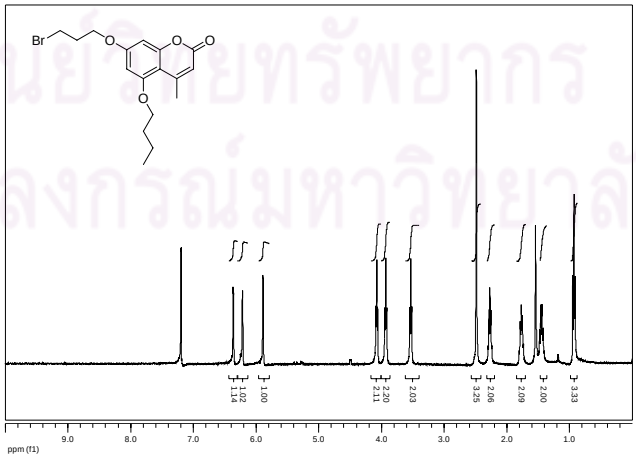


Figure A18 ^{1}H-NMR spectrum of 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

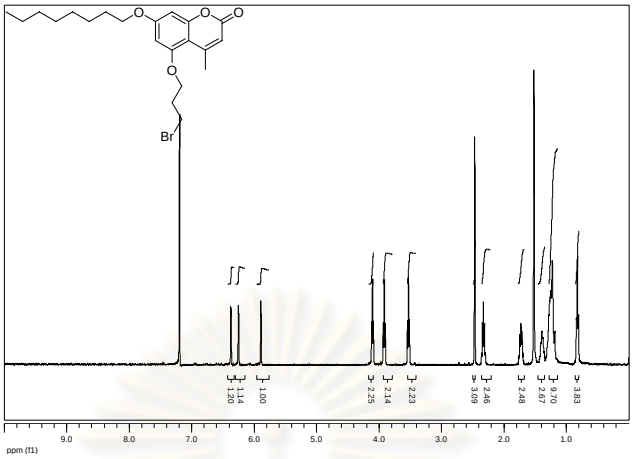


Figure A19 ^{1}H-NMR spectrum of 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

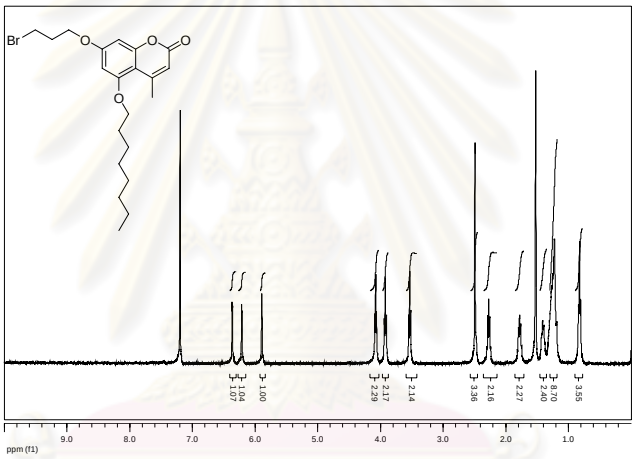


Figure A20 ^{1}H-NMR spectrum of 4-methyl-5-octoxy-7-(3′-bromo)propoxy coumarin

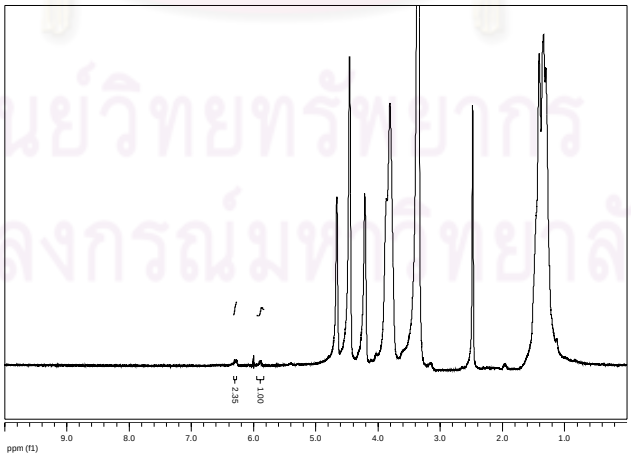


Figure A21 ^{1}H-NMR spectrum of PVA containing 5-hydroxy -4-methyl-7-(3′-bromo)propoxy-coumarin

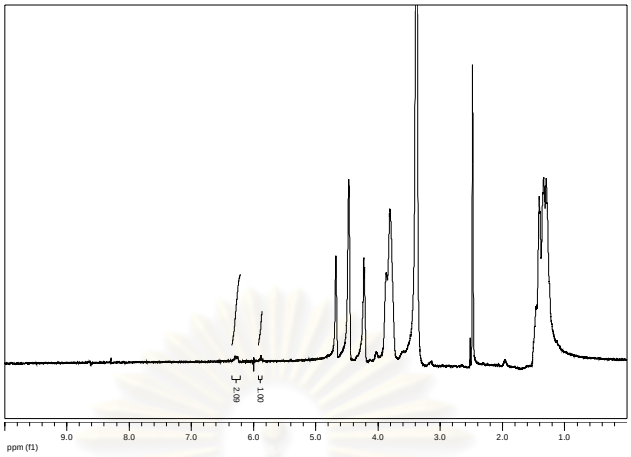


Figure A22 ^{1}H-NMR spectrum of PVA containing 7-hydroxy-4-methyl-5-(3′-bromo)propoxy-coumari

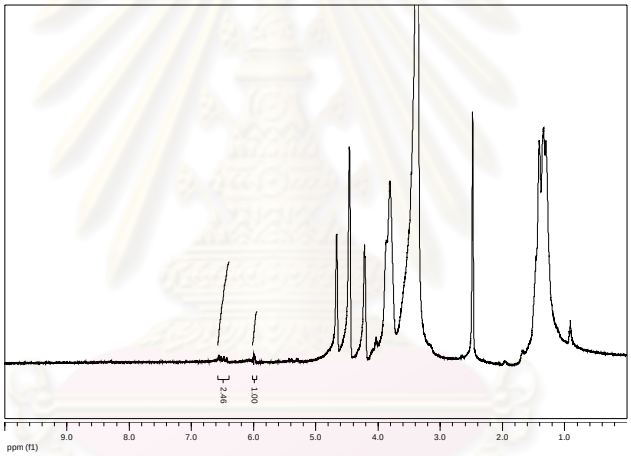


Figure A23 ^{1}H-NMR spectrum of PVA containing 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

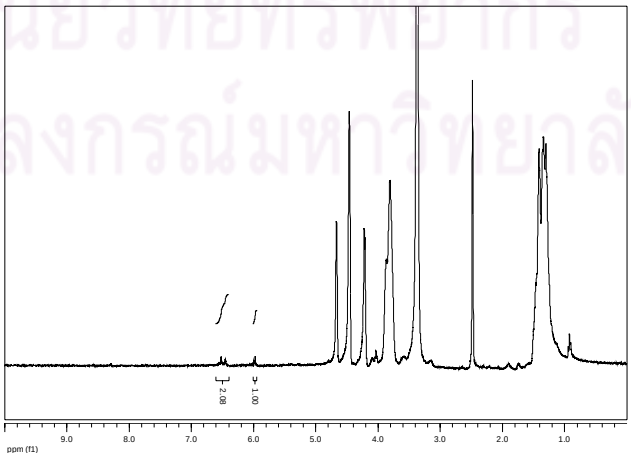


Figure A24 ^{1}H-NMR spectrum of PVA containing 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

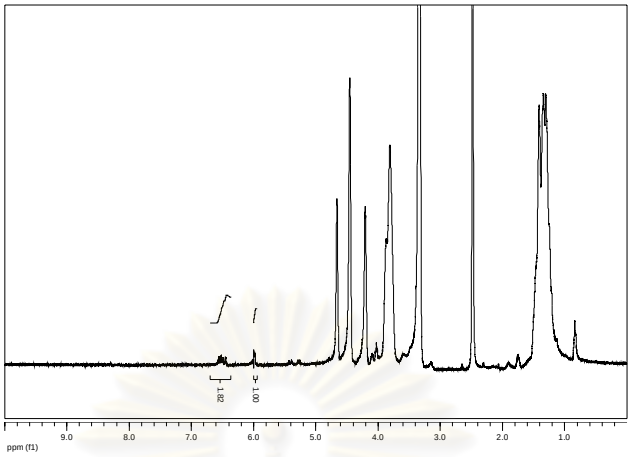


Figure A25 ^{1}H-NMR spectrum of PVA containing 4-methyl-7-octoxy -5-(3′-bromo)propoxycoumarin

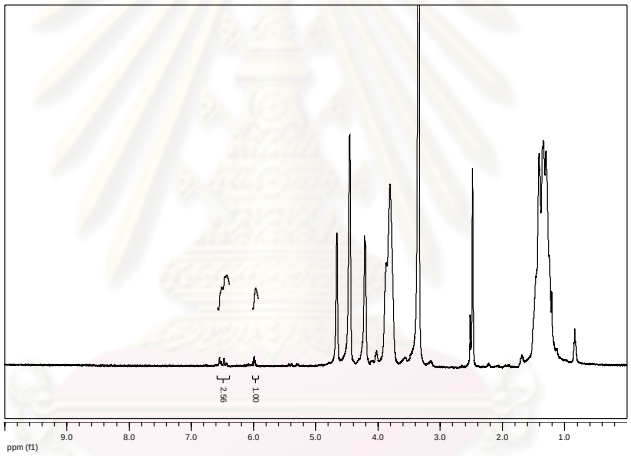


Figure A26 ^{1}H-NMR spectrum of PVA containing 4-methyl-5-octoxy -7-(3′-bromo)propoxycoumarin

