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จุฬาลงกรณ์มหาวิทยาลัย

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CHEMICAL CHARACTERIZATION OF YELLOWING PHENOMENA IN AMINO-SILICONE

Miss Jintana Pocharoen

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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งานวิจัยนี้ทำการศึกษาปัจจัยทางกายภาพคือ อุณหภูมิ แสงแดด และอากาศ ที่มีผลต่อการเหลืองของไตรเมธิลไซลิลอะโมไดเมธิโคน พบว่าอุณหภูมิที่ 60°C เป็นปัจจัยสำคัญที่สุดที่สามารถเร่งอัตราการเหลืองของอะมิโนซิลิโคนดังกล่าวได้ ปัจจัยที่มีผลรองลงมาคือการสัมผัสกับอากาศ ในส่วนของปัจจัยทางเคมีที่มีผลต่อการเหลืองของอะมิโน-ซิลิโคนในสูตรของเครื่องสำอางต่างๆพบว่า เมื่อใช้โซเดียมลอรีทซัลเฟต และโพรพิลพาราเบนร่วมกับอะมิโน-ซิลิโคนดังกล่าว จะทำให้เกิดการเหลืองอย่างรวดเร็ว เมื่อนำอะมิโนซิลิโคนที่เหลืองมาแยกโดยการกลั่นลำดับส่วนที่ความดันต่ำ การสกัดด้วยตัวทำละลาย การทำรีเวอร์สเฟสคอลัมน์โครมาโตกราฟี สามารถแยกสารเหลืองออกมาได้ 6 ส่วน นำส่วนที่เหลืองที่สุดไปหาโครงสร้างทางเคมีด้วยเทคนิคทางสเปกโตรสโคปีต่างๆ พบว่ามีโครงสร้างเป็นสารประกอบที่มีหมู่ไฮดรอกซี และคาร์บอนิลเป็นองค์ประกอบ

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ลายมือชื่อนิสิต...สาขาวิชา...
ลายมือชื่ออาจารย์ที่ปรึกษา.........................ลายมืออาจารย์ที่ปรึกษาร่วม...........................
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Among heat, sunlight and air, the most effective factor that can accelerate yellowing of trimethylsilylamodimethicone is heat (at 60^{o}C). Air exposure is the second most effective parameter in turning such amino-silicone yellow. Among 12 chemicals tested with amodimethicone , it was found that sodium laureth sulfate and propylparaben could most effectively make either amodimethicone or cosmetic formulations containing amodimethicone turn yellow. When yellow amodimethicone was subjected through low pressure fractional distillation, solvent extraction and reverse phase chromatography, 6 distinct yellow fractions were obtained. Spectroscopic identification of the most yellowish fraction gave a hydroxy and carbonyl group.

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Student’s signature………………..Field of study……………………………………...
Advisor’s signature……………….Co-advisor’s signature…………………………….
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LIST OF ABBREVIATIONS

br	broad
^{o}C	degree Celsius
cm^{-1}	unit of wavenumber (IR)
d	doublet
DMSO	dimethylsulfoxide
eq.	equation
g	gram (s)
Hz	hertz
IPA	isopropanol
IR	infrared
J	coupling constant
m	multiplet (NMR)
MeOH	methanol
mg	milligram
ml	milliliter
MS	mass spectroscopy
m/z	mass per charge
NMR	nuclear magnetic resonance
q	quartet (NMR)
qs	quantity supply
s	singlet (NMR)
t	triplet (NMR)
sol$^{\underline{n}}$	solution
UV	ultraviolet
wt	weight
λ_{max}	wavelength of maximum absorption
δ	chemical shift

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CHAPTER I

INTRODUCTION

The basic material from which the silicones are formed is quartz, i.e., silica or silicon dioxide, SiO_2. Silicon dioxide is the main constituent of ordinary white sand. The word “silicone” originally meant a compound in which silicon was present and in which each silicon atom was surrounded by two oxygens and two carbon groups. As the study of these materials expanded, the word gradually took on a wider meaning, becoming a generic term rather than a specific one.

All compounds containing only one silicon atom can be described as “silanes” of some sort. If only hydrogens are present on the silicon, giving SiH_4, the compound is known simply as “silane”. If one chlorine is present in place of one of the hydrogens to give SiH_3Cl the compound is known as “chlorosilane”. The presence of four chlorine atoms result in $SiCl_4$ or “tetrachlorosilane”.

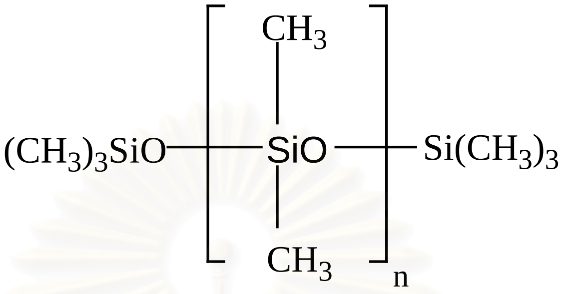
If two silicons are united in a molecule, such as $H_3Si\text{-}SiH_3$, the compound is known as a “disilane”. Similarly we may have trisilanes, tetrasilanes, etc., or polysilanes.

Now, if two or more silicons are present in a molecule and they are separated from one another by some other atom, the name “silane” is altered to describe the character of this new linkage. If the silicons are separated by an oxygen the compound is known as a “sil-ox-ane”. This, by the way, is the characteristic structure found in most silicones.

Nomenclature of siloxanes is similar to that of the silanes, for if two silicons are separated by an oxygen the compound is known as a “disiloxane”. Where three silicons are similarly separated the compound is known as a “trisiloxane”. Where there are many such groupings present the compound is known as a “polysiloxane”.

The commercially available in the forms of silicones fluids, greases, resins, and rubber are polysiloxanes. The nature of the silicone is dependent on the types of silanes used. The properties of silanes, in turn, are results of the types of groups those have replaced the hydrogens in silane.[1]

Dimethicone or dimethylpolysiloxane is a mixture of fully methylated linear siloxane polymers end blocked with trimethylsiloxy units. It conforms generally to the structure shown in Figure1.1.[2]



$$(CH_3)_3SiO-\left[\overset{CH_3}{\underset{CH_3}{SiO}}\right]_n-Si(CH_3)_3$$

Figure 1.1 Structure of dimethylpolysiloxane or dimethicone

In the United State, dimethicone may be used as an active ingredient in OTC (Over-The-Counter) drug products.[3] Dimethicone have found numerous applications in the cosmetics, detergent and coating industries.

Application of silicone

1.1 Cosmetic Applications

Silicones have been used in personal care products for over 30 years and are present in many well-known hair and skin care preparations. The use of silicones in hair care applications has been limited because of the difficulty in controlling the deposition of nonfunctional polydimethylsiloxane. Siloxanes modified with amine or polyether substituents have also been developed which provide substantive, durable conditioning properties, typically at addition levels of 1-5% in a shampoo formulation. Improved depth and color retention can also be achieved in hair dyeing by pretreating the hair with organofunctional siloxane formulations containing amino, amido or quaternary ammonium groups.

These properties are dependent on molecular weight and organic functional groups. Polar amine groups, for example, have a major effect on the deposition properties of polydimethylsiloxane. The adsorption of polyether, betain or quaternary ammonium modified siloxanes on human hair was studied by FTIR and acid dye photometry, and related to friction and combing data. The conditioning properties

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imparted by polyether functional siloxanes tend to be lost after two or three washes whereas the amine-functional analogues still show the effects of improved combing and higher gloss after six weeks. Furthermore, amine-functional polymers containing residual silanol and hydrolysable groups can undergo chain extension and cross-linking reactions, giving a partially elastomeric film on the hair and polishes which survive several detergent wash cycles.[4]

1.2 Textiles

Organofunctional siloxanes, particularly the aminosiloxanes, have been used as fabric treatments by the textile processors for many years. This is well-documented in several reviews.[5] The feel and appearance of fabrics are important, yet they are subjective properties which tend to change as fashions change. Very subtle effects can be achieved by the inclusion of low levels of reactive organic groups into siloxane textile treatments.

A polymer containing less than 0.4 mol % diaminopropyl alkoxy endgroups can be made substantive to wool and prevents shrinkage in an automatic wash cycle. Treatment of polyester fibers with a polymer containing similar pendant groups changes the fiber's physical characteristics giving bounce, resilience and enhanced air entrapment. This type of material is widely used for the fillings of continental quilts and fashion apparel. Aminofunctional siloxanes also give improved durable press appearance without the need for conventional cross-linking resins.

In some applications, like polyester cotton shirting and sheeting, a soil-releasing hydrophilic silicone is needed. This is achieved by incorporating higher levels of polar groups such as polyether, carboxylic acids or quaternary amines into the side-chains. Quaternary ammonium-functional polysiloxanes are also useful for the treatment of polyester-cotton fabrics where they are used as conditioners to impart softness but retain good rewettability. More recently microemulsions of aminofunctional siloxanes have been used as softners for improve handle and wrinkle recovery. Amino siloxanes have also been further modified by treatment with lactones to give hydroxyl amidofunctional polymers that are effective fabric treatments in production or laundering cycles.

Moreover the outstanding water-repellent properties of the silicones have prompted the use of them in a great many different fields including textiles.

1.3 Paper

Paper properly treated with hydrophobic silicones develops two valuable properties: (1) it becomes extremely water repellent; (2) it becomes non adhesive to partially cured rubber, asphalt, pressure-sensitive tapes, and to most adhesive materials.[6] The paper shows no apparent change in texture or color nor are the physical properties altered.

The high order of water repellency prevents initial wetting and greatly retards the subsequent rate of wetting. This property suggests the use of such treated paper for paper rain wear and for special purpose bags and wrapping papers.

The non-adhesive characteristics suggest its use as interleaving sheets for uncured rubber stocks, camelback, tire-tube repair patches, and pressure-sensitive rubber tape. It is also used as interleaving strips for adhesive and friction tapes and as shipping bags for materials such as asphalt.

1.4 Plastic and Resin Modification [7]

The utility of organofunctional silicones in modifying plastics for example, aminofunctional polysiloxanes have been used as additives to modify the surface characteristics of urethanes, epoxides and acrylates. The relationship between microstructure, morphology and surface properties in polycarbonate-siloxane copolymers has been studied and solvent effects in solution cast films, elucidated. The preparation and properties of various siloxane-polyimide copolymers has been described with emphasis on improved resistance to moisture and processability for these high-temperature engineering resins. Polyimides with improved impact performance are reported which use copolymers made from amine end-blocked siloxanes. Polysulphones are another important class of high-performance thermoplastics which have been modified with siloxanes. Dialkylamine terminated siloxanes were reacted with characterized.

Aminofunctional siloxanes react with caprolactam to form block copolymers which confer improved low-temperature properties to polyamides. Organofunctional silicones provided stress relief in epoxy molding compounds which are used extensively in the electronics industry and thermoplastic polyesters are reported to have improved impact strength, coefficient of friction and hydrolytic stability.

1.5 Polish Applications[8]

The use of a dimethicone as a polish for cars or furniture has gained a well-merited popularity. The silicone may be used alone or in combination with waxes.

Car polishes

As a polishing agent for cars it is favored because of the ease of application. The time required for polishing a car with the silicone fluid is variously estimated at one-half to one-quarter that required with a good hard wax. The luster is at least equal to that of a hard wax and the protective action against water and dirt is superior because there is no softening with heat. The life of a silicone film is little different from that of a wax coating.

Furniture Polishes

Furniture polish can be formulated in much the same fashion as car polishes. Although a car may be polished satisfactorily with the silicone alone, a wax addition is generally needed in a furniture polish. Hairline cracks in furniture polish appear to be filled in by the wax. The presence of the silicone gives improved luster, reduces water spotting, and makes even a hard wax easier to rub down.

Release Agent

In the molding of rubber and plastics and in the die casting of metals, there is an over-present problem of releasing the article from the mold. Some type of dressing on the mold is nearly always needed if sticking is to be avoided. The dressing is commonly referred to as a “mold release’ or a “parting material”. This may take the form of an oil, a grease, or a solid such as mica, talc, or soap. Different release agents are used for the molding of different materials and even, by different molders, for the same material.

There are certain disadvantages in the used of these agents. The oils, greases, and soaps carbonize in time as result of the heat. When rejects become too numerous, the mold must be removed for cleaning. The inorganic materials are dusty and they contaminate the molding. With complicated moldings or in cases where sharp definition is required the “down-time” of the mold must be increased if it is to be kept clean enough.

The ideal release agent should give easy release from the mol, cause no contamination of the molded part, have no odor, be nontoxic, and have long life. The dimethyl silicone fluids have been found to meet these specifications to an unusual degree. They give good release for rubber and a wide variety of plastics and even for metal die castings. They are poorly soluble in rubber and plastics and so do not affect appearance other than to give a high surface finish. Proper application calls for the use of extremely small amounts of the silicone, for the fluid wets metal readily and spreads to an even film. The high heat resistance is such that there is no decomposition and there is little or no build-up on the mold. The fluid itself has no odor and as nearly as can be determined is completely nontoxic. The life ill vary with conditions. One spraying may give good release for several cycles but most pressmen prefer to use a more dilute emulsion before each heat.

1.6 Additives Applications[9]

Paints

This holds for silicone fluids especially formulated for addition to organic paints. The amount used may vary from 1 to 50,000 ppm of the coating material. They are useful as anti-floating and anti-flooding agents in paints. They also aid gloss retention and eliminate orange peel.

Rubber

A coating or film of a dimethyl silicone on rubber prevents the rubber from sticking to other surfaces. Because of the slippery nature of the coating, abrasion of the rubber is less. The rubber is les subject to oxidation.

Some attempts have been made to incorporate the silicone into a rubber formulation in the hope of developing a rubber having the properties of non-sticking at elevated temperatures, better abrasive resistance, and improved resistance to oxidation.

Waxes

In the statement about polishes it was pointed out that the addition of a dimethyl silicone to a wax makes the rubbing-out process much easier.

The addition of very small amounts of silicone fluid to paraffin wax is claimed to given better oxidation resistance.

Antifoam

The dimethyl silicone is an effective antifoam agent for petroleum oils, hydraulic fluids, tar, thermoplastic adhesives, and similar materials. Its use has been suggested for increasing the productivity of oil wells.

Lubricants

Two points to be observed in the application of these fluids as lubricants are that the proper combination of bearing metals must be used and that only light to moderate loads should be imposed. In spite of these limitations there are many places where these fluids are more satisfactory than petroleum lubricants and are in the long run, more economical. As an example the use of these fluids in parking meters may be cited. The extremes of summer heat and winter cold have little effect on the viscosity of the silicone; it does not volatilize; it does not oxidize or become gummy. In other words it stays put and maintains its original condition over a very long period of time. This constancy of viscosity and form results in reduced servicing which, with a large number of small units, can be an item of considerable expense.

The same general considerations apply to the use of the silicone with synchronous motors, precision machinery, instruments and speedometers, and for impregnating porous bronze rings.

As lubricants for plastics the dimethyl silicones have gained wide acceptance. They have no softening effect on plastic materials and they reduce friction and wear to a minimum. This applies not only to plastics bearings but to the tools used in the cutting and machining of plastic parts.

Another application in the handling of plastics is as a lubricant and waterproofing agent in drawing plastic-covered cable into a rubber or metal conduit.

1.7 Miscellaneous Film Applications[10]

Laundries experience trouble at times from the adhesion of starch to hand irons or metal rolls. Wiping the metal with a silicone-treated cloth has been found an effective solution for the trouble.

An extremely thin coating of this liquid silicone on metal has been found to be a convenient “anti-spatter” coating to stop the adhesion of droplets of metal to the surrounding metal during a welding operation. It also prevents the metal from becoming tarnished.

The fluid is used to provide a nonstick surface for heating irons used in the heat sealing of plastics. The iron comes away cleanly from the plastic.

As a dressing for skis, particularly metal ones, there is an advantage in using silicone rather than wax in that even at extremely low temperatures the silicone does not become hard or chip off.

A dilute solution in a volatile solvent makes a simple and effective means of waterproofing a fisherman’s dry flies. Some prefer to add wax as well to increase the rigidity of the fly as it stands on the water.

The treatment of leather goods such as shoes, jackets, or luggage with a dimethyl silicone gives a water-repellent surface that is scuff-resistant. The addition of a small amount of the silicone to the resin-wax dressing on shoes is said to improve the appearance and feel of the leather.

The list of applications for silicone films could be much extended. The films are non-greasy, glossy, water-repellent, and heat-resistant. They do not allow the adhesion of other materials. Wherever any of these properties are required there is a possible application for silicone films.

Functional Silicones

Several decades ago, formulating chemists wishing to work with silicone materials were limited to dimethicone and cyclomethicone fluid only. The low surface tension and lubricious nature characteristic of dimethicone rendered these materials excellent additives in personal care products to reduce drag and impart of the carrier or delivery system for antiperspirants and deodorants, to act as fugitive emollients in skin care products, and to improve rub-in characteristics of sunscreens, liquid foundations, and anti-cellulite creams and reduce whitening that may occur during the rub-in process of creams and lotions. In addition to imparting a lubricating effect. The use of dimethicone, however, is still somewhat limited due to their inherent solubility limitations. These materials also provide a breathable barrier on the surface of the skin. The unique properties and benefits afforded by silicones in personal care product became increasingly evident, but their usage remained quite limited for many years due to their inherent solubility and incompatibility problems. With the advent of new polymeric thickeners and suspending agents, silicone emulsifiers, and organomodification of the silicone polymers themselves, the use of silicones in personal care products has dramatically increase in recent years, to the point that approximately half of all new personal care products introduced into the marketplace in 1994 contained at least one type of silicone in the formulation.[11]

Today there is a wide variety of silicone products available that provide numerous benefits in personal care formulations.[12-13] Dimethicones are still used to provide an anti-whitening effect and a breathable barrier on the skin, and for their conditioning benefits in hair care products. Organomodified silicones are being used as additives in personal care formulations, providing improved deposition characteristics and substantivity to hair and skin.[14-20] Dimethicone copolyols, or silicone glycol copolymers, are primarily used as resin plasticizers in hair-fixative products. They are also utilized in shampoo systems as resin plasticizers in hair-fixative products. They are also utilized in shampoo systems as co-solubilizers and for their ability to reduce irritation to skin and mucous membranes by primary surfactants in these formulations.[21] They may additionally provide light conditioning benefits and are widely utilized as emulsifiers in skin care compositions, particularly in antiperspirants and sunscreens. Aminofunctional siloxanes provide conditioning benefits and impart softness to hair with excellent persistent, while phenylmodified silicones are used as luster-enhancing additives in hair products and emollients for the skin. Alkyl-modified silicone polymers provide an occlusive barrier in skin products, reducing the amount of transepidermal water loss to levels similar to those observed with petrolatum.[22] Also available are specialty materials containing a wide range of functionalities grafted onto the silicone chain, including protein moieties, quarts, fatty acides, amphoteric surfactants, amino acids, and fragrance oils.[23-26]

Trimethylsilylamodimethicone or N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer is an amine-functional silicone polymer or so called amino-silicone designed to enhance the substantive properties of silicones. It is successfully used to formulate a variety of hair care products. It also compatible with several hair care formulation ingredients and various quaternary ammonium salts. Trimethylsilylamodimethicone is very substantive to hair and skin, it is, therefore, suitable for hair-skin conditioner cosmetics.

Amine-functional silicone polymers have also found applications in textile industries. It gives softening effects to fabric. Amino-silicones have been used in textiles and leather to generate softness, bounce and silk finishing.

Although with widespread uses of amino-silicone, this group of functional silicone still faces a problem on yellowing. Cosmetic formulations containing amino-silicone turn yellowish after some periods of time. Textiles treated with amino-silicone also show yellowish appearance after a period of time. These yellowing problem have seriously limited the use of amino-silicone. Derivatization of amino group into alkyl substituted amino group has solved the problem to a certain degree but has possessed some drawback of reduced persistent. These latter developed

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silicones, N-alkyl substituted amino-silicones are, therefore, not very popular. As this problem has interested us, it is quite surprising to us that characterization of yellowing mechanism of amino-silicone has not been done anywhere. We, therefore, want to look into this problem by characterizing the yellowing products of amino-silicone. More importantly, we wish to be able to help solving the problem on yellowing through the knowledge of non-compatible materials, i.e., to identify compounds that accelerate the yellowing of amino-silicone. Moreover, we also want to establish the use of anti-yellowing agent for reducing and preventing the yellowing of amino-silicone.

Amino-silicone used in this study was trimethylsilylamodimethicone or N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer. (Figure 1.2)

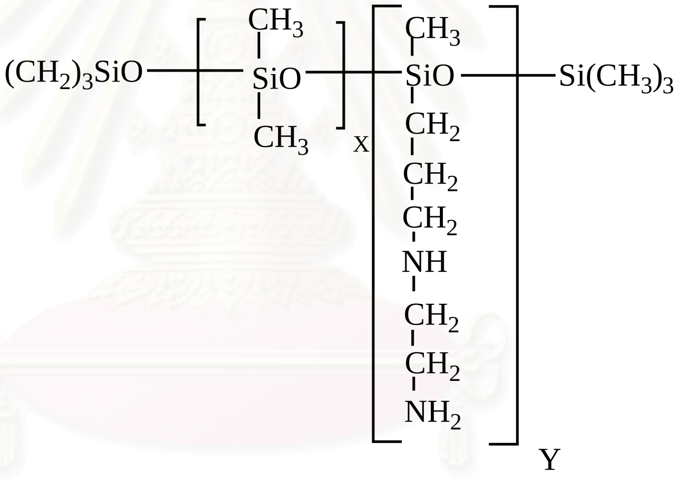

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Figure 1.2 Structure of trimethylsilylamodimethicone or N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer.

