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PHYTOCHEMICAL STUDY OF *CAESALPINIA CORIARIA* LEAVES

Miss Chaithaya Saengngoen

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By	Miss Chaithaya Saengngoen
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Thesis advisor	Witchuda Thanakijcharoenpath, Ph.D.

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(Associate Professor Rapepol Bavovada, Ph.D.)

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(Associate Professor Rutt Suttisri, Ph.D.)

.....Member

(Associate Professor Chaiyo Chaichantipyuth, Ph.D.)

ไฉทยา แสงเงิน : การศึกษาทางพฤกษเคมีของใบตันหยง (PHYTOCHEMICAL STUDY OF *CAESALPINIA CORIARIA* LEAVES) อาจารย์ที่ปรึกษา : อ.ดร. วิชชุดา ธนกิจเจริญพัฒน์, 123 หน้า. ISBN 974-14-2487-6

จากสารสกัดส่วนเฮกเซนของใบตันหยง (วงศ์ Leguminosae, วงศ์ย่อย Caesalpinoideae) สามารถแยกได้สารในกลุ่มไดเทอร์ปีนอยด์ คือ ไดเอสเทอร์ของ 7,11,15-trimethyl-3-methylene-hexadecan-1,2-diol และสารผสมของไตรเทอร์ปีนอยด์ 2 ชนิดคือ lupeol กับ germanicol รวมทั้งได้สารผสมของ β-sitosterol และ stigmasterol การพิสูจน์เอกลักษณ์ของสารเหล่านี้ทำโดยการวิเคราะห์ข้อมูล IR, MS, ^{1}H-NMR และ ^{13}C-NMR ร่วมกับการเปรียบเทียบข้อมูลที่ได้มีรายงานไว้แล้ว

ภาควิชา เภสัชพฤกษศาสตร์ ลายมือชื่อนิสิต.....

สาขาวิชา เภสัชพฤกษศาสตร์ ลายมือชื่ออาจารย์ที่ปรึกษา.....

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From the hexane extract of the leaves of *Caesalpinia coriaria* (family Leguminosae, subfamily Caesalpinoideae) a diester of an acyclic diterpenoid , 7,11,15-trimethyl-3-methylene-hexadecan-1,2-diol, a triterpenoid mixture of lupeol and germanicol, together with a mixture of β-sitosterol and stigmasterol, were isolated. Analysis of IR, MS, ^{1}H-NMR and ^{13}C-NMR data as well as comparison with reported values were used for the identification of these compounds.

Department Pharmaceutical Botany Student's signature Chaithaya Saengngoen
Field of study Pharmaceutical Botany Advisor's signature Witchuda Thanakijcharoenpath
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CHAPTER I

INTRODUCTION

Caesalpinia coriaria (Jacq.) Willd. or Divi Divi is one of about 100 species of the genus *Caesalpinia* of subfamily Caesalpinoideae of the family Leguminosae (Larsen, Larsen and Vidal, 1984). It is a small tree native to the West Indies (Backer and Van der brink, 1965) and the South America (Larsen, Larsen and Vidal, 1984). In Thailand, it is cultivated and known as "Tan Yong". Morphological characteristics of the plant are described below (Backer and Van der brink, 1965; Larsen, Larsen and Vidal, 1984).

The plant is an unarmed, crooked tree with the tops of branchlets zigzagging. The stipules an minute, subulate. The leaves are imparipinnate. The main rachis is finely hairy, on the top is usually with 3 pinnae, whereas beneath these with 3-9 pairs of pinnae. The pinnae are 2-5.5 cm long. The leaflets are sessile, in 15-28 pairs, 5-9 by 1-2 mm. They are oblong-linear, rounded, glabrous, with brownish red or black dots beneath, 4-9 mm by 1.5-2.5 cm. The flowers are small, fragrant, in terminal and axillary clusters. Inflorescences are panicle densely short-hairy, 2-6 cm long. The pedicels are 2-3 mm long. The petals are pale yellow, 3-4 mm long. The calyx and ovary are glabrous with red style. The pods are strap-shaped, flexuous and twisted, 2-6 cm by 1.5-3 cm. The seeds are 1-10, albuminous.

In Thailand, 18 species of *Caesalpinia* can be found as follows (ส่วนพฤกษศาสตร์ป่าไม้ สำนักวิชาการป่าไม้ กรมป่าไม้, 2544).

1. *Caesalpinia andamanica* (Prain) Hattink
2. *C. bonduc* (L.) Roxb.
3. *C. coriaria* (Jacq.) Willd.
4. *C. crista* L.
5. *C. cucullata* Roxb.
6. *C. decapetala* (Roth) Alston
7. *C. digyna* Rottler
8. *C. enneaphylla* Roxb.
9. *C. furfuracea* (Prain) Hattink

10. *C. godefroyana* Kuntze
11. *C. hymenocarpa* (Prain) Hattink
12. *C. major* (Medik.) Dandy & Exell
13. *C. mimosoides* Lam.
14. *C. minax* Hance
15. *C. parviflora* Prain
16. *C. pubescens* (Desf.) Hattink
17. *C. pulcherrima* (L.) Sw.
18. *C. sappan* L.

Several plants of the genus *Caesalpinia* have been used in traditional medicine for the treatment of a variety of diseases and disorders e.g. fungal infections (*C. pulcherrima*), malaria (*C. bonduc, C. crista*), dysentery (*C. minax, C. pulcherrima*), liver disorders (*C. pulcherrima*), rheumatism (*C. crista, C. decapetala, C. major*), neuralgia (*C. decapetala*) and thrombosis (*C. sappan*). Some of these plants, together with other *Caesalpinia* species, were subjected to biological investigation and the results indicated that a number of these plants contained components which exerted interesting bioactivities e.g. antiviral (*C. minax, C. pulcherrima*), antimalarial (*C. crista, C. pulcherrima, C. pluviosa, C. volkensii*), antitubercular (*C. bonduc, C. pulcherrima*), anti-inflammatory (*C. pulcherrima*), anticonvulsant (*C. sappan*) and hypoglycemic (*C. bonducella*) activities.

Chemical investigation of *Caesalpinia* species has been undertaken and a variety of compounds including diterpenoids, triterpenoids, steroids, flavonoids and other miscellaneous substances have been isolated. The most interesting compound group is cassane furanoditerpenoids which are characteristic of the plant genus.

In preliminary screening on the leaves of *C. coriaria,* the result suggested the presence of flavonoids, triterpenoids and steroids. Since there have been only a few previous reports on the phytochemical study of this plant, and such compounds as suggested by the preliminary screening have never been reported, it is interesting to conduct an investigation on the chemical composition of the plant. This study deals with the isolation of chemical constituents from the leaves of *C. coriaria* and the elucidation of their structures. The result obtained might provide useful information in the field of phytochemistry and chemotaxonomy.

Flowers

Pods

Leaves

Figure 1. *Caesalpinia coriaria* (Jacq.) Willd.

CHAPTER II

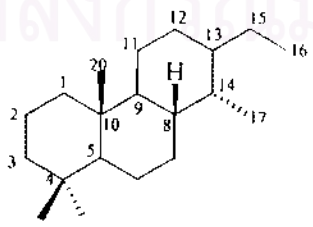
HISTORICAL

1. Chemical Constituents of *Caesalpinia* species

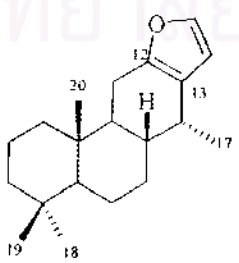
Chemical investigation of some *Caesalpinia* species has been undertaken, revealing the presence of diterpenoids as major. Other compounds found in plants of this genus include sesquiterpenoids, triterpenoids, steroids, flavonoids and other miscellaneous phytochemicals.

1.1 Diterpenoids

Plants belonging to the genus *Caesalpinia* have been proven to be a rich source of cassane furanoditerpenes which are characteristic components of the genus. The molecular skeleton of these diterpenoids is called vouacapane, which is constructed from the fusion of three cyclohexane rings and a furan ring. These compounds can be classified into five categories: (1) tricarbocyclic derivatives fused with a furan ring e.g. c-caesalpin (**39**); (2) tricarbocyclic derivatives with an α,β-butenolide e.g. neocaesalpin C (**76**); (3) tricarbocyclic derivatives with cleavage of the furan ring e.g. caesaldekarin G (**32**); (4) rearranged furanoditerpenoids with migration of the C-4 methyl group to C-3 e.g. caesalpinin (**43**); and (5) furanoditerpenoid lactones constructed from ring closure involving the oxygen atom bridged to C-7 and C-17 e.g. caesalmin A (**93**) (Jiang *et al*., 2002b). The distribution of diterpenoids in the genus *Caesalpinia* is summarized in Table 1.



cassane



vouacapane

Table 1. Distribution of diterpenoids in the genus *Caesalpinia*.

Compound	Source	Plant part	Reference
vouacapen-5α-ol (**1**)	*C. pulcherrima*	root	McPherson *et al.*, 1986
1α,5α,6α,7β,14β-pentahydroxyvouacapane (**2**)	*C. minax*	seed	Jiang *et al.*, 2002b
1α,5α-dihydroxy-14β-methoxy-6α,7β- diacetoxyvouacapane (**3**)	*C. minax*	seed	Jiang *et al.*, 2002b
1α,5α,14α-trihydroxy-6α-7β-diacetoxyvouacapane (**4**)	*C. minax*	seed	Jiang *et al.*, 2002b
6β-benzoyl-7β- hydroxyvouacapen-5α-ol (**5**)	*C. pulcherrima*	root	Promsawan *et al.*, 2003
6β-cinnamoyl-7β- hydroxyvouacapen-5α-ol (**6**)	*C. pulcherrima*	root	McPherson *et al.*, 1986; Promsawan *et al.*, 2003; Roach *et al.*, 2003
8,9,11,14-didehydrovouacapen-5α-ol (**7**)	*C. minax*	root	Roach *et al.*, 2003, McPherson *et al.*, 1986
isovouacapenol A (**8**)	*C. pulcherrima*	leaves	Roach *et al.*, 2003
isovouacapenol B (**10**)	*C. pulcherrima*	leaves	Roach *et al.*, 2003
isovouacapenol C (**11**)	*C. pulcherrima*	leaves, root	Roach *et al.*, 2003
keto- isovouacapenol C (**12**)	*C. pulcherrima*	root	Roach *et al.*, 2003
isovouacapenol C monoacetate (**13**)	*C. pulcherrima*	root	Roach *et al.*, 2003
6β-hydroxyisovouacapenol C (**14**)	*C. pulcherrima*	root	Roach *et al.*, 2003
7β-acetyl-6β- hydroxyisovouacapenol C (**15**)	*C. pulcherrima*	root	Roach *et al.*, 2003

Table 1. Distribution of diterpenoids in the genus *Caesalpinia* (continued).

Compound	Source	Plant part	Reference
isovouacapenol D (**16**)	*C. pulcherrima*	leaves	Roach *et al.*, 2003
isovouacapenol E (**9**)	*C. pulcherrima*	leaves	Ragasa *et al.*, 2003
bonducellpin A (**17**)	*C. bonduc*	root	Peter and Tinto, 1997b
bonducellpin B (**18**)	*C. bonduc*	root	Peter and Tinto, 1997b
bonducellpin C (**19**)	*C. bonduc*	root	Peter and Tinto, 1997b
7-acetoxybonducellpin C (**20**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004
bonducellpin D (**21**)	*C. bonduc*	root	Peter and Tinto, 1997b; Jiang *et al.*, 2002b
caesaldecan (**22**)	*C. decapetala*	leaves	Kiem *et al.*, 2005
caesaldekarin A (**23**)	*C. bonduc*	root	Lyder *et al.*, 1998
	C. major	root	Kitagawa *et al.*, 1994
	C. minax	seed	Jiang *et al.*, 2001a
	C. pulcherrima	leaves	Ragasa *et al.*, 2003
caesaldekarin B (**24**)	*C. major*	root	Kitagawa *et al.*, 1994
caesaldekarin C (**25**)	*C. bonducella*	root	Peter *et al.*, 1998
	C. major	root	Kitagawa *et al.*, 1996
caesaldekarin D (**26**)	*C. major*	root	Kitagawa *et al.*, 1996

Table 1. Distribution of diterpenoids in the genus *Caesalpinia*(continued).

Compound	Source	Plant part	Reference
caesaldekarin E (**27**)	*C. major*	root	Kitagawa *et al.*, 1996
2-acetoxycaesaldekarin E (**28**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005b
2-acetoxy-3-deacetoxycaesaldekarin E (**29**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005b
6- acetoxy-3- deacetoxycaesaldekarin E (**30**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004
caesaldekarin F (**31**)	*C. bonducella*	root	Peter *et al.*, 1998
caesaldekarin G (**32**)	*C. bonducella*	root	Peter *et al.*, 1998
caesaldekarin H (**33**)	*C. bonduc*	root	Lyder *et al.*, 1998
caesaldekarin I (**34**)	*C. bonduc*	root	Lyder *et al.*, 1998
caesaldekarin J (**35**)	*C. bonduc*	root	Lyder *et al.*, 1998
caesaldekarin K (**36**)	*C. bonduc*	root	Lyder *et al.*, 1998
caesaldekarin L (**37**)	*C. bonduc*	root	Lyder *et al.*, 1998
caesaljapin (**38**)	*C. decapetala*	root	Ogawa, Aoki and Sashida, 1992
ε-caesalpin (**39**)	*C. minax*	seed	Jiang *et al.*, 2001a
14-deoxy-ε-caesalpin (**40**)	*C. major*	seed kernel	Roengsumran *et al.*, 2000
caesalpin F (**41**)	*C. crista*	seed kernel	Linn *et al.*, 2005
	C. bonducella	seed kernel	Pascoe, Burke and Chan, 1986

Table 1. Distribution of diterpenoids in the genus *Caesalpinia* (continued).

Compound	Source	Plant part	Reference
14(17)-dehydrocaesalpin F (**42**)	*C. crista*	seed kernel	Linn *et al.*, 2005
caesalpinin (**43**)	*C. bonducella*	root	Peter *et al.*, 1997a
caesalpinin C (**44**)	*C. crista*	seed kernel	Linn *et al.*, 2005
caesalpinin D (**47**)	*C. crista*	seed kernel	Linn *et al.*, 2005; Kalauni *et al.*, 2005a
caesalpinin E (**45**)	*C. crista*	seed kernel	Linn *et al.*, 2005; Kalauni *et al.*, 2005a
caesalpinin F (**52**)	*C. crista*	seed kernel	Linn *et al.*, 2005; Kalauni *et al.*, 2005a
caesalpinin G (**48**)	*C. crista*	seed kernel	Linn *et al.*, 2005
caesalpinin H (**49**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin I (**50**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin J (**53**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin K (**54**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin L (**55**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin M (**56**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin N (**57**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin O (**51**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005a; Awale *et al.*, 2006
caesalpinin P (**46**)	*C. crista*	seed kernel	Awale *et al.*, 2006

Table 1. Distribution of diterpenoids in the genus *Caesalpinia* (continued).

Compound	Source	Plant part	Reference
caesalpinin MA (**58**)	*C. crista*	seed kernel	Kalauni *et al*., 2004
caesalpinin MB (**59**)	*C. crista*	seed kernel	Kalauni *et al*., 2004
caesalpinin MC (**64**)	*C. crista*	seed kernel	Kalauni *et al*., 2004
caesalpinin MD (**65**)	*C. crista*	seed kernel	Kalauni *et al*., 2004
caesalpinin ME (**67**)	*C. crista*	seed kernel	Kalauni *et al*., 2004
caesalpinin MF (**60**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin MG (**61**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin MH (**62**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin MI (**63**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin MJ (**68**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin MK(**69**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin ML (**70**)	*C. crista*	seed kernel	Kalauni *et al*., 2005a
caesalpinin MM (**71**)	*C. crista*	seed kernel	Kalauni *et al*., 2005b
caesalpinin MN (**72**)	*C. crista*	seed kernel	Kalauni *et al*., 2005b
caesalpinin MO (**73**)	*C. crista*	seed kernel	Kalauni *et al*., 2005b
caesalpinin MP (**66**)	*C. crista*	seed kernel	Kalauni *et al*., 2005b

Table 1. Distribution of diterpenoids in the genus *Caesalpinia* (continued).

Compound	Source	Plant part	Reference
neocaesalpin A (**74**)	*C. bonduc*	seed	Kinoshita *et al.*,1996; Roach *et al.*,2003
neocaesalpin B (**75**)	*C. major*	seed kernel	Kinoshita *et al.*,1996; Roengsumran *et al.*,2000
neocaesalpin C (**76**)	*C. bonduc*	seed	Kinoshita, 2000
neocaesalpin D (**77**)	*C. bonduc*	seed	Kinoshita, 2000
neocaesalpin E (**78**)	*C. pulcherrima*	root	Roach *et al.*, 2003
neocaesalpin F (**79**)	*C. pulcherrima*	root	Roach *et al.*, 2003
neocaesalpin G (**80**)	*C. pulcherrima*	root	Roach *et al.*, 2003
neocaesalpin H (**81**)	*C. crista*	leaves	Kinoshita, 2005
neocaesalpin I (**82**)	*C. crista*	leaves	Kinoshita, 2005
norcaesalpinin A (**83**)	*C. crista*	seed kernel	Linn *et al.*, 2005
norcaesalpinin B (**84**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004; Linn *et al.*, 2005
norcaesalpinin C (**90**)	*C. crista*	seed kernel	Linn *et al.*, 2005
norcaesalpinin D (**85**)	*C. crista*	seed kernel	Linn *et al.*, 2005
norcaesalpinin E (**86**)	*C. crista*	seed kernel	Linn *et al.*, 2005
norcaesalpinin F (**87**)	*C. crista*	seed kernel	Awale *et al.*, 2006

Table 1. Distribution of diterpenoids in the genus *Caesalpinia* (continued).

Compound	Source	Plant part	Reference
norcaesalpinin MA (**91**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004
norcaesalpinin MB (**92**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004
norcaesalpinin MC (**88**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004
norcaesalpinin MD (**89**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005
caesalmin A (**93**)	*C. minax*	seed	Jiang *et al.*, 2001a
caesalmin B (**94**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004; Linn *et al.*, 2005
	C. minax	seed	Jiang *et al.*, 2001a, 2002a
caesalmin C (**96**)	*C. crista*	seed kernel	Kalauni *et al.*, 2004
	C. minax	seed	Jiang *et al.*, 2001c
1-deacetylcaesalmin C (**97**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005b
1-deacetyl-1-oxocaesalmin C (**98**)	*C. crista*	seed kernel	Kalauni *et al.*, 2005b
caesalmin D (**99**)	*C. minax*	seed	Jiang *et al.*, 2001c
caesalmin E (**100**)	*C. minax*	seed	Jiang *et al.*, 2001c
	C. crista	seed kernel	Kalauni *et al.*, 2004
caesalmin F (**101**)	*C. crista*	seed kernel	Linn *et al.*, 2005
	C. minax	seed	Jiang *et al.*, 2001c

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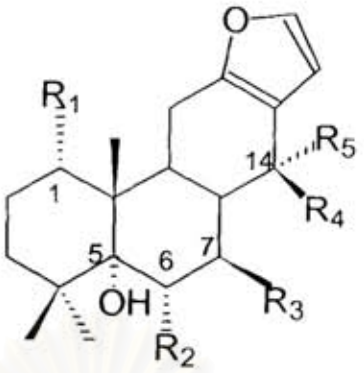
Table 1. Distribution of diterpenoids in the genus *Caesalpinia* (continued).