Appendix B

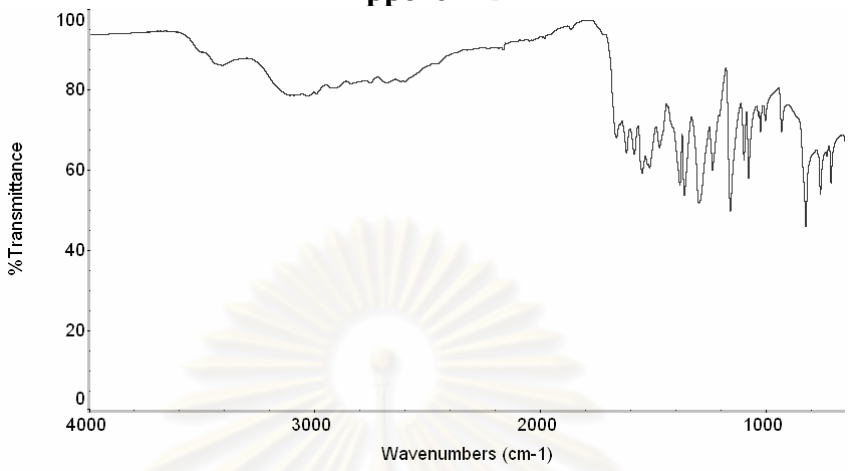


Figure B1 FTIR spectrum of 5,7-dihydroxy-4-methylcoumarin

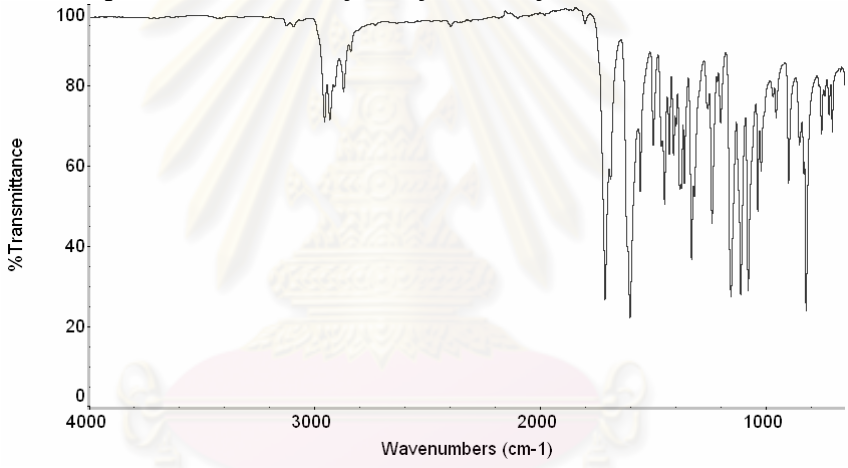


Figure B2 FTIR spectrum of 5,7-dibutoxy-4-methylcoumarin

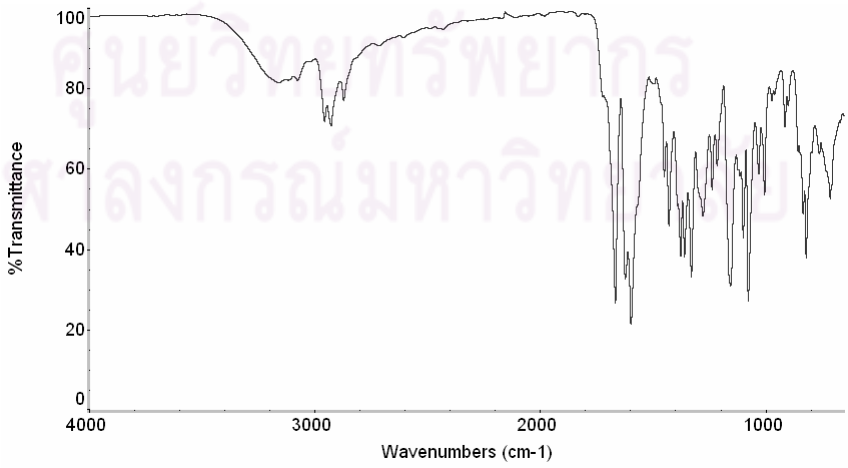


Figure B3 FTIR spectrum of 7-butoxy-5-hydroxy-4-methylcoumarin

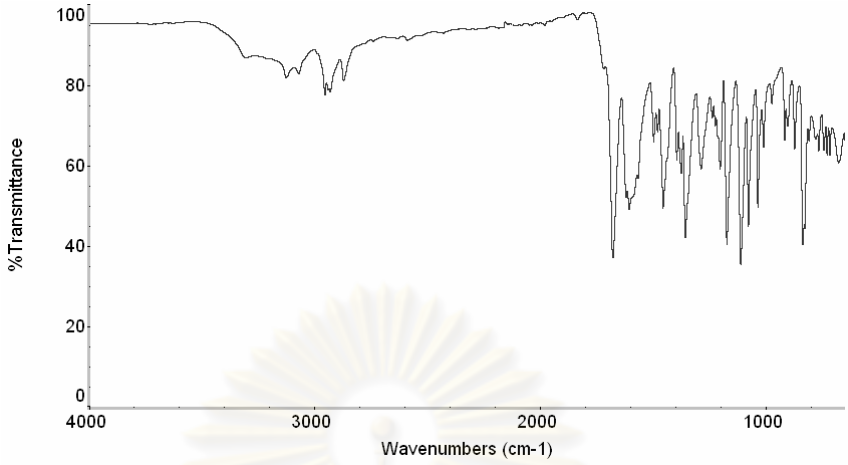


Figure B4 FTIR spectrum of 5-butoxy-7-hydroxy-4-methylcoumarin

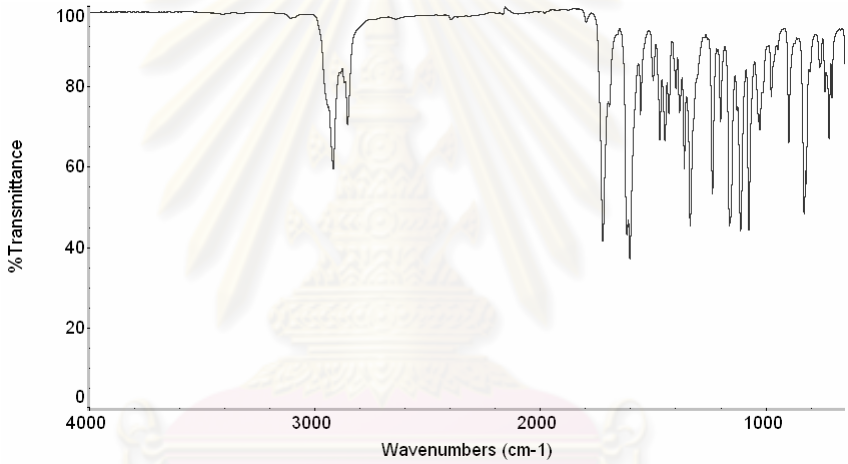


Figure B5 FTIR spectrum of 5,7-dioctoxy-4-methylcoumarin

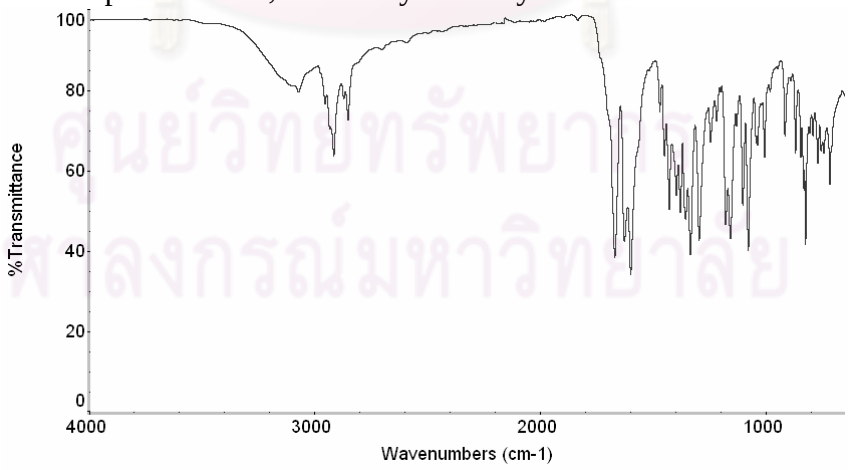


Figure B6 FTIR spectrum of 5-hydroxy-4-methyl-7-octoxy coumarin

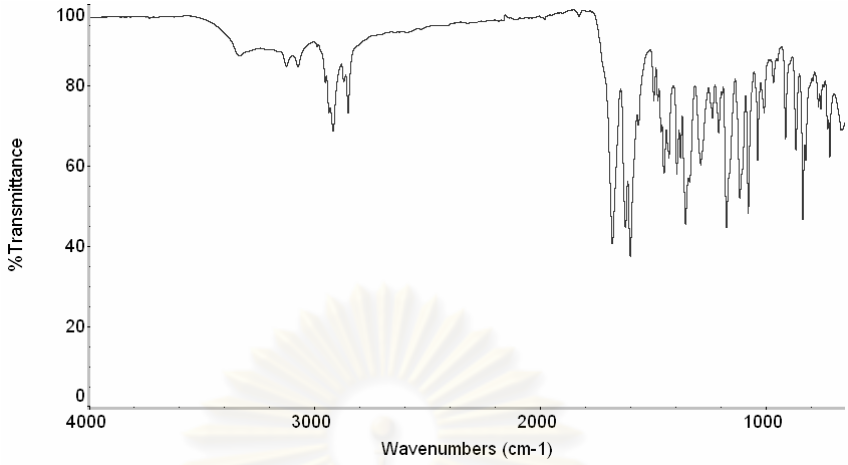


Figure B7 FTIR spectrum of 7-hydroxy-4-methyl-5-octoxycoumarin

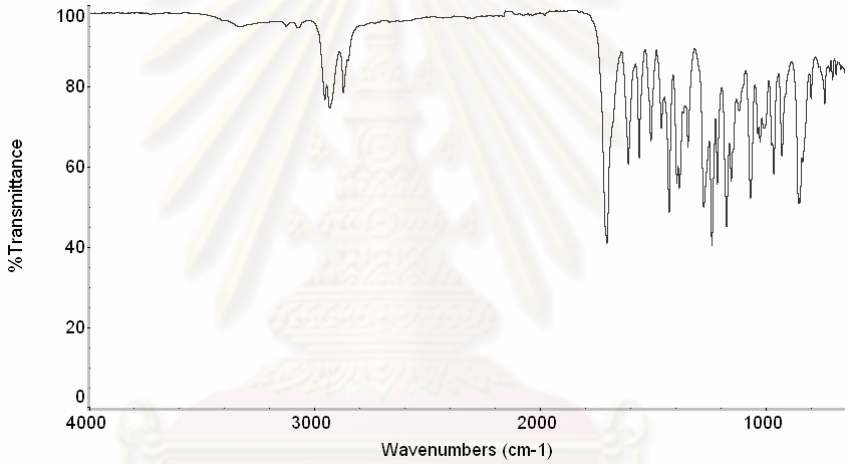


Figure B8 FTIR spectrum of 6,7-dibutoxy-4-methylcoumarin

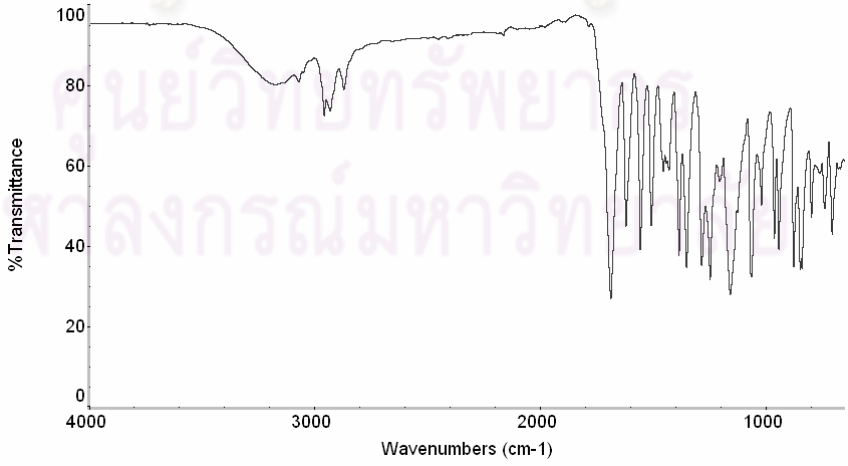


Figure B9 FTIR spectrum of 7-butoxy-6-hydroxy-4-methylcoumarin

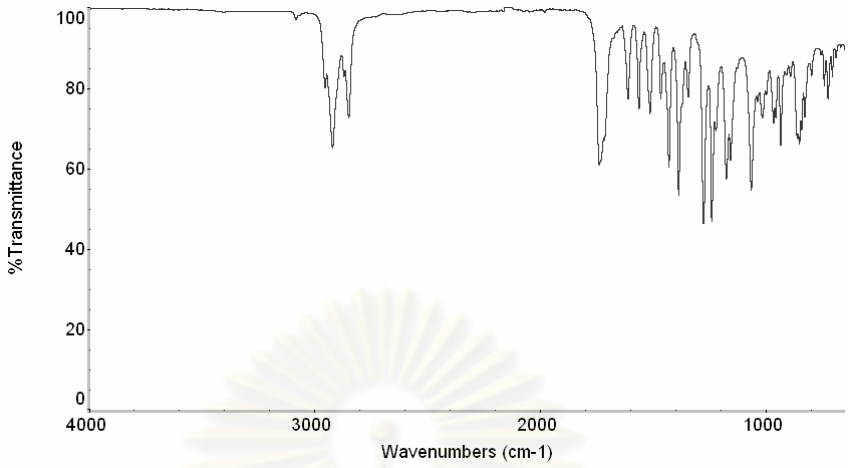


Figure B10 FTIR spectrum of 6,7-dioctoxy-4-methylcoumarin