Trimethylsilylamodimethicone or N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer is an amine-functional silicone polymer designed to enhance the substantive properties. It is successfully used to formulate a variety of hair care products. It is compatible with several hair care formulation ingredients and various quaternary ammonium salts. This functional siloxane is very substantive to hair and skin, making it suitable for hair-skin conditioner cosmetics.

The aims of this study:

1. To study physical and chemical factors affecting yellowing of N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer.
2. To identify structure of the yellow products.

Scope of this study:

Scope of this study is as follows.

1. Identifying physical and chemical factors involves in the yellowing of N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane.
2. Isolating and structural identification of the yellow products.
3. Studying the compounds that can retard the yellowing process.

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CHAPTER II

LITERATURE REVIEWS

Trimethylsilylamodimethicone or N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer is an organomodified silicone in which some of the methyl groups were replaced by amino groups. Since there are both reactive primary and secondary amine functionalities in the polymer structure, therefore the polymer is not as inert as dimethicone. Although problems on yellowing of amino silicone have long been recognized, to our surprised there are very limited studies on degradation of amine functional siloxane.

The only study involves degradation of amino-silicones is done by Hyacineth and coworkers in the study of the self-organized fibrious nanostructure of poly[(aminopropyl) siloxane] film using atomic force microscopy.[27] The authors indicated that interaction between primary amine from γ-(aminopropyl) triethoxysilane with carbondioxide and water gave n-propyl carbamate.

One common cause of polymer degradation is oxidative photodegradation. Polymer with reactive functionality such as amine groups can therefore undergoes chemical changes due to oxidation. Example of photooxidation of polymer with amine functionalties is the degradation of polybenzoxazines. Polybenzoxazines or BA-m is a polymer with phenolic and amine functionality. Its chemical structure is shown in Figure 2.1. Macko, J.A. and Ishida H. studied the photooxidative behavior of a series of polybenzoxazines and discovered that the photooxidation is obviously related to the structure of amine groups.[28]

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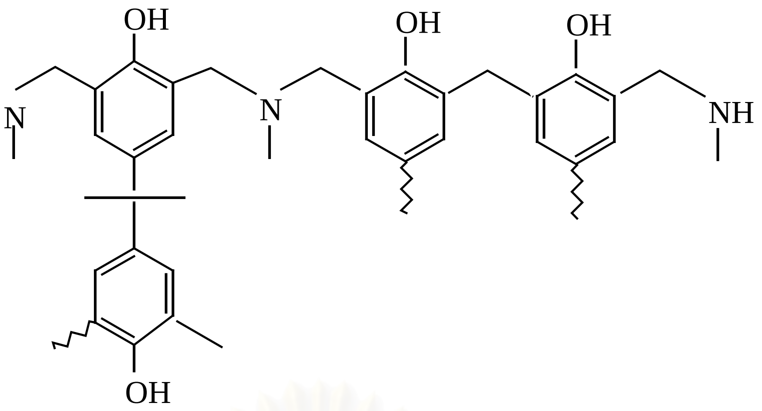

Figure 2.1 Structure of BA-m or polybenzoxazines.

Usually secondary and primary amine are basic functionalities. They are excellent nucleophile. As a result, various reactions may occur at this functional group.

Hong, J.W. and coworkers[29] studied UV-degradation chemistry of oriental lacquer coating containing hindered amine light stabilizer (amine compounds) and found that the oriental lacquer coating network degrades mostly in the unsaturated side chain. Addition of amine compounds affects the degradation at the unsaturated side chain. The postulation of this involves the competition of oxidation at amine functionalities against the unsaturated side chains.

Chang, T.C. and coworkers[30] studied characterization and degradation of hydrogen-bonded acidic polyamides linked by disiloxanes using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. With the addition of the flexible disiloxane as a segment in polyimide structure, a higher extent of imidazation an a lowering of T_g were observed.This study is the first that characterizes the degradation of amine functionality in the siloxanes environments.

Seiichi, Y. and coworkers[31] demonstrated that structure of modified silicone copolymers (ethylene oxide- or perfluoroalkyl-modified poly(dimethylsiloxane) copolymer can be characterized by matrix-assisted laser desorption/ ionization time-of-flight (MALDI-TOF) mass spectrometry. Normally desorption problem of polysiloxane had prevented the use of MALDI-TOF in structural elucidation of the polymer. With this work, it may, therefore, be possible to use such technique to characterize the polysiloxane structure.

Other studies of silicone structural identification include the study by Grumping, R. and Hirner, A.V.[32] in which inductively coupled plasma optical emission spectrometry (ICP-OES) and high-performance liquid chromatography (HPLC) were used for determination of water-soluble organosilicone species (PDMS; polydimethylsiloxane) degradation products in leachates.

Another study involves degradation study of polysiloxane are the work done by Sudarsanan, V. and coworkers.[33] They studied extraction of octamethylcyclotetrasiloxane (D_4) and its metabolites from biological matrices. This paper describes extraction of D_4 into suitable organic solvent for quantitative and structural elucidation of siloxane moieties by HPLC (water/acetonitrile) and GC-MS. The work describes an extremely efficient method for extracting D_4 and its metabolites from various biological matrices such as blood, plasma, urine, feces, liver, fat, and lung.

Silicones are widely used in textile treatments as softening agents. Amino-functional silicones provide excellent softening benefit, possibly related to their ability to form specific interactions at the fiber-silicone interface. Bereck and coworker[34] have proposed that the amino functionality can interact more strongly with highly functional (-OH) cellulose surfaces than with more inert polyester surfaces, thus the softening benefit was more pronounced on cotton fabrics compared to polyester. However, Michael, C. and coworker[35] used angle-dependent XPS to characterize the elemental composition of the outer 10 nm of treated cotton fabrics. The results indicate a preferential orientation of the amino group away from the air interface. Furthermore, the degree of endgroup depletion at the air interface was dependent on the polymer chain length and the coverage. A model is proposed in which the greatest effect occurs at near-monolayer coverage, with the endgroups adsorbed at the silicone/cellulose interface and the polymer chains forming loops the extend toward the air interface.

Berthiaume, M.D. and coworkers[36] synthesised various organofunctionalized silicone resins for personal care applications. This paper described the synthesis of several siloxysilicate resins with pendant groups consisting of organic esters, alkyls, polyethers, and phenethyl moieties, and their subsequent evaluations in personal care applications. They also discovered that the alkyl-modified siloxysilicates could impart volumizing benefits to hair conditioners without increasing combing force. The extent of the volume enhancement was dependent upon alkyl chain length. Styryl-functional siloxysilicates increased apparent luster or shine of hair, while polyether-modified silicone resins were found to offer set retention benefits for hair and could act as oil-in-water emulsifiers. Several ester-functional polysiloxane were found to possess increased substantivity and could resist water wash-off. This was applicable to skin care and color cosmetic uses.

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CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Acetone (Analytical Reagent, Labscan, Bangkok, Thailand).
2. Acetonitrile (Analytical Reagent, Labscan, Bangkok, Thailand).
3. Cetrimonium chloride (Dehyquart A, Cosmetic Grade, Henkel Corporation, Hoboken, New Jersey, USA).
4. Chloroform (Analytical Reagent, Labscan, Bangkok, Thailand).
5. Clear shampoo with perfume (Dow Corning (Thailand) Limited).
6. Clear shampoo non perfume (Dow Corning (Thailand) Limited).
7. Cocamide DEA (Comperlan KD, Cosmetics Grade, Henkel Corporation, Hoboken, New Jersey, USA).
8. Cocamidoprooyl betain (Dehyton K, Cosmetics Grade, Henkel Corporation, Hoboken, New Jersey, USA).
9. Diazolidinyl urea (Germall II, Cosmetics Grade, Sutton Laboratories, Chatham, New Jersey, USA).
10. Dibutylhydroxytoluene (BHT, Cosmetics Grade, Nipa Laboratories, Ltd., Mid Glamorgan, United Kingdom).
11. Deuterated chloroform (Analytical Reagent, Labscan, Bangkok, Thailand).
12. Deuturated DMSO (Analytical Reagent, Merck, Darmstadt, Germany).
13. Hexane (Analytical Reagent, Labscan, Bangkok, Thailand).
14. Isopropanol (Analytical Reagent, Labscan, Bangkok, Thailand).
15. Methanol (Analytical Reagent, Labscan, Bangkok, Thailand).
16. Methylparaben (Nipagin M, Cosmetics Grade, Nipa Laboratories, Ltd., Mid Glamorgan, United Kingdom).
17. Octadecyl functionalized silica (Aldrich chemical company, Milwaukee WI, USA).
18. PEG-120 methyl glucose trioleate (Glucamate LT, Cosmetics Grade, Amerchol Corporation Co., Ltd., Talmadge Road. USA).

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19. PL Gel (Crosslinked spherical polystyrene/Divinylbenzene Matrix, Polymer Laboratories, Church Stretton Shrop Shire SY6 6AX, United Kingdom).
20. Polyquaternium-10 (Celquat sc-240C, Cosmetics Grade, National Starch & Chemical Company, Bridgewater, New Jersey, USA).
21. Propylene glycol (1,2-Propylene Glycol, Cosmetics Grade, Nipa Laboratories, Ltd., Mid Glamorgan, United Kingdom).
22. Propylparaben (Nipasol M, Cosmetics Grade, Nipa Laboratories, Ltd., Mid Glamorgan, United Kingdom).
23. Shampoo car wash non perfume (Dow Corning (Thailand) Limited.)
24. Shampoo car wash with perfume (Dow Corning (Thailand) Limited.)
25. Sodium laureth sulfate (Akyposal NLS, Cosmetics Grade, KAO Corporation, Tokyo, Japan).
26. Sodium lauryl sulfate (Akyposal EO 20, Cosmetics Grade, KAO Corporation, Tokyo, Japan).
27. Sodium metabisulfite (Cosmetics Grade, Universal Preserv-A-Chem, Inc., Edison, New Jersey, USA).
28. Tetrahydrofuran (Analytical Reagent AR. Labscan, Bangkok, Thailand).
29. Trimethylsilylamodimethicone (DC-8220, Dow Corning (Thailand) Limited.
30. Tocophersolan (Vitamin E w/s, Cosmetics Grade, A&E Connock (Perfume&Cosmetics) LTD., Hampshire, United Kingdom).

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3.2 Instrument & Equipment

- The ^{1}H-, ^{13}C-NMR, HMQC, HMBC and COSY spectra were obtained in deuterated dimethylsulfoxide (DMSO-d_6) with tetramethyl silane (TMS) as an internal reference on a Bruker (Germany): ACF 200 spectrometer which operated at 399.85 MHz for ^{1}H and 100.55 MHz for ^{13}C nuclei and a JOEL : JNM-A500 spectrometer which operated at 500 MHz for ^{1}H and 100 MHz for ^{13}C nuclei.

- UV spectra were obtained with the aid of HP 8453 UV/VIS spectrophotometer (Agilent Technologies, CA, USA). The UV absorbance curves were recorded using a sample in the 1 cm quartz cell.

- Gel permeation chromatography (Water 150-CV) was performed using tetrahydrofuran (THF) as mobile phase and PL Gel (a highly crosslinked spherical polystyrene/divinylbenzene matrix) as stationary phase. Detection was done by RI (Refractive Index).
- The FT-IR spectra were recorded on a Nicolet Fourier Transform Infrared spectrophotometer: Impact 410 (Nicolet Instrument Technologies, Inc. WI, USA. Liquid samples were dropped on sodium chloride cell.

3.3 Experimentation

3.3.1 Determination of yellowing factors for pure amino-silicone.

3.3.1.1 Sunlight

Ten mL of trimethylsilylamodimethicone was placed in a closed glass container. Then it was placed under sunlight for 3 months. Observation of yellowing degree was done visibly.

3.3.1.2 Heat

. Ten mL of trimethylsilylamodimethicone was heated to 60^{o}C for 3 months. Observation of yellowing degree was done visibly.

3.3.1.3 Air

Ten mL of trimethylsilylamodimethicone was placed in an opened glass container. This air exposure was done at room temperature for 3 months. Observation of yellowing degree was done visibly.

3.3.2 Determination of yellowing factors for formulations containing amino-silicone.

Four formulations with trimethylsilylamodimethicone were prepared as described in Table 3.1. These include clear shampoo (A), clear shampoo with perfume (B), shampoo car wash (C), shampoo car wash with perfume (D).

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Table 3.1 Formulations used in yellowing study.

Clear Shampoo (A)		**Clear Shampoo with perfume (B)**	
Sodium lauryl sulfate	20%	Sodium lauryl sulfate	20.0%
Trimethylsilylamodimethicon	1.0%	Trimethylsilylamodimethicone	1.0%
Sodium laureth sulfate	5.0%	Sodium laureth sulfate	5.0%
Cocamidopropyl betain	3.0%	Cocamidopropyl betain	3.0%
Cocamide DEA	2.0%	Cocamide DEA	2.0%
Cetrimonium chloride	2.0%	Cetrimonium chloride	2.0%
PEG-120 methyl glucose trioleate	0.5%	PEG-120 methyl glucose trioleate	0.5%
Polyquaternium-10	0.5%	Polyquaternium-10	0.5%
Propylene glycol	3.0%	Propylene glycol	3.0%
Diazolidinyl urea	0.2%	Diozolidinyl urea	0.2%
Methylparaben	0.2%	Methylparaben	0.2%
Propylparaben	0.2%	Propylparaben	0.2%
Deionized water	qs to100 %	Perfume	0.3%
		Deionized water	qs to 100%

Shampoo car wash (C)		**Shampoo car wash with perfume (D)**	
Sodium lauryl sulfate	20.0%	Sodium lauryl sulfate	20.0%
Trimethylsilylamodimethicon	1.0%	Trimethylsilylamodimethicone	1.0%
Cocamidopropyl betain	3.0%	Cocamidopropyl betain	3.0%
Cocamide DEA	2.0%	Cocamide DEA	2.0%
Cetrimonium chloride	1.0%	Cetrimonium chloride	1.0%
PEG-120 methyl glucose trioleate	0.5%	PEG-120 methyl glucose trioleate	0.5%
Propylene glycol	1.0%	Propylene glycol	1.0%
Diazolidinyl urea	0.2%	Diazolidinyl urea	0.2%
Methylparaben	0.2%	Methylparaben	0.2%
Propylparaben	0.2%	Propylparaben	0.2%
Deionized water	qs to100%	Perfume	0.3%
		Deionized water	qs to 100%

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Formulation Method

- Ensure that all processing equipment is cleaned before processing the batch.
- Add the surfactant (SLS, SLES, cocamide DEA, cocamidopropyl betain), the preservative (methylparaben) and deionized water into the mixing tank. Slowly mix for 15 minutes and until it is uniform while heating them to 70-75^{o}C.
- Mix trimethylsilylamodimethicone, PEG-120 methyl glucose trioleate and propylparaben in the side kettle for 5 minutes until they are uniform.
- Slowly transfer the side kettle into the mixing tank. Jog the mill 5 times (15 seconds duration) and slowly blade mix the contents for a minimum of 10 minutes or until they are uniform.
- Slowly cool the batch to 45-50^{o}C while maintaining slow blade mixing.
- Add the fragrance, imidazolidinyl urea, cetrimonium chloride into the mixing tank and slowly blade mix the eppenbach contents for 10-15 minutes and until they are uniform.
- Slowly cool the batch to 25-30^{o}C while maintaining slow blade mixing.

Each formulation was divided into 8 portions (~ 50 mL each portion).

Each portion was placed in a glass container and subjected to various environmental exposures as indicated in table 3.2

Table 3.2 Physical conditions of each sample.

Condition	**Temperature**	**Light**	**Air**
1	room temperature	dark	N_2
2	room temperature	dark	Air exposed
3	room temperature	light	N_2
4	room temperature	light	Air exposed
5	60^{o}C	dark	N_2
6	60^{o}C	dark	Air exposed
7	60^{o}C	light	N_2
8	60^{o}C	light	Air exposed

Detection of the yellowing degree was done by UV-visible absorption spectroscopy after 2-week exposure.

3.3.3 Determination of ingredients those can stimulate yellowing of amino-silicone.

Each ingredient in formulations was individually mixed with amino-silicone. The ratio between each ingredient and amino-silicone was similar to the actual ratio used in formulation.Table 3.3 shows amounts of amino-silicone and amount of each tested ingredient.

Table 3.3 Ingredients used in each sample for the study of yellowing stimulating ingredients.

Sample#	**mL of amino-silicone**	**Tested ingredients**	**mL of tested ingredients**
1	1.00	sodium lauryl sulfate	20.00
2	1.00	sodium laureth sulfate	5.00
3	1.00	cocamidopropyl betain	3.00
4	1.00	cocamide DEA	2.00
5	1.00	cetrimonium chloride	2.00
6	1.00	PEG-120 methyl glucose trioleate	0.50
7	1.00	polyquaternium-10	0.50
8	1.00	propylene glycol	3.00
9	1.00	diazolidinyl urea	2.00
10	1.00	methylparaben	0.20
11	1.00	Propylparaben	0.20
12	1.00	fragrance	0.30

Each sample was throughly mixed and kept at 60°C. Yellowing degree was recorded by using visual observation compare with the pantone.

3.3.4 Determination of compound that can inhibit the yellowing of amino-silicone.

The most yellowing formulation used in this experiment is formulation A (clear shampoo). To the formulation, test compounds for inhibiting the yellowing of amino-silicone were added at various final concentrations. The yellowing degree of the tested samples were detected using UV-Visible spectroscopy. Compounds being tested in this experiment are sodium metabisulfite, dibutylhydroxytoluene (BHT) and tocophersolan (vitamin E water soluble).

Table 3.4 Final concentrations in the formulation of each test compounds in the formulation.

Anti-yellowing agent	Concentration in formulations (w/w)
Sodium metabisulfite	0.1, 0.3, 0.5, 0.7, 0.9, 1.0%
BHT	0.1, 0.3%
Tocophersolan	0.1, 0.3, 0.5, 0.7, 0.9, 1.0%

3.3.5 Isolation and identification of the yellowing species of amino-silicone.

3.3.5.1 Preparation of yellow amino-silicone.

Distillation of yellow amino-silicone.

Thirty mL of trimethylsilylamodimethicone was refluxed on glycerin bath at 60^{o}C for 3 months. After that, the obtained yellow amino-silicone was fractional distillated under reduced pressure. Clear colorless and yellow fraction were separately collected. The yellow fraction (fraction D) was subjected to further isolation processes.

3.3.5.2 Isolation the yellowing species in amino-silicone.

Extraction of the yellowing species

Five mL of fraction D was placed into the separating funnel and 50 mL of 65:35 acetonitrile:water mixture was added. After shaking and allowing for complete phase separation, yellowish acetonitrile:water layer was collected, and the solvent was removed by rotary evaporation. This fraction (fraction DE) was then subjected for further isolation process.

Column chromatography

One gram of fraction DE was loaded on octadecyl functionalized silica column (30 g) equilibrated with purified deionized water. Elution was done as follows :

10 mL water
10 mL 80:20 water:acetonitrile
10 mL 65:35 water:acetonitrile
10 mL 50:50 water:acetonitrile
50 mL 35:65: water:acetonitrile
10 mL 20:80 water:acetonitrile
20 mL 100 acetonitrile
30 mL 100 methanol

Distinct bands of various degree of yellowness were separately collected. The solvent was then removed from each fraction using rotary evaporator. The most yellowish fraction (fraction DEC) was subjected to spectroscopic analyses.

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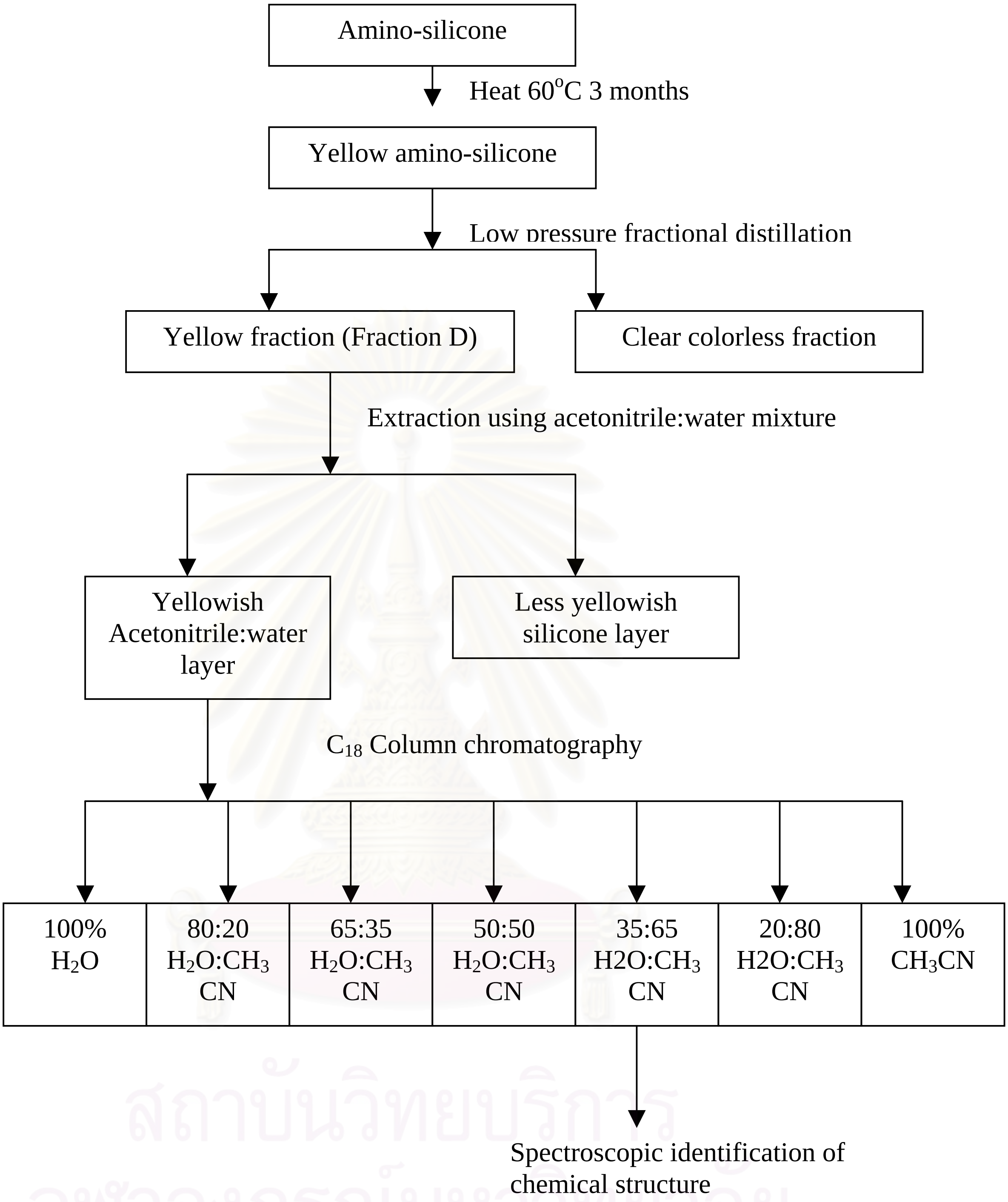

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Scheme I The separation procedures of the most yellowish fraction from amino-silicone.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Determination of factors that cause yellowing in pure amino-silicone.