Compound	Source	Plant part	Reference
taepeenin E (**115**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
taepeenin F (**116**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
taepeenin G (**117**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
taepeenin H (**118**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
taepeenin I (**119**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
vinhaticoic acid (**120**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
methyl vinhaticoate (**121**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
nortaepeenin A (**122**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
nortaepeenin B (**123**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005
17-methylvouacapane-8(14), 9(11)-diene (**124**)	*C. crista*	seed kernel	Jadhav, Kaur and Bhutani, 2003
spirocaesalmin (**125**)	*C. minax*	seed	Jiang *et al.*, 2001b
macrocaesalmin (**126**)	*C. minax*	seed	Jiang *et al.*, 2002a
ent-11β-hydroxy-rosa-5,15-diene (**127**)	*C. crista*	stems and root	Cheenpracha *et al.*, 2005



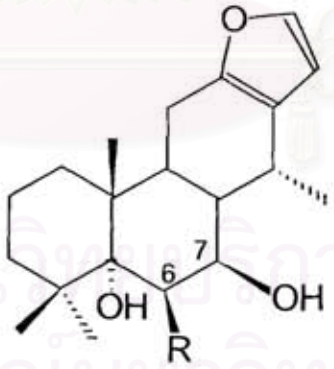
vouacapen-5α-ol **(1)**

1α,5α,6α,7β,14β-pentahydroxyvouacapane **(2)**

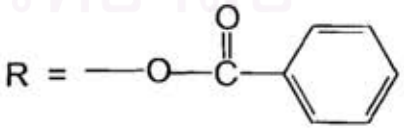
1α,5α-dihydroxy-14β-methoxy-6α,7β-diacetoxyvouacapane **(3)**

1α,5α,14α-trihydroxy-6α,7β-diacetoxyvouacapane **(4)**

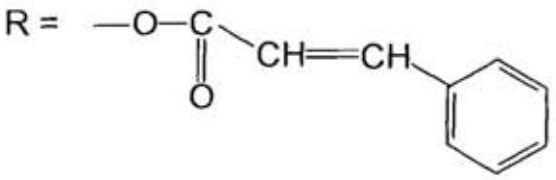
	R_1	R_2	R_3	R_4	R_5
(1)	H	H	H	H	CH_3
(2)	OH	OH	OH	OH	CH_3
(3)	OH	OAc	OAc	OCH_3	CH_3
(4)	OH	OAc	OAc	CH_3	OH

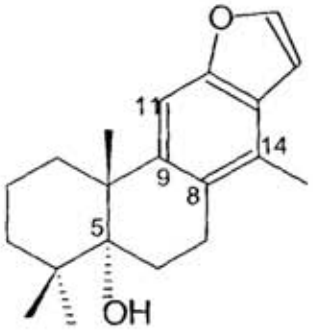


6β-benzoyl-7β-hydroxyvouacapen-5α-ol **(5)**

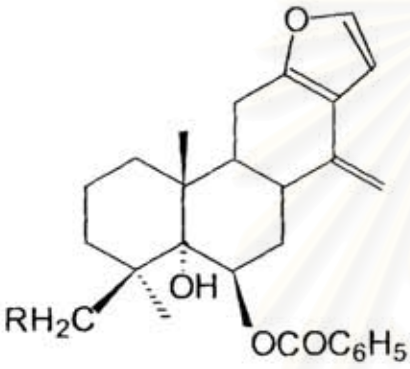


6β-cinnamoyl-7β-hydroxy vouacapen-5α-ol **(6)**



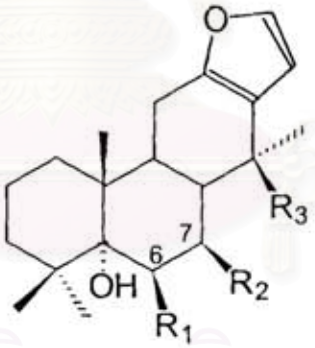


8,9,11,14-didehydrovoucapen-5α-ol (**7**)

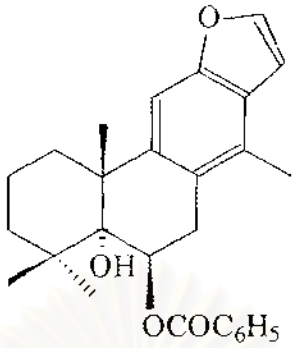


isovoucapenol A (**8**) R = H

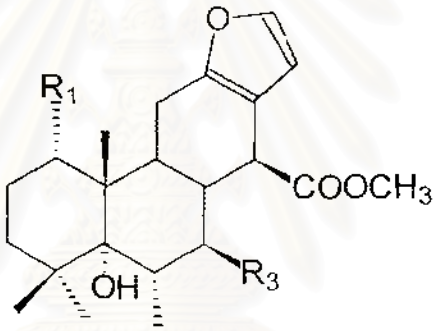
isovoucapenol E (**9**) R = $OCOC_6H_5$



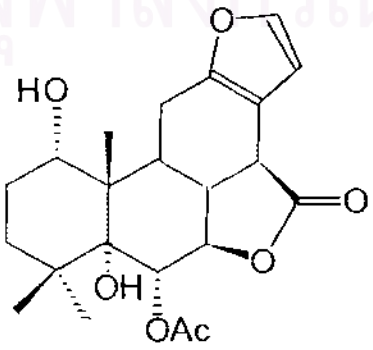
	R_1	R_2	R_3
isovouacapenol B (**10**)	$OCOC_6H_5$	H	OH
isovouacapenol C (**11**)	$OCOC_6H_5$	OH	H
keto-isovouacapenol C (**12**)	$OCOC_6H_5$	= O	H
isovouacapenol C monoacetate (**13**)	$OCOC_6H_5$	$OCOCH_3$	H
6β-hydroxy isovouacapenol C (**14**)	OH	OH	H
7β-acetyl-6β- hydroxy isovouacapenol C (**15**)	OH	$OCOCH_3$	H



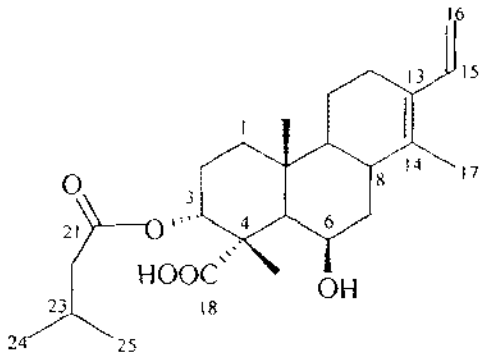
isovoucapenol D **(16)**



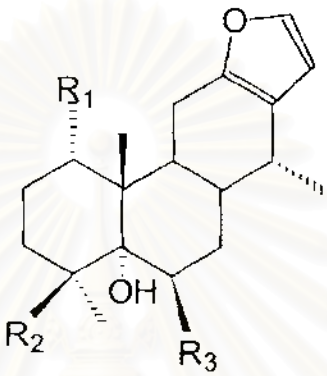
	R_1	R_2	R_3
bonducellpin A **(17)**	OAc	OAc	OH
bonducellpin B **(18)**	= O	OAc	OH
bonducellpin C **(19)**	OAc	H	OH
7-acetoxybonducellpin C **(20)**	OAc	H	OAc



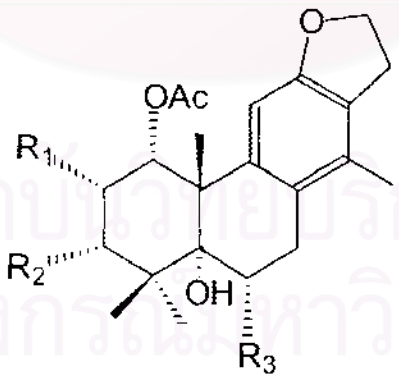
bonducellpin D **(21)**



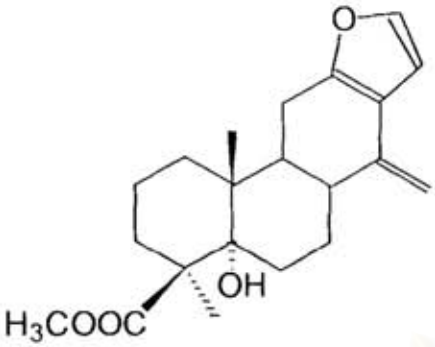
caesaldecan (**22**)



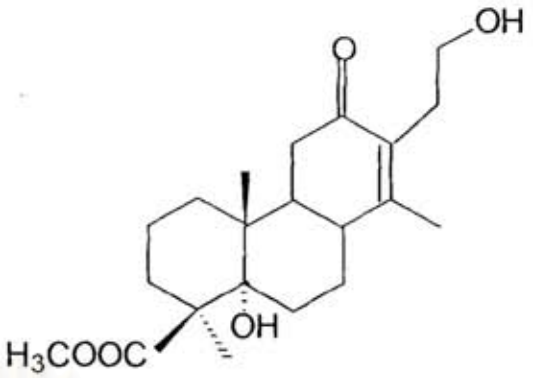
	R_1	R_2	R_3
caesaldekarin A (**23**)	H	CH_3	OAc
caesaldekarin B (**24**)	H	CH_3	OH
caesaldekarin C (**25**)	H	$COOCH_3$	H
caesaldekarin D (**26**)	OH	CH_3	OAc



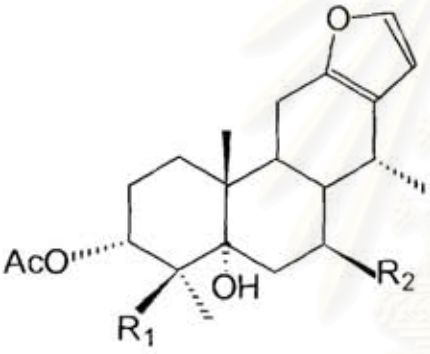
	R_1	R_2	R_3
caesaldekarin E (**27**)	H	OAc	H
2-acetoxycaesaldekarin E (**28**)	OAc	OAc	H
2-acetoxy-3-deacetoxycaesaldekarin E (**29**)	OAc	H	H
6-acetoxy-3-deacetoxycaesaldekarin E (**30**)	H	H	OAc



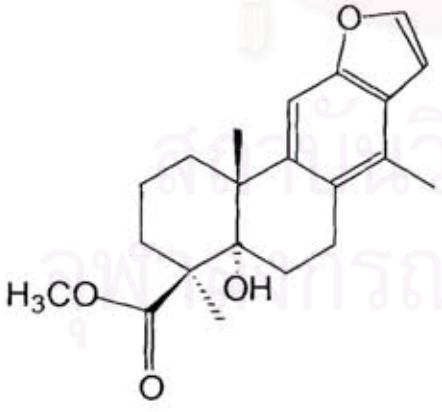
caesaldekarin F (**31**)



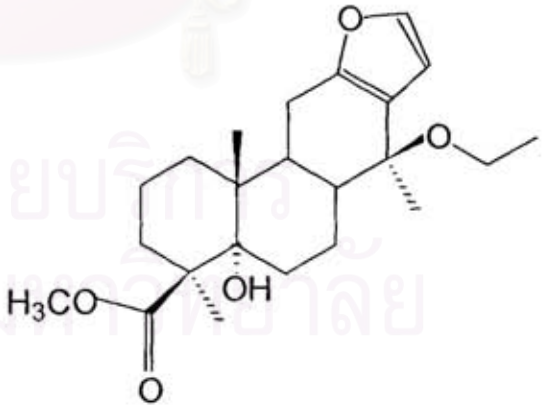
caesaldekarin G (**32**)



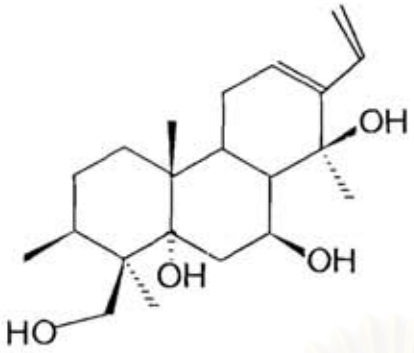
	R_1	R_2
caesaldekarin H (**33**)	CH_2OAc	H
caesaldekarin I (**34**)	CH_2OH	OH



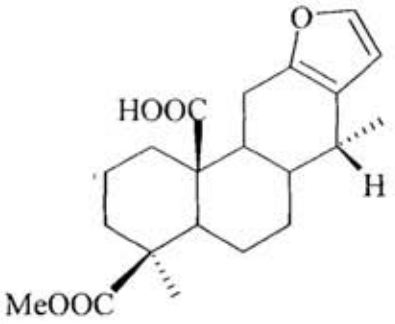
caesaldekarin J (**35**)



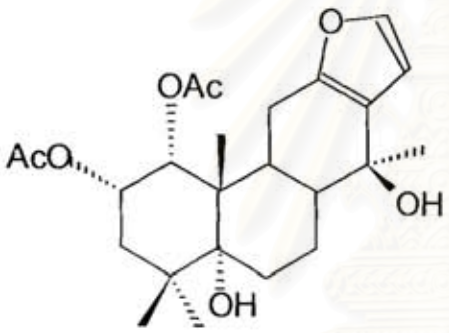
caesaldekarin K (**36**)



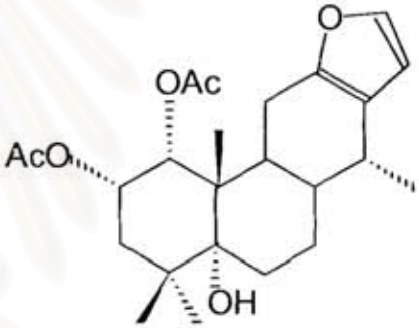
caesaldekarin L (**37**)



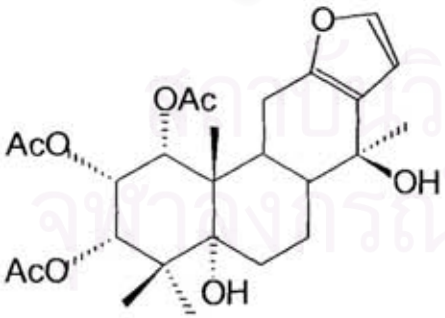
caesaljapin (**38**)



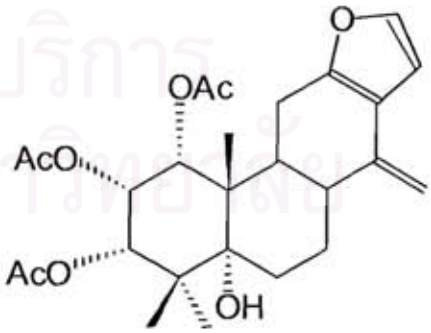
ε- caesalpin (**39**)



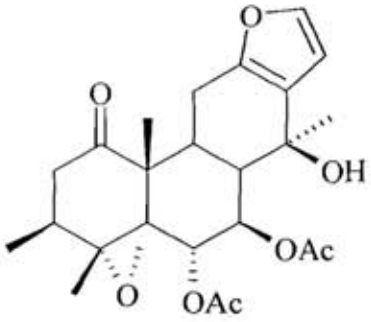
14-deoxy-ε- caesalpin (**40**)



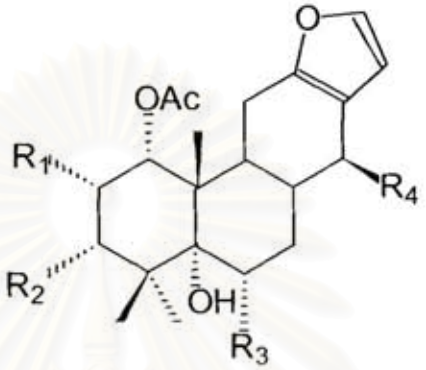
caesalpin F (**41**)



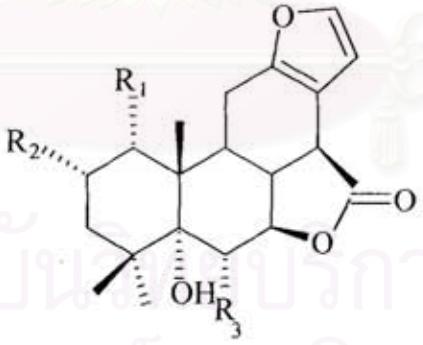
14(17)-dehydrocaesalpin F (**42**) R = $=CH_2$



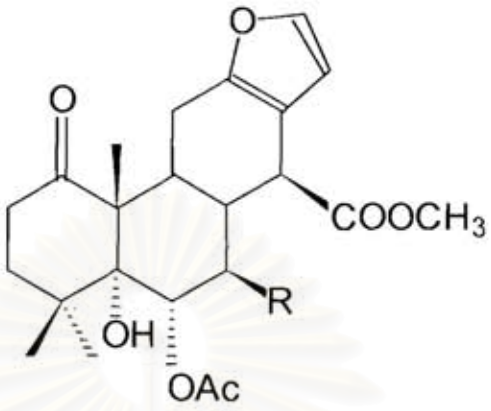
caesalpinin (**43**)



	R_1	R_2	R_3	R_4
caesalpinin C (**44**)	H	OAc	H	$=CH_2$
caesalpinin E (**45**)	H	H	OAc	$COOCH_3$
caesalpinin P (**46**)	OAc	H	H	$=CH_2$

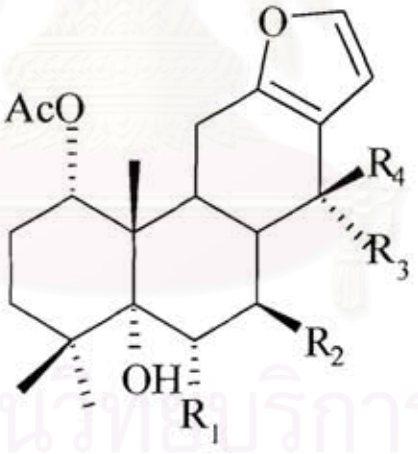


	R_1	R_2	R_3
caesalpinin D (**47**)	OAc	H	OAc
caesalpinin G (**48**)	OAc	OAc	H
caesalpinin H (**49**)	OH	H	OAc
caesalpinin I (**50**)	=O	H	OAc
caesalpinin O (**51**)	OAc	H	OH

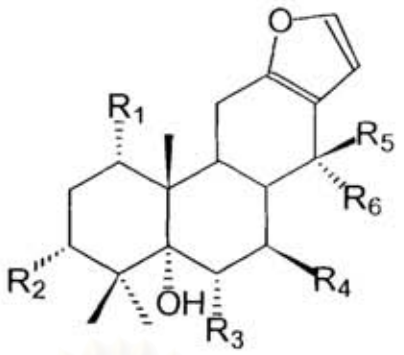


caesalpinin F (**52**) R = H

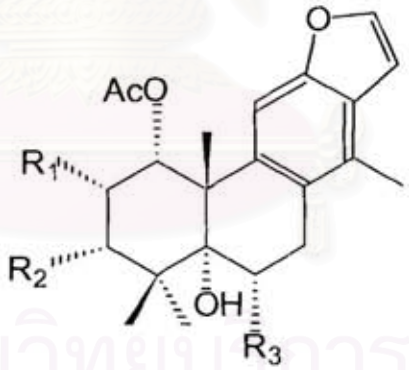
caesalpinin J (**53**) R = OAc



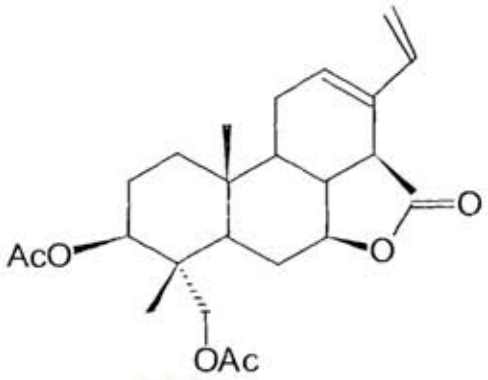
	R_1	R_2	R_3	R_4
caesalpinin K (**54**)	H	OH	CH_3	H
caesalpinin L (**55**)	H	OAc	OH	CH_3
caesalpinin M (**56**)	OH	OAc	H	$COOCH_3$
caesalpinin N (**57**)	H	OH	H	CHO



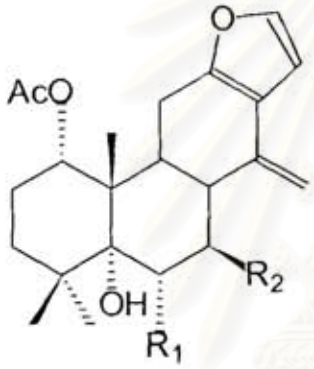
	R_1	R_2	R_3	R_4	R_5	R_6
caesalpinin MA **(58)**	OAc	OAc	H	H	H	CH_3
caesalpinin MB **(59)**	OAc	H	H	H	$COOCH_3$	H
caesalpinin MF **(60)**	OAc	OAc	H	H	$COOCH_3$	H
caesalpinin MG **(61)**	OAc	H	OAc	OAc	$COOCH_3$	H
caesalpinin MH **(62)**	OAc	H	OAc	OH	COOH	H
caesalpinin MI **(63)**	H	H	H	OH	H	CH_3

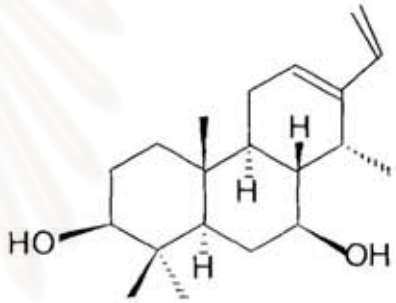


	R_1	R_2	R_3
caesalpinin MC **(64)**	H	OAc	H
caesalpinin MD **(65)**	OAc	H	OAc
caesalpinin MP **(66)**	H	H	H



caesalpinin ME **(67)**

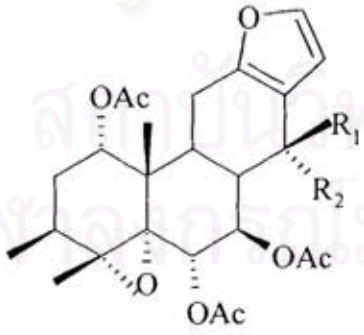


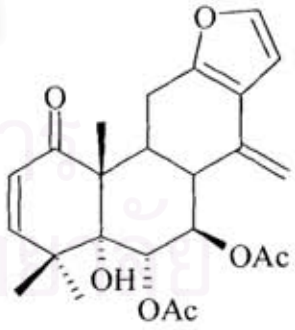


caesalpinin MJ **(68)** R_1 = H, R_2 = OAc

caesalpinin MK **(69)** R_1 = OAc, R_2 = H

caesalpinin ML **(70)**

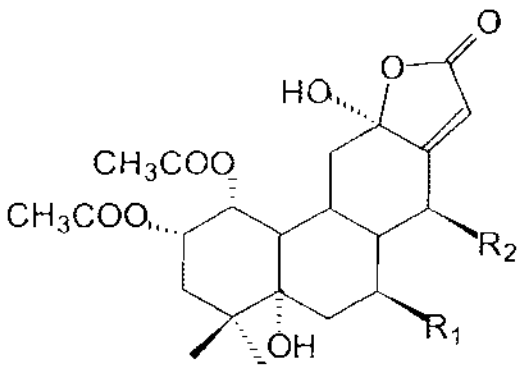




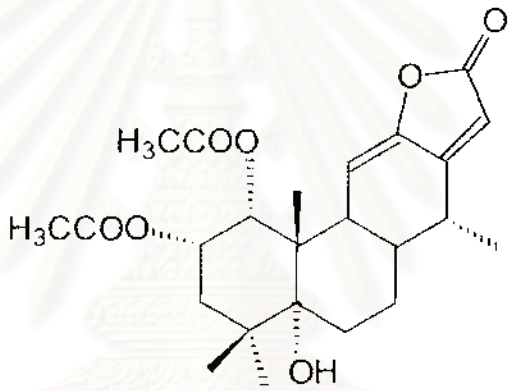
caesalpinin MM **(71)** R_1= CH_3, R_2= OH

caesalpinin MN **(72)** R_1= OH, R_2= CH_3

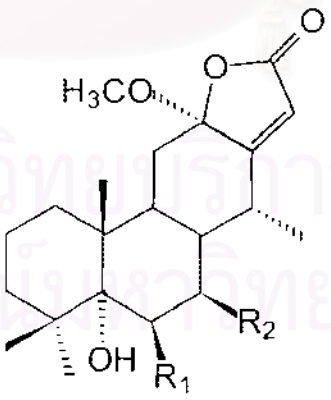
caesalpinin MO **(73)**



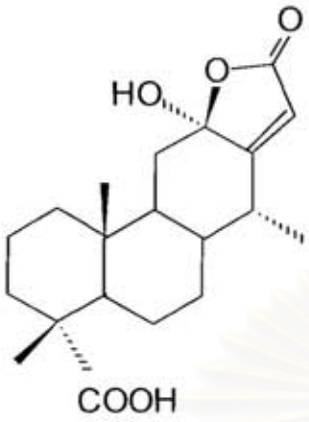
	R_1	R_2
neocaesalpin A (**74**)	H	OH
neocaesalpin B (**75**)	H	H
neocaesalpin C (**76**)	OH	H