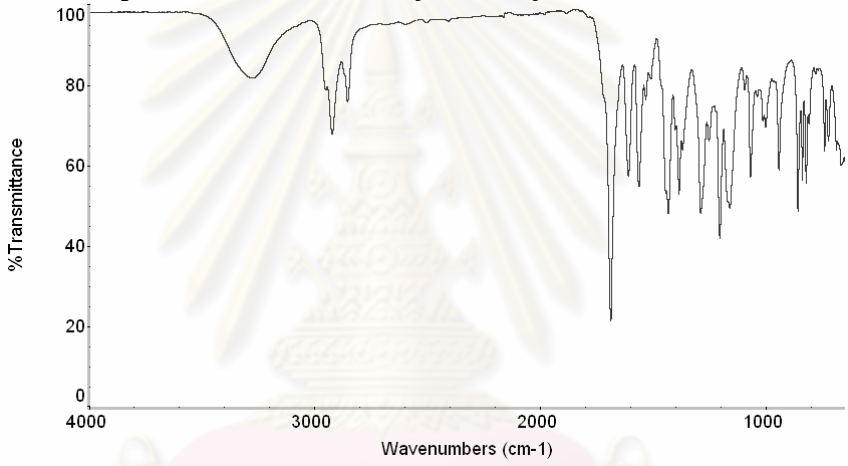


Figure B11 FTIR spectrum of 6-hydroxy-4-methyl-7-octoxycoumarin

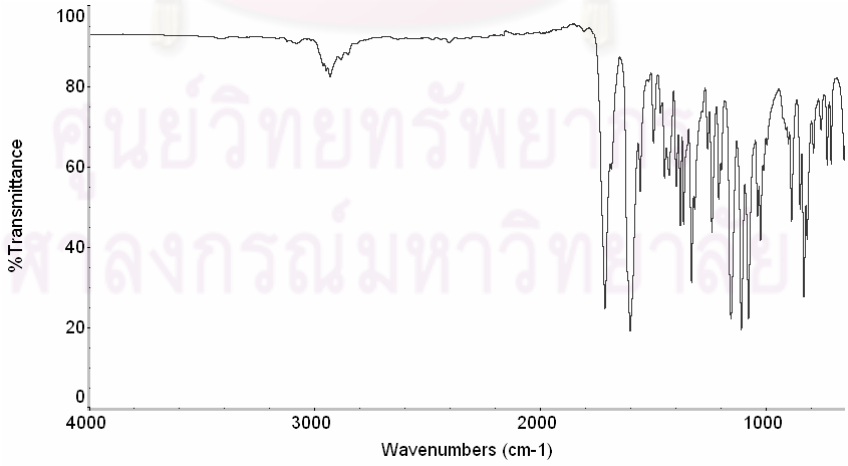


Figure B12 FTIR spectrum of 5,7-di(3′-bromo)propoxy-4-methylcoumarin

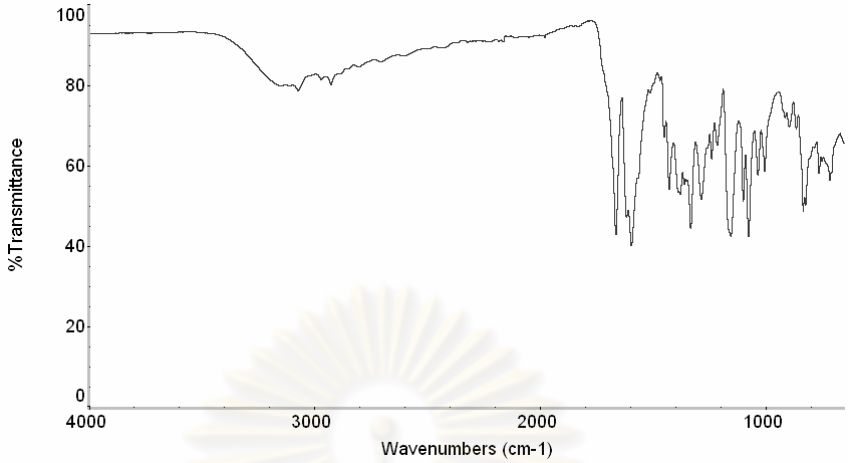


Figure B13 FTIR spectrum of 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

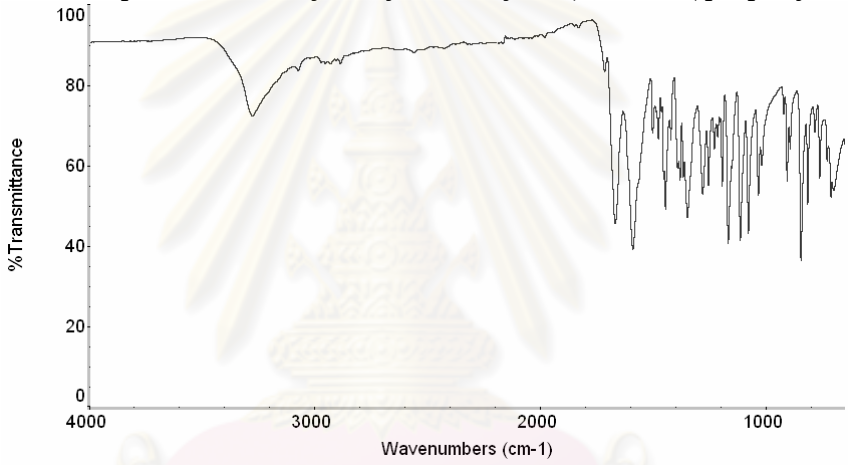


Figure B14 FTIR spectrum of 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

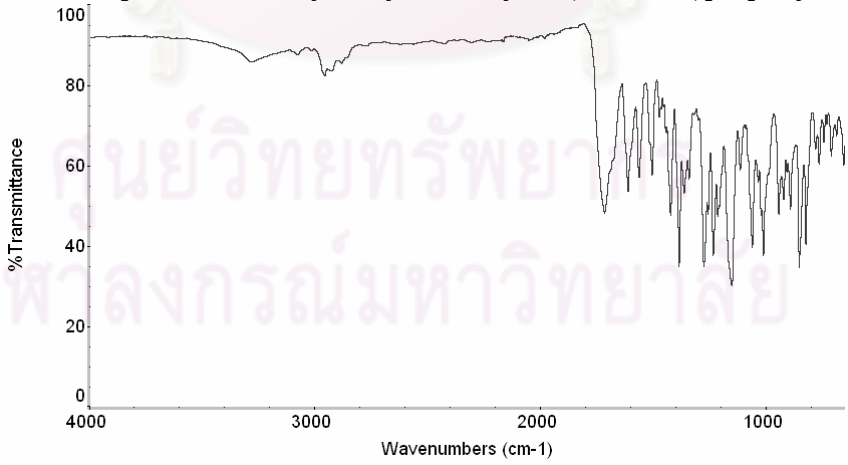


Figure B15 FTIR spectrum of 6,7-di(3′-bromo)propoxy-4-methylcoumarin

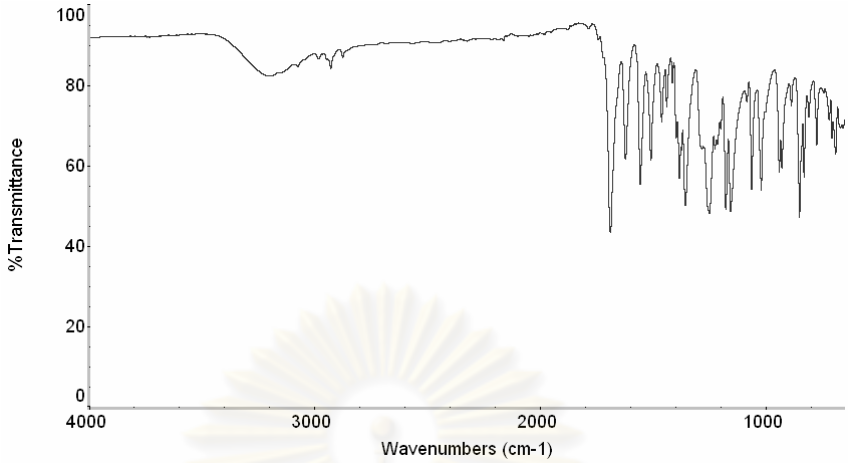


Figure B16 FTIR spectrum of 6-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

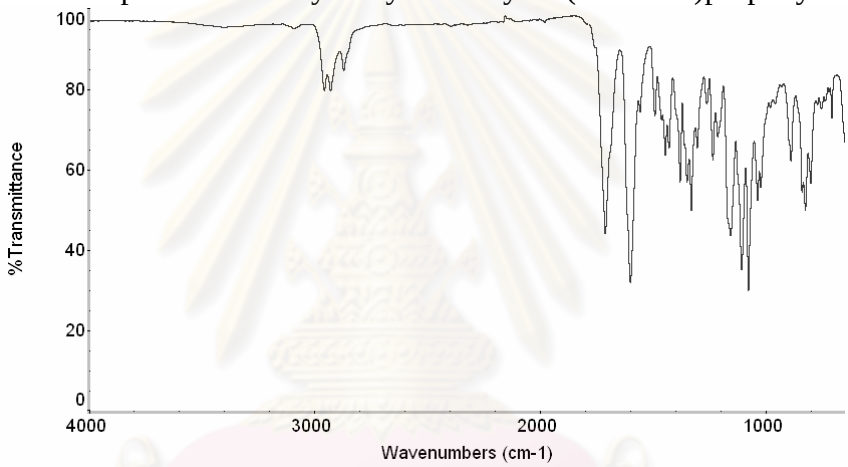


Figure B17 FTIR spectrum of 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

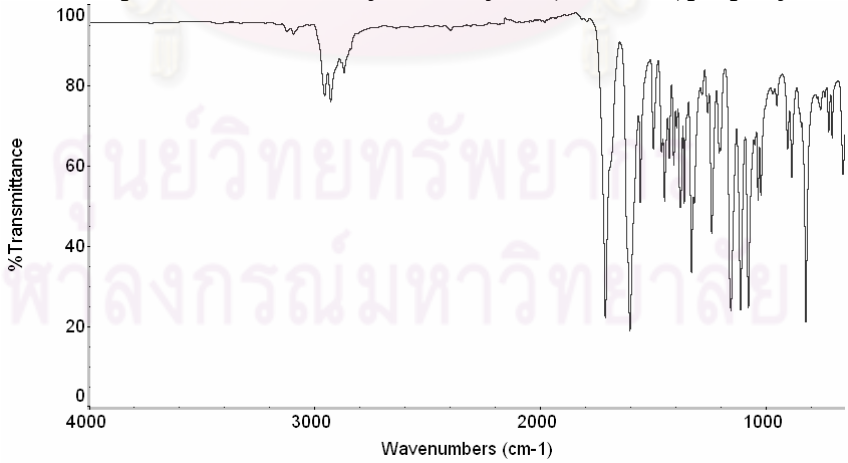


Figure B18 FTIR spectrum of 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

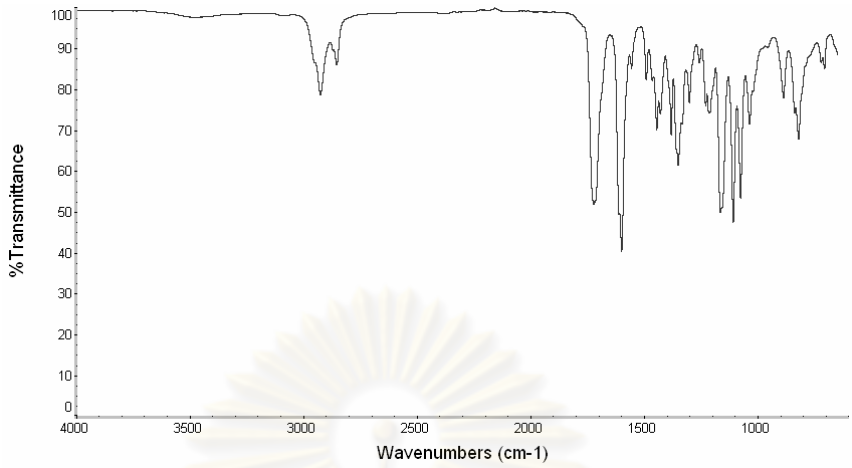


Figure B19 FTIR spectrum of 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