When N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer was subjected to different physical environmental exposured including heat (at 60°C), air and light. It was found that heat was the most effective factor for inducing yellowness in the polymer. Heat at 60°C alone (without air or light exposure) can effectively induce visible yellowness within 1 month. On the other hand, heat with air can effectively accelerate the yellowing process of amino-silicone.

When tested at room temperature, air and sunlight can also cause yellowing in amino-silicone but at a much slower rate when compared to those performed at 60°C. Comparing between air and sunlight, air is more effective in causing yellowness to amino-silicone than sunlight.

Since heat is the most important factor in yellowing process of amino-silicone, the process is probably, thermal degradation.

4.2 Determination of factors that cause yellowing in formulations containing amino-silicone.

As we now know that heat and air are important factors in turning colorless pure amino-silicone into yellowish fluid. We now want to investigate whether this is so when amino-silicone is not pure but rather formulated as personal care products. Therefore 4 formulations naming formulation A (clear shampoo), B (clear shampoo with perfume), C (shampoo car wash) and D (shampoo car wash with perfume) were picked for this study. These formulations are the existing formulations commonly used in various products. Each formulation was prepared (see section 3.3.2) and subjected to various storage conditions (see table 3.2). The plot between the absorbances at maximum absorption wavelength and the storage times of each formulation kept at each condition are depicted in Figures 4.1-4.8.

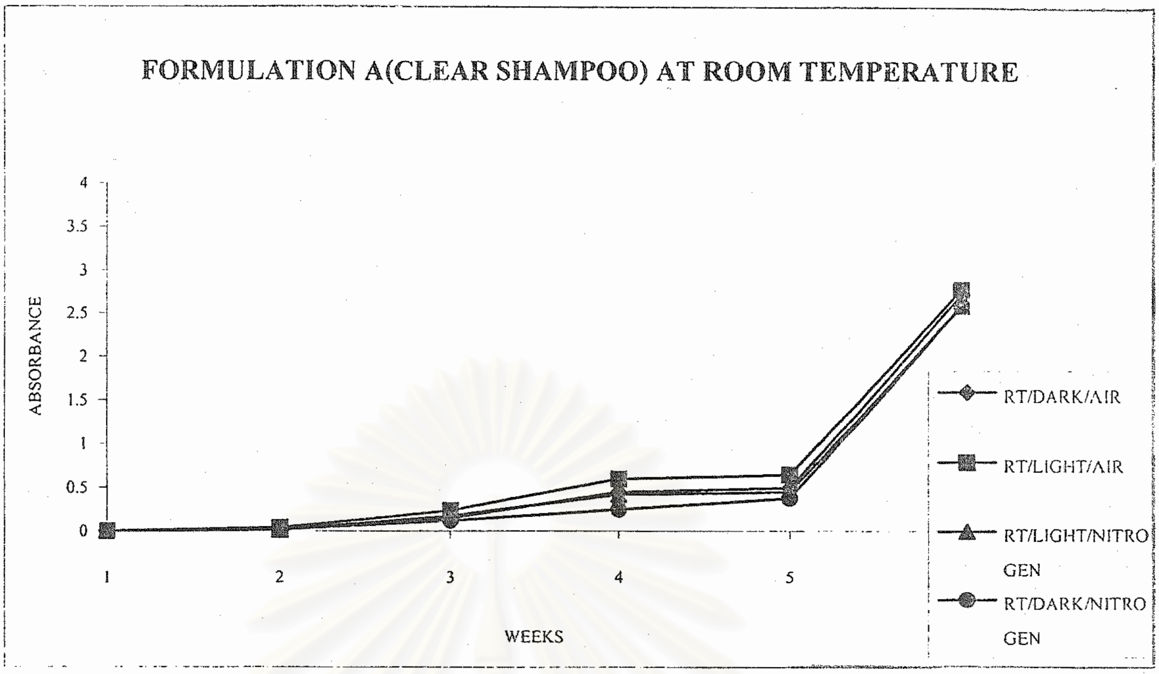

Figure 4.1 Absorbance (at maximum absorption) of formulation A at room temperature.

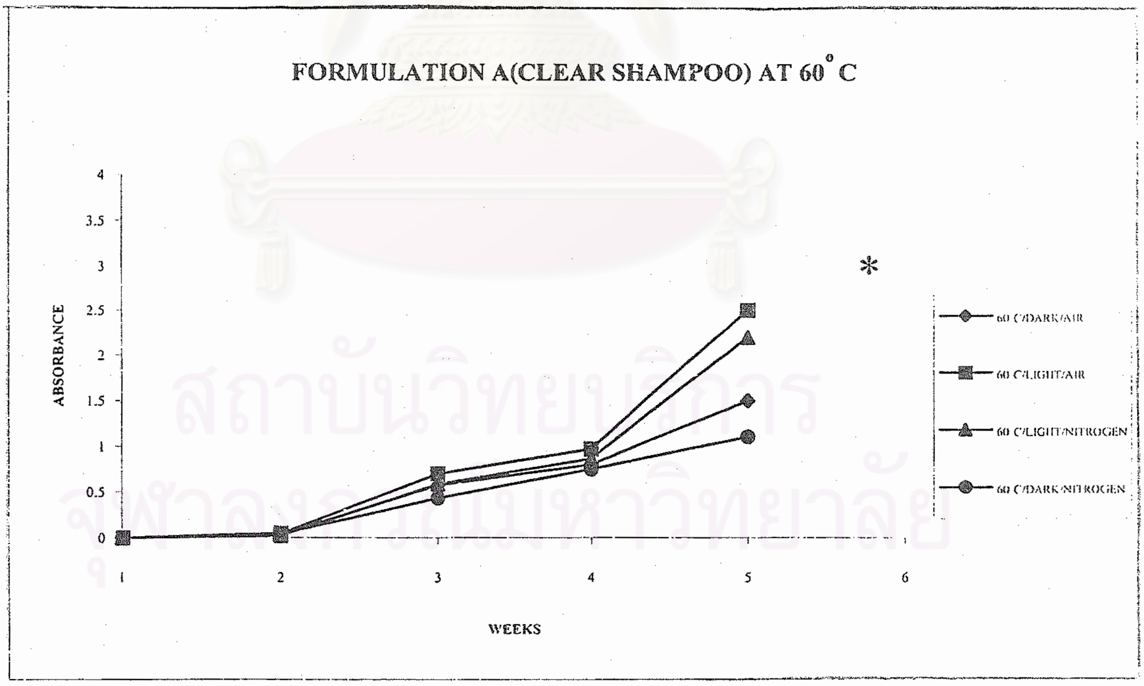

Figure 4.2 Absorbance (at maximum absorption) of formulation A at 60°C.

* The solution became cloudy therefore the absorbance could not be measured.

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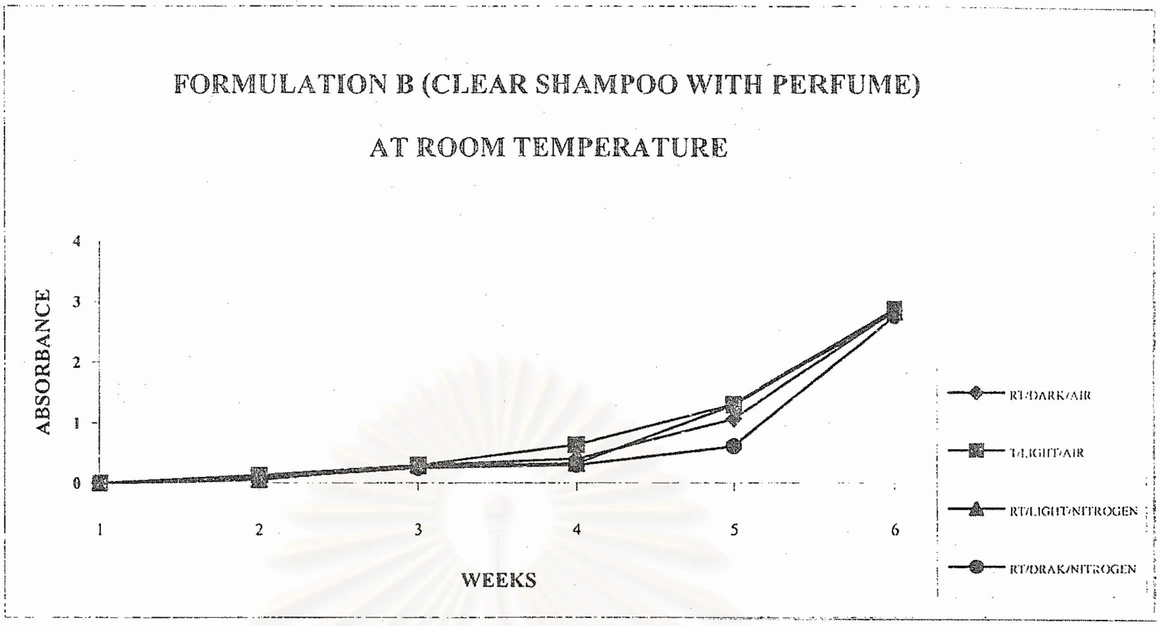

Figure 4.3 Absorbance (at maximum absorption) of formulation B at room temperature.

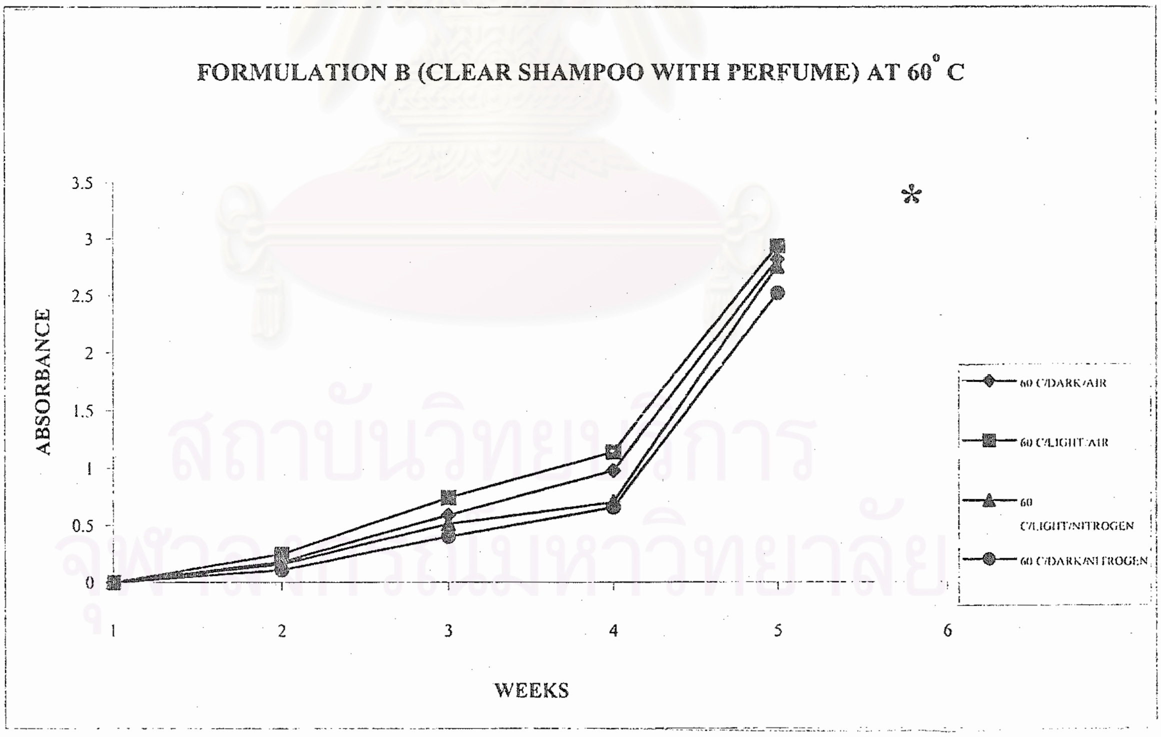

Figure 4.4 Absorbance (at maximum absorption) of formulation B at 60°C.

* The solution became cloudy therefore the absorbance could not be measured.

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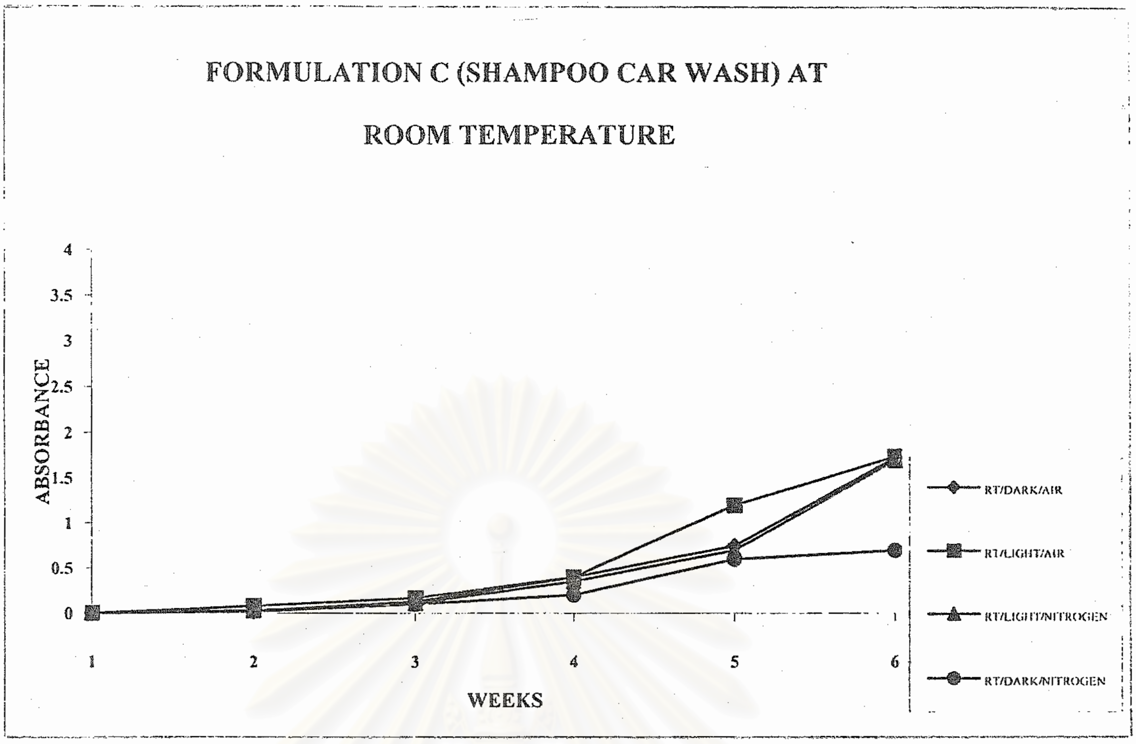

Figure 4.5 Absorbance (at maximum absorption) of formulation C at room temperature.

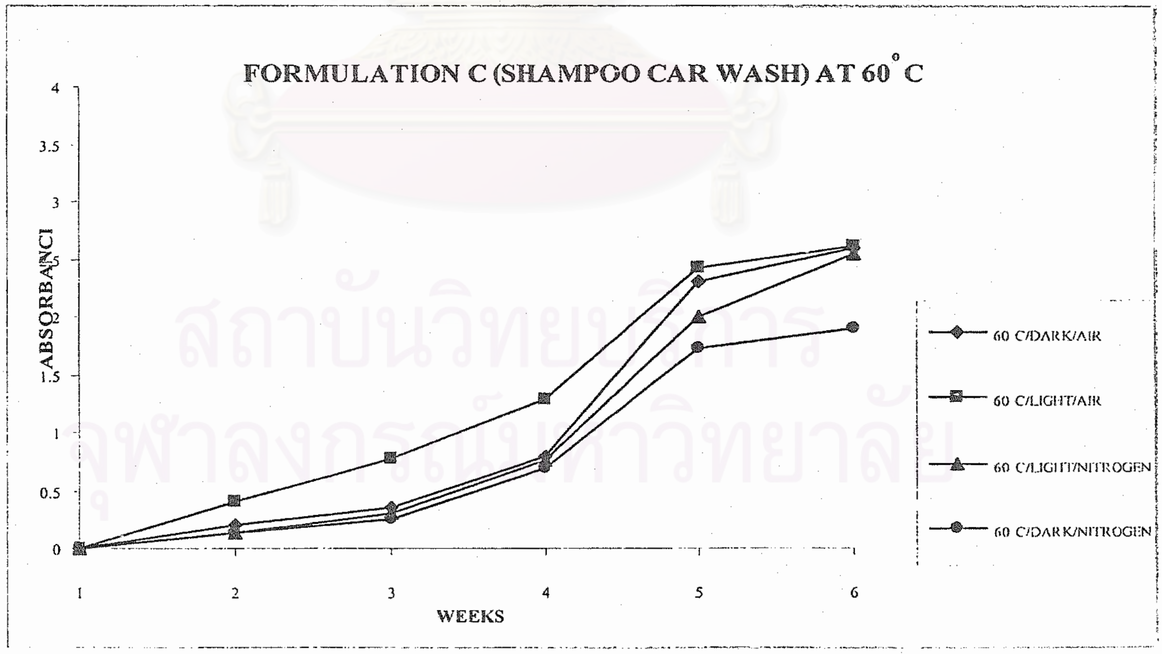

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Figure 4.6 Absorbance (at maximum absorption) of formulation C at 60°C.

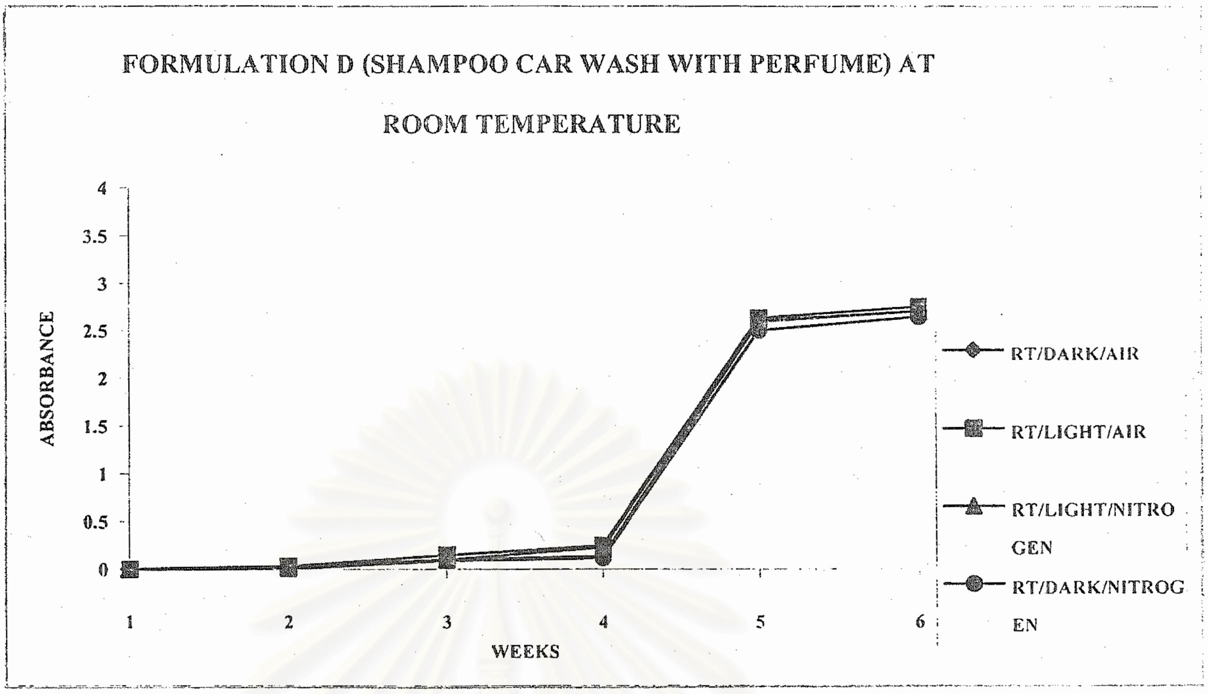

Figure 4.7 Absorbance (at maximum absorption) of formulation D at room temperature.