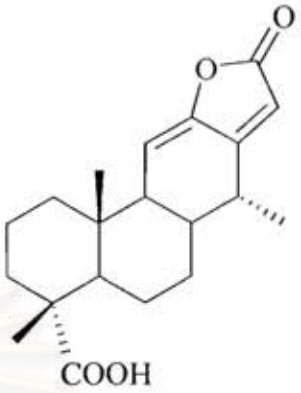
neocaesalpin D (**77**)



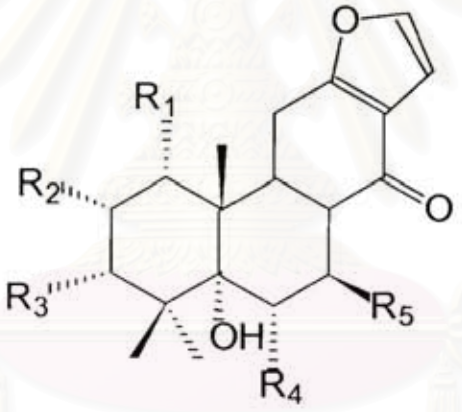
neocaesalpin E (**78**)	R_1= H	R_2= H
neocaesalpin F (**79**)	R_1= $OCOC_6H_5$	R_2= OH
neocaesalpin G (**80**)	R_1= $OCOCH=CHC_6H_5$	R_2= OH



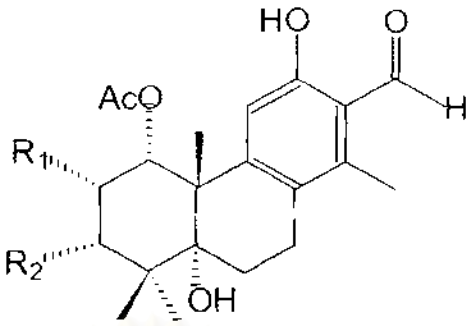
neocaesalpin H (**81**)



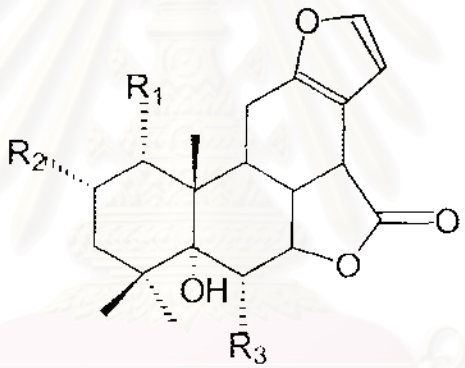
neocaesalpin I (**82**)



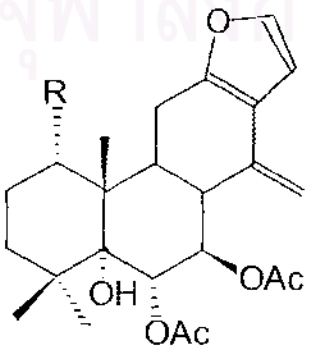
	R_1	R_2	R_3	R_4	R_5
norcaesalpinin A (**83**)	OAc	OAc	H	H	H
norcaesalpinin B (**84**)	OAc	H	OAc	H	H
norcaesalpinin D (**85**)	OAc	OAc	OAc	H	H
norcaesalpinin E (**86**)	OAc	H	H	OH	H
norcaesalpinin F (**87**)	= O	H	H	OH	OAc
norcaesalpinin MC (**88**)	OAc	H	H	OAc	H
norcaesalpinin MD (**89**)	= O	H	H	OAc	OAc



	R_1	R_2
norcaesalpinin C (**90**)	OAc	H
norcaesalpinin MA (**91**)	H	OAc
norcaesalpinin MB (**92**)	OAc	OAc



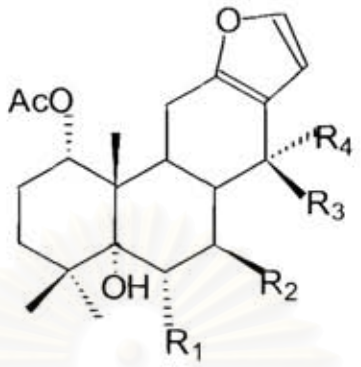
	R_1	R_2	R_3
caesalmin A (**93**)	OH	OH	OAc
caesalmin B (**94**)	OAc	H	H
caesalmin G (**95**)	OH	H	H



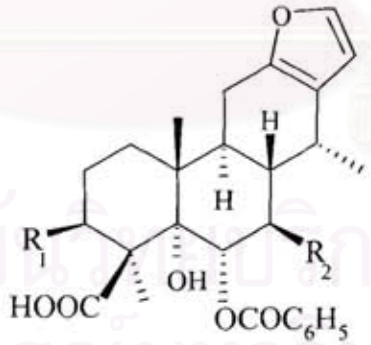
caesalmin C (**96**) R = OAc

1-deacetylcaesalmin C (**97**) R = OH

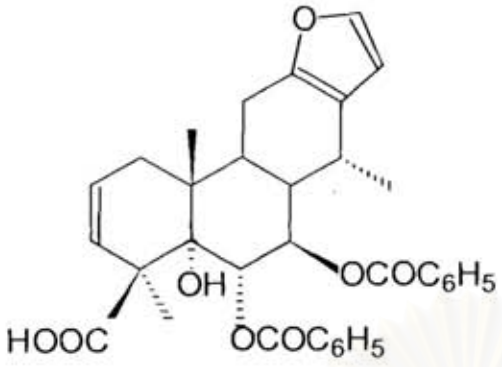
1-deacetoxy-1-oxocaesalmin C (**98**) R = =O



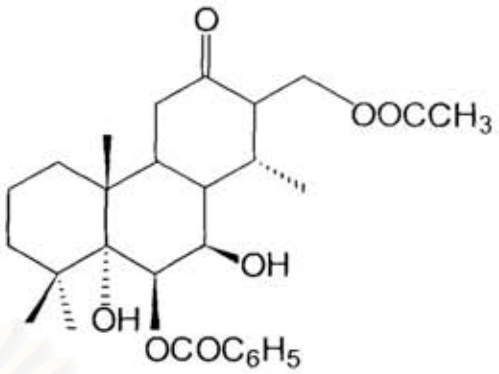
	R_1	R_2	R_3	R_4
caesalmin D (**99**)	OAc	OAc	OH	CH_3
caesalmin E (**100**)	OAc	OAc	CH_3	OH
caesalmin F (**101**)	OAc	OAc	CH_3	OCH_3
caesalmin H (**102**)	H	OH	H	CH_3
14(17)-dehydro caesalmin F (**103**)	OAc	OAc	R_3 R_4 =	$=CH_2$



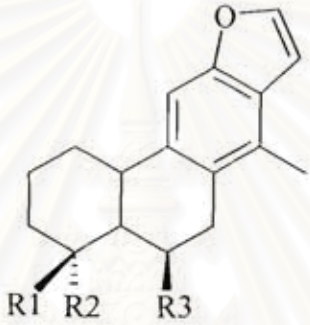
	R_1	R_2
pulcherrimin A (**104**)	OH	$OCOC_6H_5$
pulcherrimin C (**105**)	H	$OCOC_6H_5$
pulcherrimin D (**106**)	$OCOCH_3$	$OCOC_6H_5$
pulcherrimin E (**107**)	$OCOC_6H_5$	$COCH_3$
pulcherrimin F (**108**)	$OCOCH_3$	$OCOCH_3$



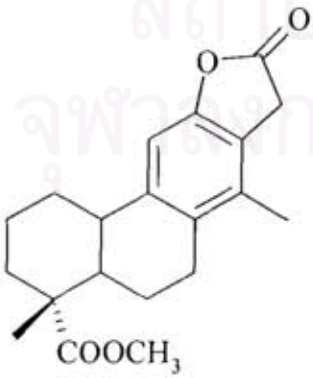
pulcherrimin B (**109**)



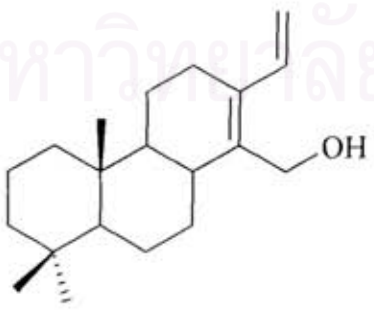
pulcherralpin (**110**)



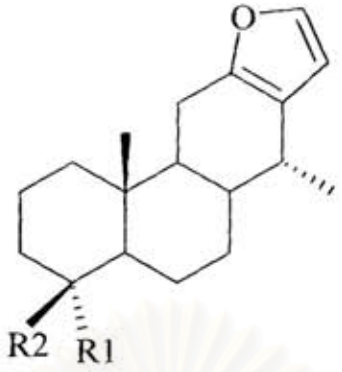
	R_1	R_2	R_3
taepeenin A (**111**)	$COOCH_3$	CH_3	H
taepeenin B (**112**)	COOH	CH_3	H
taepeenin C (**113**)	$COOCH_3$	CH_3	OH
taepeenin D (**114**)	$COOCH_3$	CH_3	$OCOCH_3$
taepeenin E (**115**)	$COOCH_3$	CHO	H



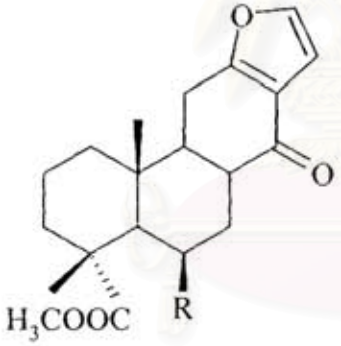
taepeenin F (**116**)



taepeenin G (**117**)

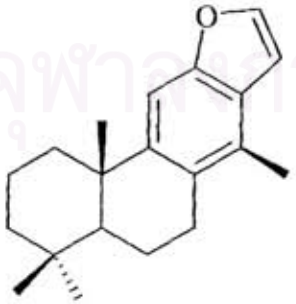


	R_1	R_2
taepeenin H (**118**)	$COOCH_3$	CHO
taepeenin I (**119**)	$COOCH_3$	CH_2OH
vinhaticoic acid (**120**)	COOH	CH_3
methyl vinhaticoate (**121**)	$COOCH_3$	CH_3

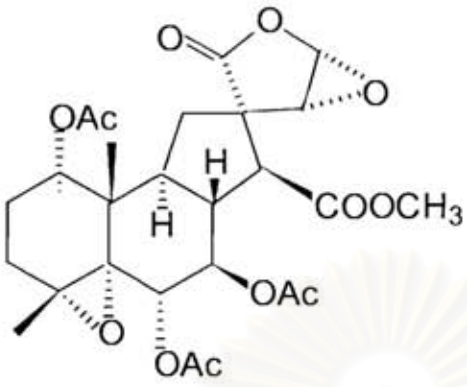


nortaepeenin A (**122**) R = H

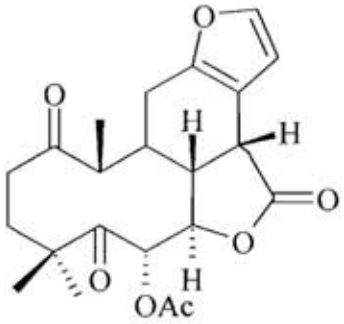
nortaepeenin B (**123**) R = OH



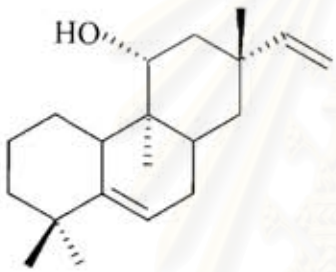
17-methylvouacapane-8(14), 9(11)-diene (**124**)



spirocaesalmin **(125)**



macrocaesalmin **(126)**



ent-11β-hydroxy-rosa-5,15-diene **(127)**

1.2 Other Compounds

In addition to diterpenoids which are a major group of compounds found in the genus *Caesalpinia*, sesquiterpenoids, triterpenoids, steroids and flavonoids, together with miscellaneous substances, have also been isolated from *Caesalpinia* species. The distribution of these compounds are summarized in Table 2.

Table 2. Distribution of compounds other than diterpenoids in the genus *Caesalpinia*.

Compounds	Source	Plant part	Reference
1. Sesquiterpenoids			
caryophyllene oxide (**128**)	*C. pulcherrima*	leaves	Rangasa *et al*., 2003
4,5-epoxy-8(14)-caryophyllene (**129**)	*C. decapetala*	leaves	Kiem *et al*., 2005
spathulenol (**130**)	*C. pulcherrima*	leaves	Rangasa *et al*., 2003
	C. decapetala	leaves	Kiem *et al*., 2005
2. Triterpenoids			
squalene (**131**)	*C. decapetala*	leaves	Kiem *et* al., 2005
oleanolic acid (**132**)	*C. pyraguariensis*	-	Woldemichael *et al*., 2003
3-*O*-(E)-hydroxycinnamoyl oleanolic acid (**133**)	*C. pyraguariensis*	-	Woldemichael *et al*., 2003
lupeol (**134**)	*C. decapetala*	leaves	Kiem *et* al., 2005
		root	Ogawa, Aoki and Sashida, 1992
	C. pyramidalis	leaves	Mendes *et al*., 2002
	C. pulcherrima	flower	Ragasa, Hofilene and Rideout, 2002

Table 2. Distribution of compounds other than diterpenoids in the genus *Caesalpinia* (continued).

Compounds	Source	Plant part	Reference
lueol acetate (**135**)	*C. pyraguariensis*	flower	Ragasa, Hofilene and Rideout, 2002
betulinic acid (**136**)	*C. pyraguariensis*	root	Woldemichael *et al*, 2003
3-*O*-(E)-hydroxycinnamoyl betulinic acid (**137**)	*C. pyraguariensis*	-	Woldemichael *et al*., 2003
friedelin (**138**)	*C. minax*	stem	Jiang *et al*, 2002b
epifriedelinol (**139**)	*C. minax*	stem	Jiang *et al*, 2002b
3. Steroids			
β-sitosterol (**140**)	*C. pulcherrima*	flower, stem	Jiang *et al*., 2001c Ragasa; Hofilena and Rideout, 2002; Ragasa *et al*., 2003
stigmast-5-en-3-*O*-β-glucopyranoside	*C. paraguariensis*	-	Woldemichael *et al*., 2003
stigmast-5-en-3-*O*-β-6'-stearoylglucopyranoside	*C. paraguariensis*	-	Woldemichael *et al*., 2003
stigmast-5-en-3-*O*-β-6'-palmitoylglucopyranoside	*C. paraguariensis*	-	Woldemichael *et al*., 2003

Table 2 . Distribution of compounds other than diterpenoids in the genus *Caesalpinia* (continued).

Compounds	Source	Plant part	Reference
4. Flavonoids and related compounds			
quercetin **(141)**	*C. pulcherrima*	flower	Rao *et al*., 1978
rhamnetin **(142)**	*C. sappan*	heart wood	Namikoshi, Nakata and Saitoh, 1987
ombuin **(143)**	*C. sappan*	heart wood	Namikoshi, Nakata and Saitoh, 1987
quercimeritrin **(144)**	*C. pulcherrima*	stem bark	Awasthi, Kumar and Misra, 1980;
myricetin **(145)**	*C. pulcherrima*	flower	Rangasa, Hofilena and Rideout, 2002
myricetin glycoside	*C. pulcherrima*	leaves	Rangasa, Hofilena and Rideout, 2002
rutin **(146)**	*C. pulcherrima*	stem	Rao *et al*., 1978
astragalin **(147)**	*C. decapetala*	root	Kiem *et al*., 2005
aghatisflavone **(148)**	*C. pyramidalis*	leaves	Mendes *et al*., 2002
5,7-dimethoxyflavanone **(149)**	*C. pulcherrima*	aerial part	Srinivas *et al*., 2003
5,7-dimethoxy-3',4'-methylenedioxyflavone **(150)**	*C. pulcherrima*	aerial part	Srinivas *et al*., 2003
pulcherrimin **(151)**	*C. pulcherrima*	stem	McPherson *et al*., 1983
6-methoxypulcherrimin **(152)**	*C. pulcherrima*	stem	McPherson *et al*., 1983

Table 2 . Distribution of compounds other than diterpenoids in the genus *Caesalpinia* (continued).

Compounds	Source	Plant part	Reference
4,4'-dihydroxy-2'-methoxychalcone (**153**)	*C. sappan*	heart wood	Namikoshi, Nakata and Saitoh, 1987
2'-hydroxy-2,3,4',6'-tetramethoxychalcone(**154**)	*C. sappan*	aerial part	McPherson *et al.*, 1983
catechin (**155**)	*C. decapetala*	root	Ogawa *et al.*, 1992
leucodelphinidin (**156**)	*C. pulcherrima*	Stem bark	Rao *et al.*, 1978
bonducellin (**157**)	*C. pulcherrima*	aerial	Srinivas *et al.*, 2003
	C. pulcherrima	stem	McPherson *et al.*, 1983
isobonducellin (**158**)	*C. pulcherrima*	aerial	Srinivas *et al.*, 2003
8-methoxybonducellin (**159**)	*C. pulcherrima*	stem	McPherson *et al.*, 1983
7-hydroxy-3-(4'-hydroxybenzylidene)-chroman-4-one (**160**)	*C. sappan*	heart wood	Namikoshi, Nakata and Saitoh, 1987
3,7-dihydroxy-3-(4'-hydroxybenzyl)-charoman-4-one (**161**)	*C. sappan*	heart wood	Namikoshi, Nakata and Saitoh, 1987
3,4,7-trihydroxy-3-(4'-hydroxybenzyl)-chroman (**162**)	*C. sappan*	heart wood	Namikoshi, Nakata and Saitoh, 1987
hematoxylin (**163**)	*C. sappan*	heart wood	Xie *et al.*, 2000
brazilin(brasilin) (**164**)	*C. sappan*	heart wood	Fuke *et al.*, 1985

Table 2. Distribution of compounds other than diterpenoids in the genus *Caesalpinia* (continued).