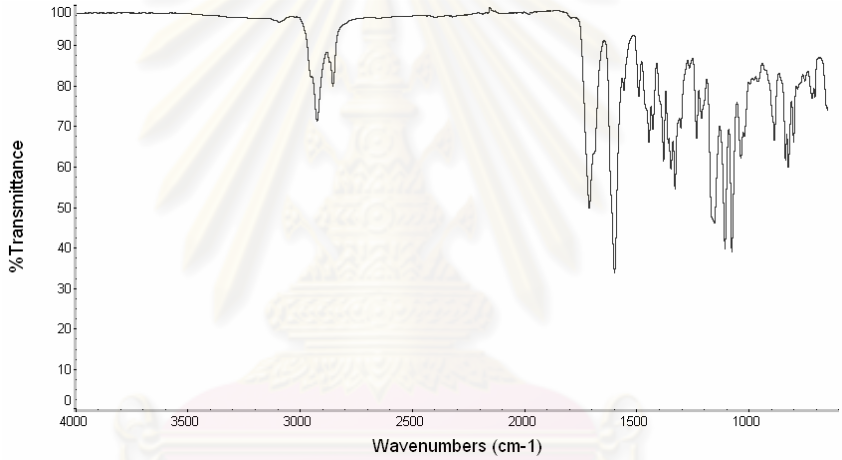


Figure B20 FTIR spectrum of 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin