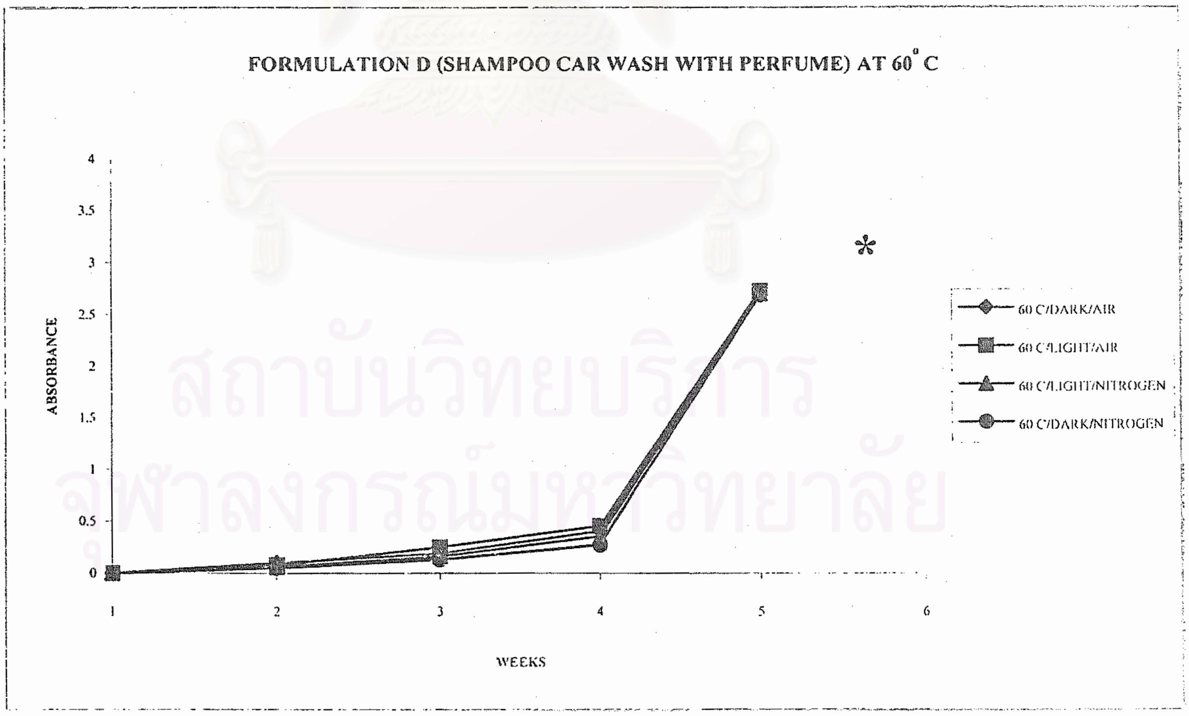

Figure 4.8 Absorbance (at maximum absorption) of formulation D at 60°C.

* The solution became cloudy therefore the absorbance could not be measured.

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From Figures 4.1-4.8, it is obvious that degree of yellowing is much more pronounced when experiments were performed at 60°C. This is consistent with previous experiment in which pure amino-silicone was used. Among 4 formulations, formulation B (clear shampoo with perfume) was most yellow. This result again indicates that the yellowing process in formulation with amino-silicone is probably a thermal degradation process.

4.3 Determination of ingredients that can stimulate yellowing of amino-silicone.

When pure amino-silicone was subjected to various physical factors in order to induce yellowness, the time required for it to turn yellow was more than 2 months. However, when only a small amount of amino-silicone was mixed other ingredients, the formulation turned yellow within a week. This result suggests that there must be some chemical interactions between amino-silicone and ingredients in the formulation facilitating the yellowing process. In other words, particular ingredients in the formulation must act as an accelerator of yellowing of amino silicone. We, therefore, wanted to identify the component that accelerate such yellowness. Mixtures of amino-silicone with each ingredient were then prepared. The ratio between the two chemicals was similar to the actual ratio in the formulation (see Table 3.3 for details). Table 4.1 describes appearances of the mixtures kept at 60°C.

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Table 4.1 Appearances of mixtures between amino-silicone and test ingredients.

Ingredient mixed with amino-silicone	**Appearance of the mixtures on day**						
	1	2	3	4	5	6	7
Propylene glycol	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq
Cetrimonium chloride	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq
Glucamate	white clear liq	white clear liq	white clear liq	clear yellow liq	clear yellow liq	clear yellow liq	clear yellow liq
Polyquaternium-10	white clear liq	white clear liq	white clear liq	clear yellow liq	clear yellow liq	clear yellow liq	clear yellow liq
Cocamidopropyl betain	white clear liq	white clear liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq
Cocamide DEA	white clear liq	white clear liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq
Sodium lauryl sulfate	white clear liq	white clear liq	white clear liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq
Sodium laureth sulfate	**white clear liq**	**clear yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**
Diazolidinyl urea	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq	white milky liq
Propylparaben	**white clear liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**
Perfume	pale yellow liq	pale yellow liq	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**	**strong yellow liq**
Methylparaben	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq	pale yellow liq

From Table 4.1, it is obvious that sodium laureth sulfate and propylparaben are the two most yellow stimulating ingredients. Sodium laureth sulfate (see structure in appendix I p.64) is an anionic surfactant used frequently in the formulation of cleansing agent. This surfactant can be avoided by the use of disodium laureth sulfosaccinate. Propylparben (see structure in appendix I p.68) is a common preservative that can inhibit the growth of bacteria (gram+ and gram-) and fungus. To avoid yellowing, other preservative such as methylparaben, benzylalcohol and phenoxyethanol can be employed in place of propylparaben in formulation with amino-silicone. It should be noted here that formulations with methylparaben, benzylalcohol and phenoxyethanol were prepared and tested for yellowing. These latter formulation showed no yellowing problem. As can be seen in the table, perfume could also cause strong yellow when mixed with amino-silicone. Therefore some experiments should be done before selecting fragrance for each formulation. There results agreed well with the previous result which indicated that among formulations A, B, C and D, formulation B showed problem on yellowing. When look into the formulation ingredients (Table 3.1), formulation B contains all those troubled ingredients, i.e., sodium laureth sulfate, propylparaben and perfume.

4.4 **Determination of compounds that can inhibit the yellowing of amino-silicone.**

Since the result from structural identification of yellow product (see section 4.5) indicated that oxidation product at the aminopropyl aminoethyl group is the main yellow constituent. Antioxidants such as sodium metabisulfite, dibutylhydroxytoluene (BHT) and tocophersolan (see structures in appendix) were tested for their abilities to prevent yellowing. This was done by adding test antioxidant into formulation at various concentrations and following the yellowness of the formulation using UV-visible spectroscopy.

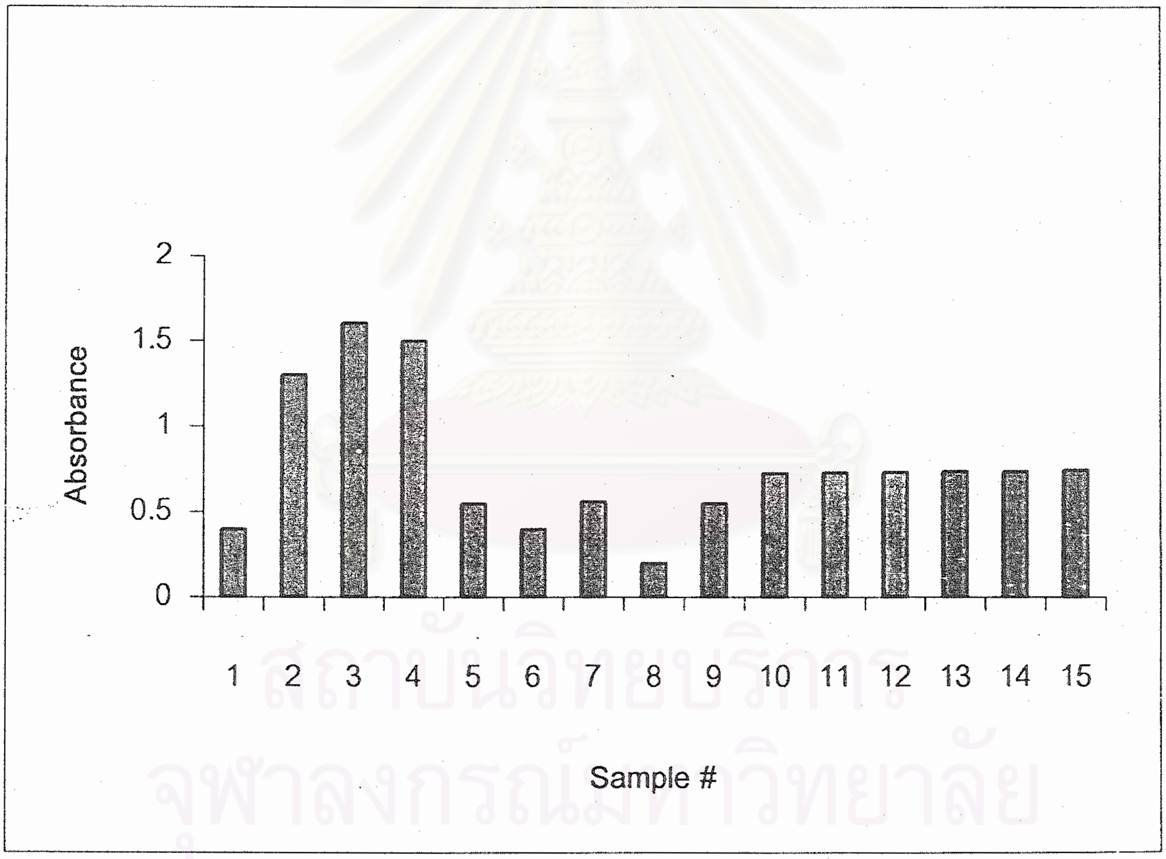

Figure 4.9 Absorbance at maximum absorption of formulations added with various yellowing inhibitors taken after 2-week storage at 60°C. See Table 4.2 for sample descriptions.

Table 4.2 Descriptions of samples in Figure 4.9

Sample #	Description
1	clear shampoo without added antioxidant.
2	clear shampoo with 0.1% BHT.
3	clear shampoo with 0.3% BHT.
4	clear shampoo with 0.1% sodium metabisulfite.
5	clear shampoo with 0.3% sodium metabisulfite.
6	clear shampoo with 0.5% sodium metabisulfite.
7	clear shampoo with 0.7% sodium metabisulfite.
8	clear shampoo with 0.9% sodium metabisulfite.
9	clear shampoo with 1.0% sodium metabisulfite.
10	clear shampoo with 0.1% tocophersolan
11	clear shampoo with 0.3% tocophersolan
12	clear shampoo with 0.5% tocophersolan
13	clear shampoo with 0.7% tocophersolan
14	clear shampoo with 0.9% tocophersolan
15	clear shampoo with 1.0% tocophersolan

From Figure 4.9, it is clear that none of the antioxidants tested can effectively inhibit the yellowing of the formulation. This is probably because the yellowing is the thermal degradation process rather than an oxidation process.

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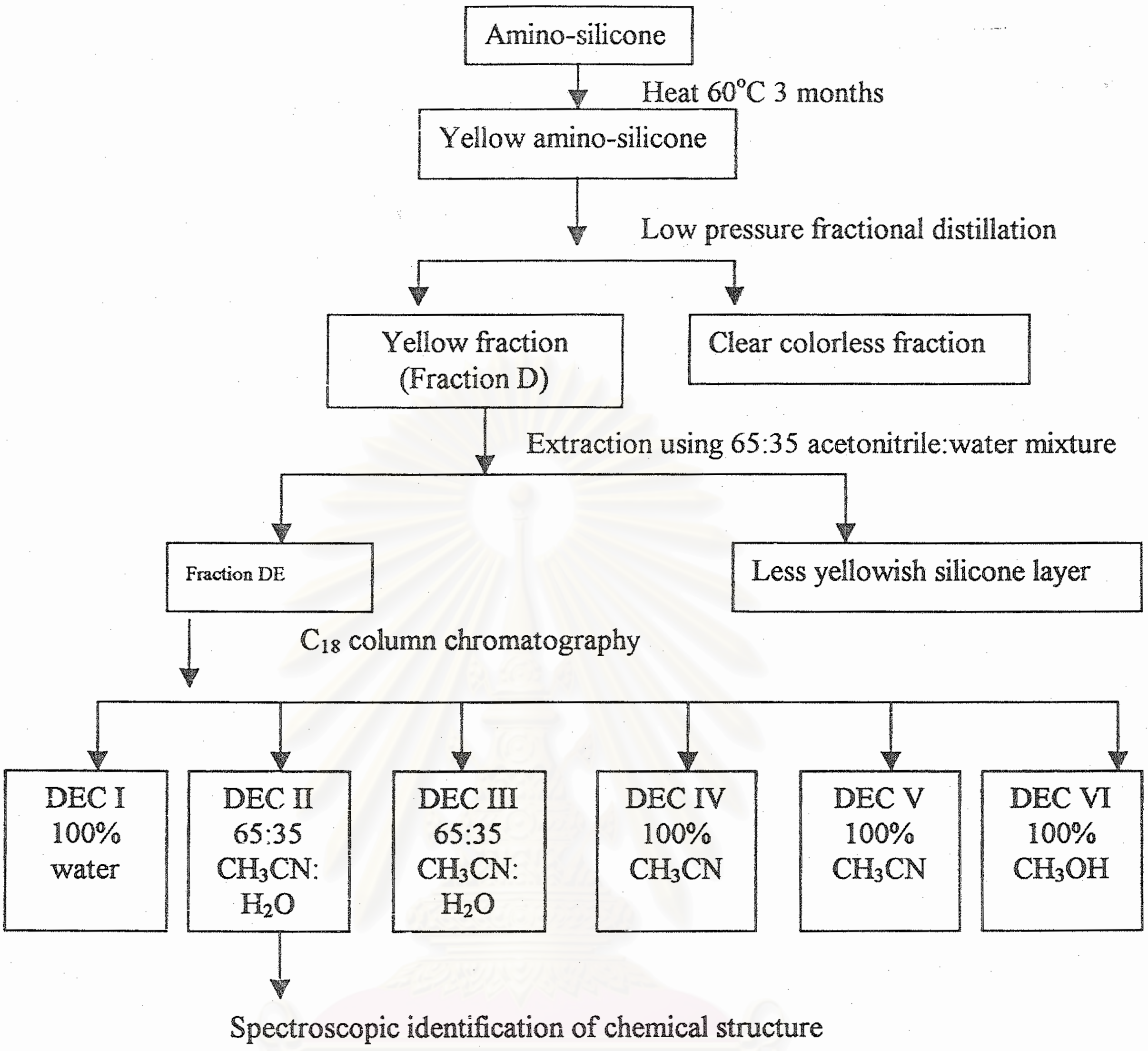

Scheme II The separation procedures of the most yellowish fraction from amino-silicone and details of column fractionation.

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4.5 Isolation and identification of the yellowing constituents of amino-silicone

4.5.1 Preparation of yellow amino-silicone by distillation

Vacuum distillation of yellow amino-silicone yields 2 fractions; clear colorless liquid (169-208°C) and clear yellow liquid (218-248°C fraction D).

4.5.2 Isolation the yellowing species of amino-silicone

To 5 mL of yellow fraction (fraction D) 100 mL of acetonitrile/water (65:35% W/W) mixture was added. After vigorously shaking the mixture was allowed to sit until layer separation complete. Yellow specieses probably migrated into the acetonitrile/water layer because this layer became yellowish while the silicone became less yellow. The yellow acetonitrile/water fraction (fraction DE) was then subjected to rotary evaporation to remove solvent. Yellow viscous liquid was tested for its solubility in various solvents. The results were shown in Table 4.3.

Table 4.3 Solubility of fraction DE comparing with amodimethicone.

Solvent	Amodimethicone	Fraction DE
water	no	yes
methanol	no	yes
ethanol	Slightly soluble (1:10 amino-silicone:ethanol)	yes
acetonitrile	no	yes
ethyl acetate	yes	yes
isopropanol	yes	no
chloroform	yes	no
hexane	yes	no

4.5.3 Column chromatography

Six clearly-separated bands can be seen when fraction DE was chromatographed through C-18 column. Since separation can be obviously seen in the column, therefore, collection of each fraction was done visually. The column chromatography was gradiently eluted starting from 100% water to 100% acetonitrile and to 100% methanol (Table 4.4).

Table 4.4 Fraction order obtained from gradient elution of fraction DE

Fraction number	Appearance on the column	Weight (g)	Eluents
DEC I	wide pale yellow band	0.01	100% water
DEC II	distinct intense yellow narrow band	0.02	65:35 $CH_3CN:H_2O$
DEC III	wide pale yellowish band	0.01	65:35 $CH_3CN:H_2O$
DEC IV	yellow narrow band	0.01	100% CH_3CN
DEC V	wide pale yellow band	0.03	100% CH_3CN
DEC VI	wide pale yellow band	0.04	100% CH_3OH

Since it is very obvious that fraction DEC II is not only well separated but also the most yellowish fraction, this fraction was, therefore, subjected to spectroscopic analyses including NMR, IR, UV-vis and MS. After solvent removal the DEC II fraction appeared as yellow viscous liquid.

4.5.4 Spectrometry analyses of the most yellowing fraction.

The functional groups of DEC II were determined using FT-IR, ^{1}H-NMR, HMQC, HMBC, COSY-NMR and MS. The IR spectrum of DEC II is shown in Figure 4.10. The assignments of major peaks are shown in Table 4.5.

Table 4.5 Peak assignments of DEC II IR spectrum.

Wave Number, cm.$^{-1}$	**Peak Assignment**
3800-3000	O-H stretching of hydroxy group
2250, 2100	Si-O-Si
1650	C=O stretching of RCONH$_2$, RCONHR

Figures 4.11 and 4.12 show the ^{1}H NMR spectra and ^{13}C NMR of DEC II in DMSO-d_6 , respectively. Figure 4.13-4.27 represent HMQC, HMBC and COSY spectra of the DEC II.

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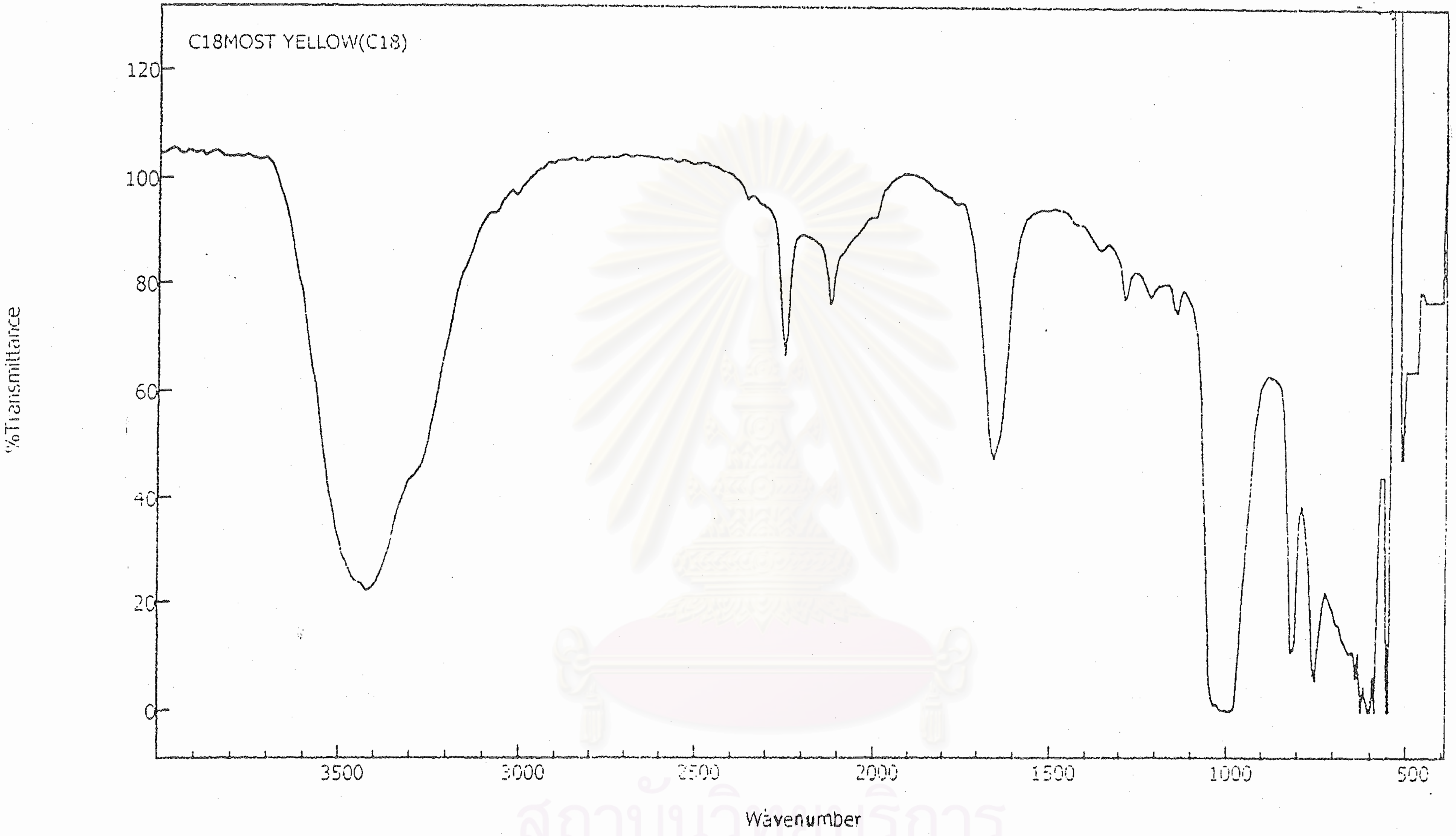

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Figure 4.10 IR spectrum of DEC II fraction.