Compounds	Source	Plant part	Reference
brazilein(brasilein) **(165)**	*C. sappan*	heart wood	Xie *et al*., 2000
3-deoxysappanchalcone	*C. decapetala*	root	Ogawa *et al*., 1992
sappanchalcone	*C. decapetala*		Ogawa *et al*., 1992
5. Miscellaneous compounds			
aucubin (iridoid glycoside)	*C. coriaria*	pod	Nageshwar, Radhakrishnaiah and Narayana, 1984
bilobetin	*C.paraguariensis*	-	Woldemichael *et al*., 2003
4-*O*-β-glucopyranosyloxy-(*Z*)-7-hydroxycinnamic acid	*C. pyramidalis*	leaves	Mendes *et al*., 2002
4-*O*-β-glucopyranosyloxy-(*Z*)-8-hydroxycinnamic acid	*C. pyramidalis*	leaves	Mendes *et al*., 2002
trans-resveratrol	*C. decapetala*	leaves	Kiem *et al*., 2005
gallic acid	*C. pulcherrima*	flower	Rangasa, Hofilena and Rideout, 2002

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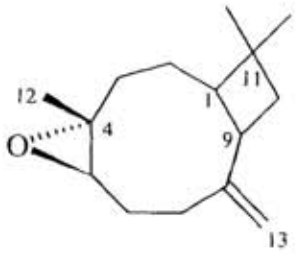
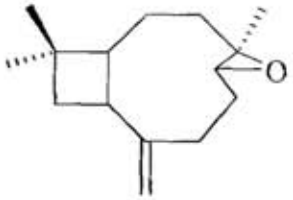
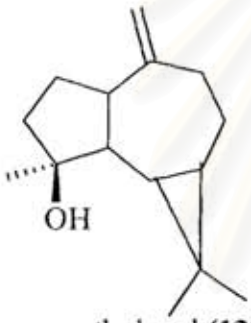


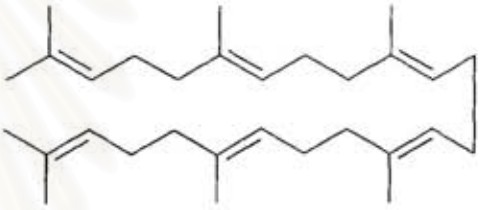
caryophyllene oxide (**128**)



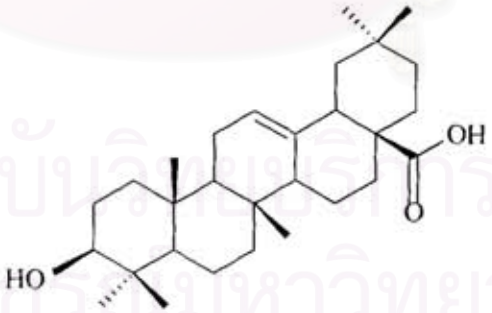
4,5-epoxy-8(14)--caryophyllene(**129**)



spathulenol (**130**)

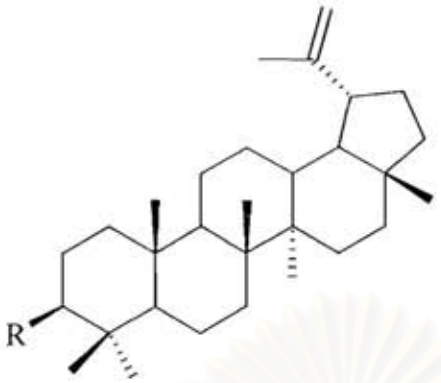


squalene (**131**)



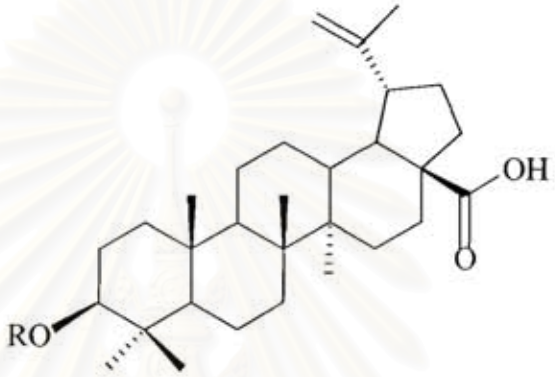
oleanolic acid (**132**) R = OH

3-*O*-(E)-hydroxycinnamoyl oleanolic acid (**133**) R = $OCOCH{=}CHC_6H_4OH$



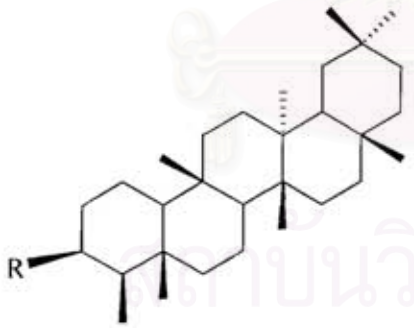
lupeol (**134**) R = OH

lupeol acetate (**135**) R = OAc



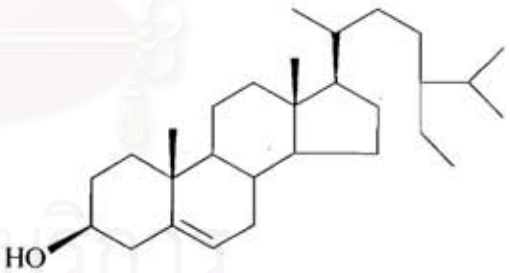
betulinic acid (**136**) R = OH

3-*O*-(E)- hydroxycinnamoyl betulinic acid (**137**) R = $OCOCH{=}CHC_6H_4OH$

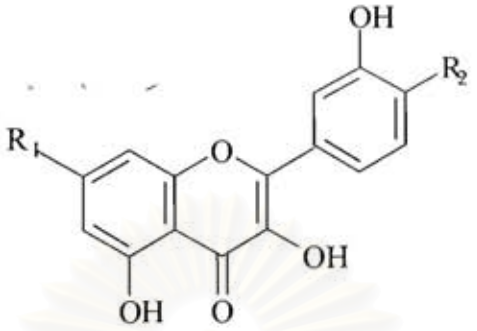


friedelane (**138**) R = =O

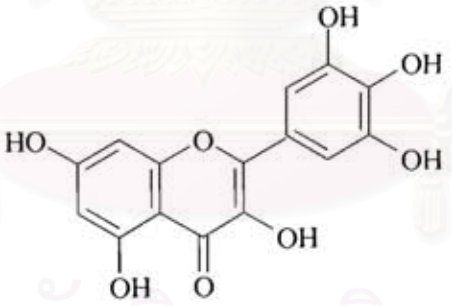
epifriedelinol (**139**) R = OH



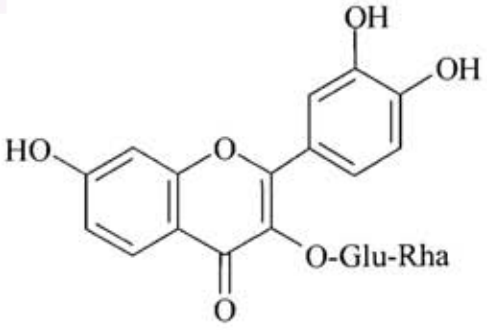
β-sitosterol (**140**)



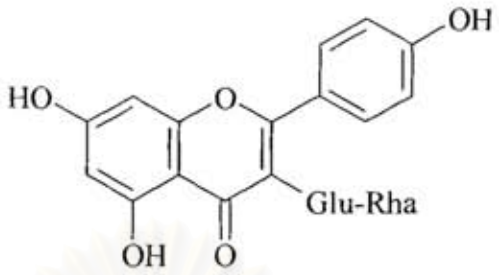
	R_1	R_2
quercetin **(141)**	OH	OH
rhamnetin **(142)**	OCH_3	OH
ombuin **(143)**	OCH_3	OCH_3
quercimeritrin **(144)**	O-Glu	OH



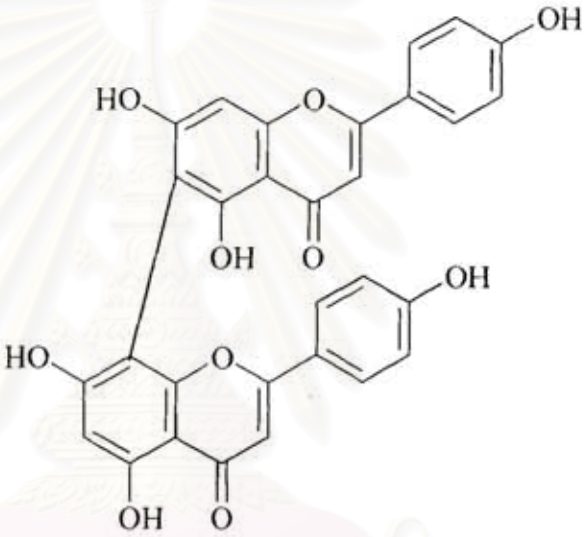
myricetin **(145)**



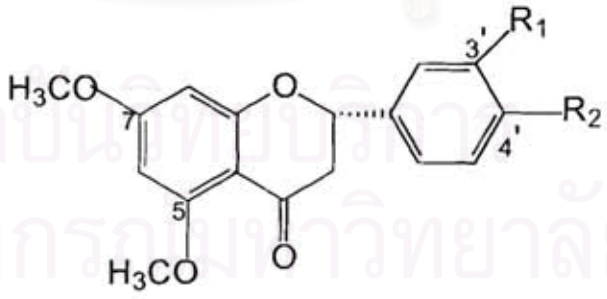
rutin **(146)**



astragalin (**147**)

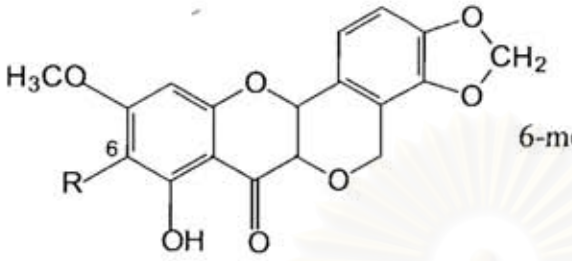


aghatisflavone (**148**)



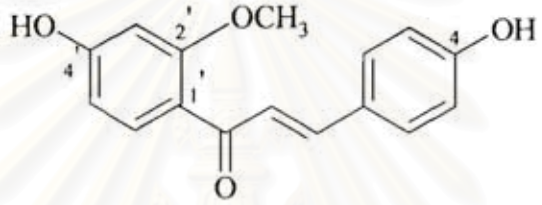
5,7-dimethoxyflavanone (**149**) R_1,R_2 = H

5,7-dimethoxy-3',4'-methylenedioxyflavanone (**150**) R_1,R_2 = -OCH_2O-

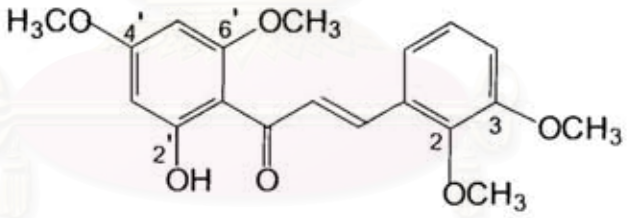


pulcherrimin (**151**) R = H

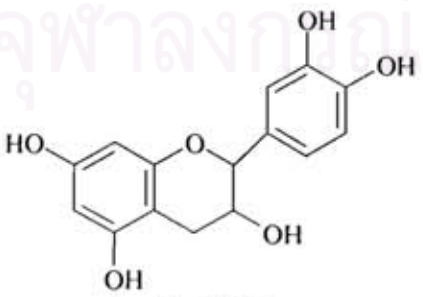
6-methoxypulcherrimin (**152**) R = OCH_3



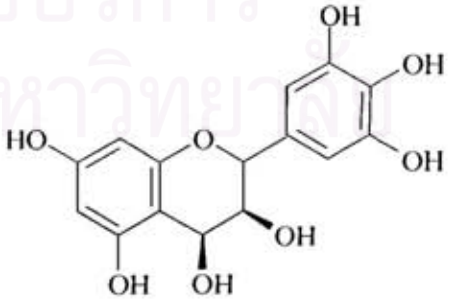
4,4'-dihydroxy-2'-methoxychalcone (**153**)



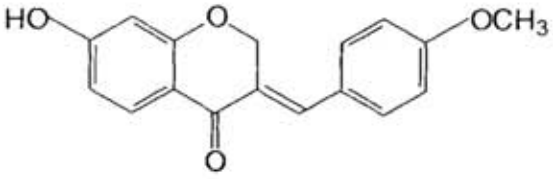
2'-hydroxy-2,3,4',6'-tetramethoxychalcone (**154**)



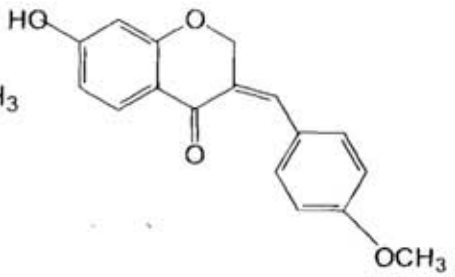
catechin (**155**)



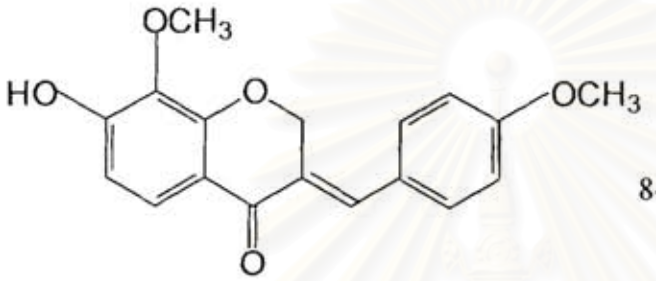
leucodelphinidin (**156**)



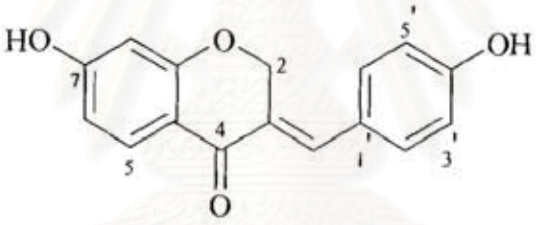
bonducellin (**157**)



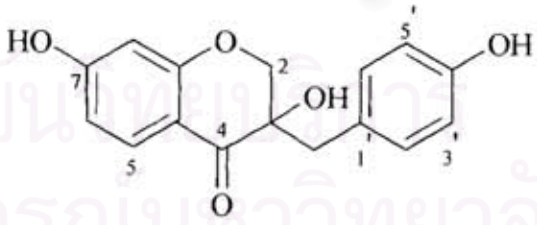
isobonducellin (**158**)



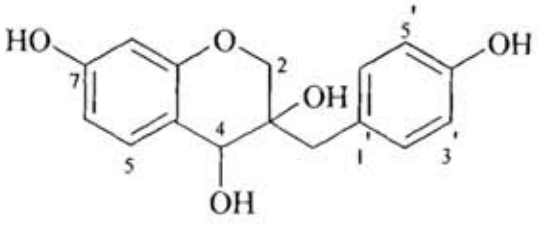
8-methoxybonducellin (**159**)



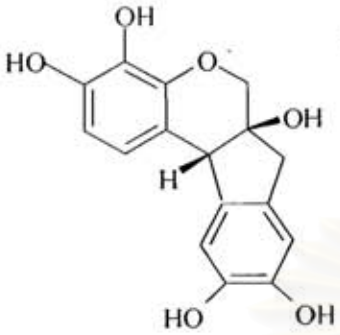
7-hydroxy-3-(4'-hydroxybenzylidene)-chroman-4-one (**160**)



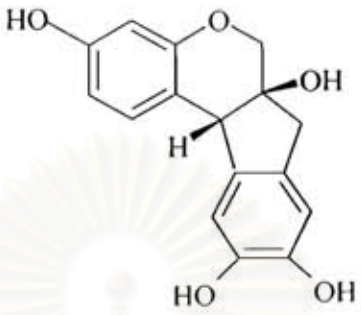
3,7-dihydroxy-3-(4'-hydroxybenzyl)-chroman-4-one (**161**)



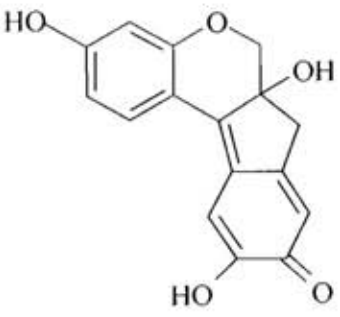
3,4,7-trihydroxy-3-(4'-hydroxybenzyl)-chroman (**162**)



hematoxylin **(163)**



brazilin **(164)**



brazilein **(165)**

2. Ethnomedicinal Uses of *Caesalpinia* species

Plants of the genus *Caesalpinia* have been known for their uses in traditional medicine of several countries. Ethnomedicinal uses of these plants are described below.

Calumbibit is an important crude drug used in Philippines, botanically originated from the seeds of *Caesalpinia bonduc*. It is regarded as a febrifuge and purgative and is also considered to be effective for the treatment of malaria (Kinoshita, 2002).

C. bonducella is a prickly shrub found throughout the coastal region of India and is reported to have antipyretic, antidiuretic, anthelmintic, antibacterial, antianaphylactic, antidiarrhoeal, antiviral, antiasthmatic, antiemetic and antiestrogenic properties. Traditionally, the tribes of Andaman and Nicobar Island use the aqueous decoction of its seeds to eliminate the symptoms of diabetes mellitus (Chakrabati *et al.*, 2005).

The seed of *C. crista*, locally known as " Ka-lain" in Myanmar, are used as an anthelmintic, antipyretic, anti-inflammatory, and antimalarial agent. In Indonesia, this plant is known as "Bagore" and a decoction of its roots has been used as a tonic and for the treatment of rhumatism and back-ache (Kalauni *et al.*, 2004). In Thailand, the plant is known as " Tapee" and the leaves , root, and fruits are used as a tonic and an antiperiodic (Cheenpracha *et al.*, 2005).

The roots of *C. decapetala* var. *japonica* are used as a folk medicine to treat neuralgia in Kagoshima, Japan (Ogawa, Aoki and Sashida, 1992). In Vietnam, the plant has been used as an immunomodulatory and anti-inflammatory agent (Kiem *et al.*, 2005).

C. major is used as a medicinal plant in various regions of the tropics. For example, the decoction of the roots has been used as a tonic and an anthelmintic as well as for treatment of rheumatism and back-ache. In Thailand, the seeds of this plant are used as an expectorant and antitussive agent (Roengsumran *et al.*, 2000).

C. minax is used in China to treat the common cold, fever and dysentery (Jiang *et al.*, 2001a, b).

The stem of *C. pulcherrima* is used as an abortifacient and emmenagogue, while decoctions of the leaves, roots and bark are used to alleviate fungal infections, reduce fever and treat liver disorders as well as ulcers of the mouth and throat (Roach *et al*, 2003). Decoction of the plant is applied to treat various infections (Srinivas *et al.*, 2003). The fruit is used to stop bleeding and prevent diarrhea and dysentery (Ragasa, Hofilena and Rideout, 2002).

Stem bark of *C. pluviosa* is used by the Tacana, a native tribe of Bolivia, as a treatment against dysentery (sometimes due to protozoal infestation) and antimalaria (Deharo *et al.*, 2001).

The heartwood of *C. sappan* has long been used in oriental folk medicine to promote blood circulation and as an emmenagogue, analgesic and anti-inflammatory agent. In China, the drug is also used as hemostatic and in for the treatment of contusion and thrombosis (Yang *et al.*, 2002).

In Kenya, *C. volkensii* is most frequently used to treat malaria. The leaves of this plant are bitter-tasting and are used in soup mainly for malaria while its roots are used for gonorrhea. The seed are used for stomach ulcer (Kuria *et al.*, 2001).

3. Biological Activities of *Caesalpinia* Species

Several species of the genus *Caesalpinia* have been investigated pharmacologically and the results indicated that they contained components (extracts/isolated compound) to exhibit interesting bioactivities. The biological activities of extracts and isolated compounds from these plants are summarized in Table 3.

Table 3. Biological activities of *Caesalpinia* species.

Species	Plant part	Extract/Isolated compound	Activity	Reference
C. bonduc	seed	methanol extract; bondenolide	antibacterial, antifungal	Simin *et al.*, 2001
C. bonducella	seed	aqueous extract	hypoglycemic	Chakrabarti *et al.*, 2003
C. crista	seed kernels	CH_2Cl_2 extract; caesalpinin K, norcaesalpinin F	antimalarial	Awale *et al.*, 2006
		CH_2Cl_2 extract - 2-acetoxy-3-deacetoxycaesaldekarin e - 14(17)-dehydrocaesalpin F	antimalarial	Linn *et al.*, 2005
C. minax	seed	$CHCl_3$ extract; caesalmin B, bonducellpin D	antiviral	Jiang *et al.*, 2002 b
		macrosaesalmin	antiviral	Jiang *et al.*, 2002 a
		caesalmins C-G	antiviral	Jiang *et al.*, 2001c
C. paraguariensis	NS	oleanolic acid	antibacterial	Woldemichael *et al.*, 2003
C. pluviosa	NS	crude extract	antimalarial	Baelmans *et al.*, 2002

Table 3. Biological activities of *Caesalpinia* species (continued).

Species	Plant part	Extract/isolated compound	Activity	Reference
C. pulcherrima	aerial part	5,7-dimethoxyflavanone	anti-inflammatory	Rao, Fang and Tzeng, 2005
		5,7-dimethoxy-3',4'-	antibacteria, antifungal	Banskota *et al.*, 2003
		mehthoxylenedioxyflavanone	anti-inflammatory	Rao, Fang and Tzeng, 2005
		isobonducellin		Banskota *et al.*, 2003
				Rao, Fang and Tzeng, 2005
		2'-hydroxy-2,3,4',6'-		Banskota *et al.*, 2003
		tetramethoxychalcone		Rao, Fang and Tzeng, 2005
		bonducellin	anti-inflammatory	Rao, Fang and Tzeng, 2005
	fruit, seed,	aqueous extract	antiviral	Chiang *et al.*, 2003
	stem, leaf, flower	flavonoids		
	root	pulcherrimins A&B	cytotoxic	Pati *et al.*, 1997; Roach *et al.*, 2003
		isovouacapenols A –D	antibacteria, antifungal	Roach *et al.*, 2003
		6β-benzoyl-7β-hydroxy	antitubercular, cytotoxic	Promsawan *et al.*, 2003
		vouacapen-5α-ol		
		diterpene benzoates	cytotoxic	Che *et al.*, 1986

Table 3. Biological activities of *Caesalpinia* species (continued).