Appendix C

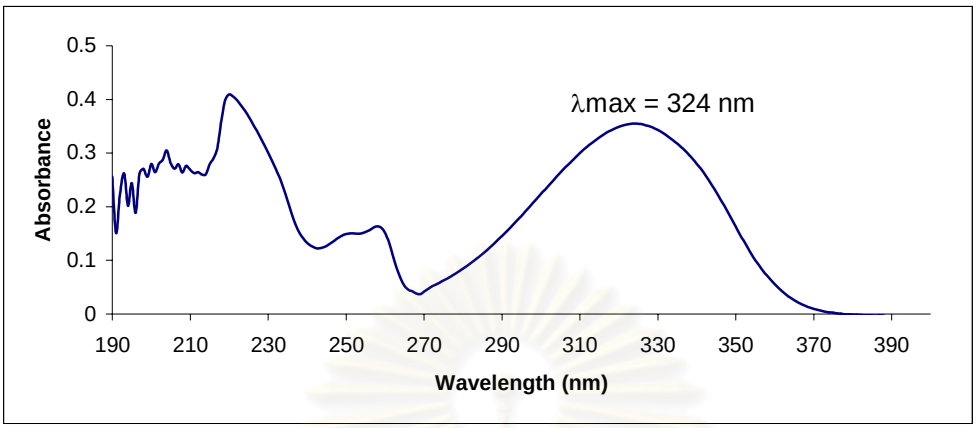


Figure C1 UV absorption spectrum of 5,7-dihydroxy-4-methylcoumarin

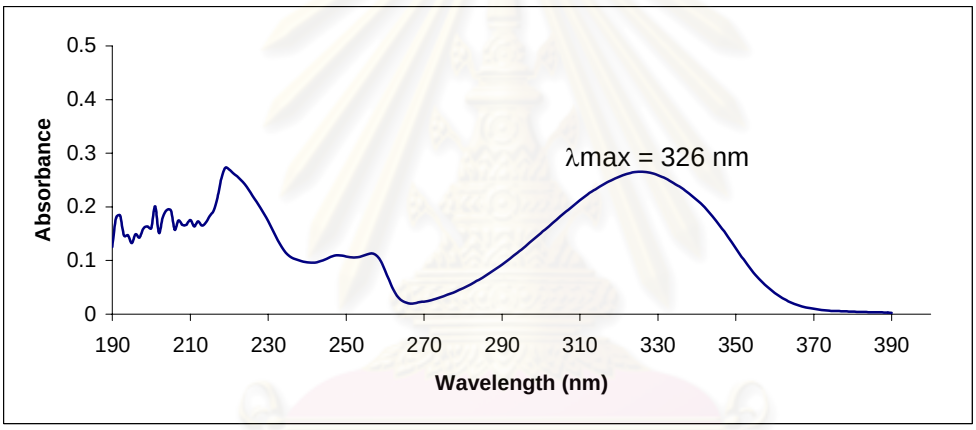


Figure C2 UV absorption spectrum of 5,7-dibutoxy-4-methylcoumarin

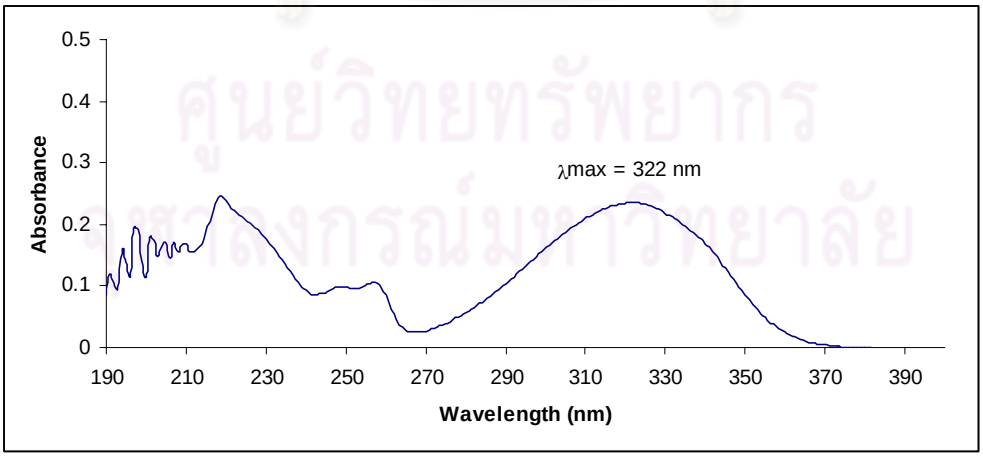


Figure C3 UV absorption spectrum of 7-butoxy-5-hydroxy-4-methylcoumarin

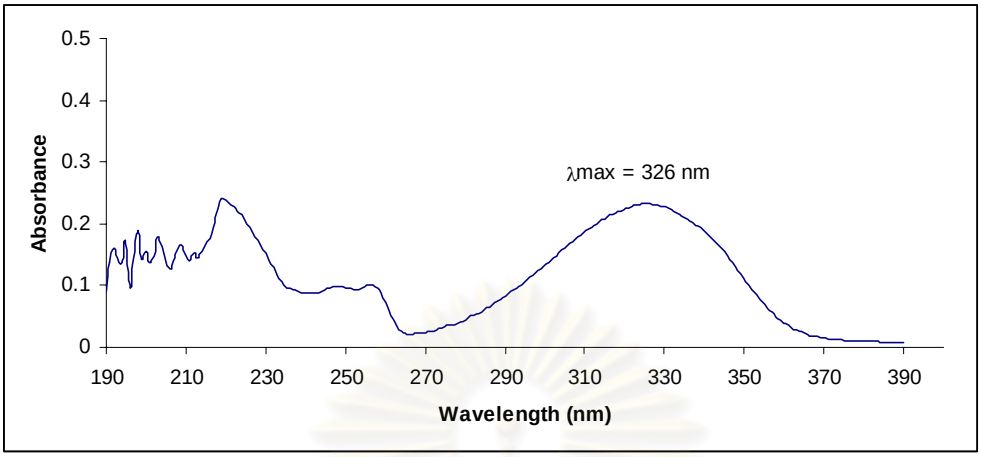


Figure C4 UV absorption spectrum of 5-butoxy-7-hydroxy-4-methylcoumarin

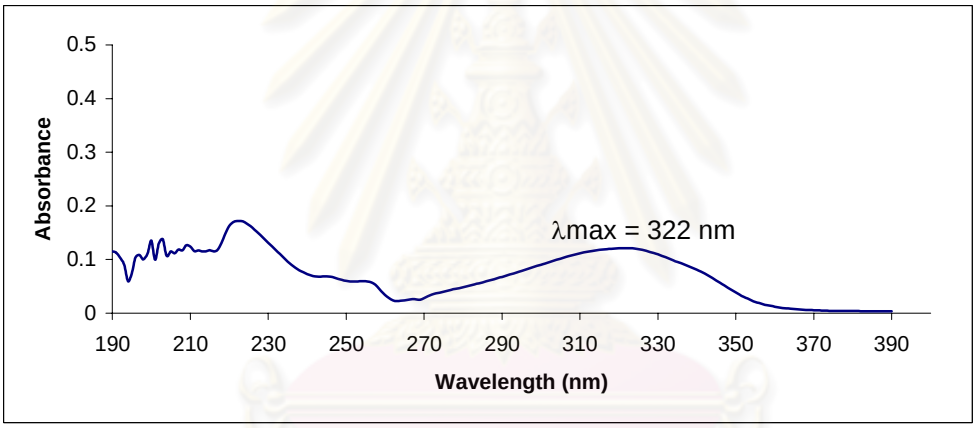


Figure C5 UV absorption spectrum of 5,7-dioctoxy-4-methylcoumarin

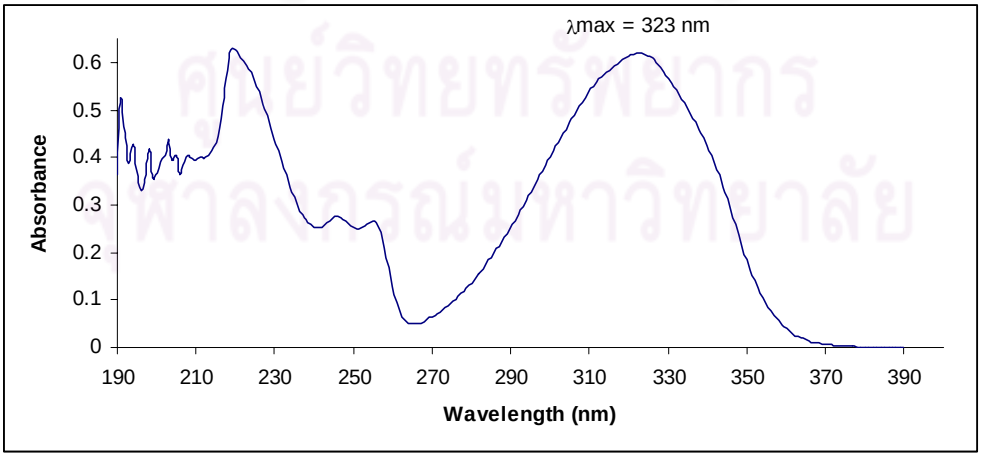


Figure C6 UV absorption spectrum of 5-hydroxy-4-methyl-7-octoxycoumarin

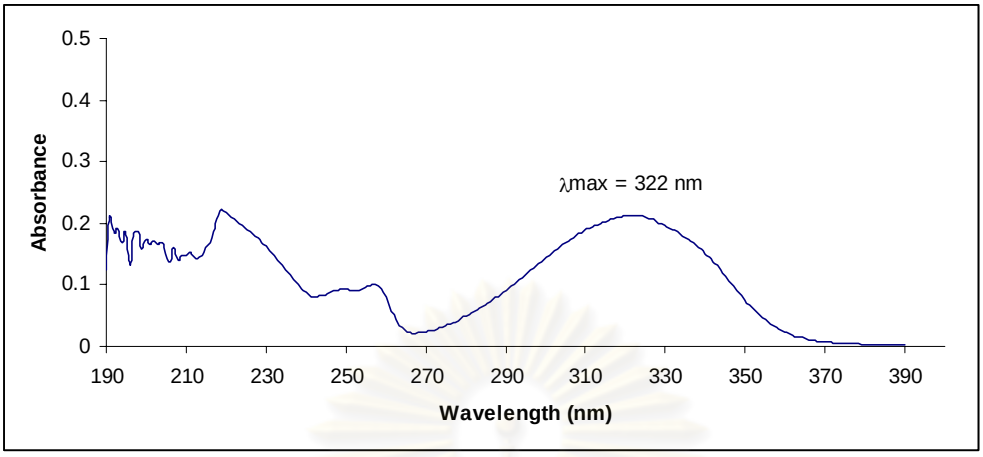


Figure C7 UV absorption spectrum of 7-hydroxy-5-octoxy-4-methylcoumarin

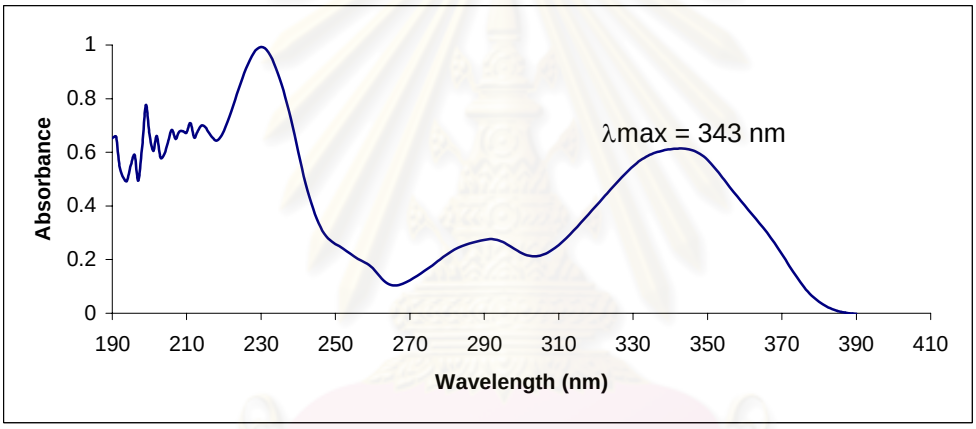


Figure C8 UV absorption spectrum of 6,7-dibutoxy-4-methylcoumarin

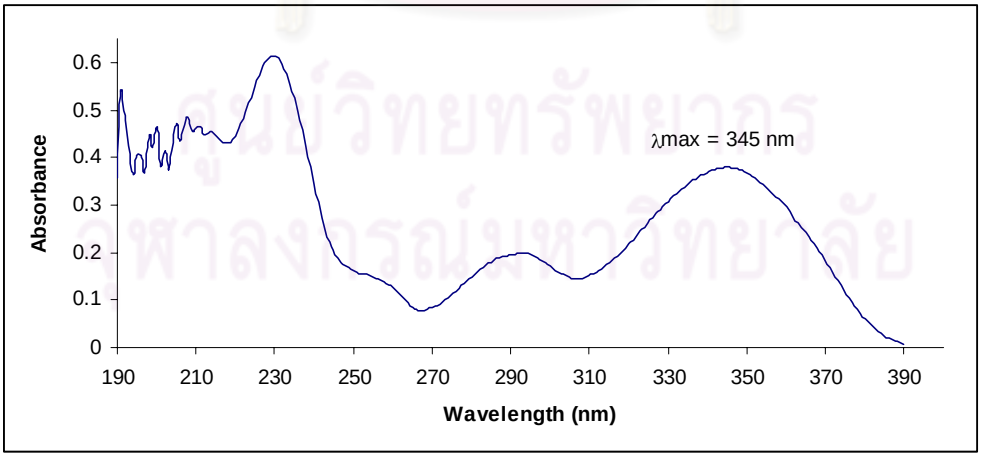


Figure C9 UV absorption spectrum of 7-butoxy-6-hydroxy-4-methylcoumarin

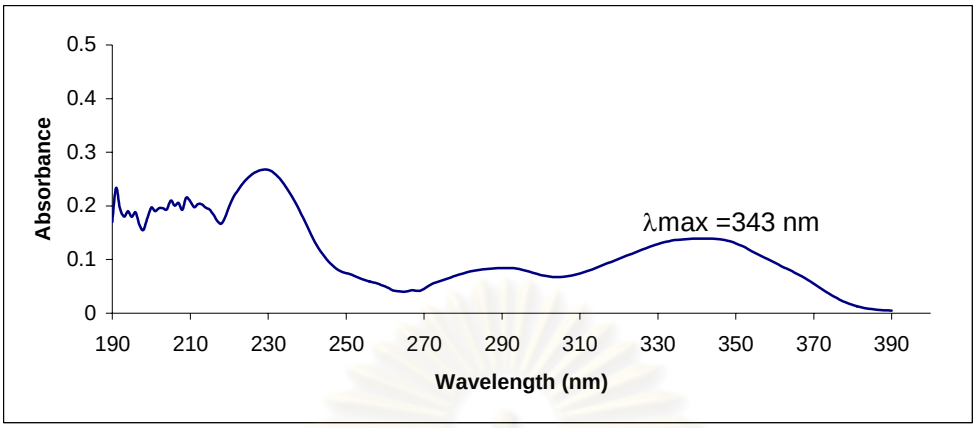


Figure C10 UV absorption spectrum of 6,7-dioctoxy-4-methylcoumarin

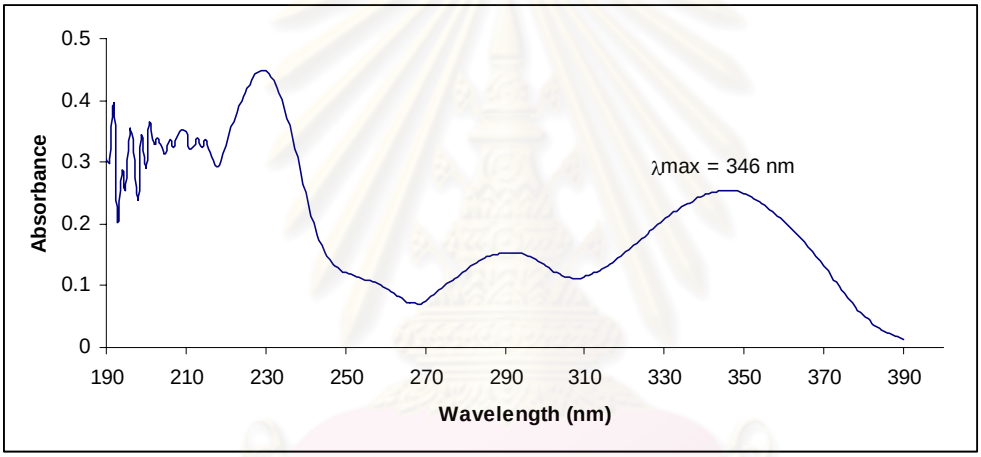


Figure C11 UV absorption spectrum of 6-hydroxy-4-methyl-7-octoxycoumarin

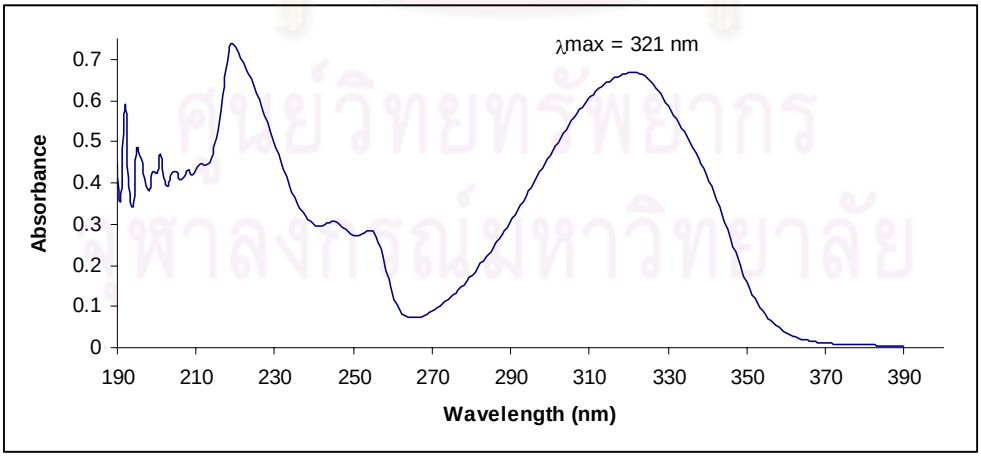


Figure C12 UV absorption spectrum of 5,7-di(3′-bromo)propoxy-4-methylcoumarin

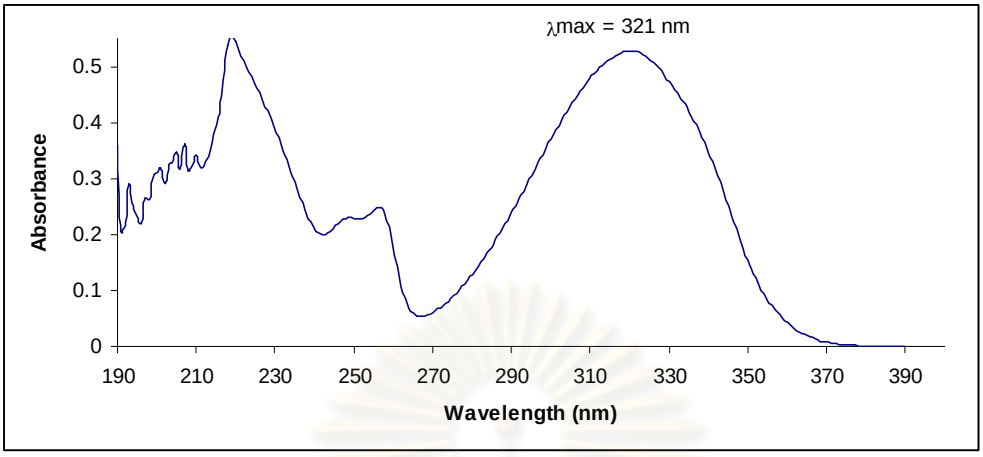


Figure C13 UV absorption spectrum of 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

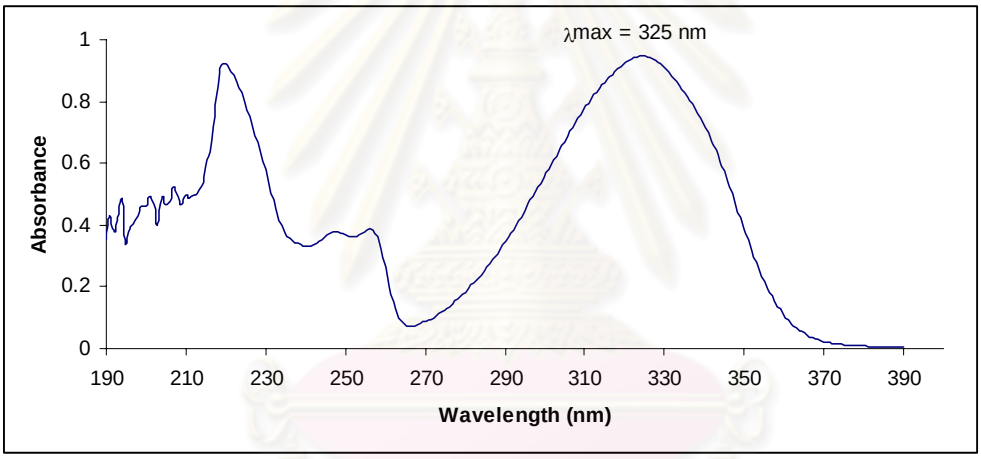


Figure C14 UV absorption spectrum of 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