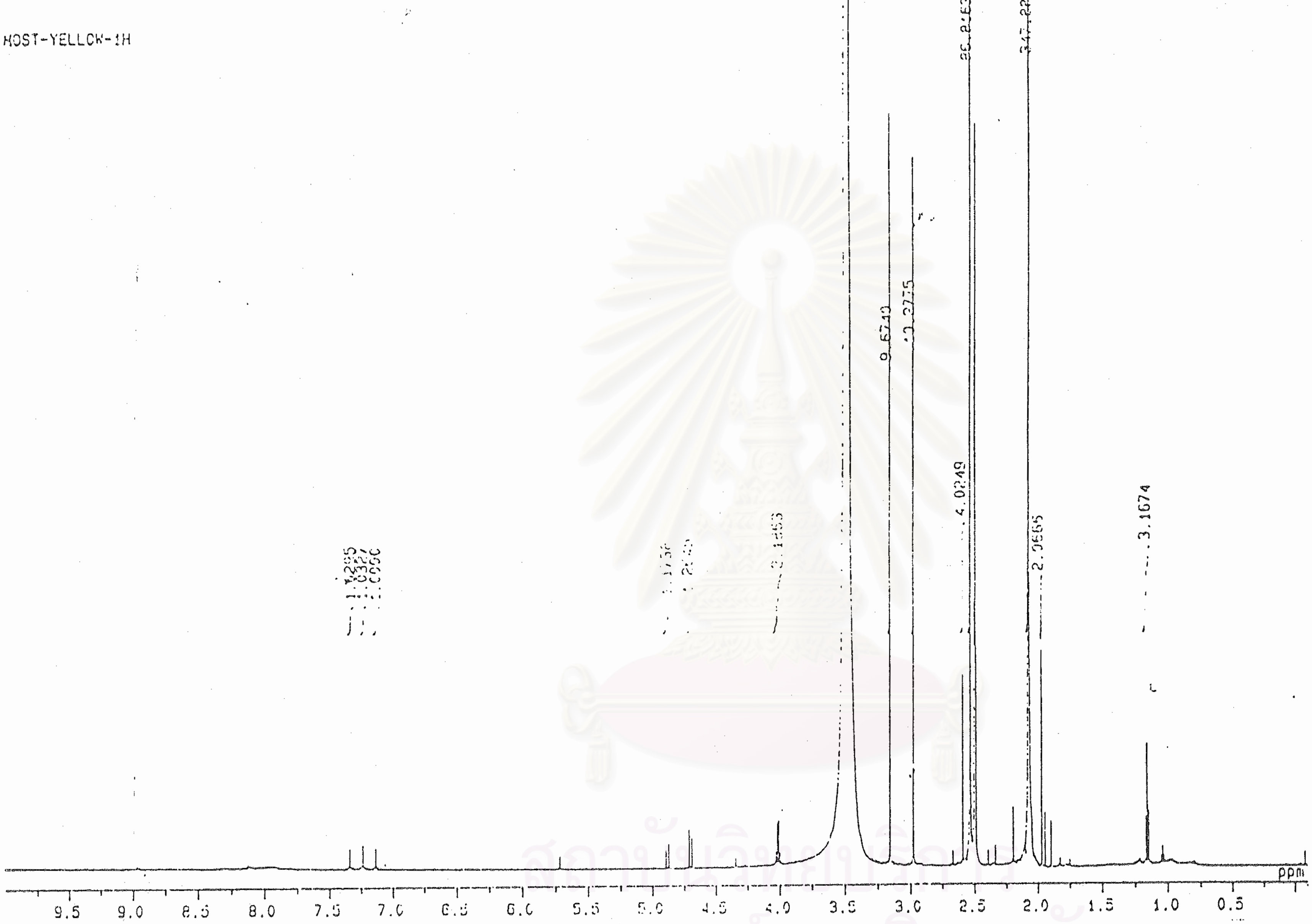

Figure 4.11 ^{1}H NMR spectrum of the DEC II fraction.

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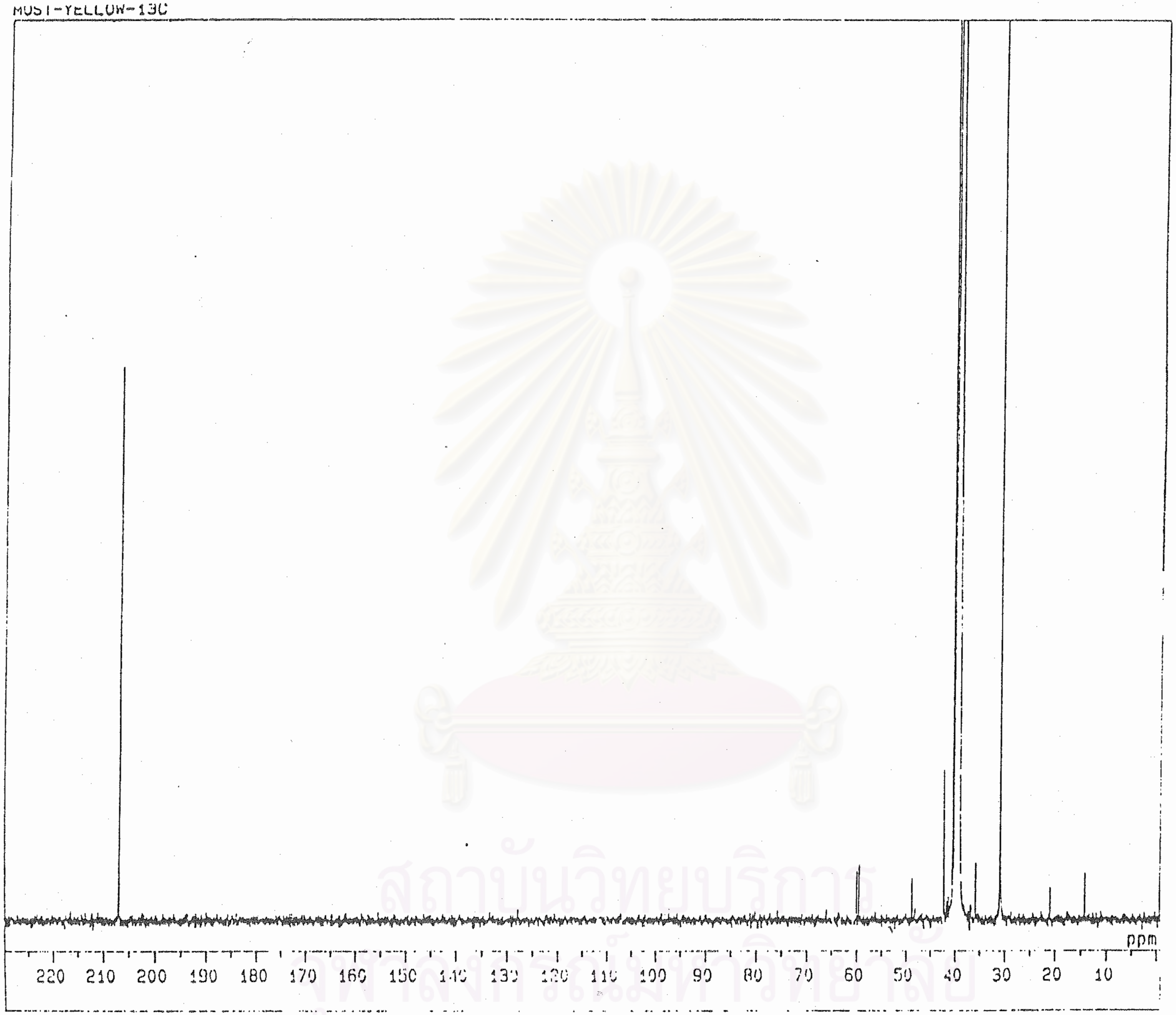

Figure 4.12 ^{13}C NMR spectrum of DEC II fraction.

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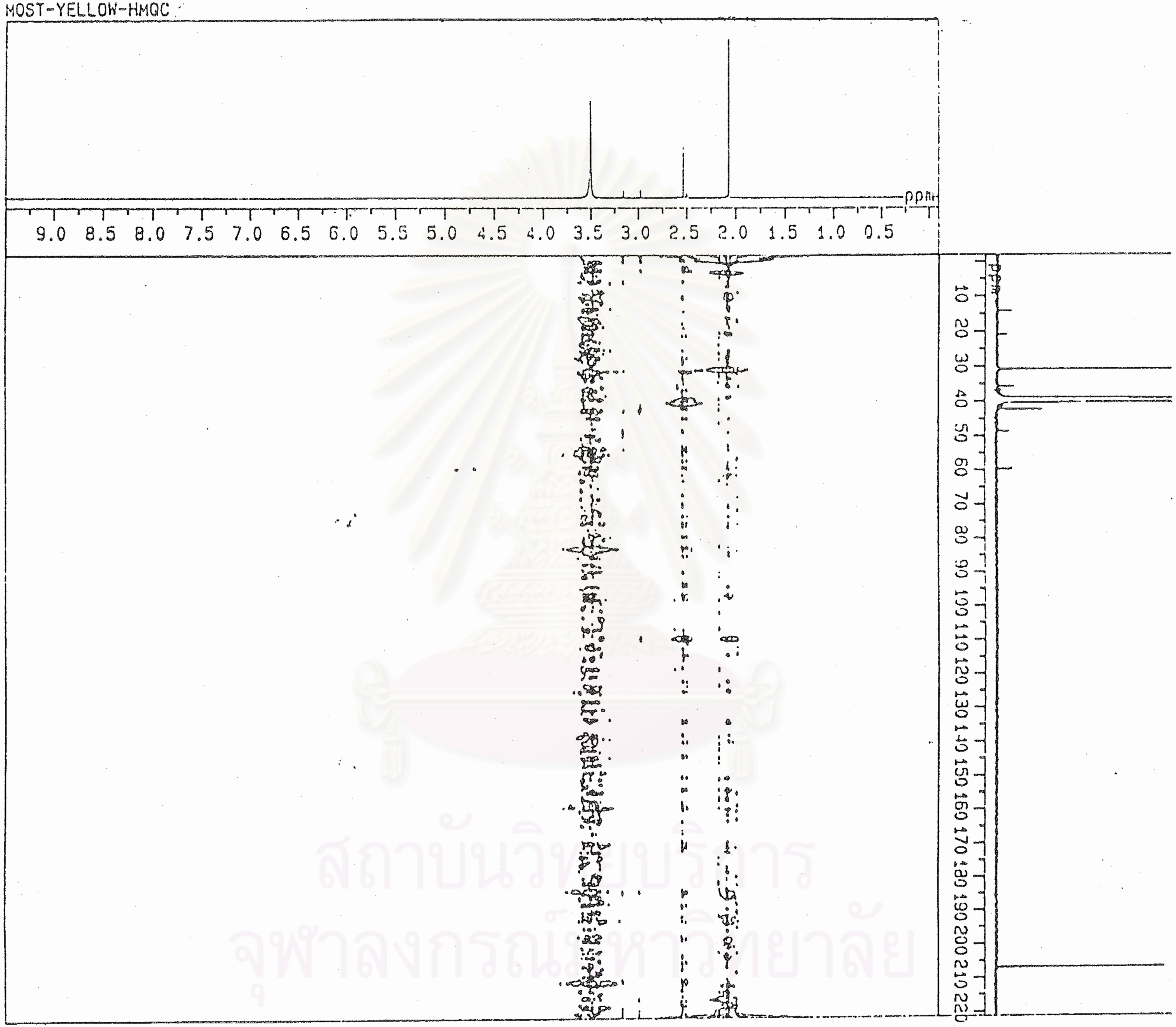

Figure 4.13 HMQC NMR spectrum of DEC II fraction.

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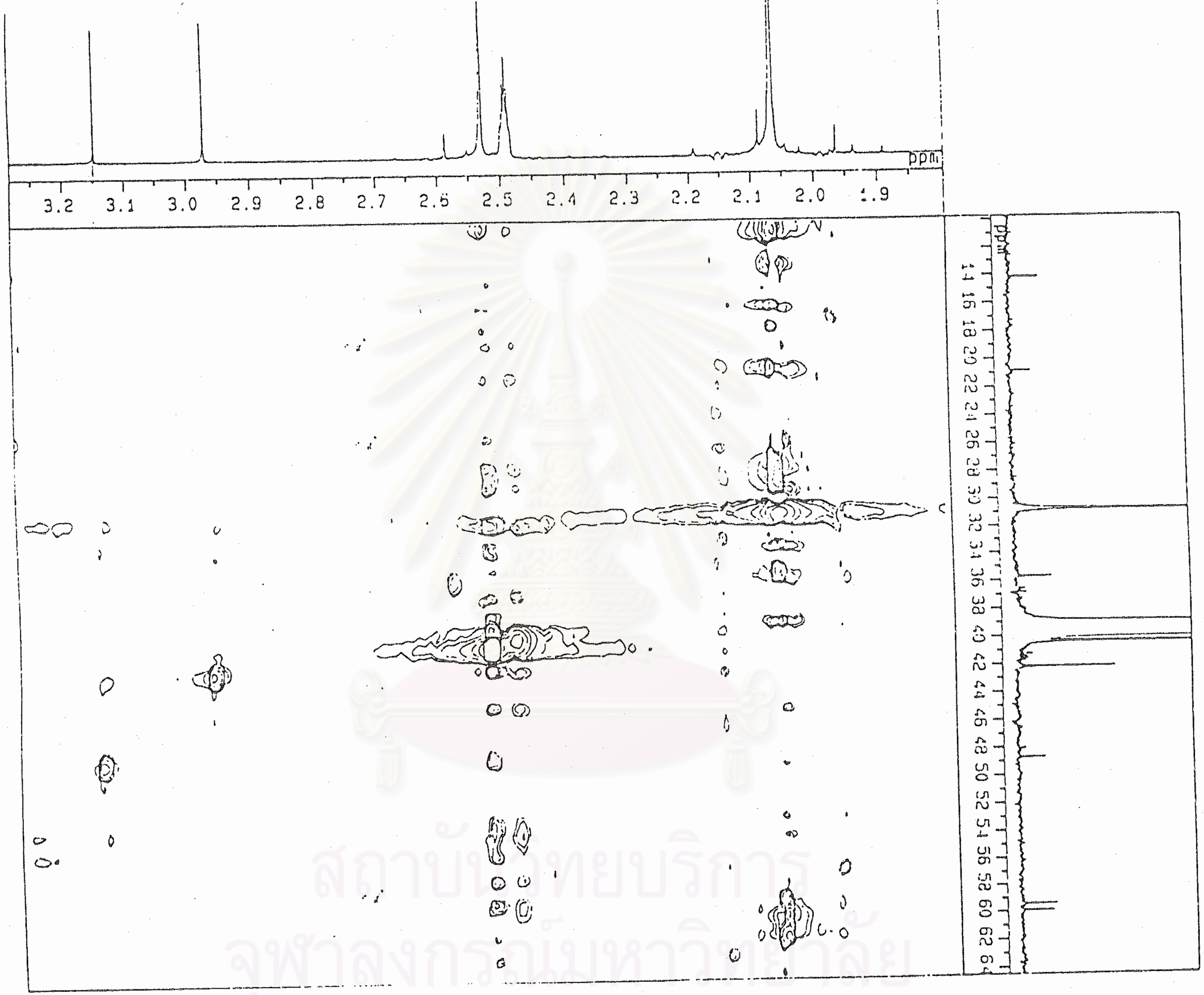

Figure 4.14 HMQC NMR spectrum of DEC II fraction.

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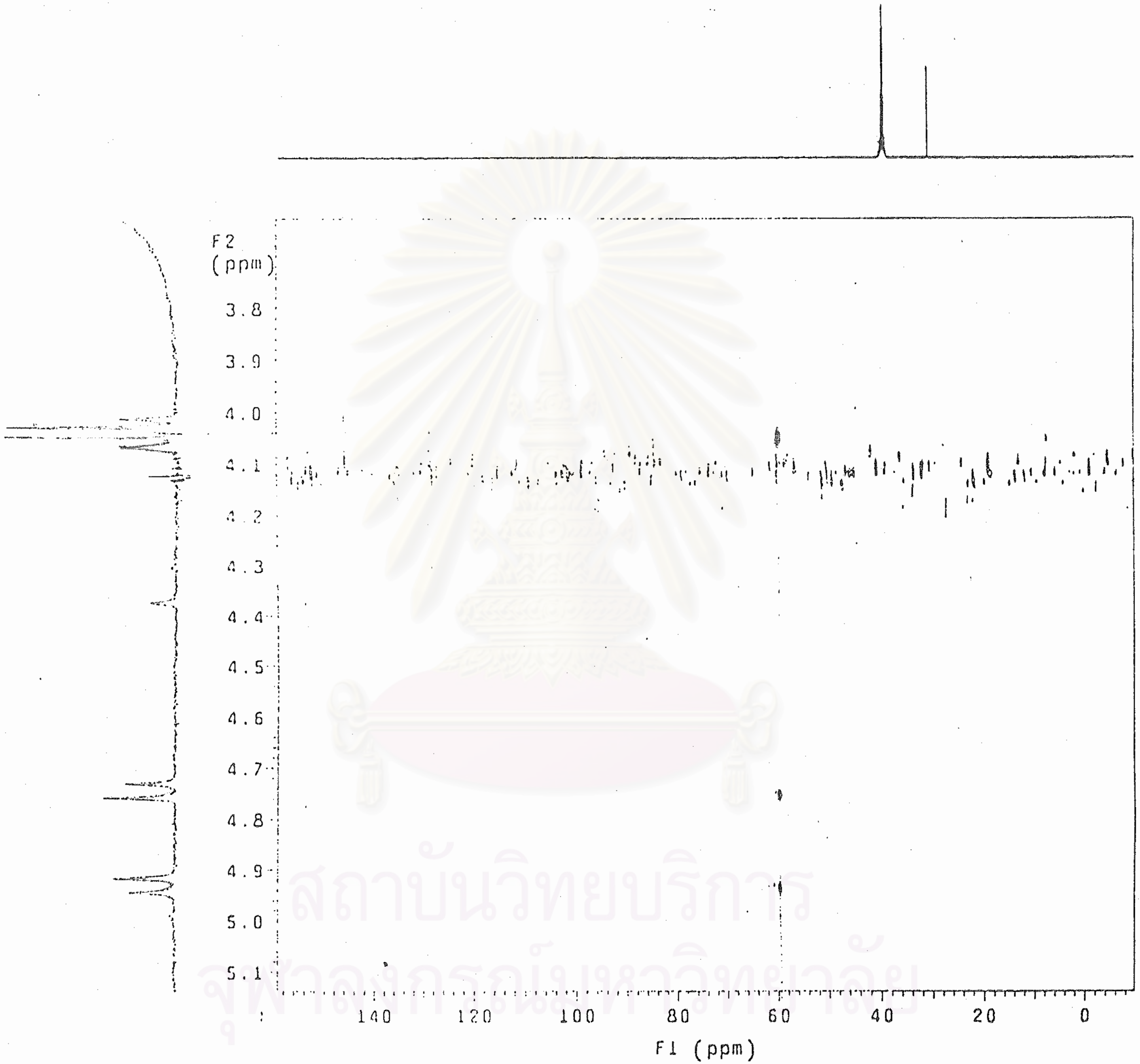

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Figure 4.15 HMQC NMR spectrum of DEC II fraction.

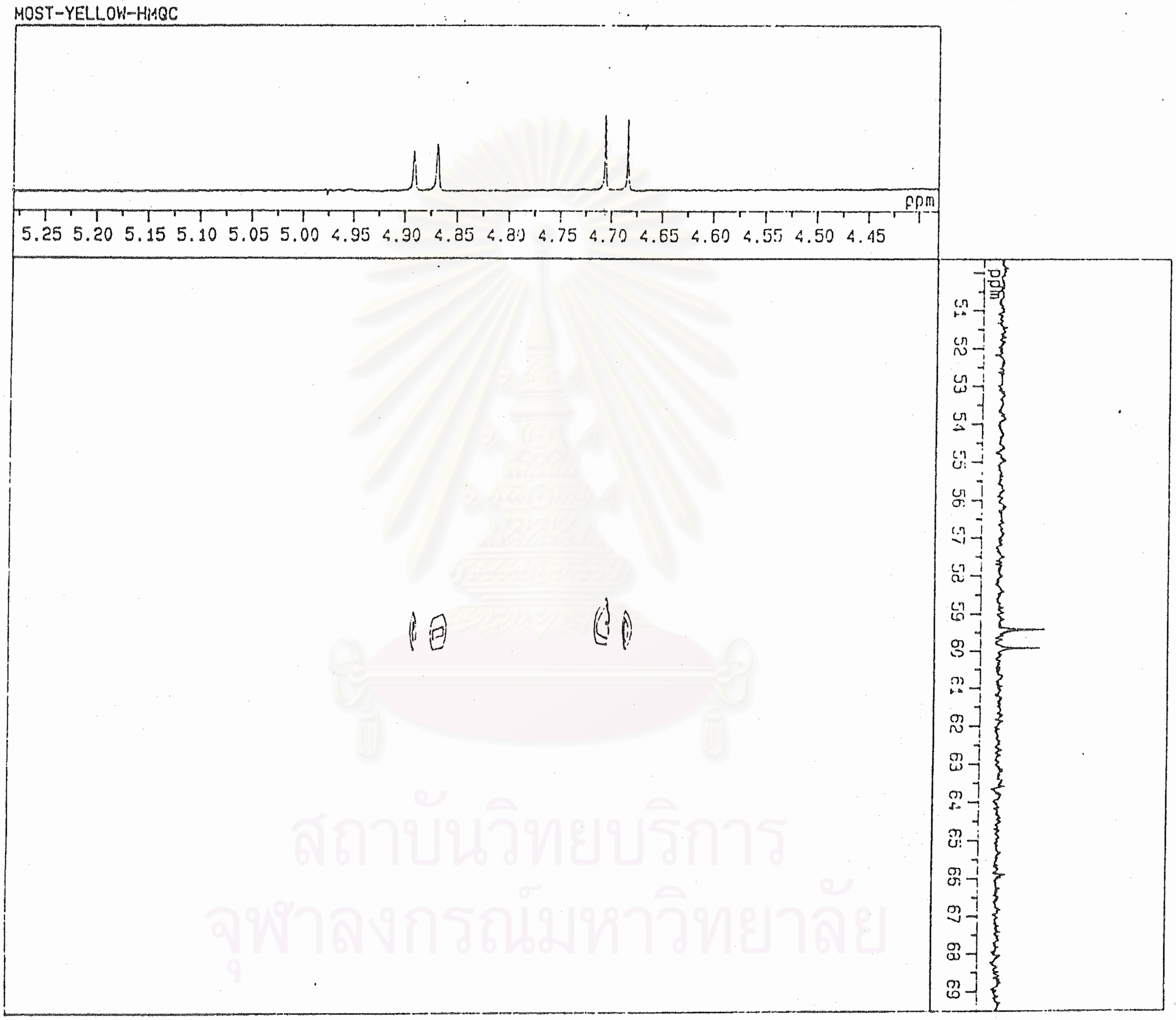

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Figure 4.16 HMQC NMR spectrum of DEC II fraction.