Species	Plant part	Extract/isolated compound	Activity	Reference
C. pulcherrima	stem	pulcherralpin	fertility regulator, antitumor	Che *et al.*, 1986
		2,6-dimethoxybenzoquinone	cytotoxic	
		4'-methoxyisoliquritrigen		
C. sappan	heartwood	aromatic compound - 1',4'-dihydro-spiro [benzofuran-3(2H),3'-[3H-2]benzopyran]-1',6',6',7'-tetrol - 3-[[4,5-dihydroxy-2(hydroxymethyl)phenyl]-methyl]-2,3-dihydro-3,6-benzofurandiol	antioxidant	Safitri *et al.*, 2003
		methanolic extract; brazilin, hematoxylin	vascular relaxant effect	Xie *et al.*, 2000
		sappanchalcone, brazilin	anticonvulsant	Baek *et al.*, 2000
C. sappan	heartwood	aqueous extract	antioxidant	Mendes *et al.*, 2002; Badami *et al.*, 2003
C. volkensii	heartwood	aqueous extract,	antimalarial	Kuria *et al.*, 2001

NS = not stated

CHAPTER III

EXPERIMENTAL

1. Source of Plant Material

The leaves of *Caesalpinia coriaria* (Jacq.) Willd. were collected from Bangkoknoi District, Bangkok, Thailand in November, 2003. Authentication was performed by comparison with herbarium specimens (BKF 28360) at the Bangkok Herbarium of the National Park and Plant Conservation Department, Ministry of Natural Resource and Environment.

2. General Techniques

2.1 Chromatographic Techniques

2.1.1 Thin- Layer Chromatography (TLC)

Technique : One Way ascending

Adsorbent : Silica gel $60F_{254}$ (E. Merck) precoated plate

Layer thickness : 0.2 mm

Solvent system : Various solvent systems depending on materials.

Distance : 6 cm

Temperature : Laboratory temperature (28-35 °C)

Detection : 1. Ultraviolet light (254 and 356 nm)
2. 10% Sulfuric acid in ethanol
3. Liebermann-Burchard reagent (acetic anhydride-sulphuric acid).
4. anisaldehyde reagent

2.1.2 Column Chromatography

Column : Flat bottom glass column (various diameter)

Adsorbent : Silica gel 60 (No. .9385, E. Merck) particle size 0.040-0.063 mm (230-400 mesh ASTM)

Packing method : Dry and wet packing

Sample loading : 1) Dry packing : The sample was dissolved in a small amount of suitable organic solvent, mixed with a small quantity of adsorbent, triturated, dried and then loaded on the top of the column.

2) Wet packing : The sample was dissolved in a small amount of the eluent, then loaded on the top of the column.

Solvent system : Various solvent systems depending on materials.

Detection : Fractions were examined by TLC observing under UV light at the wavelengths of 254 and 365 nm. The plate was then sprayed with 10% sulfuric acid in ethanol or with anisaldehyde and heated at 110° C. Fractions with similar chromatographic pattern were combined.

2. 2 Spectroscopy

2.2.1 Infrared (IR) Absorption Spectra

IR spectra (KBr disc) were obtained on a Perkin Elmer FT-IR 1760X spectrometer (Scientific and Technological Research Equipment Center, Chulalongkorn University)

2.2.3 Mass Spectra (MS)

Electron impact mass spectra (EIMS) were recorded on a Polaris Q serial number MS 210179 mass spectrometer (Department of Chemistry, Faculty of Science, Mahidol University) operating at 15 eV.

2.2.4 Proton and Carbon-13 Nuclear Magnetic Resonance (^{1}H and ^{13}C-NMR) Spectra

^{1}H-NMR (500 MHz) and ^{13}C-NMR (125MHz) spectra were obtained either on a JEOL JNM-A500 (Alpha series) NMR spectromether (Scientific and Technological Research Equipment Center, Chulalongkorn University) or a Bruker-AV 500 MHz (National Science and Technology Development Agency)

NMR solvents used in this study were deuterated chloroform ($CDCl_3$). Chemical shifts were reported in ppm scale using the chemical shift of the solvent as the reference signal.

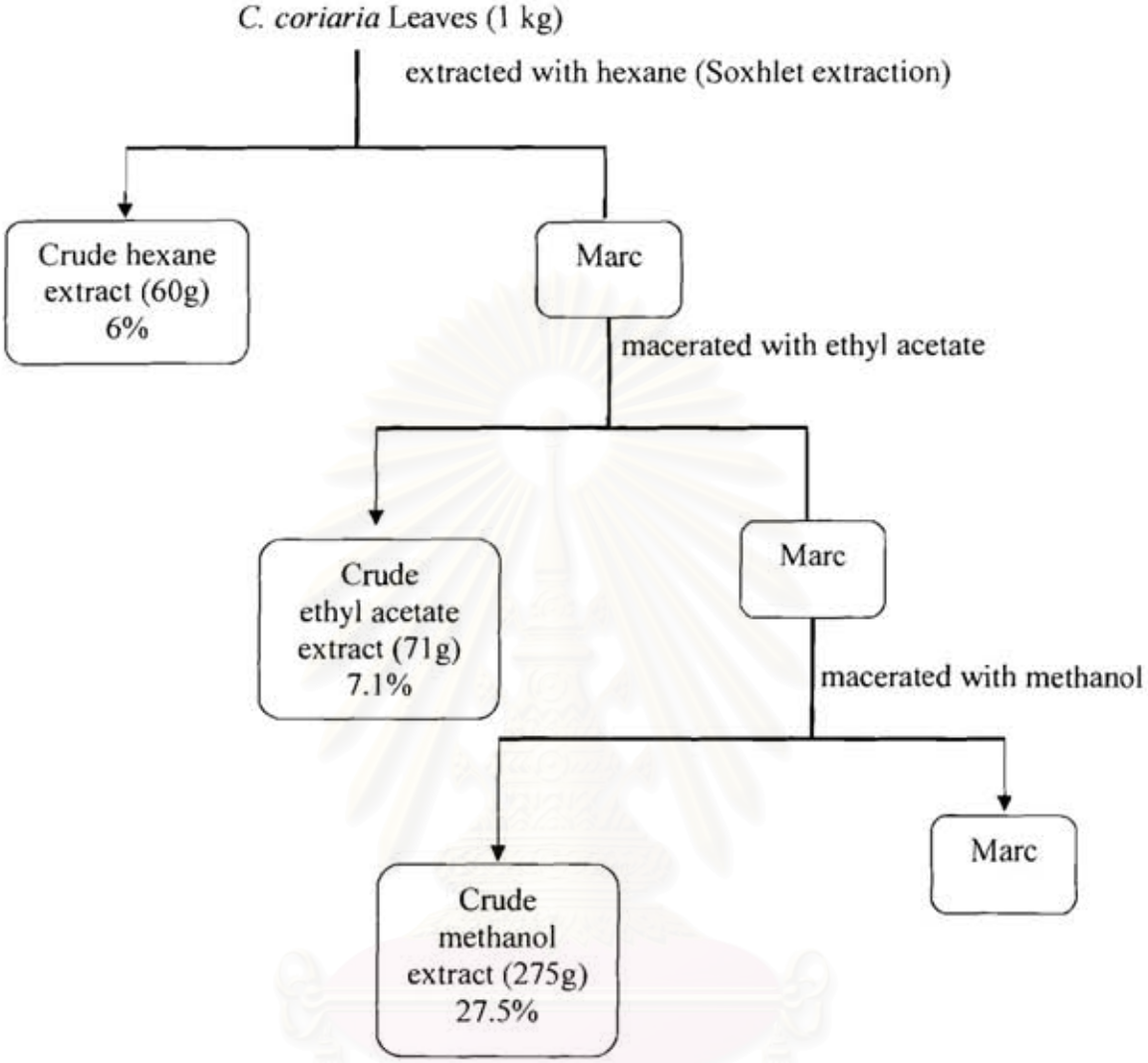
2.3 Solvents

Throughout this work, all organic solvents were of commercial grade and were redistilled prior to use.

3. Extraction and Isolation

3.1 Extraction

Dried, coarsely powdered leaves (1 kg) of *Caesalpinia coriaria* (Jacq.) Willd. were extracted with hexane by soxhlet extraction to afford 60 g of crude hexane extract (6% of dry weight). The marc was then extracted by maceration with ethyl acetate and methanol, respectively, to yield 71 g of crude ethyl acetate extract (7.1% of dry weight) and 275 g of crude methanol extract (27.5% of dry weight).



Scheme 1. Extraction of *Caesalpinia coriaria* leaves.

3.2 Isolation

The hexane extract (30 g) was first fractionated on a silica gel column (750 g, 10x23.5 cm) eluted with hexane-dichloromethane mixture of increasing polarity (from 1:1 to 1:9) to give 223 fractions of 50 ml each and then washed down with methanol. The fractions were combined according to their TLC pattern into 9 portions as shown in Table 4.

Table 4. Combined fractions from the hexane extract

Portion	Solvent	Number of fraction	Weight (g)
H1	hexane-CH_2Cl_2 1:1	1-17	4.41
H2	hexane-CH_2Cl_2 1:1	18-27	7.82
H3	hexane-CH_2Cl_2 1:1	28-41	1.13
H4	hexane-CH_2Cl_2 4:6	42-73	1.74
H5	hexane-CH_2Cl_2 3:7	74-116	5.62
H6	hexane-CH_2Cl_2 2:8	117-179	4.00
H7	hexane-CH_2Cl_2 2:8	180-203	0.55
H8	hexane-CH_2Cl_2 1:9	204-223	2.85
H9	methanol	224	1.40

3.2.1 Isolation of Compound CC1

Portion H3 (1.13 g) was subjected to a silica gel column (80 g , 2.5x30 cm) eluted with hexane-dichloromethane mixture of increasing polarity (from 8:2 to 6:4) to give 230 fractions of 30 ml each and then washed down with methanol. The fractions were then combined according to their TLC pattern into 9 portions, as shown in Table 5.

Table 5. Combined fractions from H3

Portion	Solvent	Number of fraction	Weight (mg)
H10	hexane-CH_2Cl_2 8:2	1-15	54.6
H11	hexane-CH_2Cl_2 8:2	16-20	54.2
H12	hexane-CH_2Cl_2 8:2	21-36	297.3
H13	hexane-CH_2Cl_2 8:2	37-46	63.5
H14	hexane-CH_2Cl_2 7:3	47-136	45.7
H15	hexane-CH_2Cl_2 7:3	137-140	22.3
H16	hexane-CH_2Cl_2 6:4	141-156	45.4
H17	hexane-CH_2Cl_2 6:4	157-162	12.6
H18	hexane-CH_2Cl_2 6:4	163-230	153.5
H19	methanol	231	236.9

Portion H16 (126.0 mg) which gave one major blue spot and another violet spot on TLC under detection with anisaldehyde reagent, was further separated on preperative TLC using hexane-dichloromethane (8:2) as developing solvent, to give compound CC1 as white amorphous powder (35.0 mg)

3.2.2 Isolation of Compound CC2

Portion H6 (4.0 g) was subjected to a silica gel column (120 g, 3x44 cm) eluted with solvent mixture of increasing polarity (hexane-dichloromethane 2:8 to dichloromethane-methanol 95:5) to give 110 fractions of 30 ml each and then washed down with methanol. The fractions were then combined according to their TLC pattern into 6 portions, as shown in Table 6.

Table 6. Combined fra tions from H6

Portion	Solvent	Number of fraction	Weight (mg)
H20	hexane:CH_2Cl_2:MeOH 1: 4 : 0	1-10	220
H21	hexane:CH_2Cl_2:MeOH 1: 9 : 0	11-22	453
H22	hexane:CH_2Cl_2:MeOH 1: 9 : 0	23-34	860
H23	hexane:CH_2Cl_2:MeOH 0: 1 : 0	35-46	127
H24	hexane:CH_2Cl_2:MeOH 0: 1 : 0	47-94	834
H25	hexane:CH_2Cl_2:MeOH 0: 95 : 5	95-110	1,079
H26	methanol	111	389

Portion H22 (860.0 mg) was further separated on a silica gel column (30 g, 2x15 mg) eluted with solvent mixture of hexane and dichloromethane (1:9 and 1:19) to give 65 fractions (10 ml each). These fraction were combined according to their TLC pattern into 6 portions as shown in Table 7.

Table 7. Combined fractions from H22

Portion	Solvent	Number of fraction	Weight (mg)
H27	hexane : CH_2Cl_2 1 : 9	1-10	48.6
H28	hexane : CH_2Cl_2 1 : 9	11-39	167.7
H29	hexane : CH_2Cl_2 1 : 19	40-46	318.0
H30	hexane : CH_2Cl_2 1: 19	47-56	57.3
H31	hexane : CH_2Cl_2 1 : 19	57-65	36.5
H32	methanol	66	197.2

Portion H30 which gave a single violet spot on TLC under reaction with Liebermann-Burchared reagent, was purified by recrytallization in methanol to give compound CC2 as white amorphous powder (33.6 mg).

Portion H23 (127.4 mg) was further separated on a silica gel column(40 g, 2x30 cm) eluted with solvent mixture of hexane and dichloromethane (4:6 to 2:8) to give 43 fractions of 20 ml each and then washed down with methanol. The fractions were then combined according to their TLC pattern into 6 portions as shown in Table 8.

Table 8. Combined fractions from H23

Portion	Solvent	Number of fraction	Weight of fraction (mg)
H33	hexane : CH_2Cl_2 4 : 6	1-4	7.7
H34	hexane : CH_2Cl_2 4 : 6	5-7	27.4
H35	hexane : CH_2Cl_2 3 : 7	8-10	20.6
H36	hexane : CH_2Cl_2 3 : 7	11	8.0
H37	hexane : CH_2Cl_2 2 : 8	12-25	23.9
H38	hexane : CH_2Cl_2 2 : 8	26-43	24.2
H39	methanol	44	11.0

Portion H34, which gave a single violet spot on TLC under detection with Liebermann-Burchared reagent, was purified by recrystallization in methanol to give another (19.5 mg) of compound CC2.

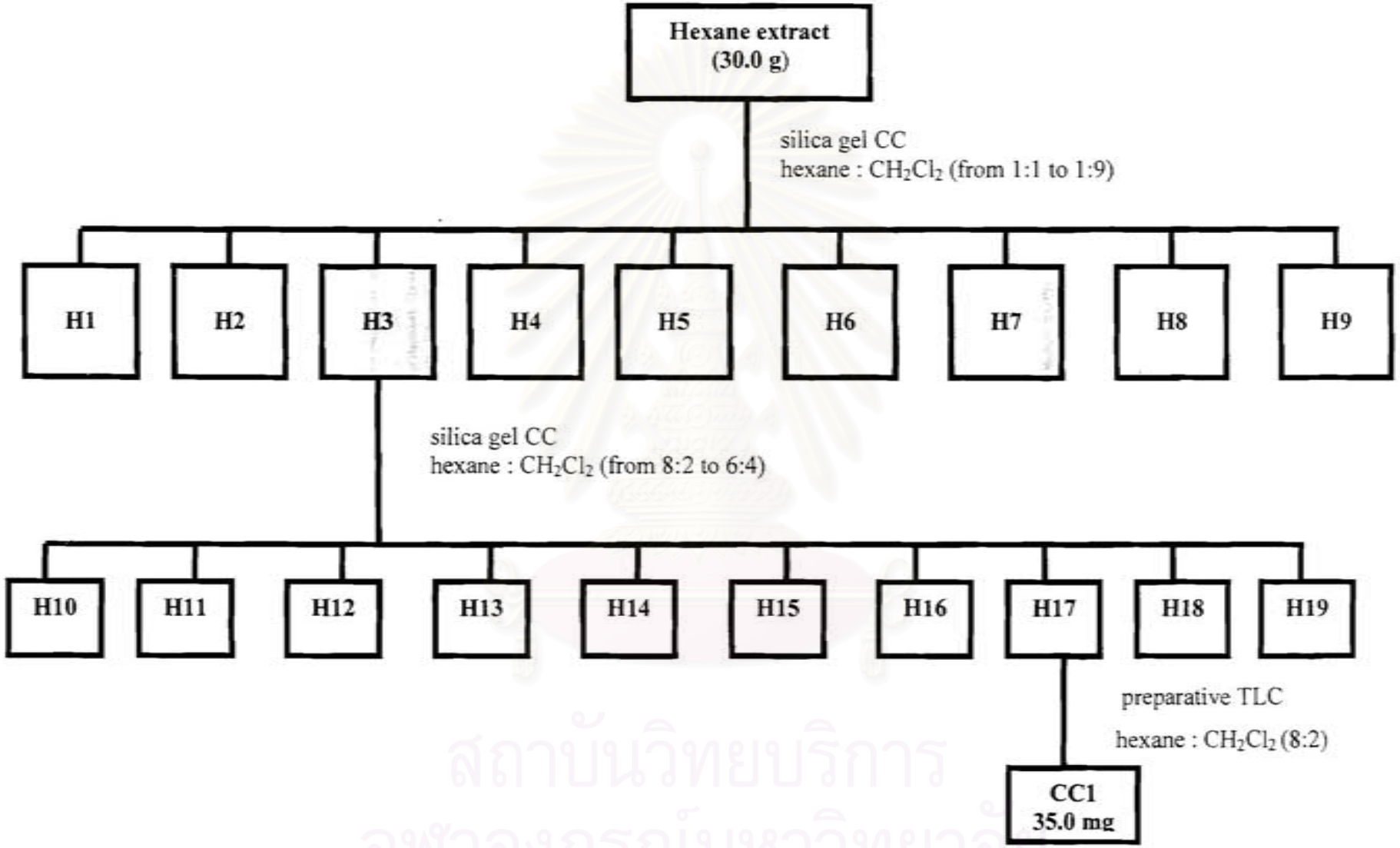
3.2.3 Isolation of Compound CC3

Portion H7 (550 mg) was subjected to a silica gel column (20 g 2x16 cm), eluted with dichloromethane to give 24 fractions of 20 ml each and then washed down with methanol. The fractions were then combined according to their TLC pattern to give 7 portions as shown in Table 9.

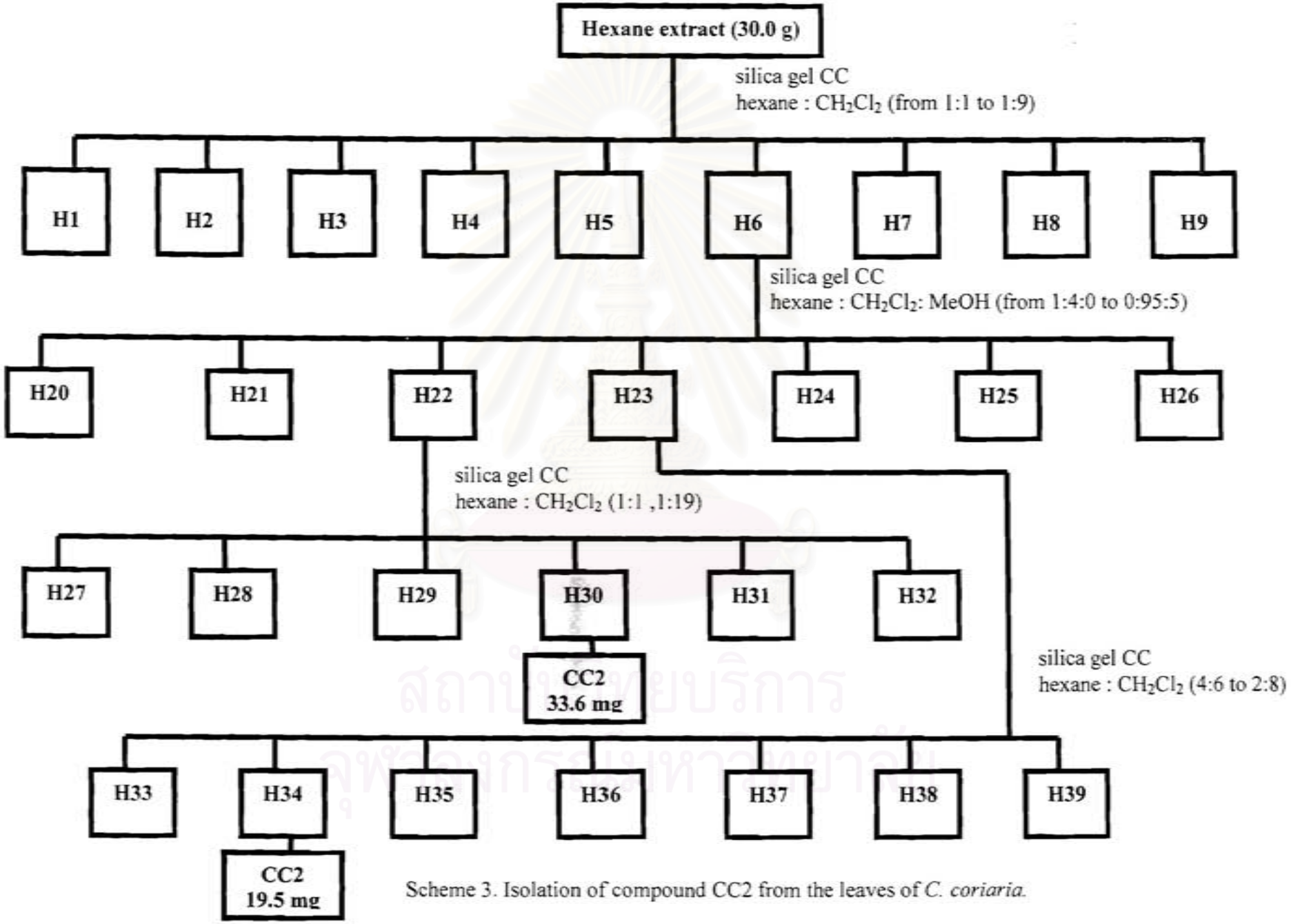
Table 9. Combined frac ion from H7

Portion	Number of fraction	Weight of fraction(mg)
H40	1-4	19.5
H41	5-6	36.4
H42	7-9	68.5
H43	10-14	136.5
H44	15-18	62.6
H45	19-24	65.2
H46	25	114.8