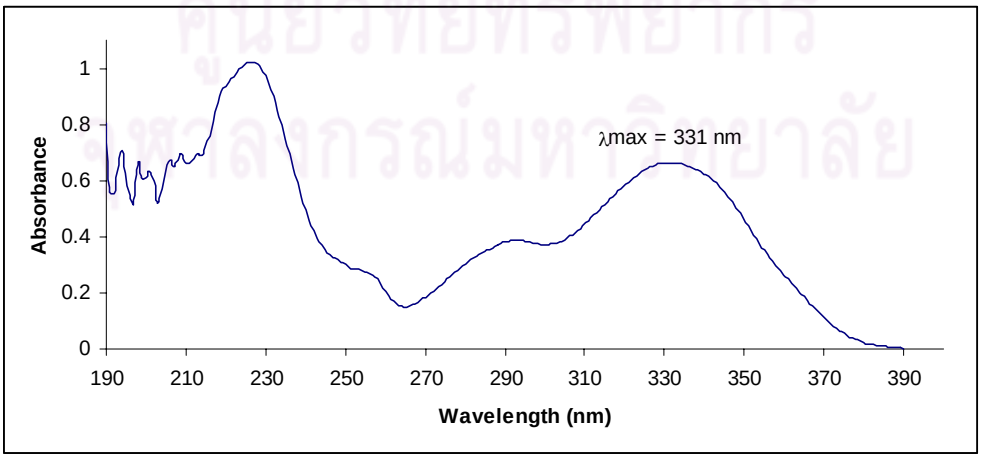


Figure C15 UV absorption spectrum of 6,7-di(3′-bromo)propoxy-4-methylcoumarin

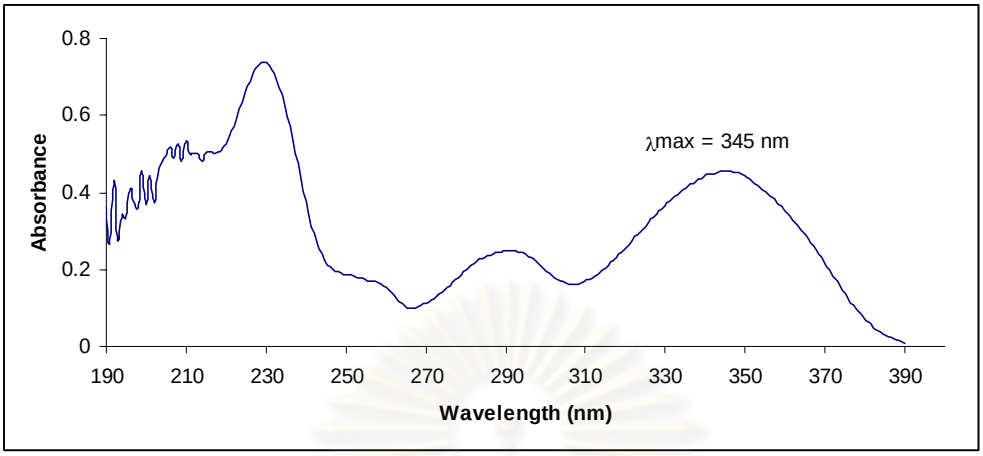


Figure C16 UV absorption spectrum of 6-hyroxy-4-methyl-7-(3′-bromo)propoxy coumarin

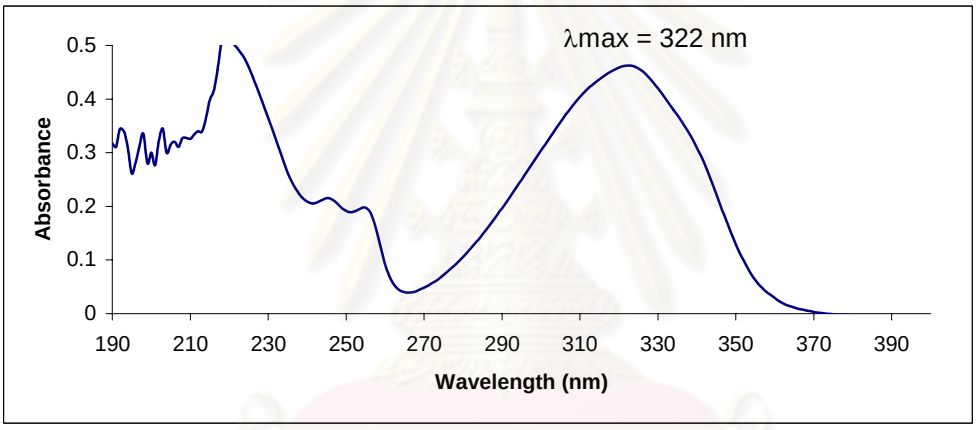


Figure C17 UV absorption spectrum of 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

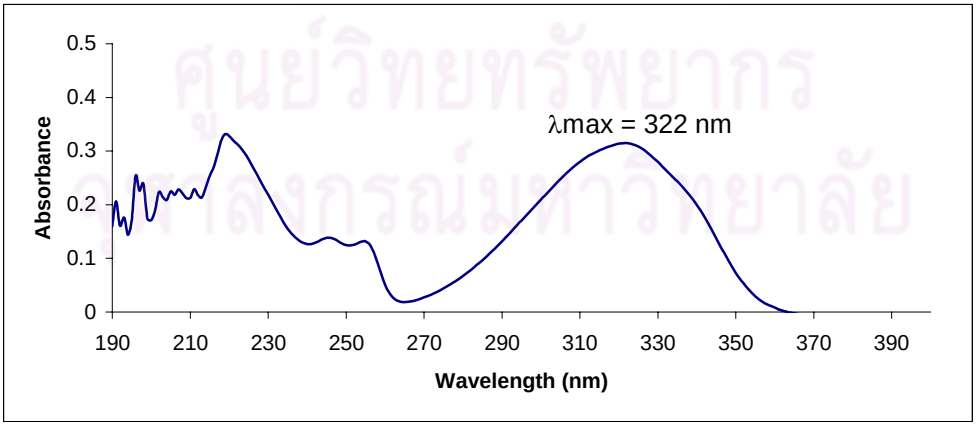


Figure C18 UV absorption spectrum of 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

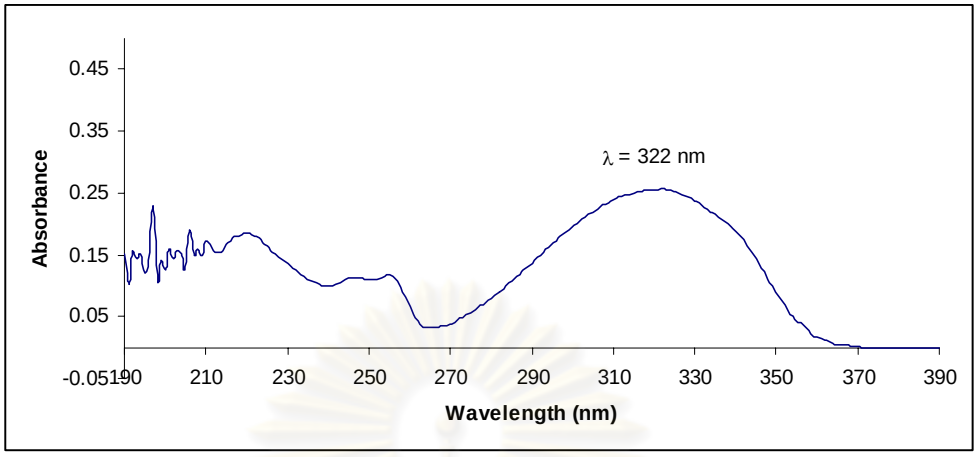


Figure C19 UV absorption spectrum of 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

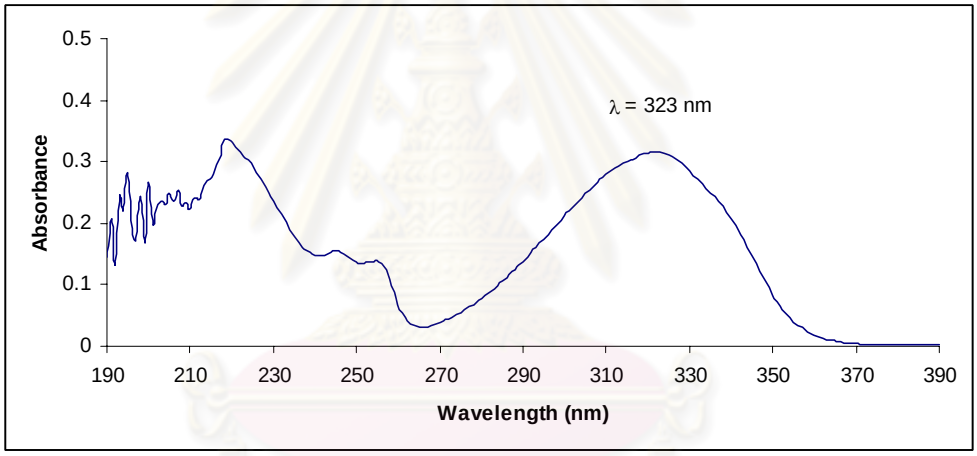


Figure C20 UV absorption spectrum of 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin