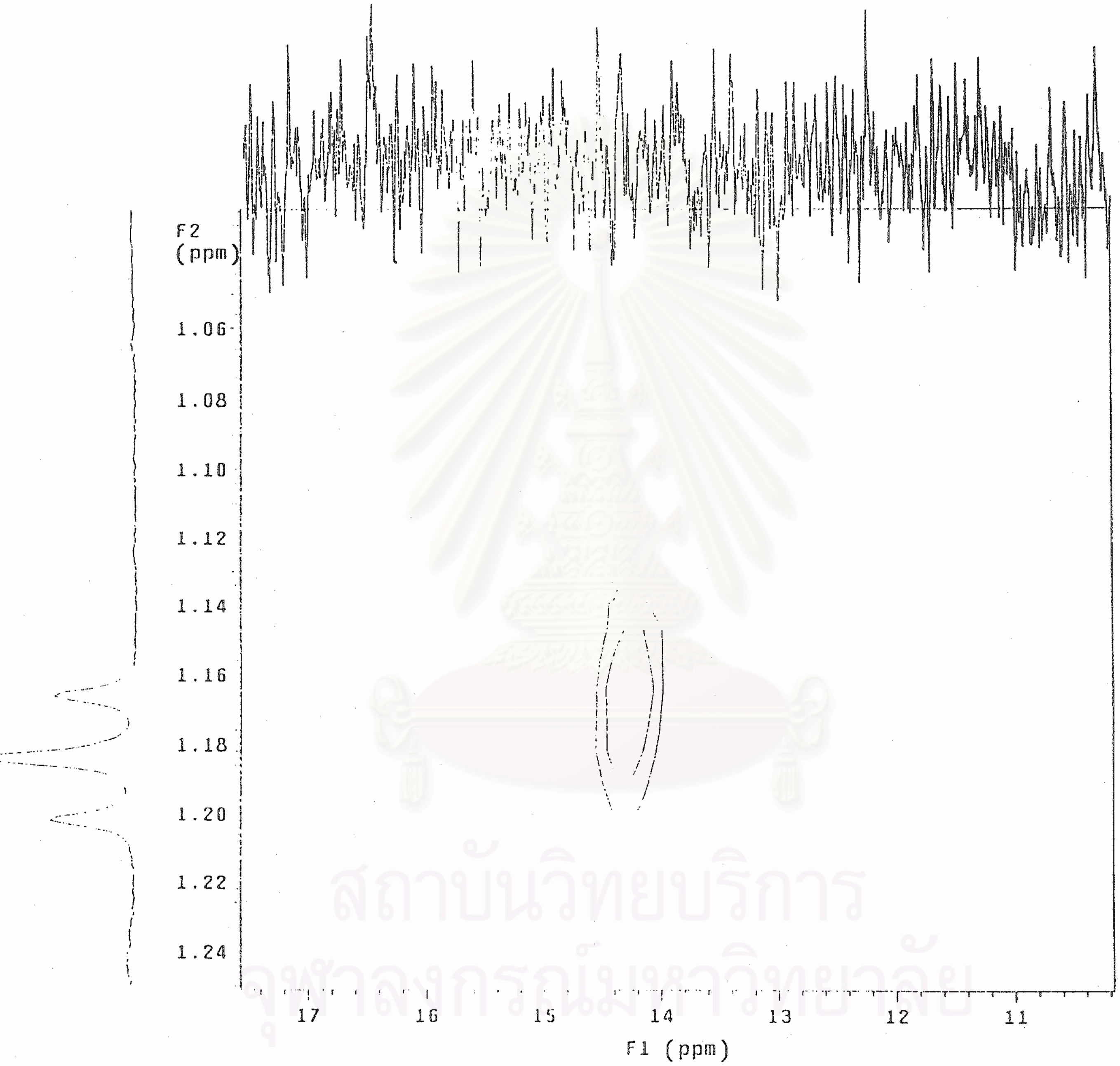

Figure 4.17 HMQC NMR spectrum of DEC II fraction.

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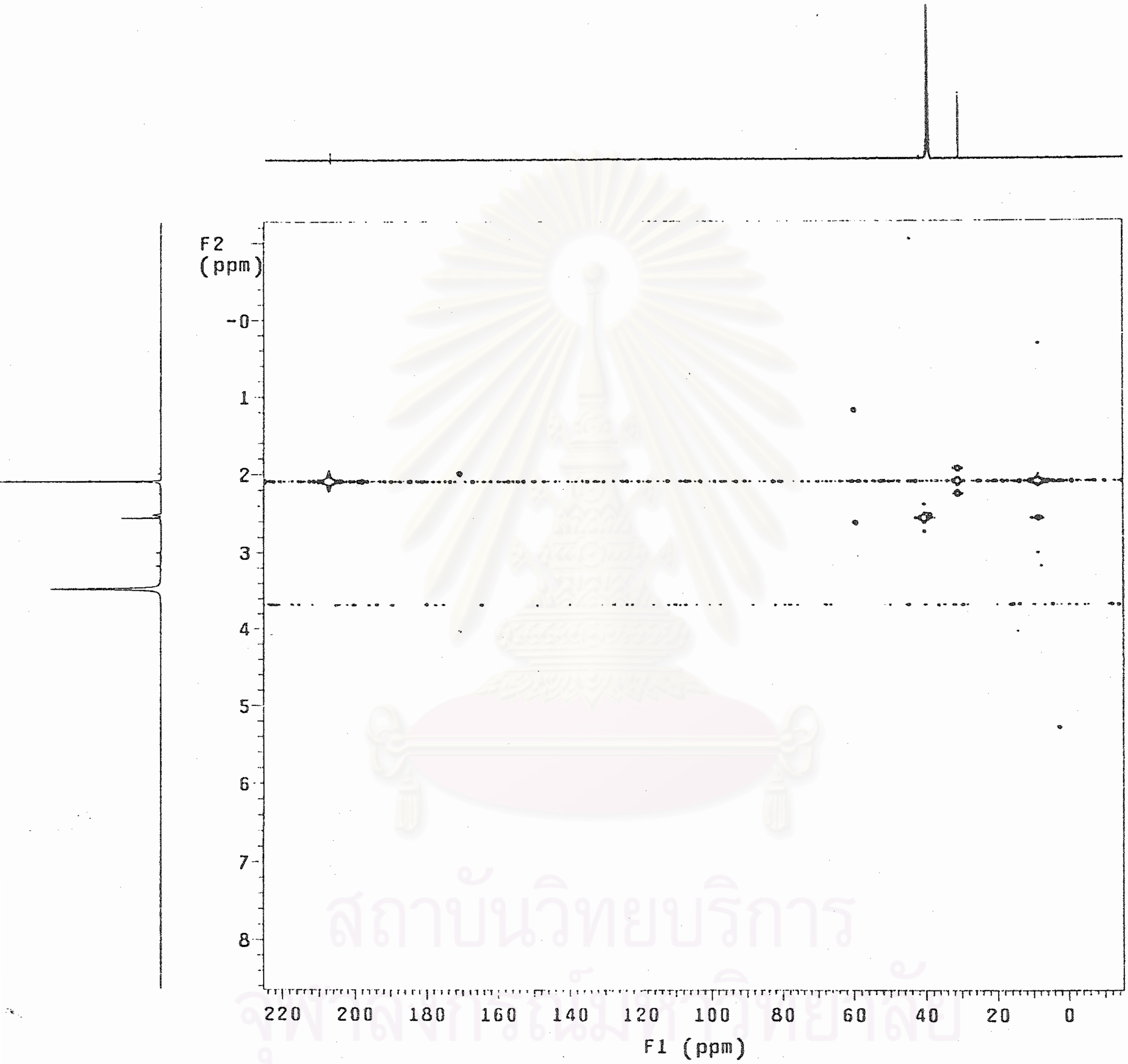

Figure 4.18 HMBC NMR spectrum of DEC II fraction.

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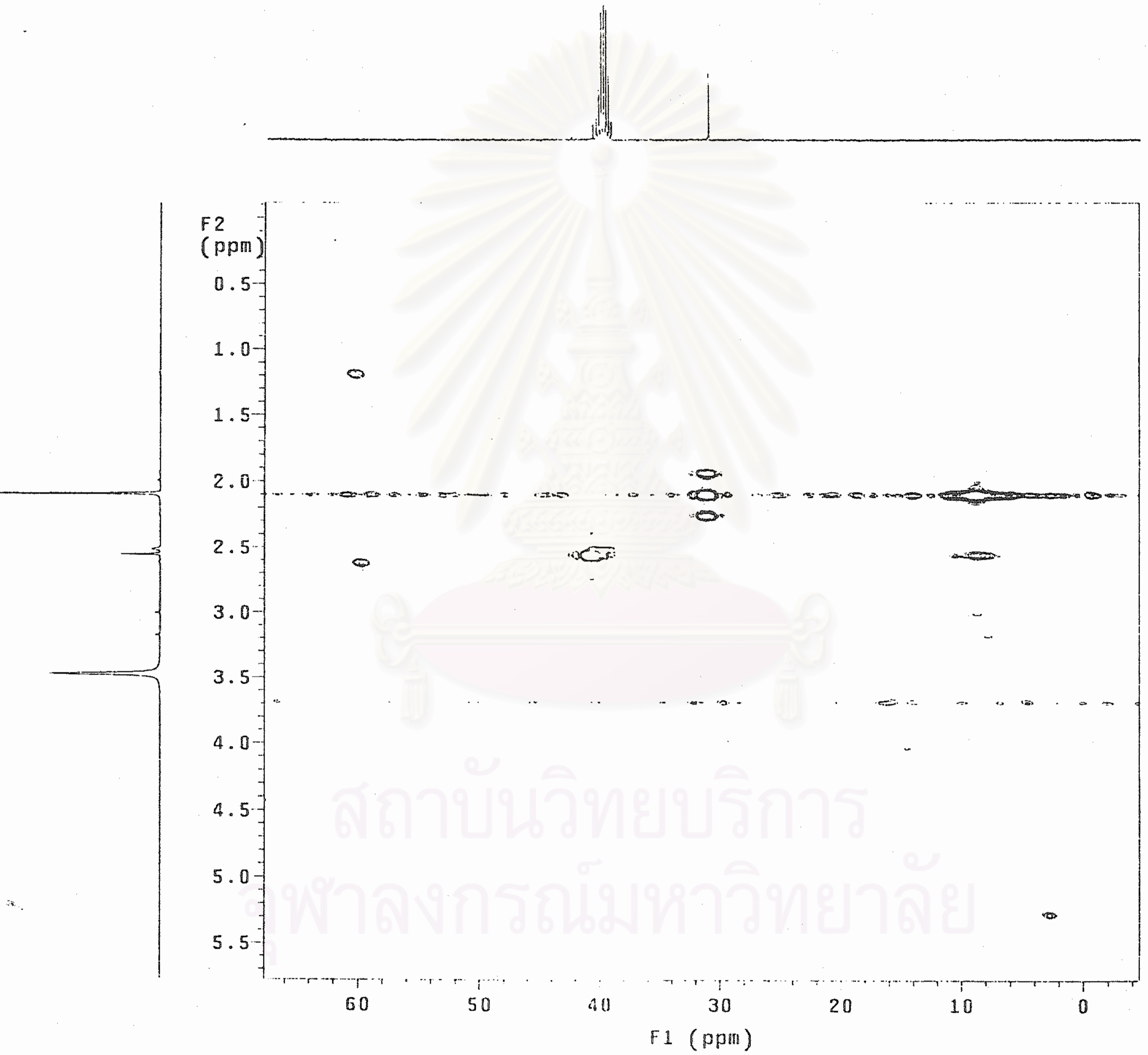

Figure 4.19 HMBC NMR spectrum of DEC II fraction.

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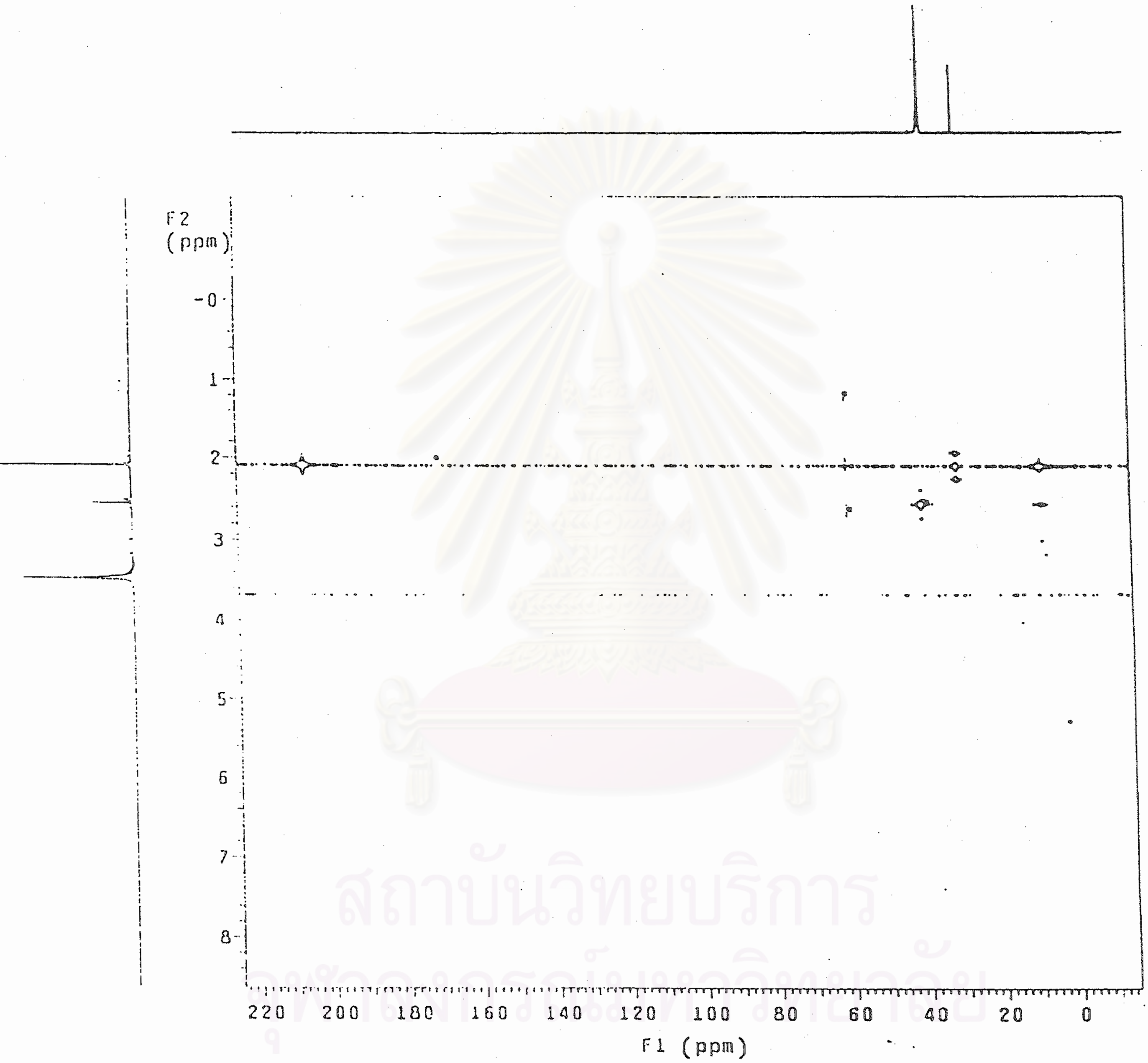

Figure 4.20 HMBC NMR spectrum of DEC II fraction.

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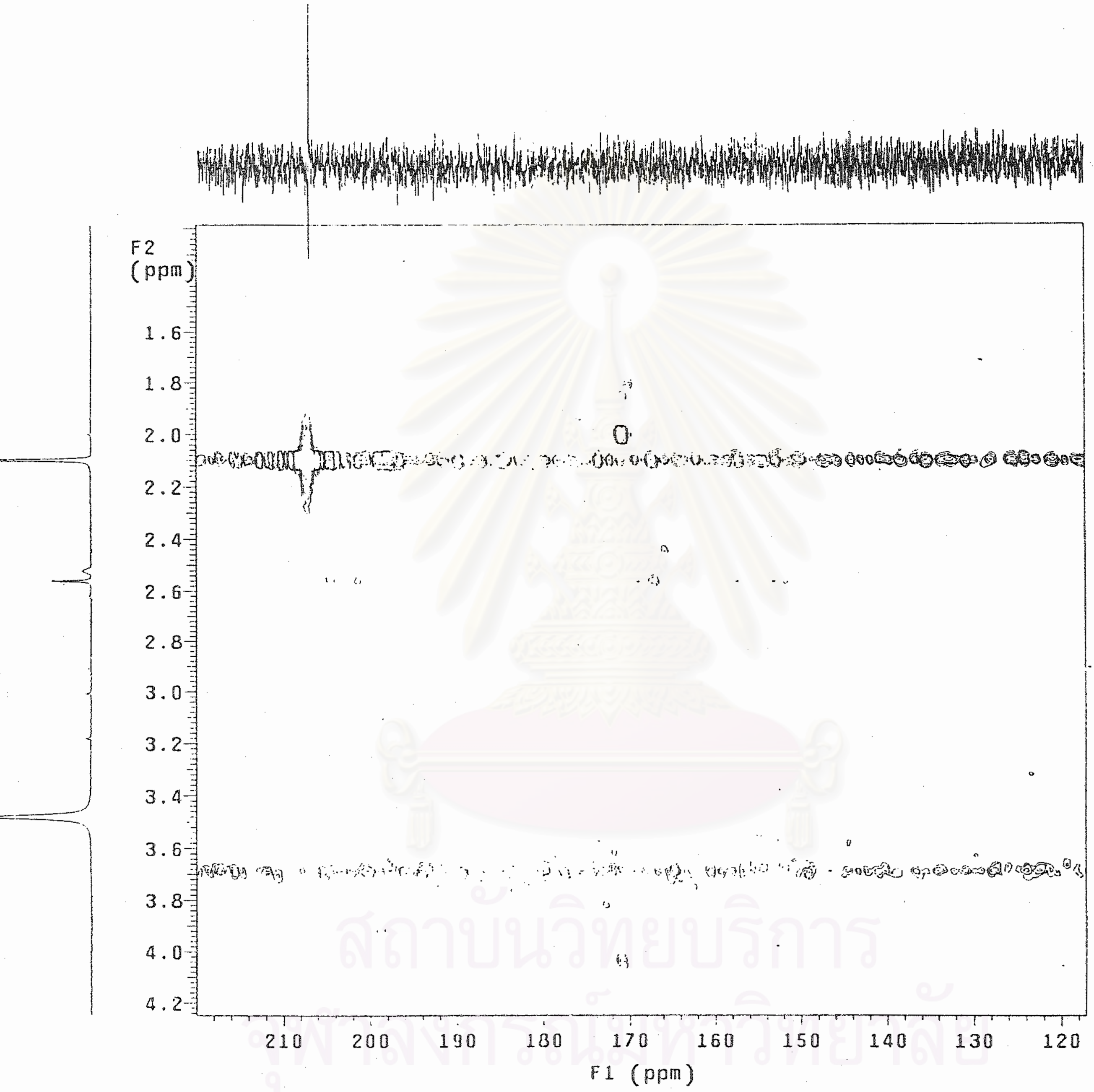

Figure 4.21 HMBC NMR spectrum of DEC II fraction.