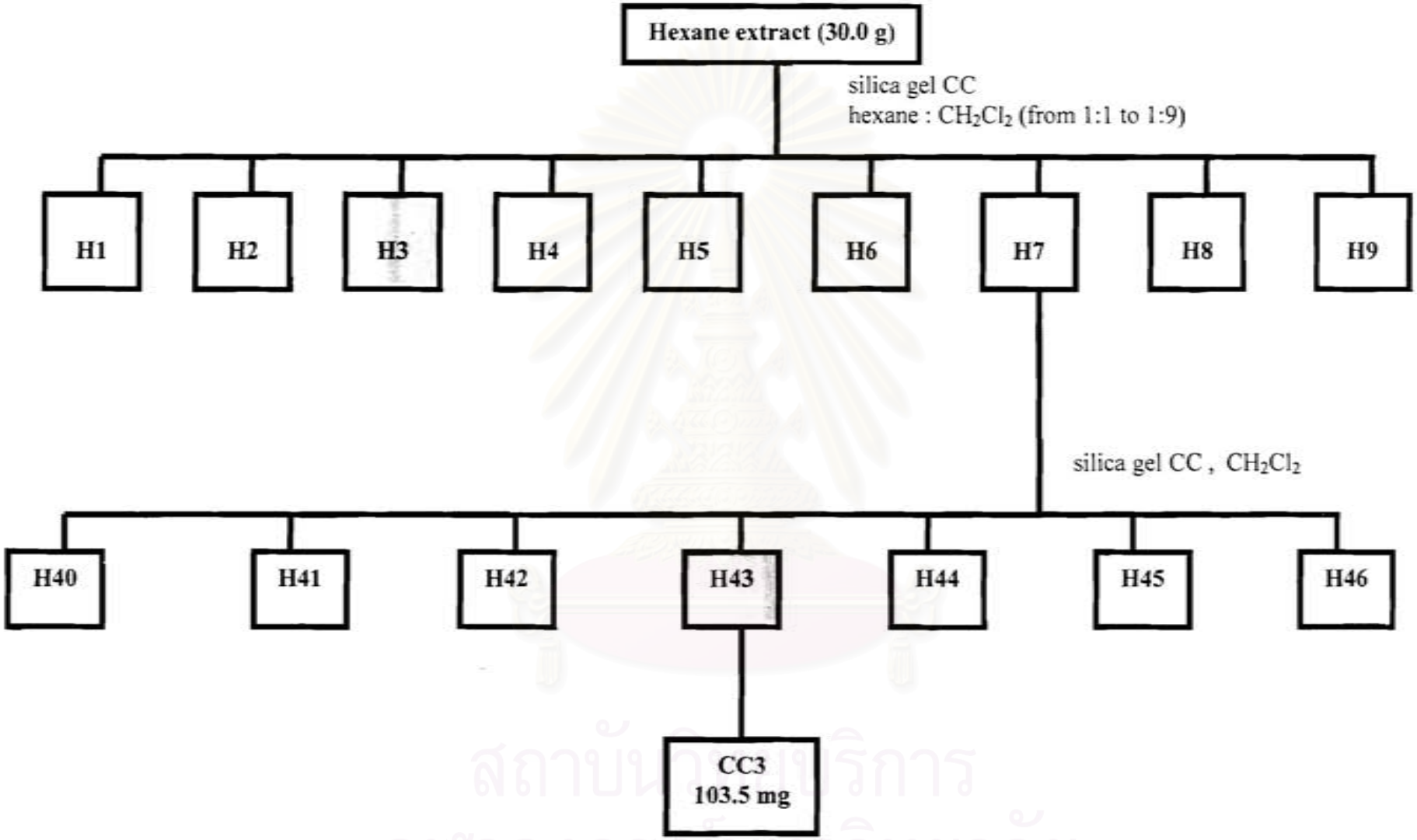
Portion H43, which gave a major violet-red spot on TLC under detection with Liebermann-Burchared reagent, was recrytallized in methanol to give compound CC3 as colorless needle (103.5mg).



Scheme 2. Isolation of compound CC1 from the leaves of *C. coriaria*.



Scheme 3. Isolation of compound CC2 from the leaves of *C. coriaria*.



Scheme 4. Isolation of compound CC3 from the leaves of *C. coriaria*.

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4. Characterization of Isolated Compounds

4.1 Compound CC1

Appearance : white amorphous powder

Solubility : Soluble in hexane and CH_2Cl_2

IR ν_{max} (KBr) cm^{-1} : 3451, 2955, 2871, 2853, 2850, 1734, 1455, 1373, 1261, 1166, 1097 and 803 (Figure 2, page 70)

EIMS *m/z* (%rel. inten.) : 323 (5), 309 (9), 280 (12), 279 (33), 239 (12), 211 (14), 197 (18), 183 (12), 167 (100), 149 (95), 125 (31), 111 (44), 97 (53), 85 (51), 71 (53), 57 (59) (Figure 9, page 87)

^{1}H-NMR (δ ppm, 500MHz, $CDCl_3$) : 5.40 (1H, *m*), 5.09 (1H, *s*), 4.99 (1H, *s*), 4.27 (1H, *dd* , *J* = 11.3, 3.2), 4.13 (1H, *dd*, *J* = 11.3, 8.4), 2.05 (*t*, *J* = 7.7), 0.84- 0.92 (18H) (Figures 3a-3c, page 71-73)

^{13}C-NMR (δ ppm, 125MHz, $CDCl_3$) : 144.9, 112.3, 73.7, 64.3, 39.4, 37.5, 37.3, 36.8, 33.2, 32.8, 32.7, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.0, 25.2, 24.9, 24.8, 24.5, 22.7, 22.6, 19.7, 19.6, 14.1 (Figures 5a-5c, page 76-78)

4.2 Compound CC2

Appearance : white amorphous powder

Solubility : Soluble in hexane and CH_2Cl_2

EIMS *m/z* (%rel. int.) : 426 (24), 411 (21), 409 (14), 393 (9), 229 (17), 219 (31), 218 (95), 205 (36), 204 (83), 203 (55), 190 (50), 189 (100), 177 (45), 175 (39), 161(41), 148 (29), 135 (35), 121 (38), 124 (21), 111 (42), 108 (24), 97 (51), 95 (46), 81 (32), 67 (25)

(Figure 15, page 110)

^{1}H-NMR (δ ppm, 500MHz, $CDCl_3$) : 4.87 (1H, *br s*), 4.70 (1H, *dd*, *J* = 2.1), 4.58 (1H, *br s*), 3.21 (2H, *m*), 2.39 (1H, *dd*, *J* = 11.1, 5.8), 2.28 (1H, *d*, *J* = 12.5), 1.70 (3H, *s*), 1.09 (3H, *s*), 1.04 (3H, *s*), 1.03 (3H, *s*), (0.99 (3H, *s*), 0.98 (3H, *s*), 0.96 (3H, *s*), 0.95 (6H, *s*), 0.89 (3H, *s*), 0.84 (3H, *s*), 0.80 (3H, *s*), 0.78 (6H, *s*), 0.75 (3H, *s*)

(Figures 10a-10c, page 96-98)

^{13}C-NMR (δ ppm, 125MHz, $CDCl_3$) : 151.0, 142.8, 129.7, 109.3, 79.0, 55.5, 55.3, 51.2, 50.5, 48.3, 48.0, 43.3, 43.0, 42.8, 40.9, 40.8, 40.0, 39.0, 38.9, 38.7, 38.4, 38.1, 37.7, 37.4, 37.2, 35.6, 34.6, 34.4, 34.3, 33.3, 32.3, 31.3, 29.9, 29.2, 28.0, 27.5, 27.4, 26.2, 25.3, 25.2, 21.1, 20.9, 19.3, 18.3, 18.0, 16.7, 16.1, 16.0, 15.4, 14.6

(Figures 12a-11 b, page 99-100)

4.3 Compound CC3

Appearance : Colorless needles

Solubility : Soluble in hexane and dichloromethane

^{1}H-NMR (δ ppm, 500MHz, $CDCl_3$) : 5.33 (1H, *br s*), 5.15 (1H), 5.00 (1H), 3.50 (1H, *m*), 1.25 (3H, *s*), 0.93 (3H, *d*), 0.88 (3H, *t*), 0.85 (3H, *d*), 0.82 (3H, *d*), 0.70 (3H, *s*)
(Figure 16, page 113)

^{13}C-NMR (δ ppm, 125MHz, $CDCl_3$) : 140.6, 138.1, 129.1, 121.6, 71.8, 56.8, 56.1, 50.2, 45.9, 42.4, 39.9, 37.3, 36.6, 36.2, 34.0, 32.0, 31.9, 29.8, 28.3, 26.2, 24.4, 23.2, 21.2, 20.0 19.5, 19.2, 18.9, 12.1, 11.9
(Figures 17a-17b, page 114-115)

CHAPTER IV

RESULTS AND DISCUSSION

In this chemical investigation on the leaves of *Caesalpinia coriaria* (Jacq.) Willd., three compounds were isolated from its hexane extract. The identification of the isolated compounds were based on the interpretation of their spectral data and further confirmed by comparison with those values reported in the literature. The details are as follows.

Identification of Isolated Compounds

1. Identification of Compound CC1

Compound CC1 was obtained as white amorphous powder (35.0 mg, 0.007 % yield). The compound gave violet-blue color to anisaldehyde-sulfuric acid reagent. Its IR spectrum (Figure 2) showed the carbonyl absorption at 1734 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra of CC1 gave evidences which suggested that the compound was a diester of an unsaturated acyclic diterpenoid, 7,11,15-trimethyl–3-methylene hexadecan-1,2-diol.

The ^{1}H-NMR spectrum (Figures 3a-3c) exhibited overlapped signals due to six methyl groups in the region of δ 0.84 – 0.92 ppm. Two sites of esterification in the molecule of CC1 were inferred from two partially overlapped triplets at δ 2.31 (2H, J = 7.5 Hz; H-2") and 2.35 ppm (2H, J = 7.5 Hz; H-2'). A pair of singlets at δ 4.99 and 5.09 ppm (1H each; H-17), which showed correlation with each other in the COSY spectrum (Figures 4a-4b), implied the presence of an exo-methylene group. Another pair of correlated signals at δ 4.13 (1H, *dd*, J = 11.3, 8.4 Hz; H-1a) and 4.27 ppm (1H, *dd*, , J = 11.3, 3.2 Hz; H-1b) and the most downfield signal at δ 5.40 ppm (1H, *m*, H-2) were attributable to protons due to oxymethylene and oxymethine groups at the site of ester formation, respectively. The proximity of these two groups was confirmed by the correlation between their corresponding protons observed in the COSY spectrum.

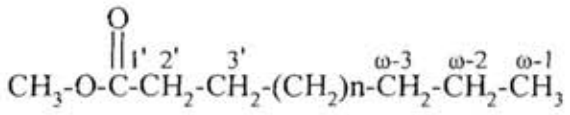
The ^{13}C-NMR spectrum (Figures 5a-5c) exhibited a number of signals in the region of δ 14.0-40.0 ppm and four signals in the more downfield region at δ 64.3, 73.7, 112.3 and 144.9 ppm . The DEPT experiments (Figures 6a-6b) and ^{1}H-^{13}C HMQC spectrum (Figure 7) were useful in differentiating these signals. The signals at δ 112.3 and 144.9 ppm. represented the unsaturation due to the exo-methylene group while those at δ 64.3 and 73.7 ppm were attributed to methylene and methine carbons connecting to the ester oxygen, respectively. Surprisingly, no carbonyl signals were observed. However, the presence of such signals was evident from the HMBC spectrum (Figures 8a-8e) in which the triplets at δ 2.31 (H-2") and 2.35 (H-2') ppm displayed correlation with the unobservable carbon signals at δ 173.5 (C-1") and 173.2 ppm (C-1'), respectively. In addition, the signal at δ 173.2 ppm (C-1') also showed correlation with the signal of oxymethylene proton at δ 4.13 ppm (H-1a). Correlation observed for the pair of singlets at δ 4.99 and 5.09 ppm (H-17) with the carbon signal at δ 73.7 ppm (C-2) in the HMBC spectrum indicated the location of the exo-methylene group at the quaternary carbon (C-3) next to the oxymethine one (C-2).

Comparison of ^{1}H- and ^{13}C-NMR assignments of the diterpenoid part of CC1 with the reported data of 7,11,15-trimethyl-3-methylene hexadecan-1,2-diol (Urones *et al.*, 1987) are shown in Table 10. The structure elucidation of two acyl moieties of CC1 could not be achieved on the basis of available data, including those from the EIMS (Figure 9). However, some information about the acyl part was obtained from the ^{13}C-NMR spectrum. In addition to those of carbons of the diterpenoid part, the ^{13}C-NMR spectrum of CC1 exhibited signals at δ 14.1, 22.7, 25.2, 31.9, 34.2 ppm and a number of signals at around δ 29.0-30.0 ppm. All of these signals, as suggested by the DEPT experiments, belonged to methylene carbons except for the most upfield one which was due to methyl carbons. Chemical shifts of these signals were similar to those of methyl alkanoates (Gunstone, Pollard, and Scrimgeor, 1976.) as shown in Table 11. As can be seen from the Table, the carbon at each position, except for the carbonyl, was represented by only one signal of CC1, suggesting that both acyl moieties of the compound had the same structure.

Table10. ^{1}H and ^{13}C-NMR assignments of compound CC1 and the reported data of 7,11,15-trimethyl-3-methylene-hexadecan-1,2diol (in $CDCl_3$).

Position	CC1		7,11,15-trimethyl-3-methylene-hexadecan-1,2diol	
	δH	δC	δH	δC
1	4.27 (*dd*, *J* = 11.3, 3.2) 4.13 (*dd*, *J* = 11.3, 8.4)	64.3	3.69 (*dd*, *J* = 11.23, 3.42) 3.57 (*dd*, *J* = 11.23, 7.32)	65.8
2	5.40 (*m*)	73.7	4.21 (*dd*, *J* = 11.23, 3.42)	75.1
3		144.9		148.9
4	2.05 (*t*, *J* = 7.7)	33.2		33.1
5		24.9		25.6
6		36.8		36.9
7		32.7		32.8
8		37.5*		37.5
9		24.5		24.5
10		37.5*		37.5
11		32.8		32.9
12		37.3*		37.4
13		24.8		24.8
14		39.4		39.5
15		28.0		28.0
16	0.88 (*d*, *J* = 6.6)	22.6	0.86 (*d*, *J* = 6.6)	22.6
17	5.09 (*s*), 4.99 (*s*)	112.3	5.13 (*s*), 4.98 (*s*)	110.6
18	0.87 (*d*, *J* = 6.6)	19.7	0.85 (*d*, *J* = 6.4)	19.8**
19	0.86 (*d*, *J* = 6.6)	19.7	0.84 (*d*, *J* = 6.4)	19.7**
20	0.88 (*d*, *J* = 6.6)	22.7	0.86 (*d*, *J* = 6.6)	22.7
1'		173.2		
1"		173.5		
2'	2.35 (*t*, *J* = 7.5)	34.2		
2"	2.31 (*t*, *J* = 7.5)	34.2		
$\underline{CH_3}(CH_2)_nCOO$	0.90 (*t*, *J* = 6.7)	14.1		
	0.89 (*t*, *J* = 6.7)	14.1		

*, ** The values may be interchanged.

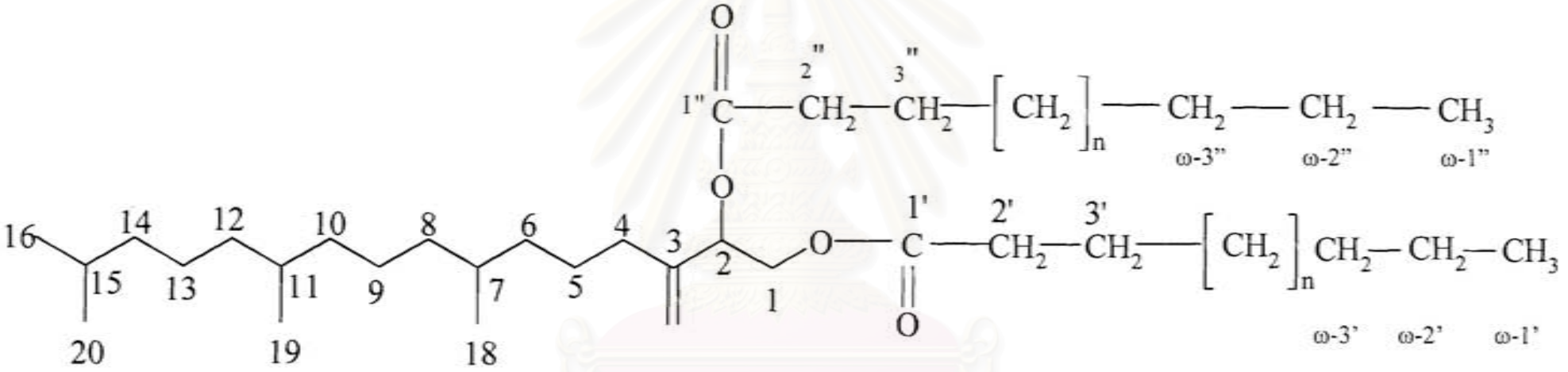


methyl alkanoate

Table 11. ^{13}C-NMR data of the acyl moiety of CC1 and reported values of methyl alkanoates (in $CDCl_3$).

Carbon	δ (ppm)	
	methyl alkanoates	CC1 (the acyl moiety)
C-1'	174.0-174.3	173.2 / 173.5
C-2'	34.1 - 34.2	34.2
C-3'	25.0 - 25.2	25.2
$(CH_2)_n$	29.2 – 29.9	29.1 - 30.0
ω-3	31.9 - 32.2	31.9
ω-2	22.7 - 22.9	22.7
ω-1	14.1 -14.2	14.1

Therefore, it was concluded that CC1 was a diester of 7,11,15-trimethyl-3-methylene hexadecan-1,2-diol, of which two acyl moieties were derived from the same saturated fatty acid.



Compound CC1

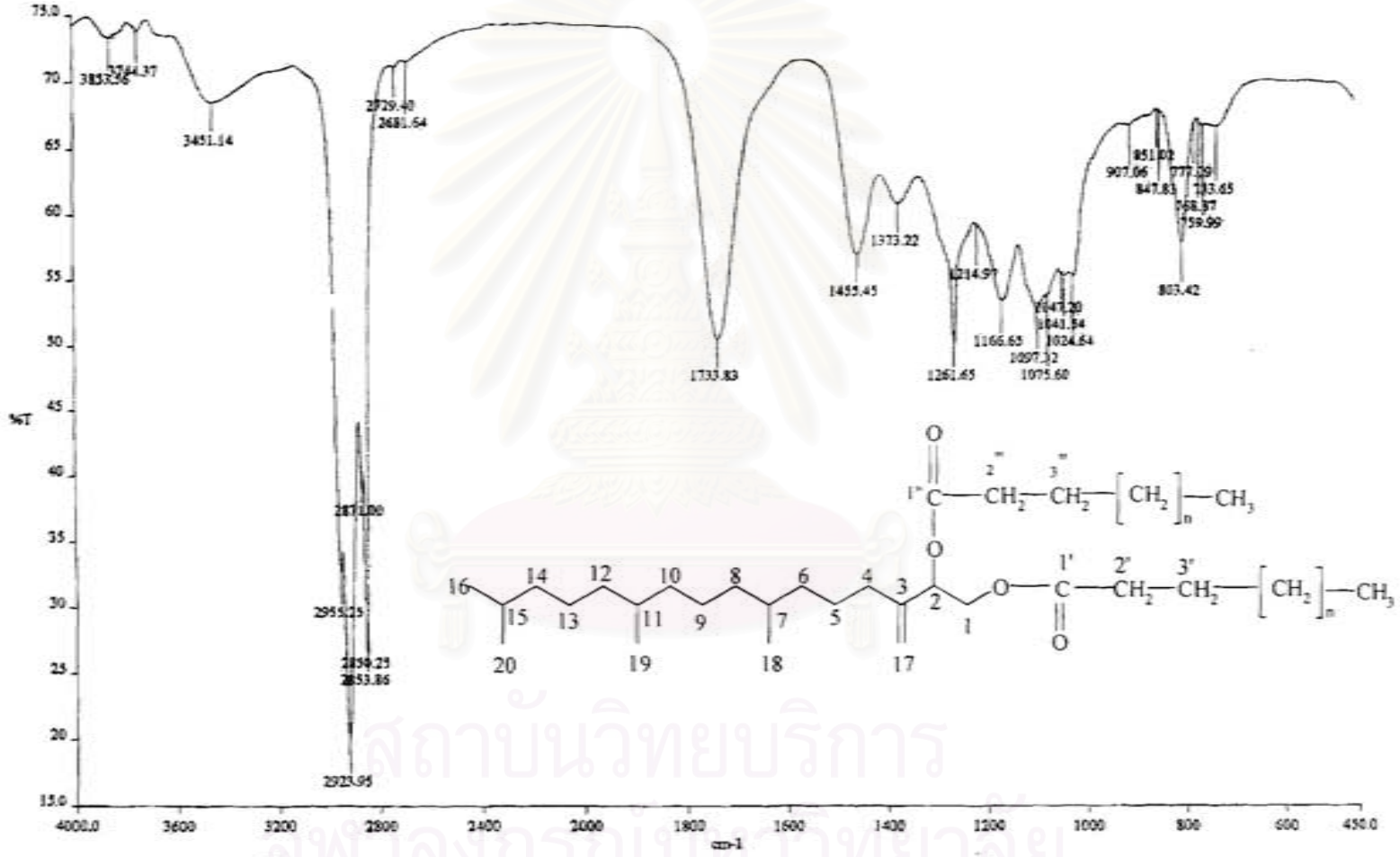


Figure 2. IR spectrum of compound CC1.