Appendix D

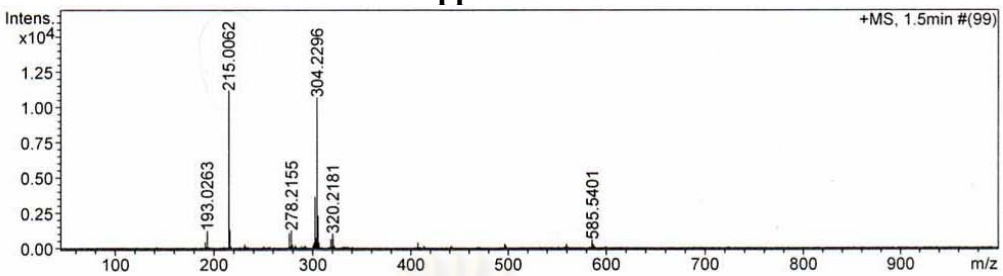


Figure D1 Mass spectrum of 5,7-dihydroxy-4-methylcoumarin

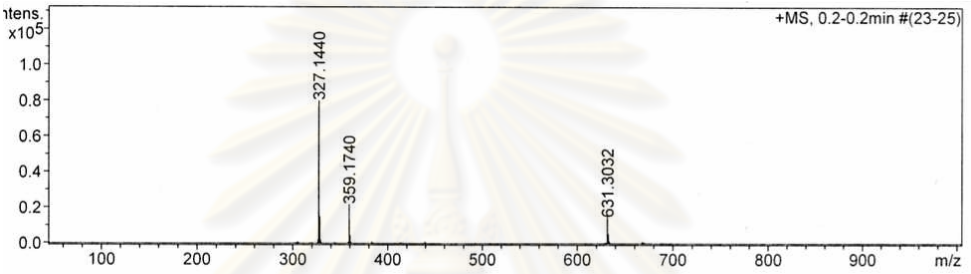


Figure D2 Mass spectrum of 5,7-dibutoxy-4-methylcoumarin

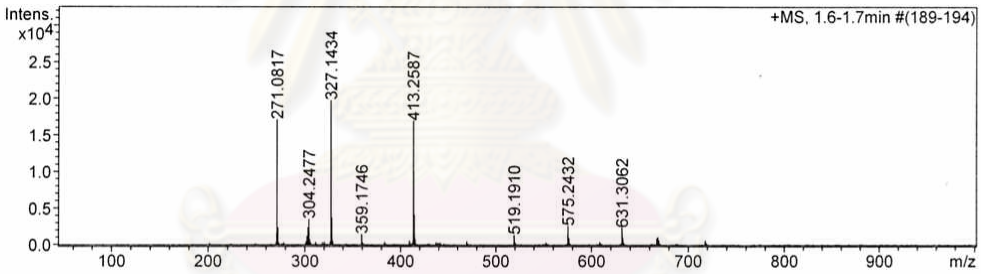


Figure D3 Mass spectrum of 7-butoxy-5-hydroxy-4-methylcoumarin

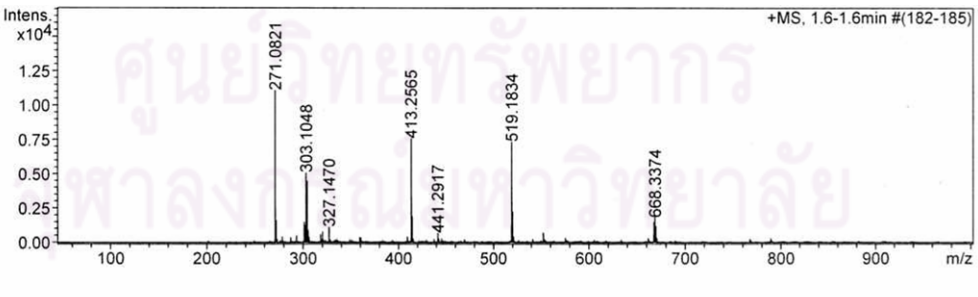


Figure D4 Mass spectrum of 5-butoxy-7-hydroxy-4-methylcoumarin

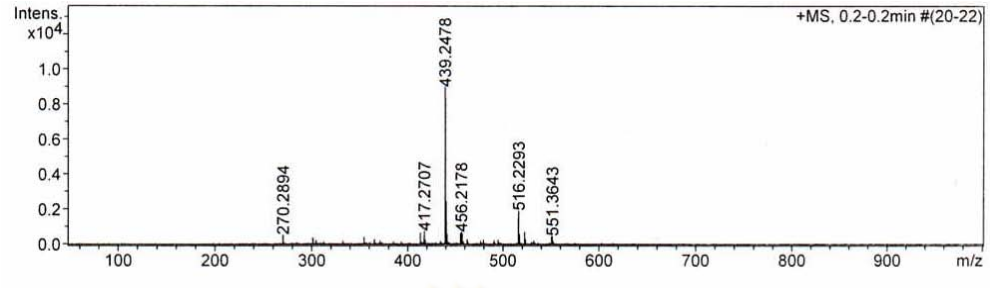


Figure D5 Mass spectrum of 5,7-dioctoxy-4-methylcoumarin

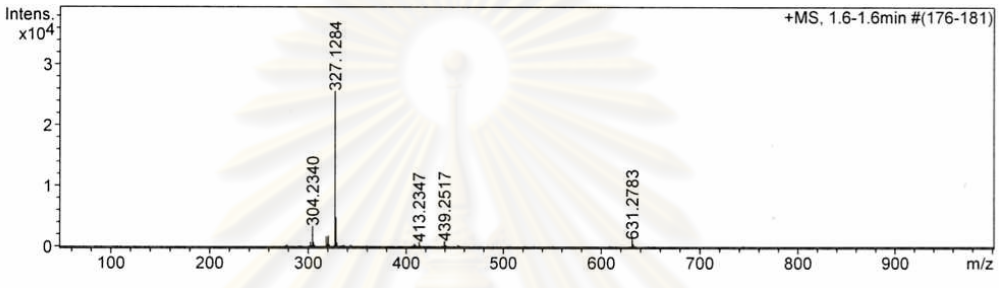


Figure D6 Mass spectrum of 5-hydroxy-4-methyl-7-octoxycoumarin

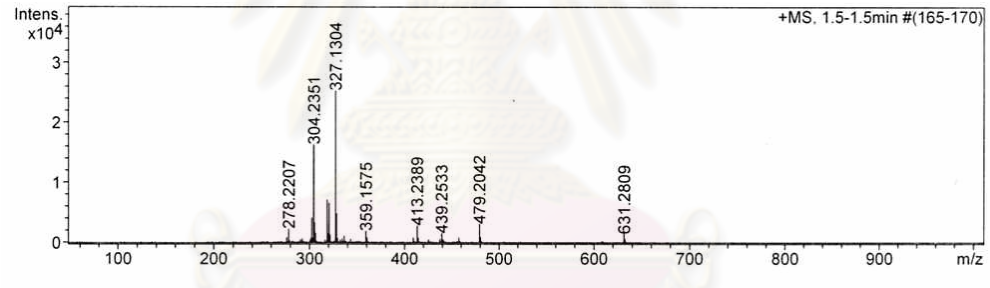


Figure D7 Mass spectrum of 7-hydroxy-4-methyl-5-octoxycoumarin

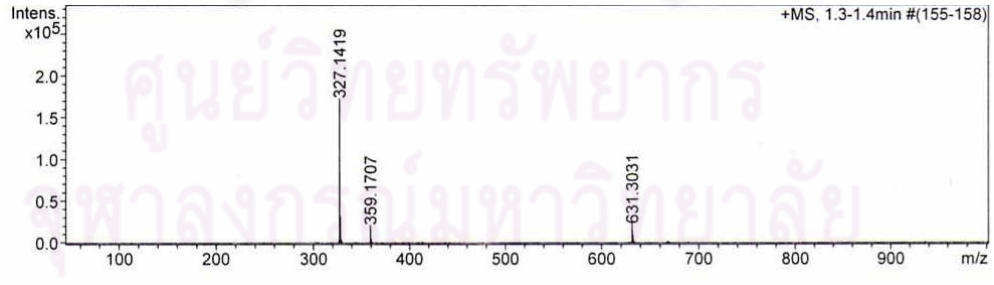


Figure D8 Mass spectrum of 6,7-dibutoxy-4-methylcoumarin

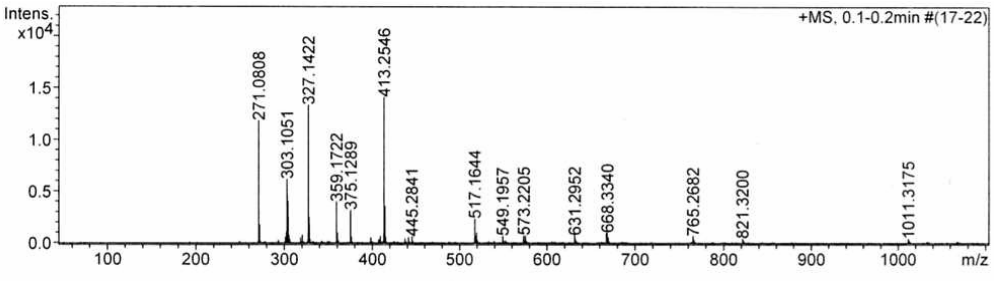


Figure D9 Mass spectrum of 7-butoxy-6-hydroxy-4-methylcoumarin

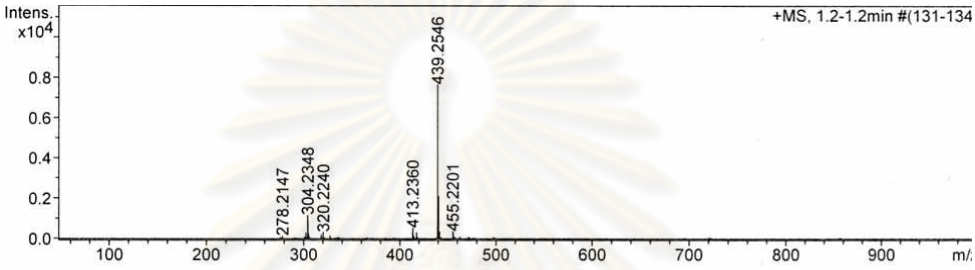


Figure D10 Mass spectrum of 6,7-dioctoxy-4-methylcoumarin

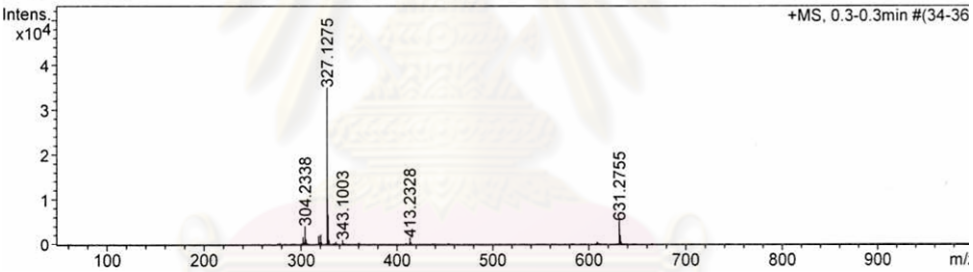


Figure D11 Mass spectrum of 6-hydroxy-4-methyl-7-octoxycoumarin

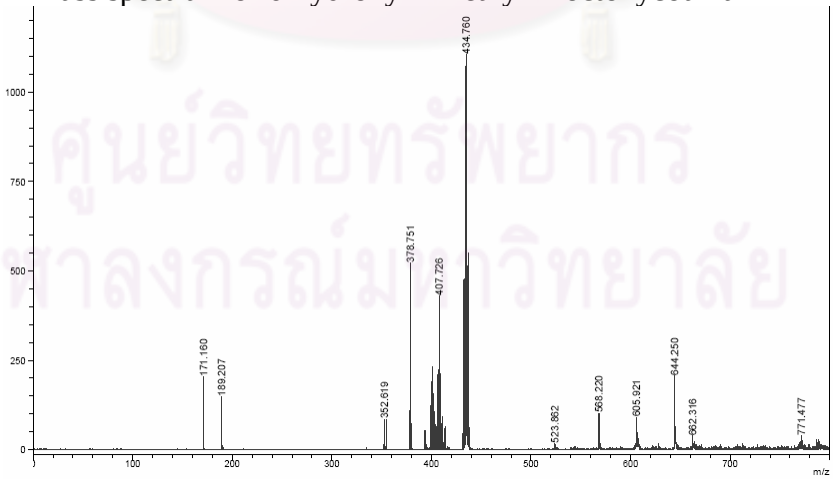


Figure D12 Mass spectrum of 5,7-di(3′-bromo)propoxy-4-methylcoumarin

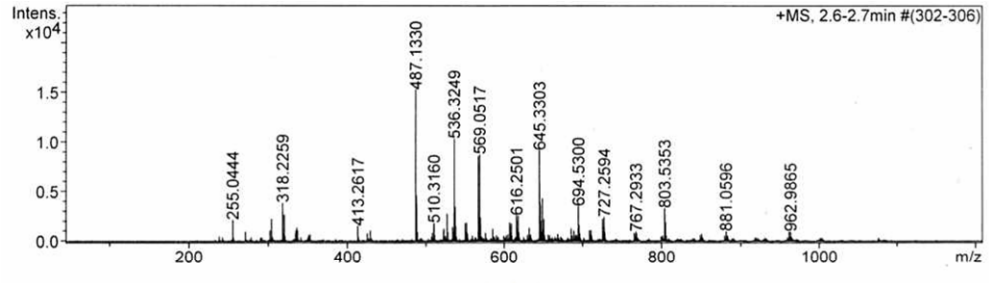


Figure D13 Mass spectrum of 5-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

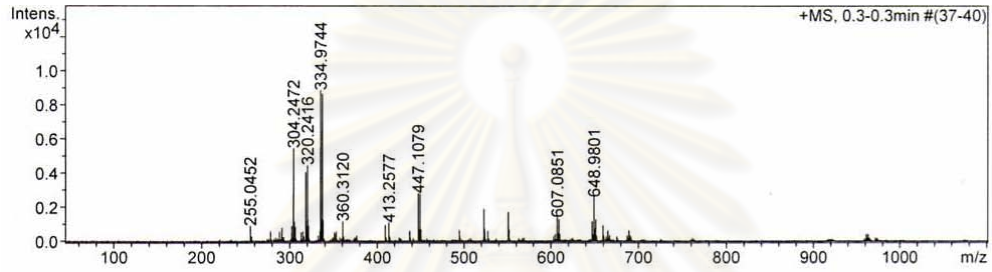


Figure D14 Mass spectrum of 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