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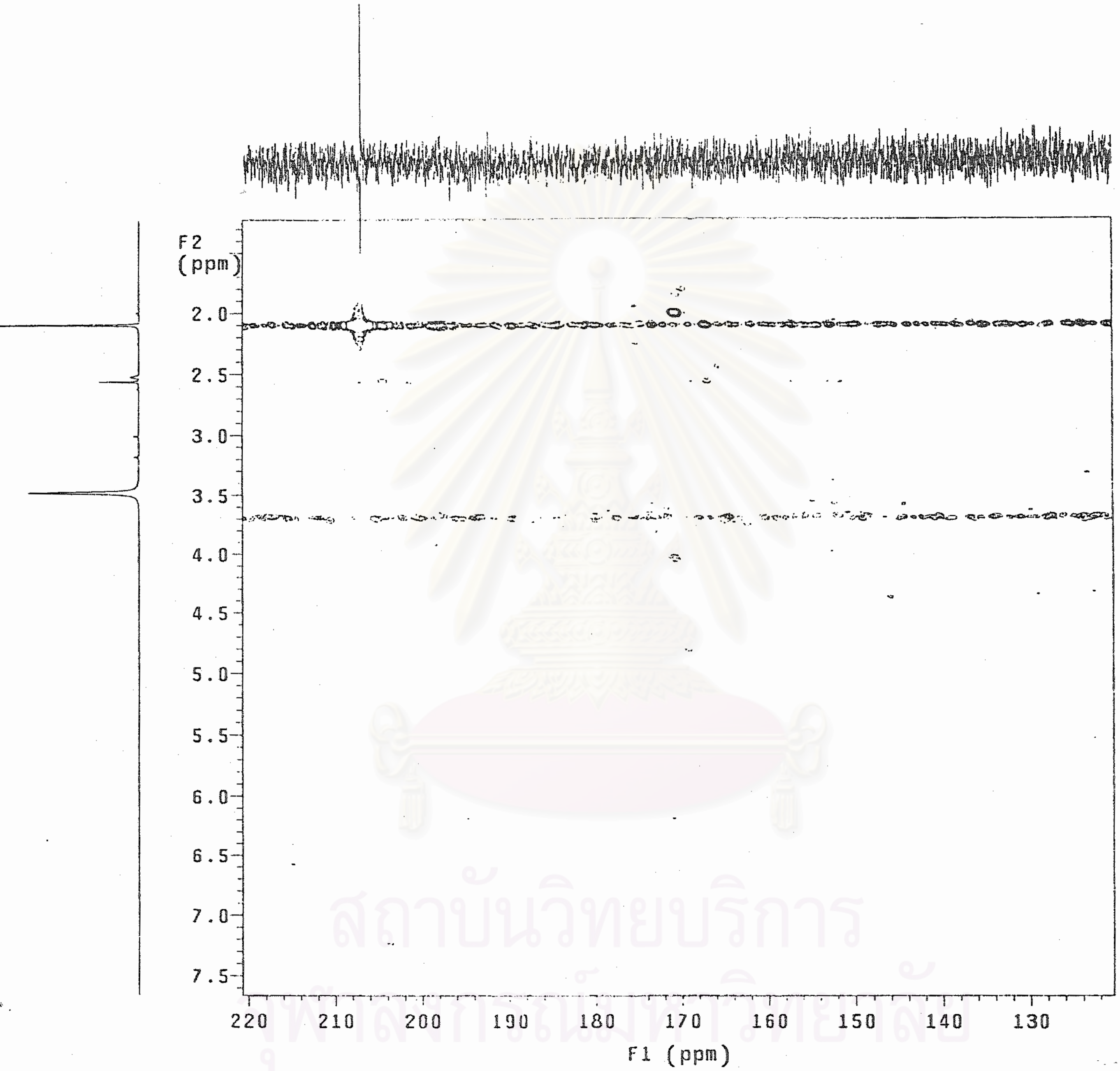

Figure 4.22 HMBC NMR spectrum of DEC II fraction.

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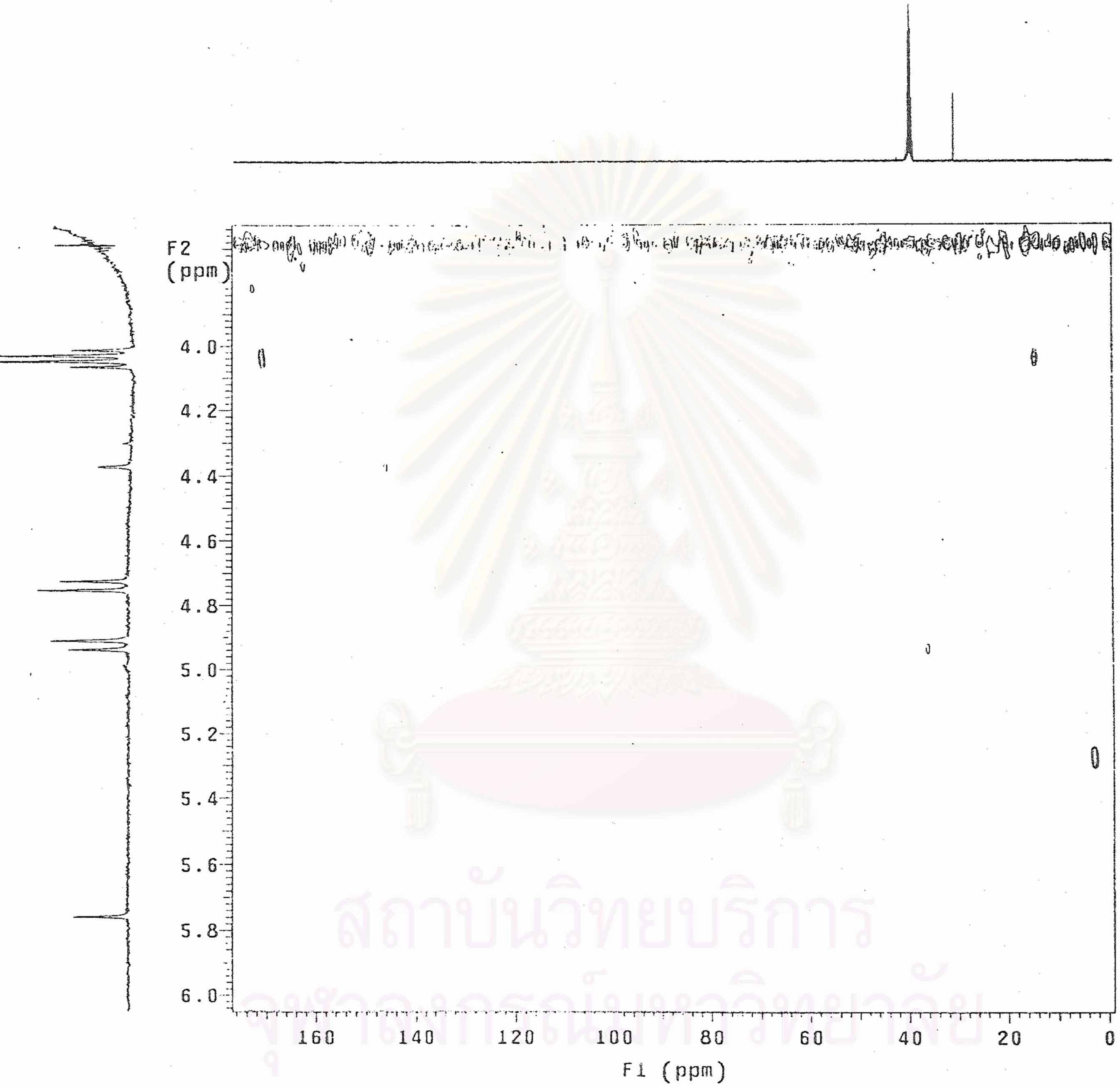

Figure 4.23 HMBC NMR spectrum of DEC II fraction.

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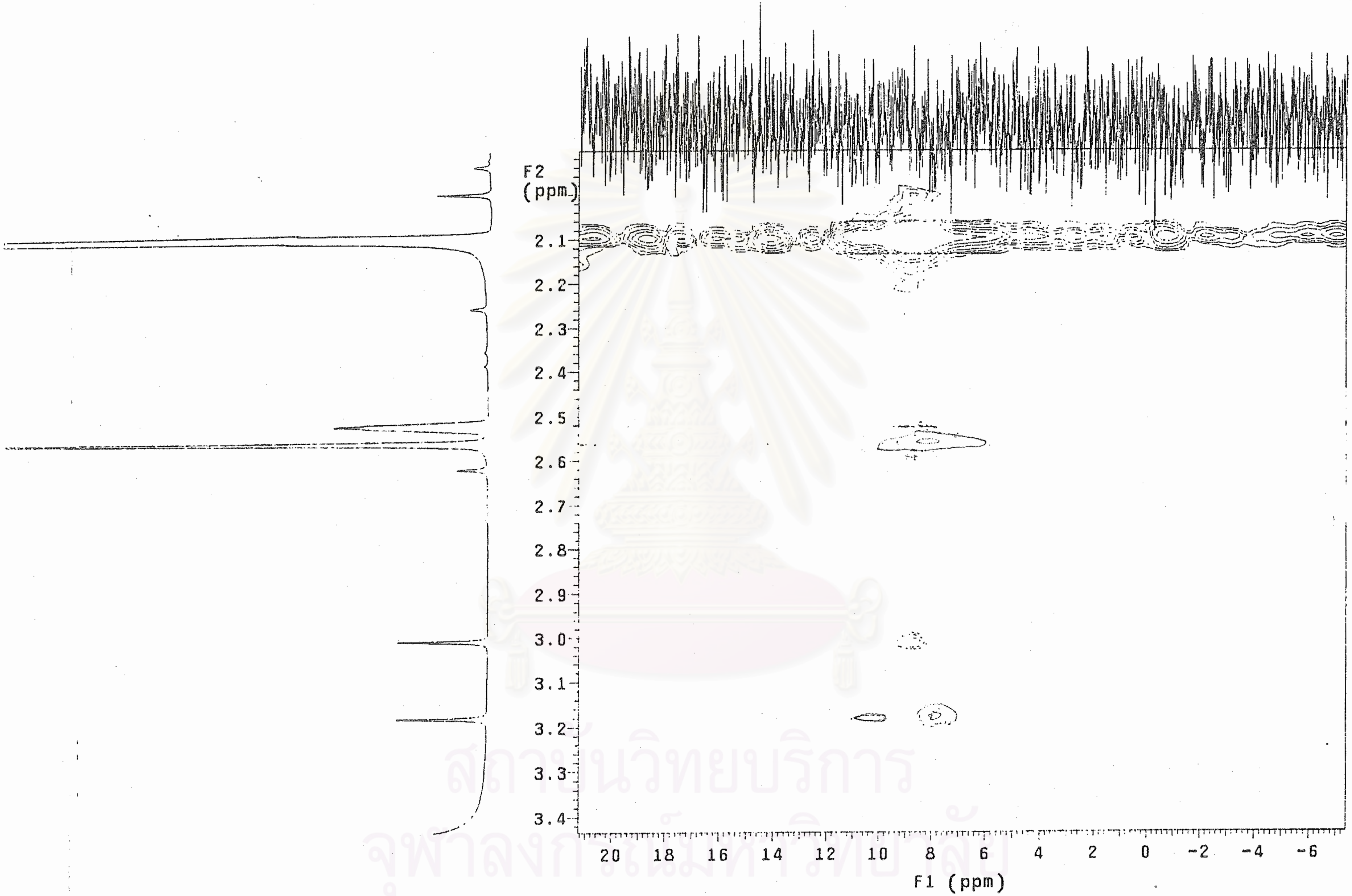

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Figure 4.24 HMBC NMR spectrum of DEC II fraction.

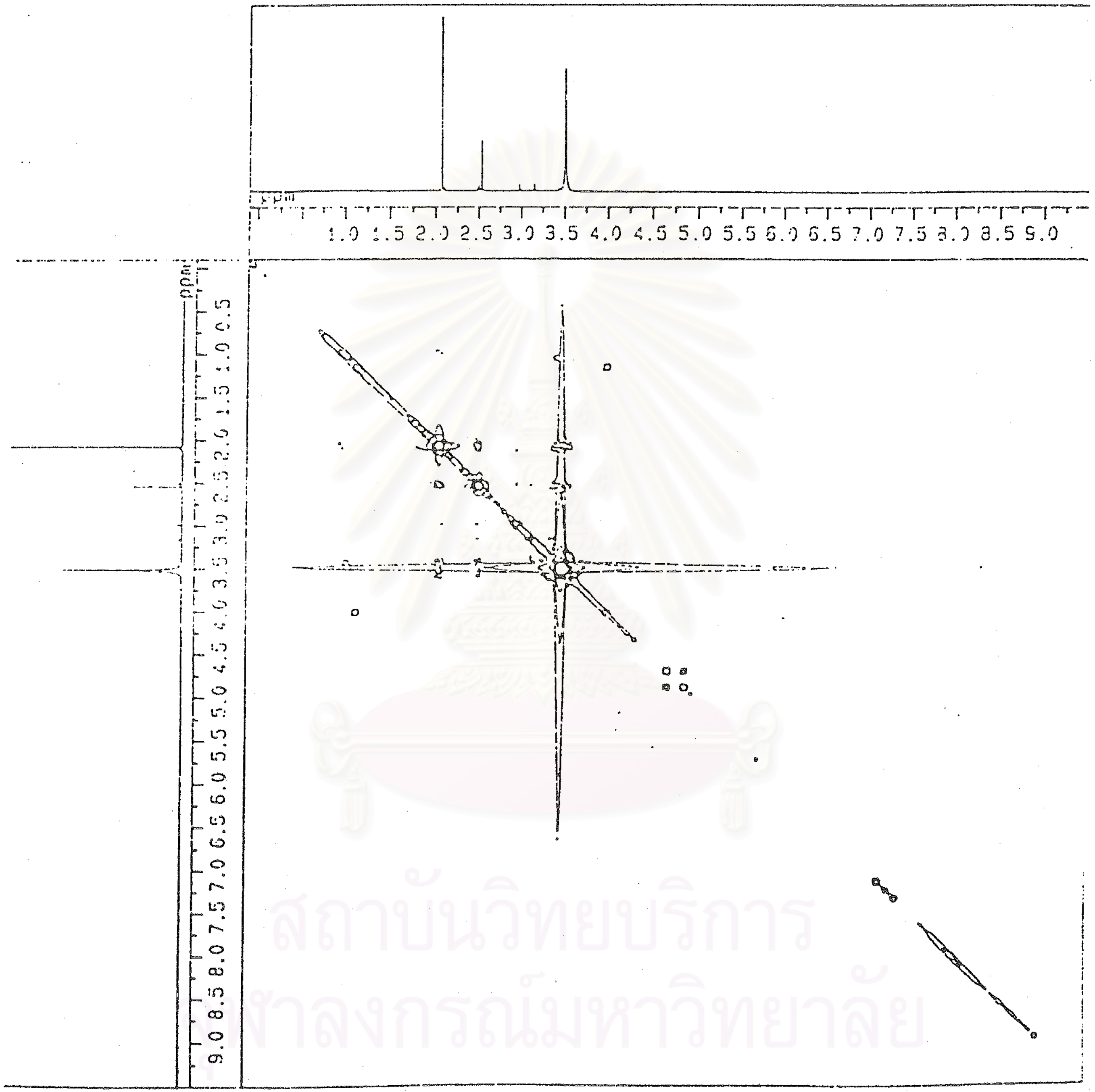

Figure 4.25 COSY NMR spectrum of DEC II fraction.

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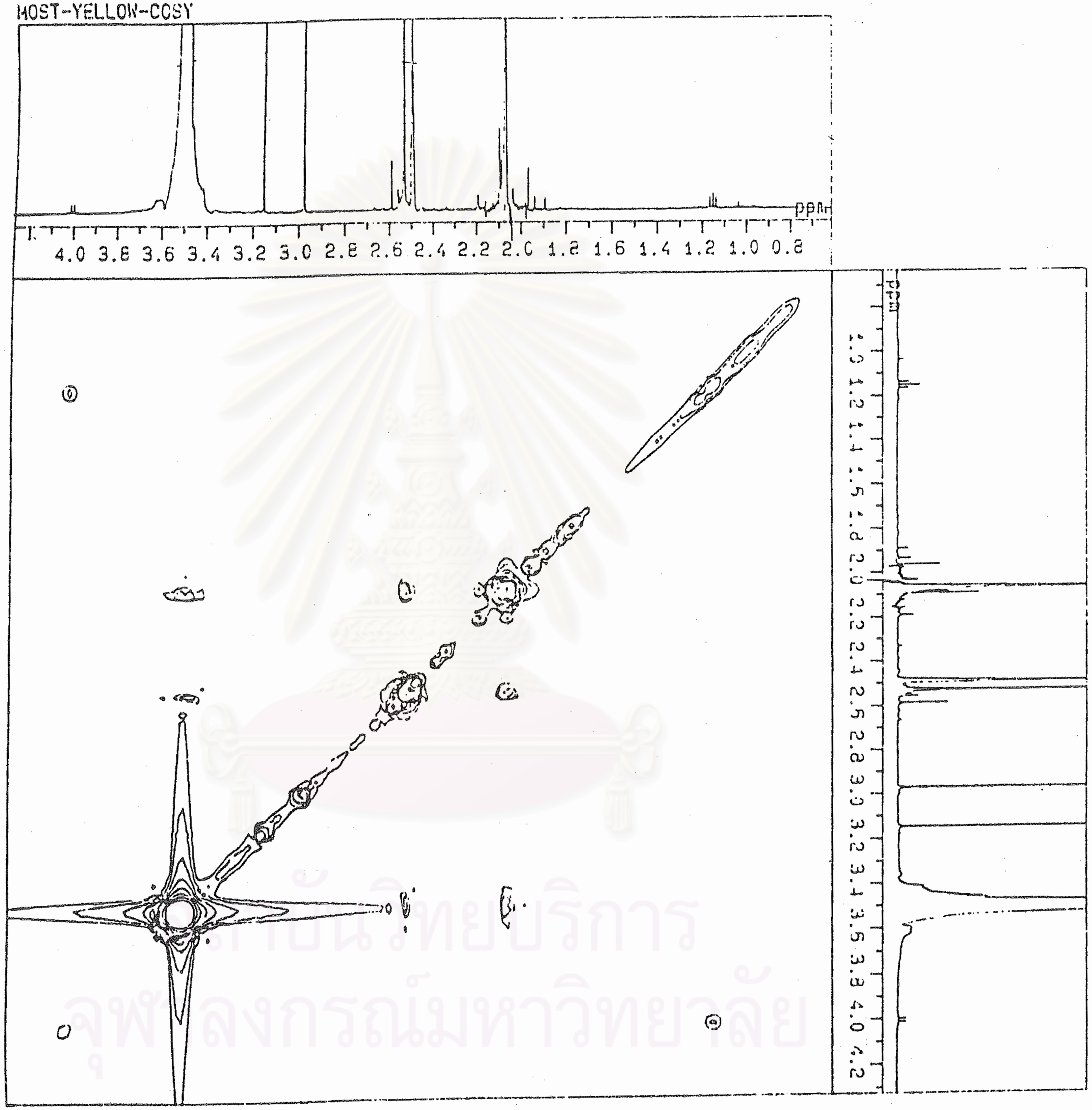

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Figure 4.26 COSY NMR spectrum of DEC II fraction.

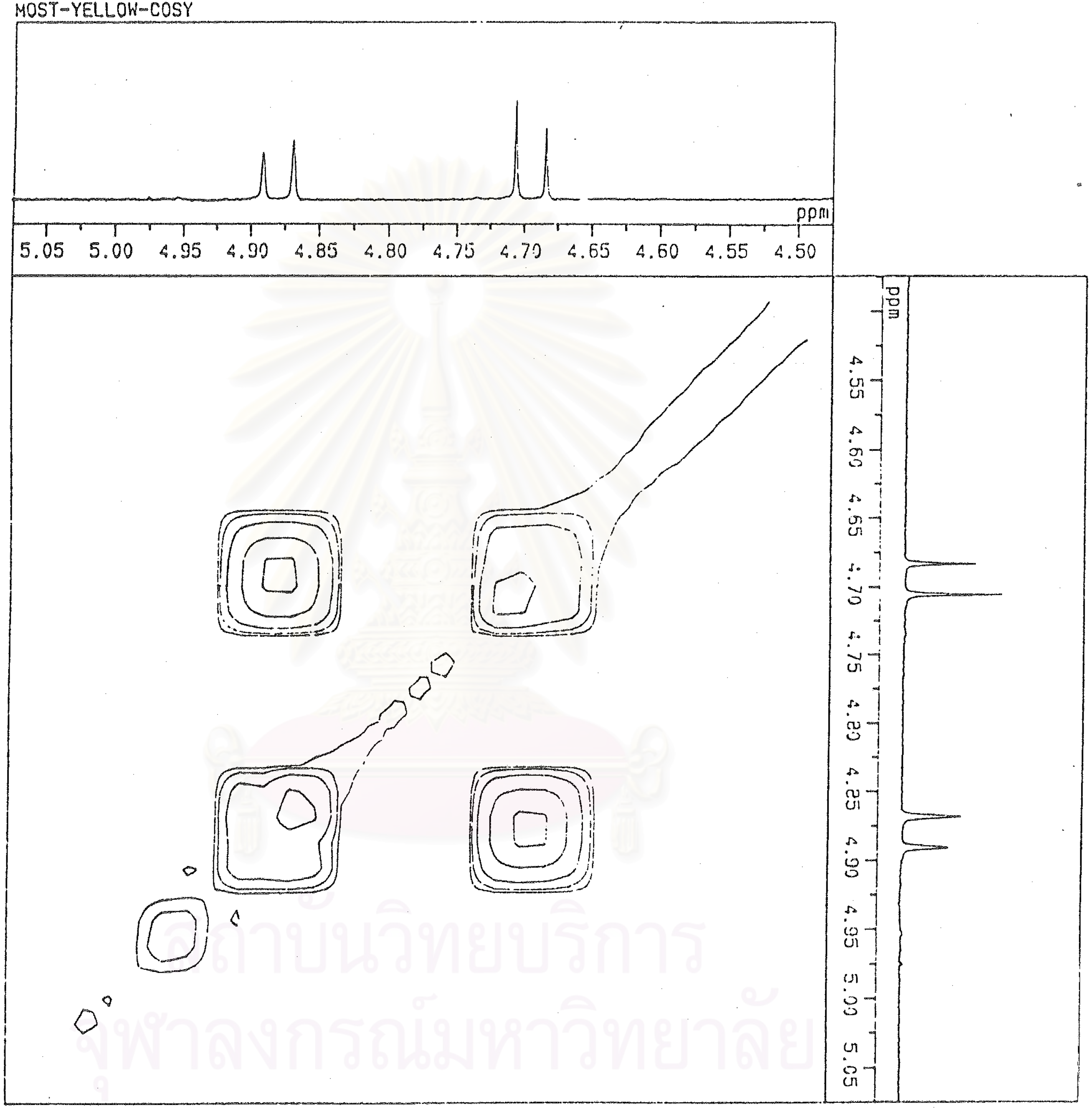

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Figure 4.27 COSY NMR spectrum of DEC II fraction.

From the NMR data, structure of compound A was deduced. Details of ^1H, ^{13}C and 2-d correlations are presented in Figure 4.28-4.32.