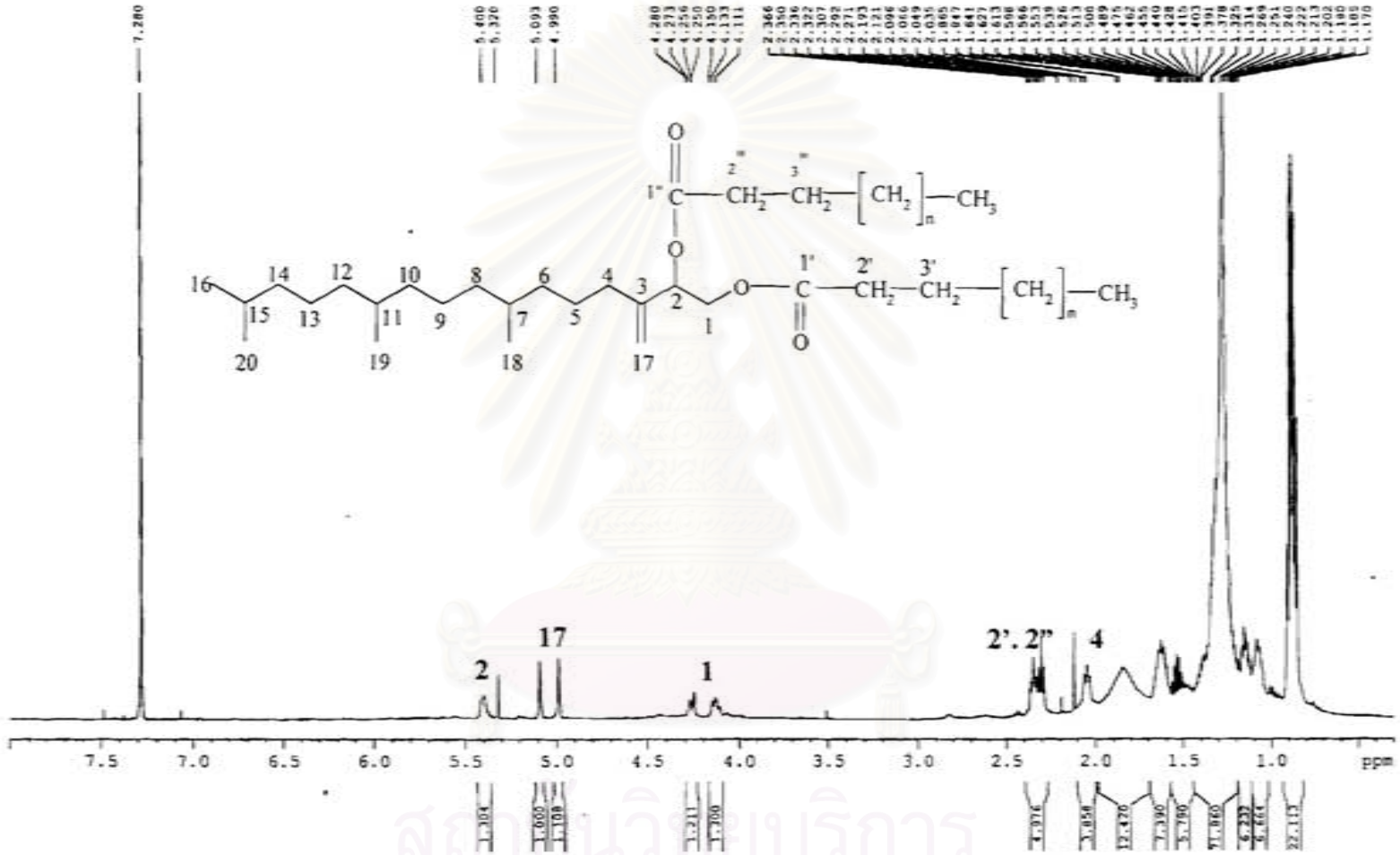


Figure 3a. The 500 MHz ^{1}H-NMR spectrum of compound CC1.

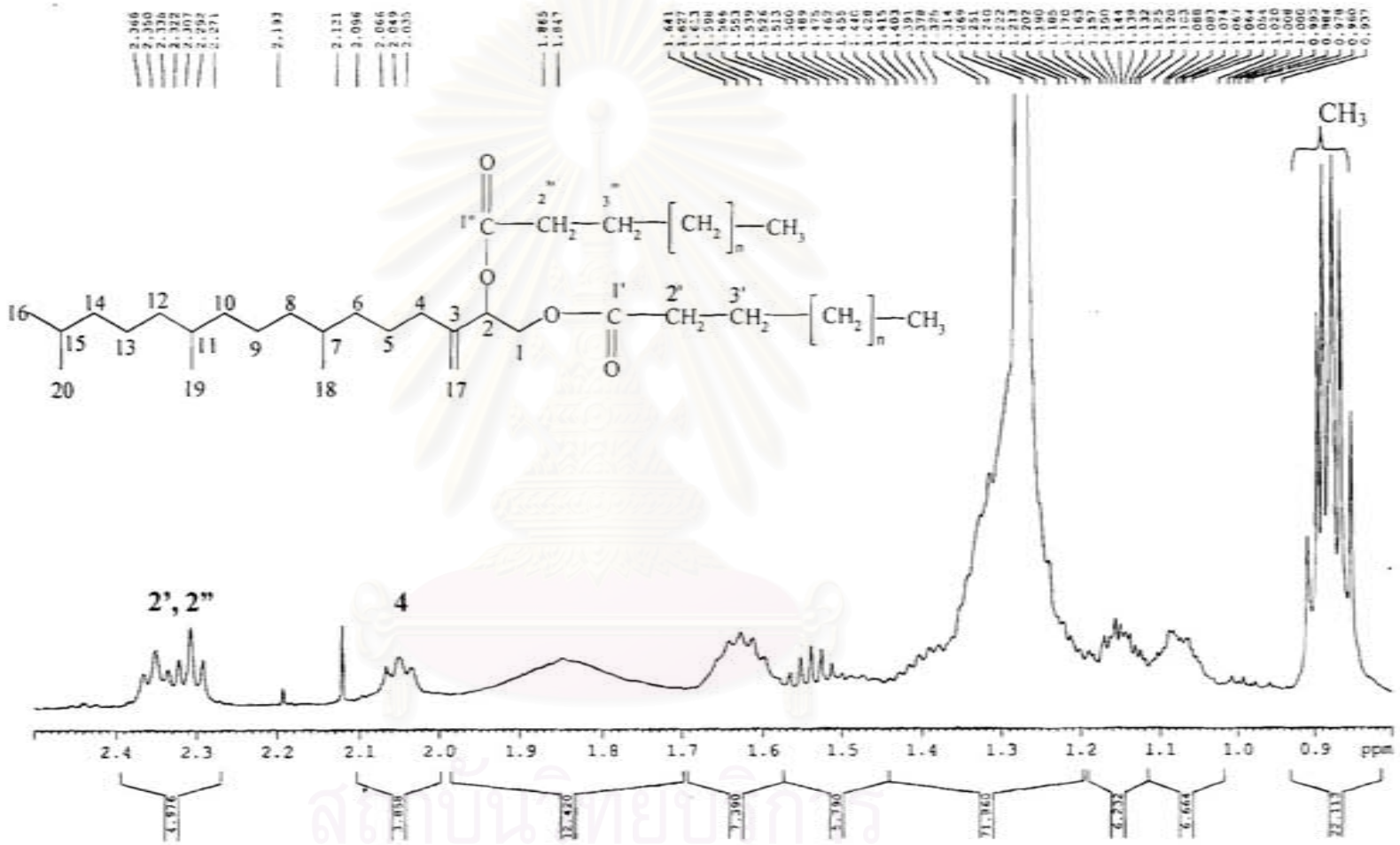


Figure 3b. The 500 MHz ^{1}H-NMR spectrum of compound CC1 (expanded).

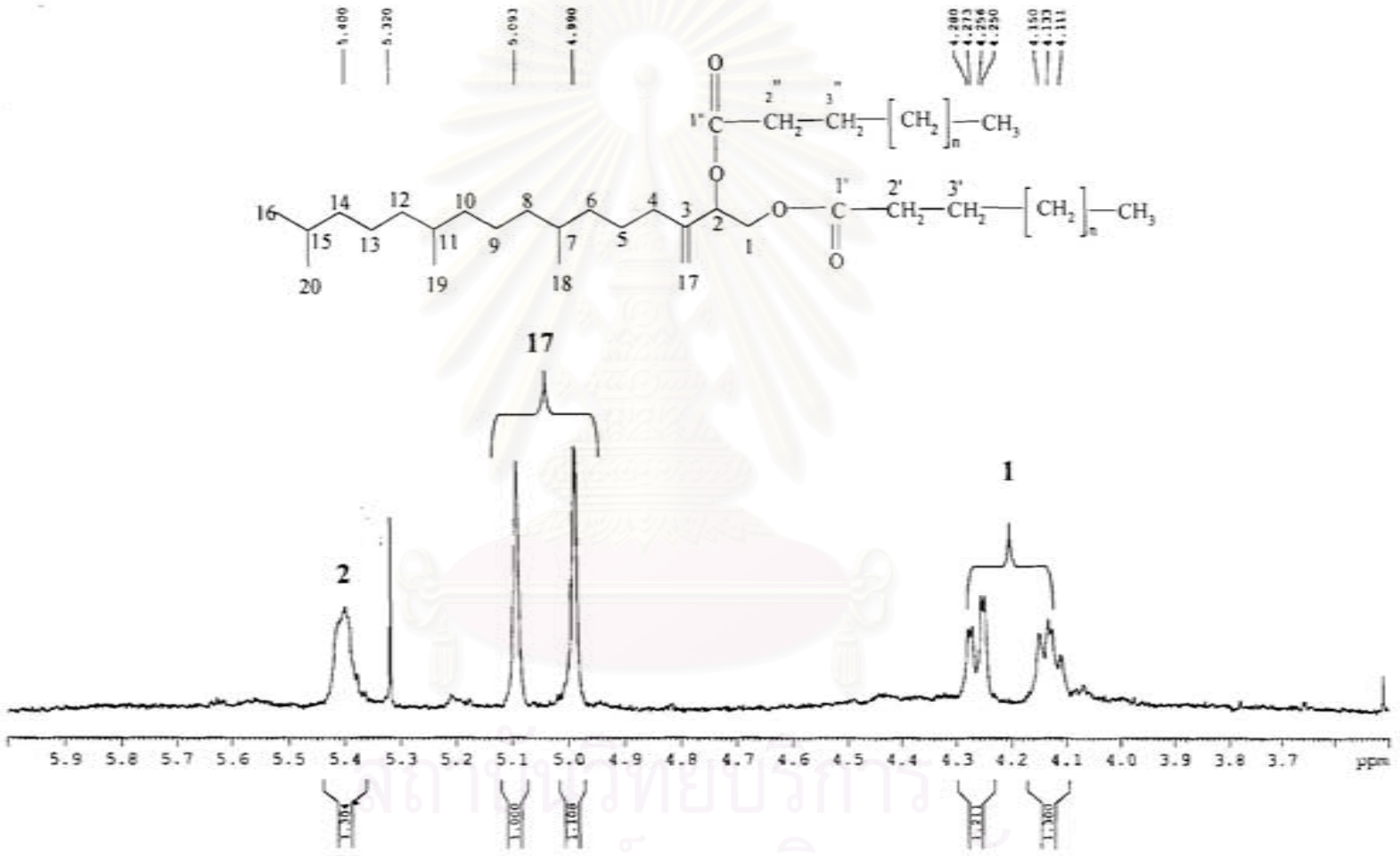


Figure 3c. The 500 MHz ^{1}H-NMR spectrum of compound CC1 (expanded).

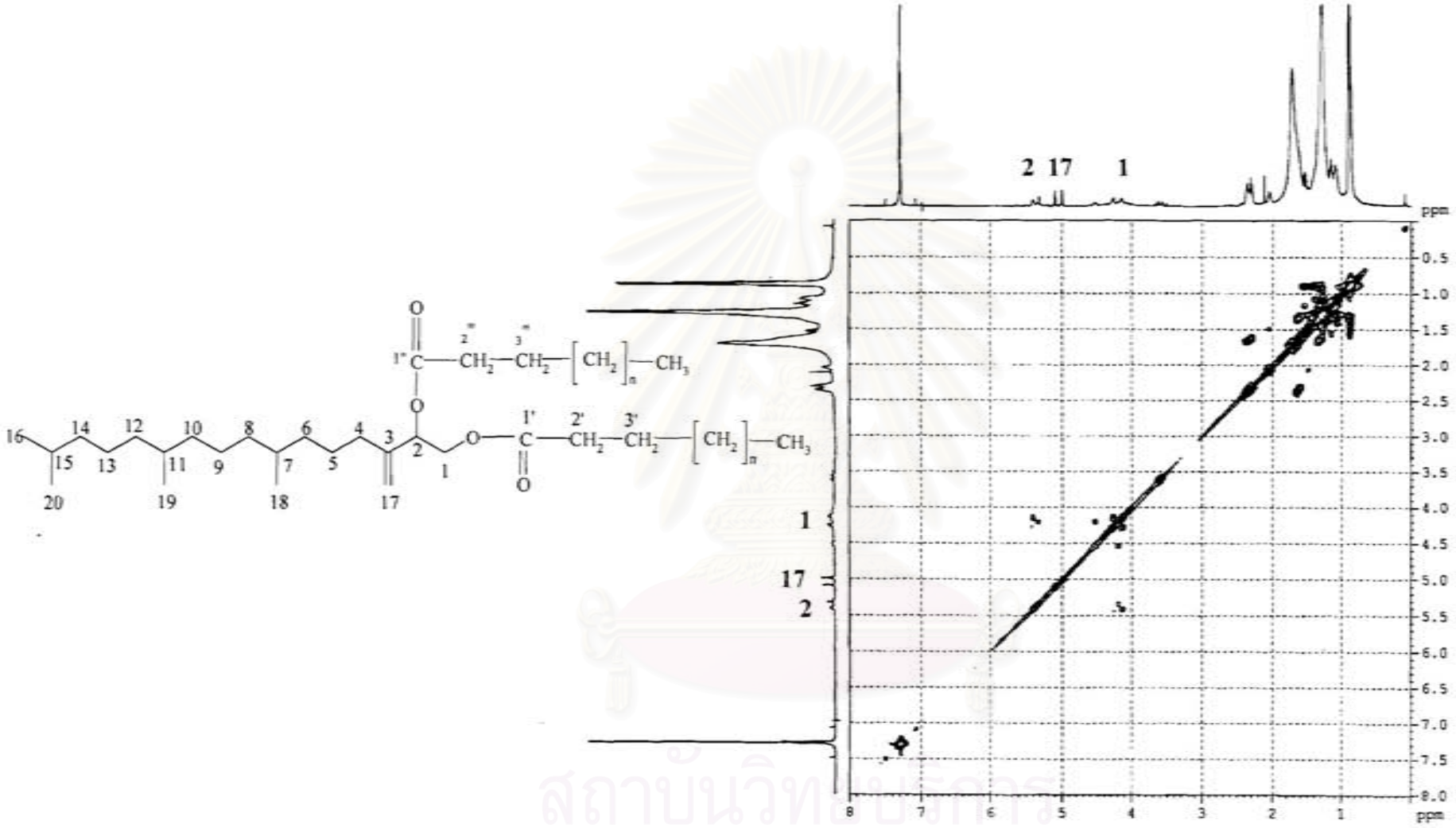


Figure 4a. The ^{1}H ^{-1}H COSY NMR spectrum of compound CC1.

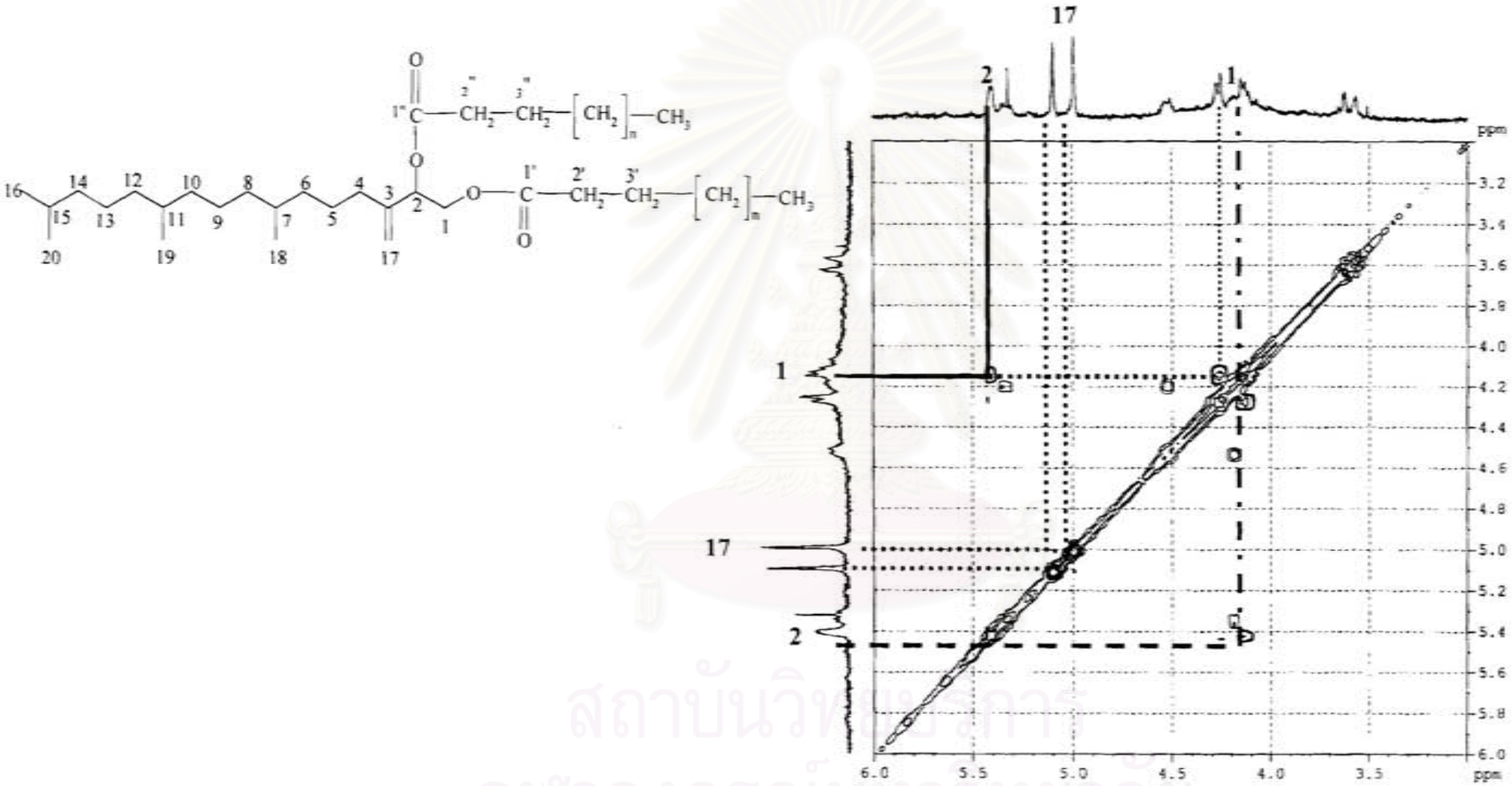


Figure 4b. The ^{1}H ^{-1}H COSY NMR spectrum of compound CC1 (expanded).