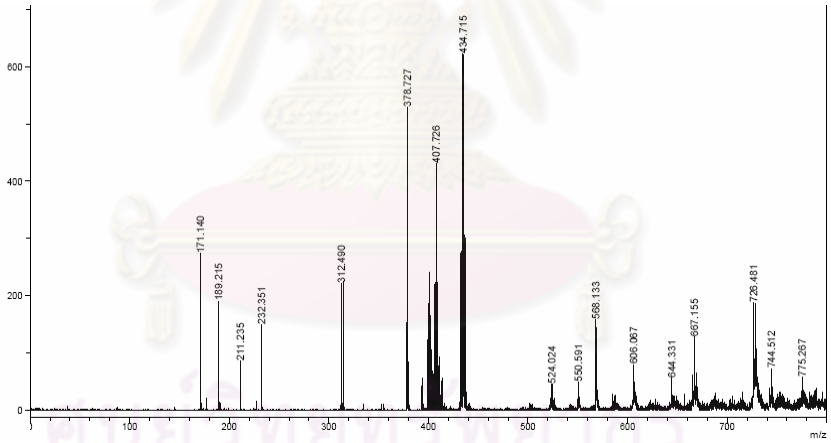


Figure D15 Mass spectrum of 6,7-di(3′-bromo)propoxy-4-methylcoumarin

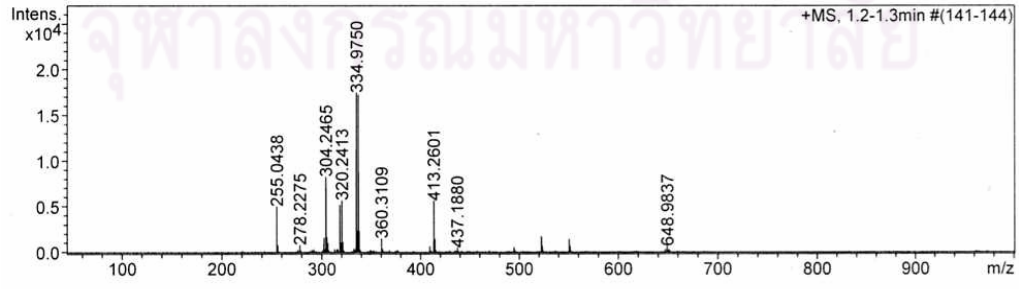


Figure D16 Mass spectrum of 6-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

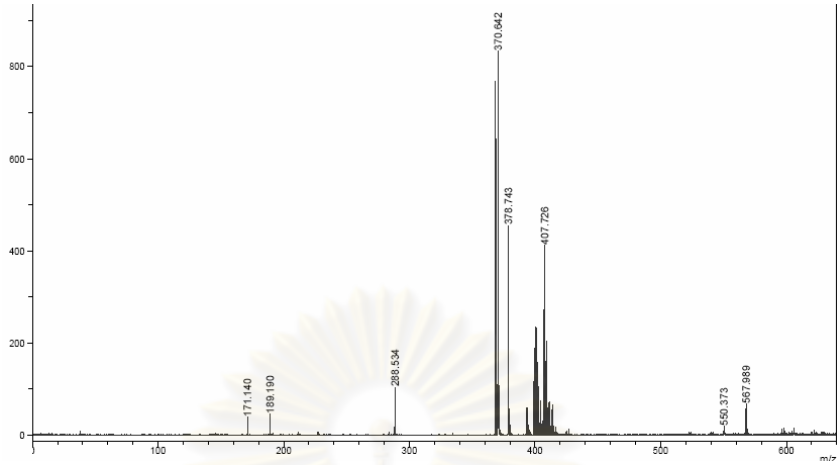


Figure D17 Mass spectrum of 7-butoxy-4-methyl-5-(3′-bromo)propoxycoumarin

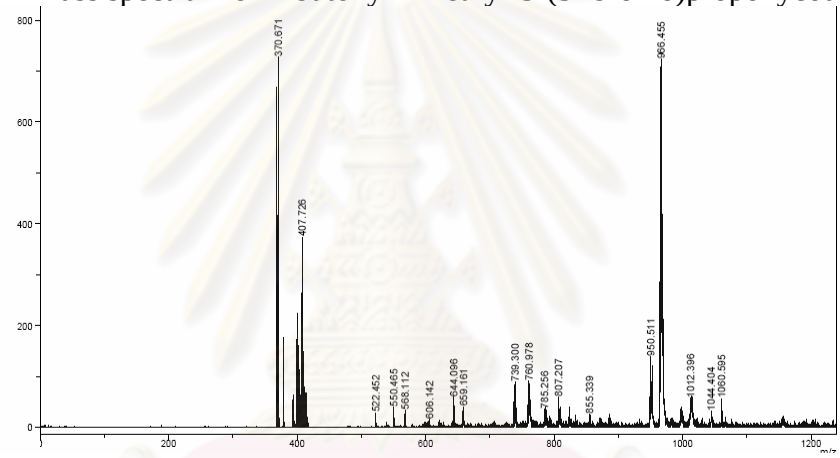


Figure D18 Mass spectrum of 5-butoxy-4-methyl-7-(3′-bromo)propoxycoumarin

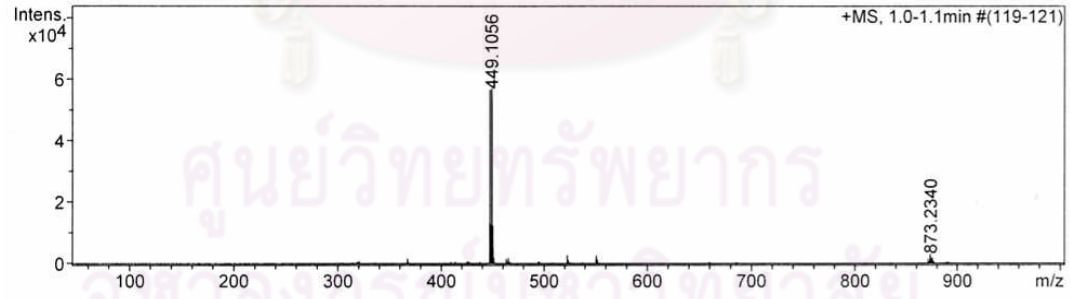


Figure D19 Mass spectrum of 4-methyl-7-octoxy-5-(3′-bromo)propoxycoumarin

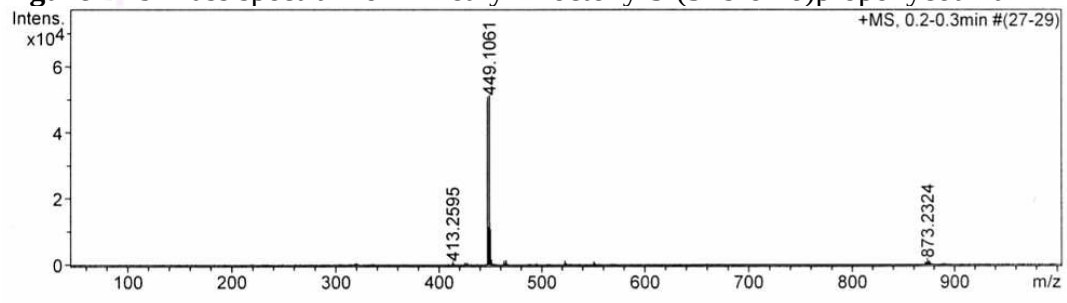


Figure D20 Mass spectrum of 4-methyl-5-octoxy-7-(3′-bromo)propoxycoumarin

Appendix E

Calibration curves

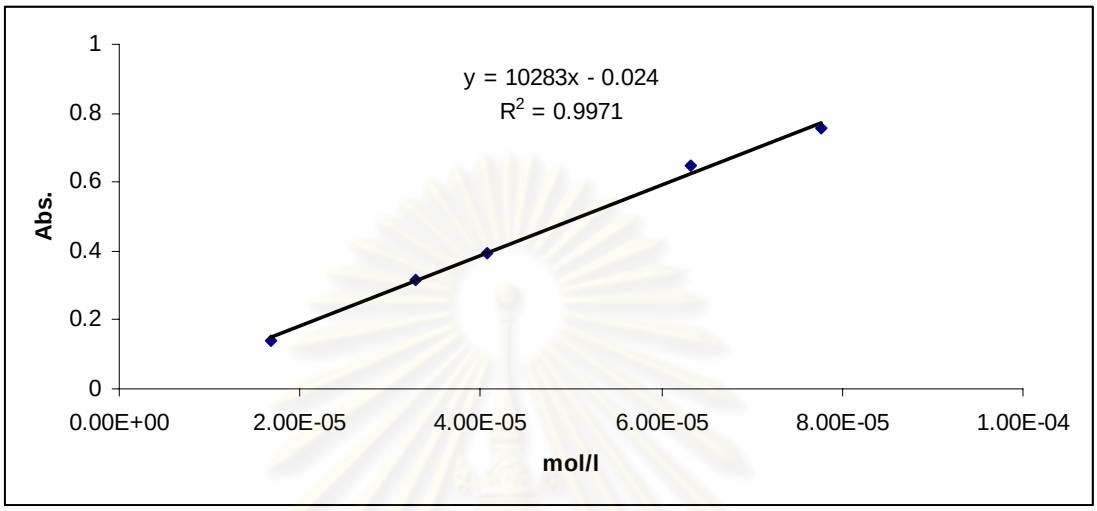
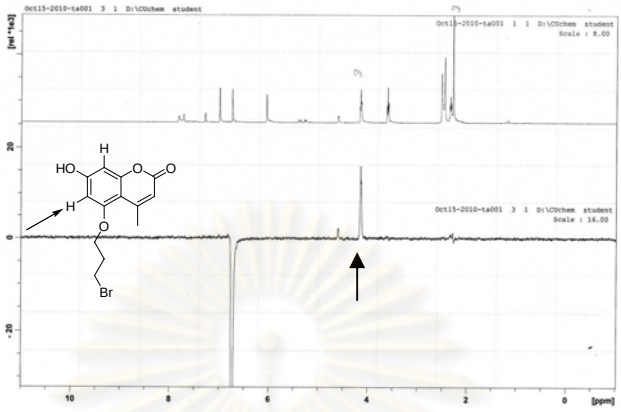
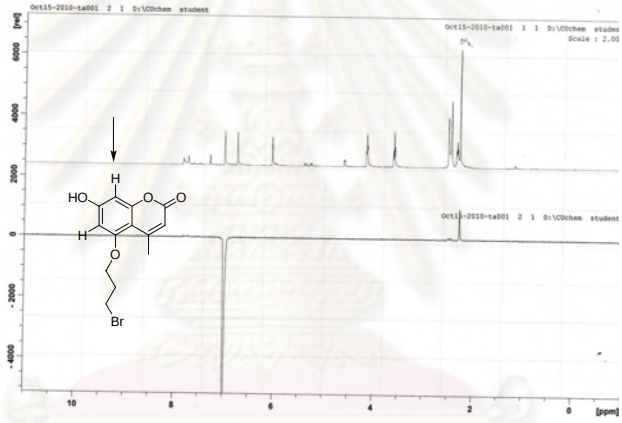


Figure E1 Calibration curve of 5,7-dihydroxy-4-methylcoumarin

Appendix F



NOE difference spectrum resulting from irradiation of H-6



NOE difference spectrum resulting from irradiation of H-8

Figure F1 NOE difference of 7-hydroxy-4-methyl-5-(3′-bromo)propoxycoumarin

NOE difference spectrum resulting from irradiation of H-5

Figure F2 NOE difference of 6-hydroxy-4-methyl-7-(3′-bromo)propoxycoumarin

VITAE

Mister Theerawat Tosawan was born on June 4, 1985 in Nakhonpanom, Thailand. He graduated with a Bachelor's degree of Science, Faculty of Science, Mahidol University in 2008. He has continued his study in Master's degree, majoring in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2009 and finished her study in 2011.

-Presentation at the Pure and Applied Chemistry International Conference (PACCON 2011) in the topic of "SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE POLY(VINYL ALCOHOL) CONTAINING ALKOXYCOUMARINS"