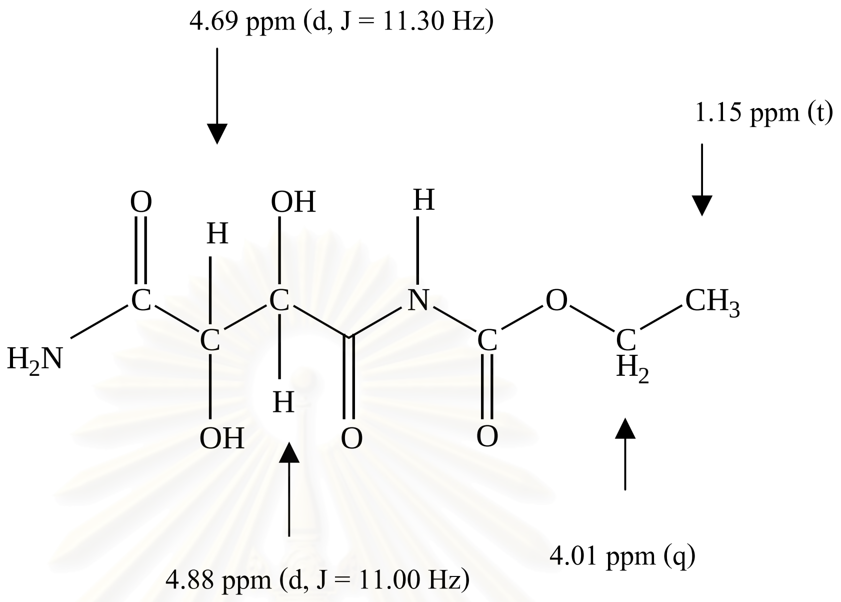

Figure 4.28 Assignments of ^1H NMR for compound A.

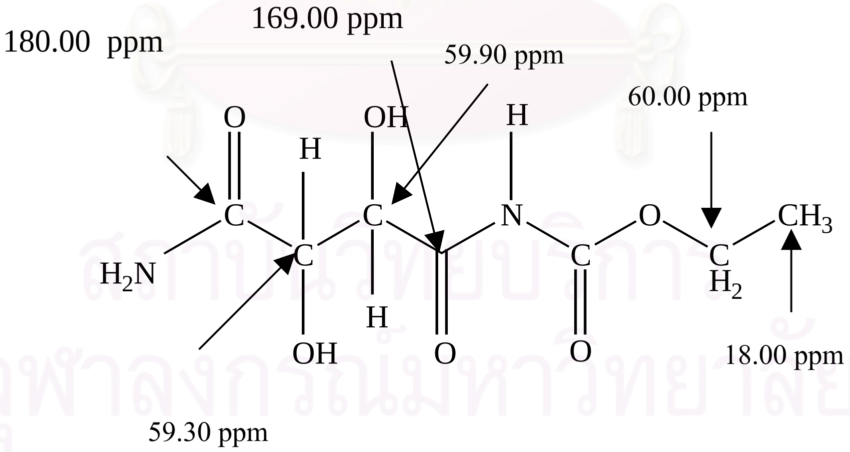

Figure 4.29 Assignments of ^{13}C NMR for compound A.

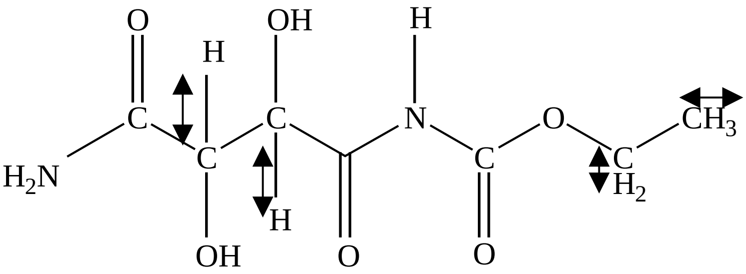

Figure 4.30 Assignments of HMQC spectra for compound A.

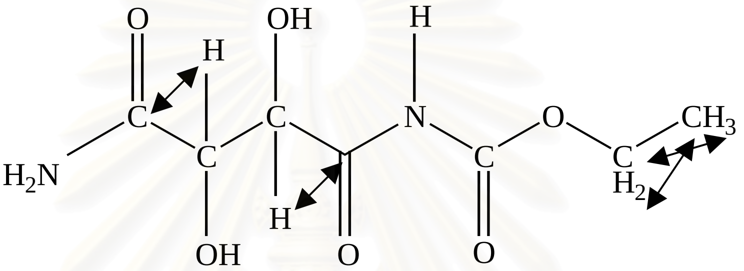

Figure 4.31 Assignments of HMBC correlation spectra for compound A.

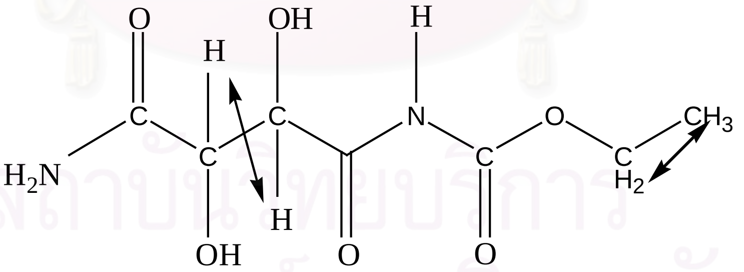

Figure 4.32 Assignments of COSY correlation spectra of compound A

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Confirmation of structure of compound A should be done by mass spectrometry. Moreover, the isolation process should also be repeated to confirm that compound A will always be present as a degradation product.

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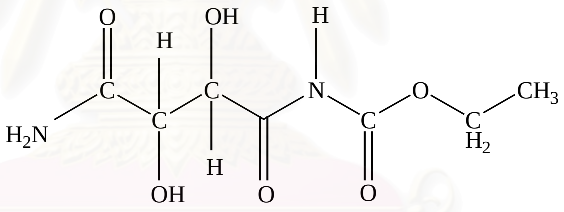
CHAPTER V

CONCLUSIONS AND SUGGESTION

1. Physical factors that most affecting the yellowing of N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer are in the order of heat, air and sunlight. Since heat is the most important factor in yellowing process of amino-silicone, the process is probably, thermal degradation.

2. Chemicals that could induce the yellowing of N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer are propylparaben and sodium laureth sulfate.

3. By using low pressure fractional distillation, solvent extraction and C-18 column chromatography, the most yellowish constituent in yellow N-(aminoethyl)aminopropyl methyl dimethyl polysiloxane copolymer could be isolated. Spectroscopic analyses yielded structure as shown below:



However, confirmation of this structure should be done by mass spectrometry.

4. Sodium laureth sulfate and propylparaben are the most yellow stimulating ingredients.

Suggestion for further works:

This work should be further studied by allowing amino-silicone to be yellow using air and sunlight. Then isolation of yellow species should be done. Comparison of the yellow species from the heat, air and sunlight should be done.

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APPENDICES

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APPENDIX I

Definition of active ingredients in shampoo

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Definition of active ingredients in shampoo

1. Akyposal EO

INCI Name : Sodium Laureth Sulfate

Definition : Sodium laureth sulfate is the sodium salt of sulfated ethoxylated lauryl alcohol that conforms generally to the formula: $CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOSO_3Na$

Where n averages between 1 and 4.

Chemical Classes : Alkyl ether sulfates; sulfonic acids

Function : Surfactant, cleansing agent, emulsifying agent

2. Akyposal NLS

INCI Name : Sodium Luaryl Sulfate

Empirical Formula : $C_{12}H_{26}O_4S.Na$

Definition : Sodium lauryl sulfate is the sodium salt of lauryl sulfate that conforms to the formula: $CH_3(CH_2)_{10}CH_2OSO_3Na$

Chemical Class : Alkyl sulfates

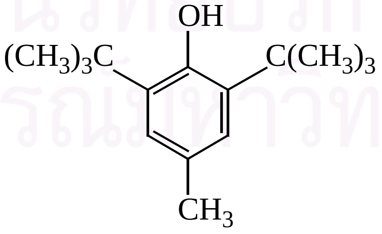
Function : Surfactant, cleansing agent

3. BHT

INCI Name : BHT

Empirical Formula : $C_{15}H_{24}O$

Definition : BHT is a substituted toluene that conforms to the formula:



Chemical Class : Phenols

Functions : Antioxidant, fragrance ingredient

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4. Celquat SC-230M

INCI Name : Polyquaternium-10

Definition : Polyquaternium-10 is a polymeric quaternary ammonium salt of hydroxyethylcellulose reacted with a trimethyl ammonium substituted epoxide.

Chemical Classes : Quaternary ammonium compounds; synthetic polymers

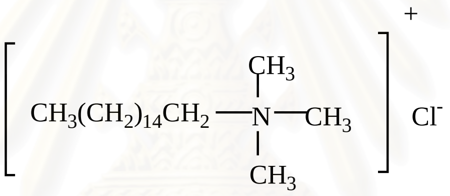
Functions : Antistatic agent; film former; hair fixative; hair conditioning agent

5. Cetrimonium Chloride

INCI Name : Cetrimonium Chloride

Formula : $C_{19}H_{42}N.Cl$

Definition : Cetrimonium chloride is a quaternary ammonium salt that conforms generally to the formula:



$$\left[CH_3(CH_2)_{14}CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} - CH_3 \right]^+ Cl^-$$

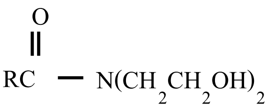
Chemical Classes : Quaternary ammonium compounds

Function : Antiststic agent, cosmetic biocide, surfactant-emulsifying agent

6. Comperland KD

INCI Name : Cocamide DEA

Definition : Cocamide DEA is a mixture of ethanolamides of cocos nucifera (coconut) acid. It conforms generally to the formula:



$$R\overset{\displaystyle O}{\overset{\|}{C}} - N(CH_2CH_2OH)_2$$

Where RCO^- represents the fatty acids derived from cocos nucifera (coconut) oil.

Chemical classes : Alkanolamides

Functions : Surfactant-foam booster; viscosity increasing agent

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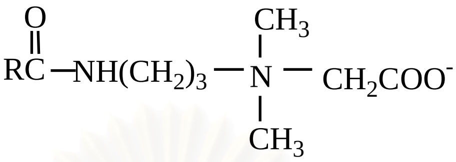
7. Dehyton K

INCI Name : Cocamidopropyl Betain

Definition : Cocamidopropyl betain is the switterion (inner salt).That conforms generally to the formula:



$$\overset{O}{\overset{\|}{RC}}-NH(CH_2)_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{N}}}}-CH_2COO^-$$

Where RCO^- represents the fatty acids derived from coconut oil.

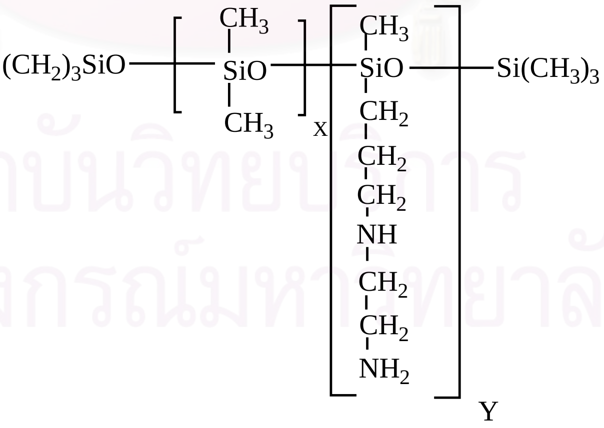
Chemical Classes : Betains

Function : Antistatic agent, hair conditioning agent, skin conditioning agent, miscellaneous, surfactant-cleansing agent, surfactant-foam booster, viscosity increasing agent

8. Dow Corning Q2-8220

INCI Name : Trimethylsilylamodimethicone

Definition : Trimethylsilylamodimethicone is a silicone polymer that conforms generally to the formula:



$$(CH_2)_3SiO-\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_x-\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_2\\ |\\ NH\\ |\\ CH_2\\ |\\ CH_2\\ |\\ NH_2\end{array}\right]_Y-Si(CH_3)_3$$

Chemical Classes : Amines; silicone and silanes

Functions : Antistatic agent; hair conditioning agent; skin conditioning agent-emollient

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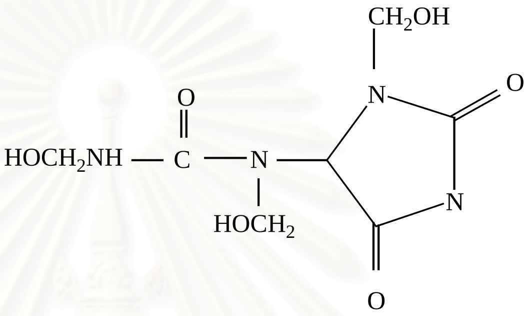
9. Germaban II

INCI Name : Propylene Glycol (&) Diazolidinyl Urea (&) Methylparaben (&) Propylparaben

Diazolidinyl Urea

Formula : $C_8H_{14}N_4O_7$

Definition : Diazolidinyl urea is the heterocyclic substituted urea that conforms to the formula:

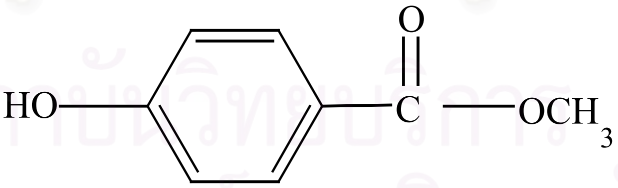


Function : Preservative

Methylparaben

Formula : $C_8H_8O_3$

Definition : Methylparaben is the ester of methyl alcohol and *p*-hydroxybenzoic acid it conforms to the formula:



Chemical Classes : Esters, phenols

Function : Preservative

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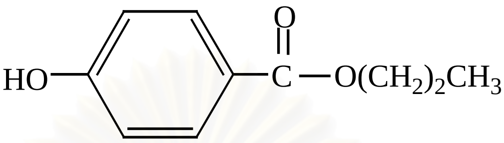
Propyparaben

Formula : $C_{10}H_{12}O_3$

Definitions : Propylparaben is the ester of *n*-propyl alcohol and *p*-hydroxybenzoic acid it conforms to the formula:



Chemical Classes :Ester, phenols

Function : Fragrance ingredient, preservative.

10. Glucamate LT

INCI Name : PEG-120 Methyl Glucose Trioleate

Definition : PEG-120 methyl glucose trioleate is the polyethylene glycol ether of the triester of methyl glucose and oleic acid with an average of 120 moles of ethylene oxide.

Chemical Classes : Alkoxylated alcohols ; carbohydrates

Functions : Skin-conditioning agent-emollient, surfactant, cleansing agent, viscosity increasing agent

11. Phenyl Trimethicone

INCI Name : Phenyl Trimethicone

Empirical Formula : $C_3H_9SiO\ (C_9H_{15}SiO_2)_X\ SiC_3H_9$

Definition : Phenyl trimethicone is the siloxane polymer that conforms generally
to the formula:

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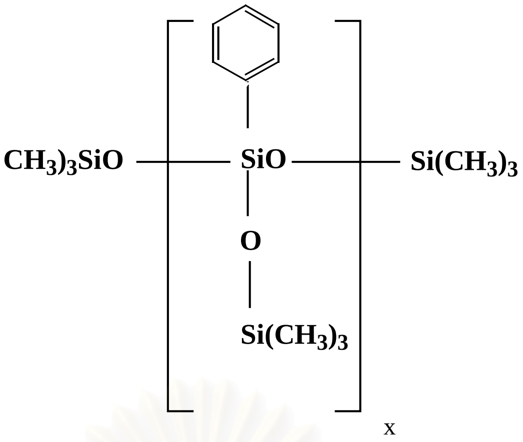


Chemical Classes : Silicones and silanes

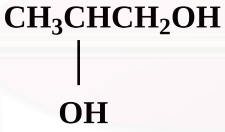
Function : Antifoaming agent; hair conditioning agent; skin-conditioning agent-occlusive

12. Propylene Glycol

INCI NAME : Propylene Glycol

Formula : $C_3H_8O_2$

Definition : Propylene glycol is the aliphatic alcohol that conforms generally to the formula:



$$CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_2OH$$

Functions : Fragrance ingredient, humectant, skin-conditioning agent, solvent, viscosity decreasing agent.

13. Sodium Metabisulfite

INCI Name : Sodium Metabisulfite

Empirical Formula : $H_2O_5S_2.2Na$

Definition : Sodium metabisulfite is the inorganic salt that conforms to the formula: $Na_2S_2O_5$

Chemical Class : Inorganic salts

Functions : Antioxidant; reducing agent

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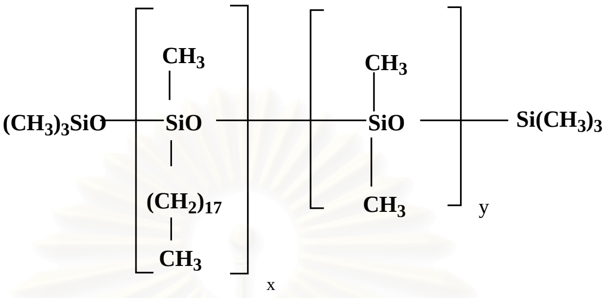
14. Stearyl Dimethicone

INCI Name : Stearyl Dimethicone

Empirical Formula : $C_3H_9SiO\ (SiOC_{19}H_{40})_x\ (SiOC_2H_6)_y\ SiC_3H_9$

Definition : Stearyl dimethicone is the silicone polymer that conforms generally to the formula:



Chemical Classes : Silicones and silanes

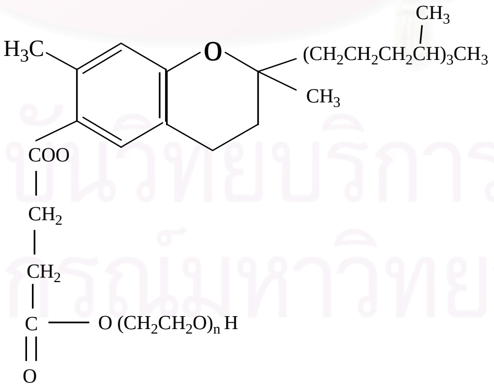
Function : Skin-conditioning agent-occlusive

15. Tocophersolan

INCI Name : Tocosphersolan

Empirical Formula : $C_{33}H_{54}O_5\ .\ (C_2H_4O)_n$

Definition : Tocophersolan is the organic compound that conforms to the formula: Where n has an average value of 22.



Chemical Classes : Alkoxylated carboxylic acids; esters, heterocyclic compounds

Function : Antioxidant

APPENDIX II

UV-absorbance data of shampoo A, B, C and D

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Table I UV-absorption of shampoo formulation A, B, C and D.

Formulation	Storage condition	Absorbance/weeks					
		1	2	3	4	5	6
A	RT/Dark/Air	0	0.02	0.15	0.45	0.50	2.72
	RT/Light/Air	0	0.04	0.24	0.60	0.65	2.78
	RT/Light/Nitrogen	0	0.01	0.18	0.42	0.45	2.59
	RT/Dark/Nitrogen	0	0.02	0.12	0.25	0.38	2.59
	60^{o}C/Dark/Air	0	0.04	0.57	0.80	1.50	3.00
	60^{o}C/Light/Air	0	0.05	0.70	0.97	2.50	3.02
	60^{o}C/Light/Nitrogen	0	0.02	0.59	0.86	2.20	2.90
	60^{o}C/Dark/Nitrogen	0	0.04	0.43	0.75	1.10	2.84
B	RT/Dark/Air	0	0.10	0.30	0.40	1.06	2.85
	RT/Light/Air	0	0.13	0.30	0.63	0.31	2.88
	RT/Light/Nitrogen	0	0.05	0.28	0.32	0.29	2.82
	RT/Dark/Nitrogen	0	0.08	0.25	0.30	0.61	2.76
	60^{o}C/Dark/Air	0	0.18	0.59	0.98	2.82	3.00
	60^{o}C/Light/Air	0	0.25	0.74	1.14	2.94	3.50
	60^{o}C/Light/Nitrogen	0	0.16	0.51	0.70	2.76	3.00
	60^{o}C/Dark/Nitrogen	0	0.10	0.40	0.66	2.52	3.00
C	RT/Dark/Air	0	0.023	0.13	0.40	0.75	1.73
	RT/Light/Air	0	0.08	0.17	0.40	1.2	1.74
	RT/Light/Nitrogen	0	0.03	0.11	0.35	0.70	1.70
	RT/Dark/Nitrogen	0	0.02	0.10	0.20	0.60	0.70
	60^{o}C/Dark/Air	0	0.20	0.20	0.80	2.30	2.60
	60^{o}C/Light/Air	0	0.40	0.40	1.28	2.43	2.61
	60^{o}C/Light/Nitrogen	0	0.14	0.30	0.76	2.00	2.55
	60^{o}C/Dark/Nitrogen	0	0.13	0.25	0.70	1.73	1.90
D	RT/Dark/Air	0	0.03	0.10	0.14	2.59	2.70
	RT/Light/Air	0	0.032	0.15	0.25	2.63	2.75
	RT/Light/Nitrogen	0	0.01	0.10	0.23	2.60	2.70
	RT/Dark/Nitrogen	0	0.008	0.09	0.12	2.50	2.64
	60^{o}C/Dark/Air	0	0.10	0.19	0.40	2.70	2.74
	60^{o}C/Light/Air	0	0.08	0.25	0.45	2.73	2.79
	60^{o}C/Light/Nitrogen	0	0.06	0.16	0.35	2.70	2.70
	60^{o}C/Dark/Nitrogen	0	0.05	0.13	0.27	2.69	2.69

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VITA

Miss Jintana Pocharoen was born on June 23, 1978 in Bangkok province, Thailand. She graduated with a degree of Bachelor of Science in Chemistry from Chulalongkorn University in 1999. In the same year, she was admitted into a Master Degree Program of Petrochemistry and Polymer Science, Faculty of Science at Chulalongkorn University and she completed the program in 2003.

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