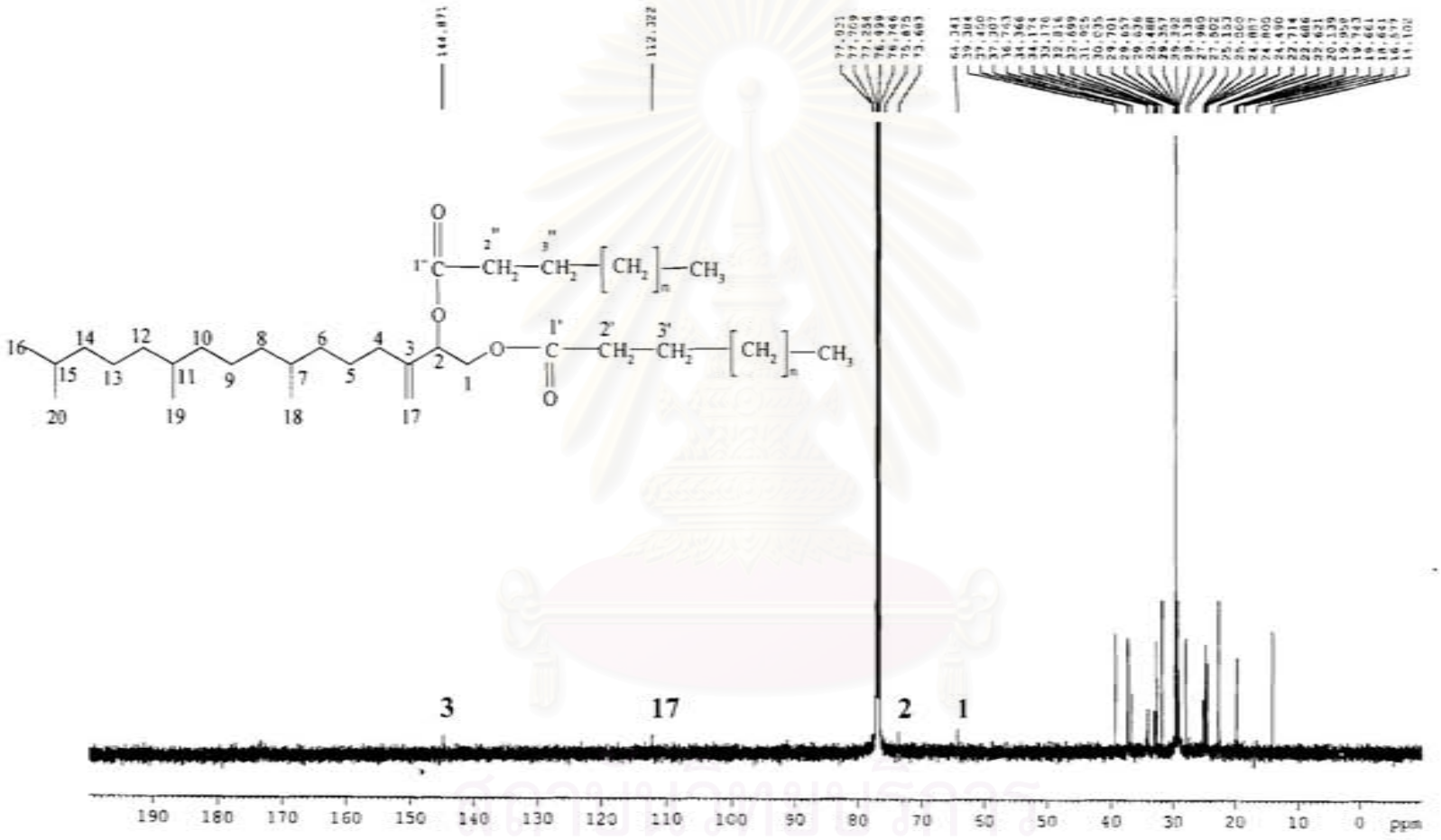


Figure 5a. The 125MHz ^{13}C-NMR spectrum of compound CC1.

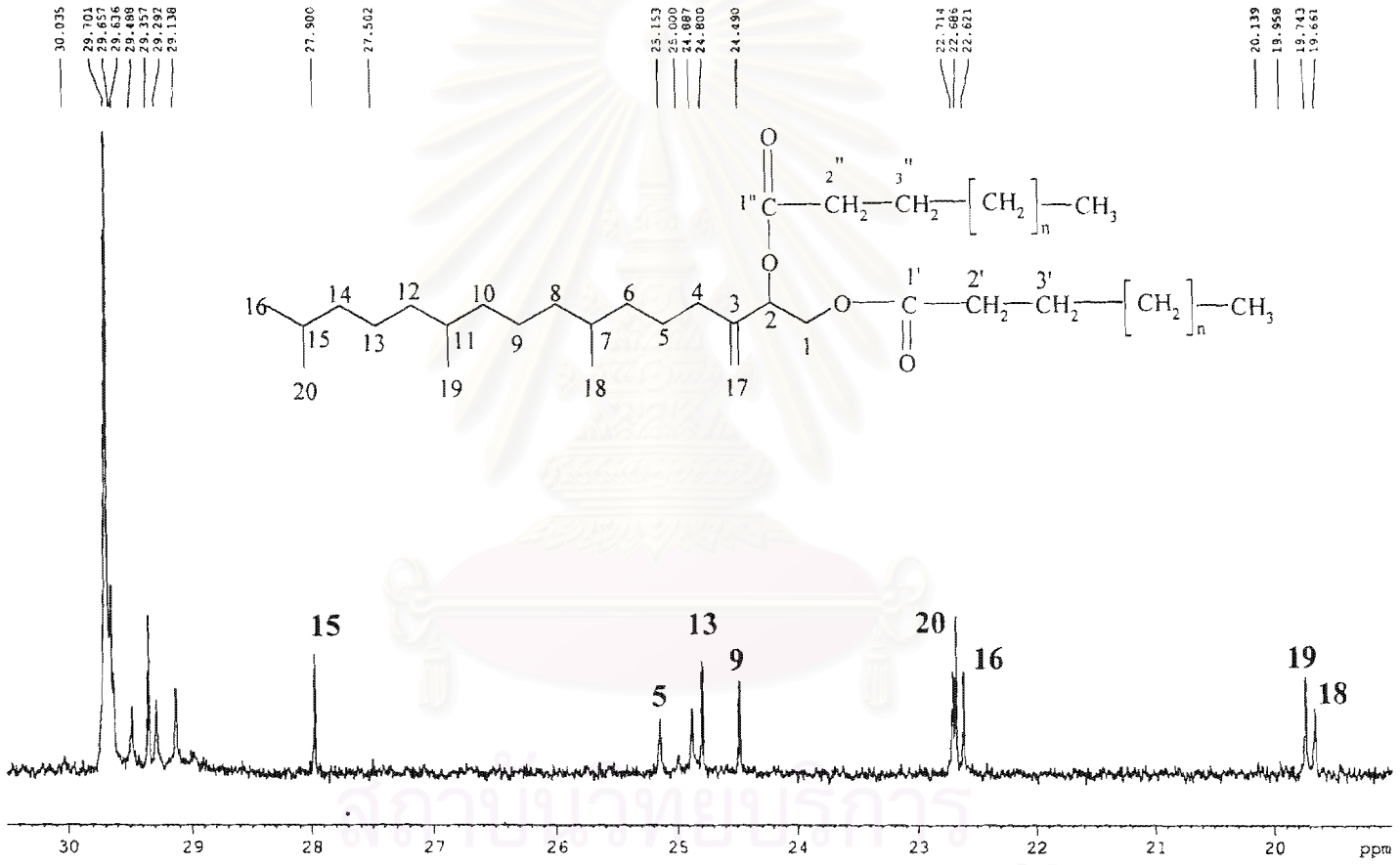


Figure 5b. The 125MHz ^{13}C-NMR spectrum of compound CC1 (expanded).

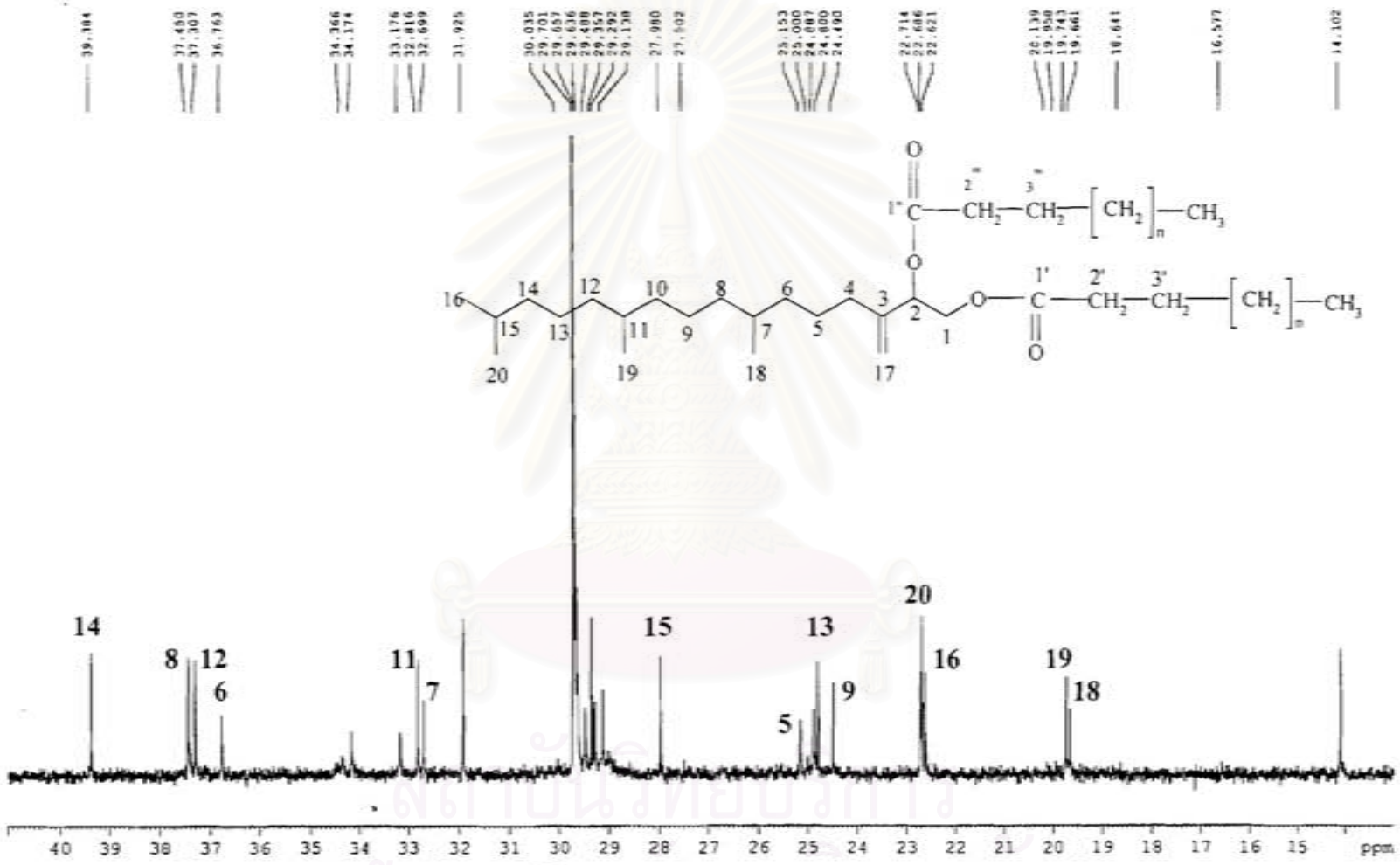


Figure 5c. The 125MHz ^{13}C-NMR spectrum of compound CC1 (expanded).

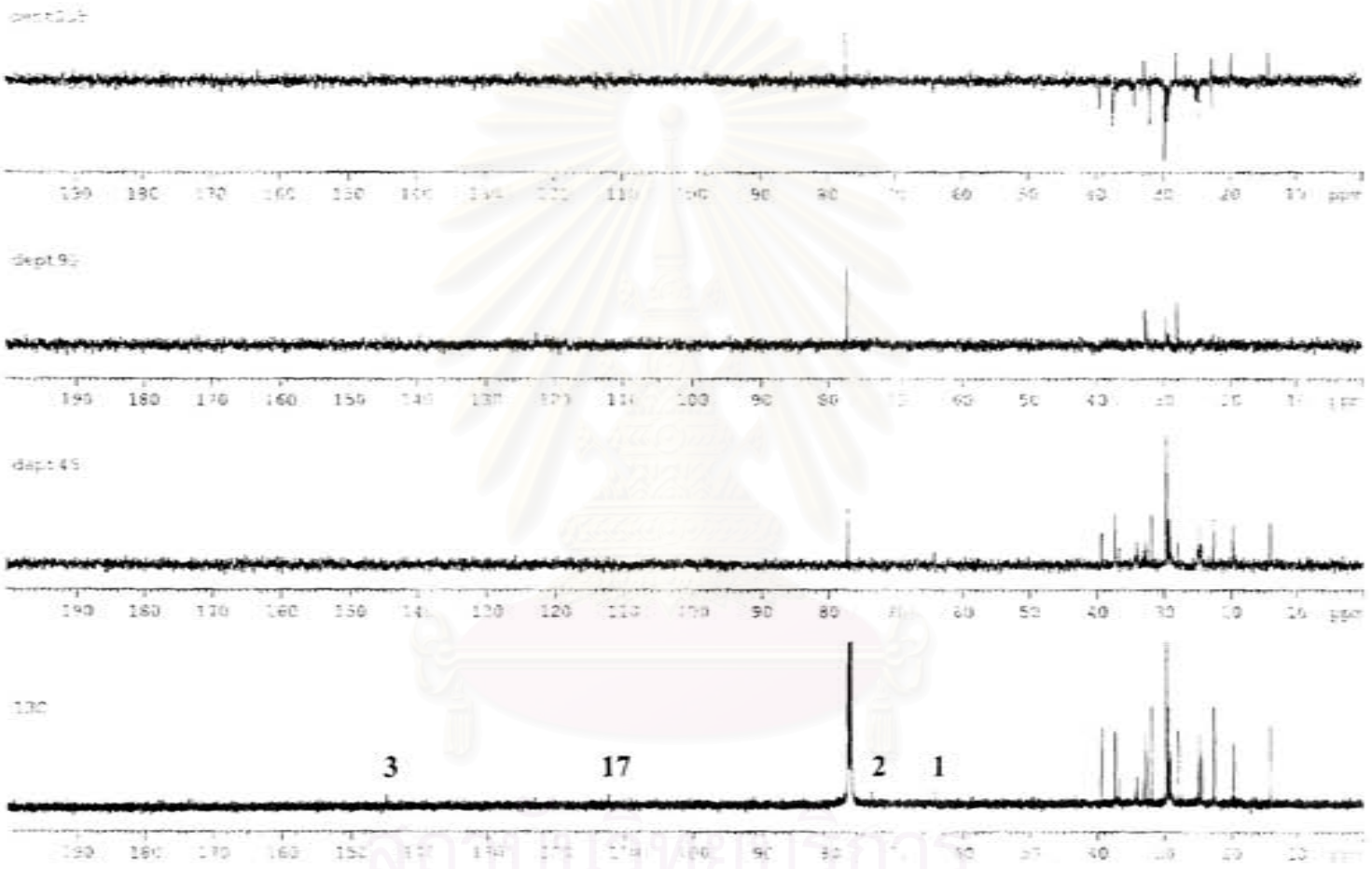


Figure 6a. The 125MHz ^{13}C-DEPT NMR spectrum of compound CC1

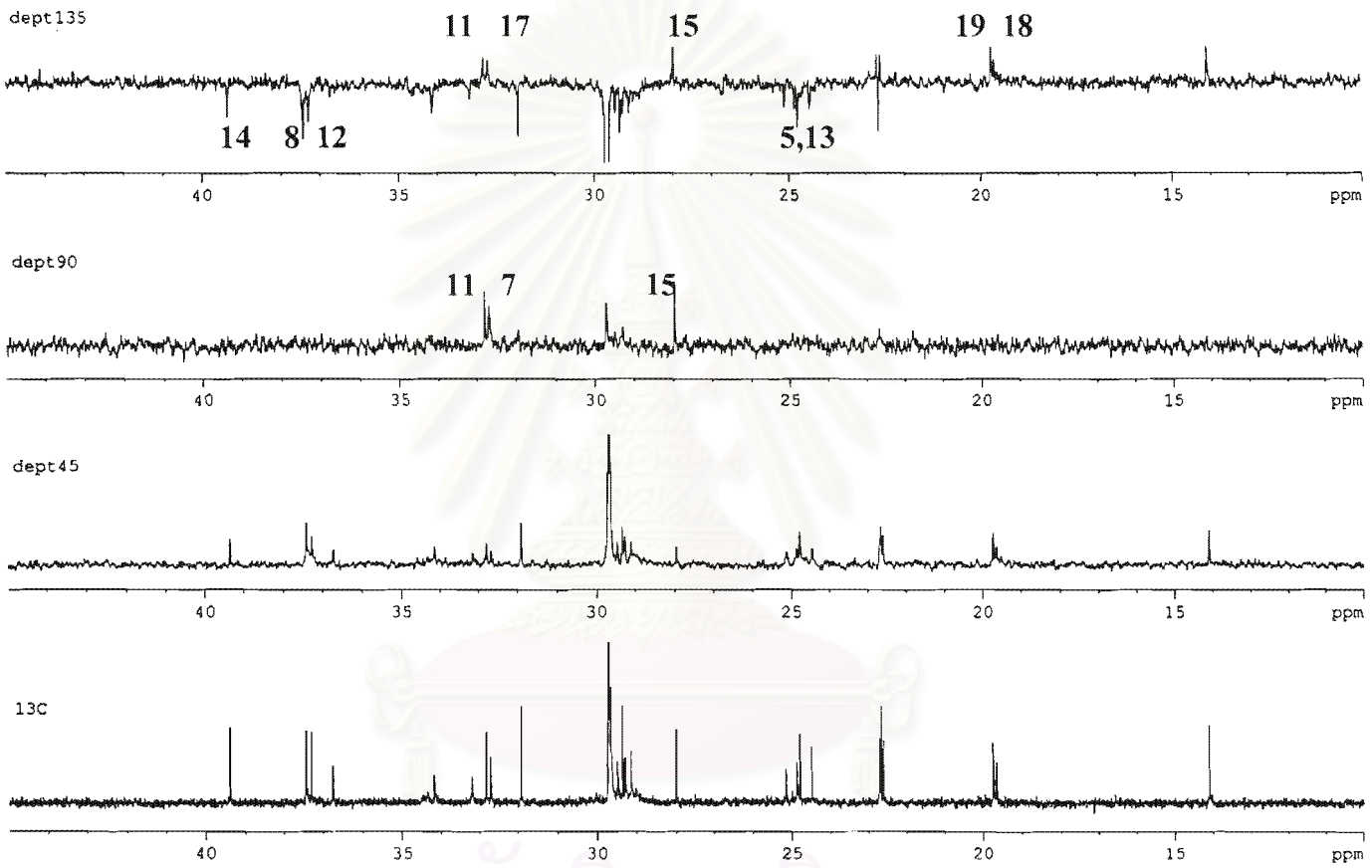


Figure 6b. The 125MHz ^{13}C-DEPT NMR spectrum of compound CC1 (expanded).

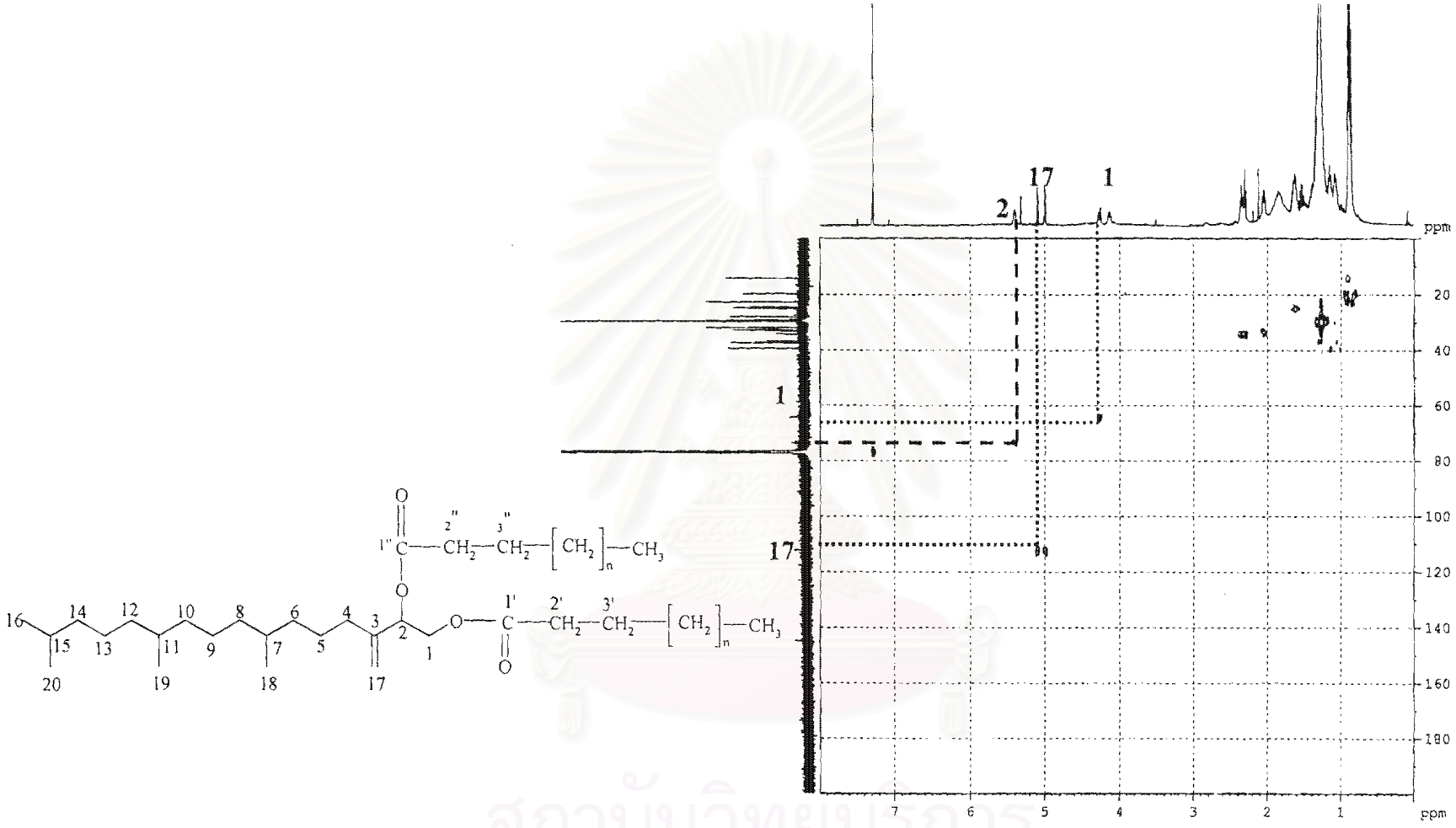


Figure 7. The HMQC NMR spectrum of compound CC1.

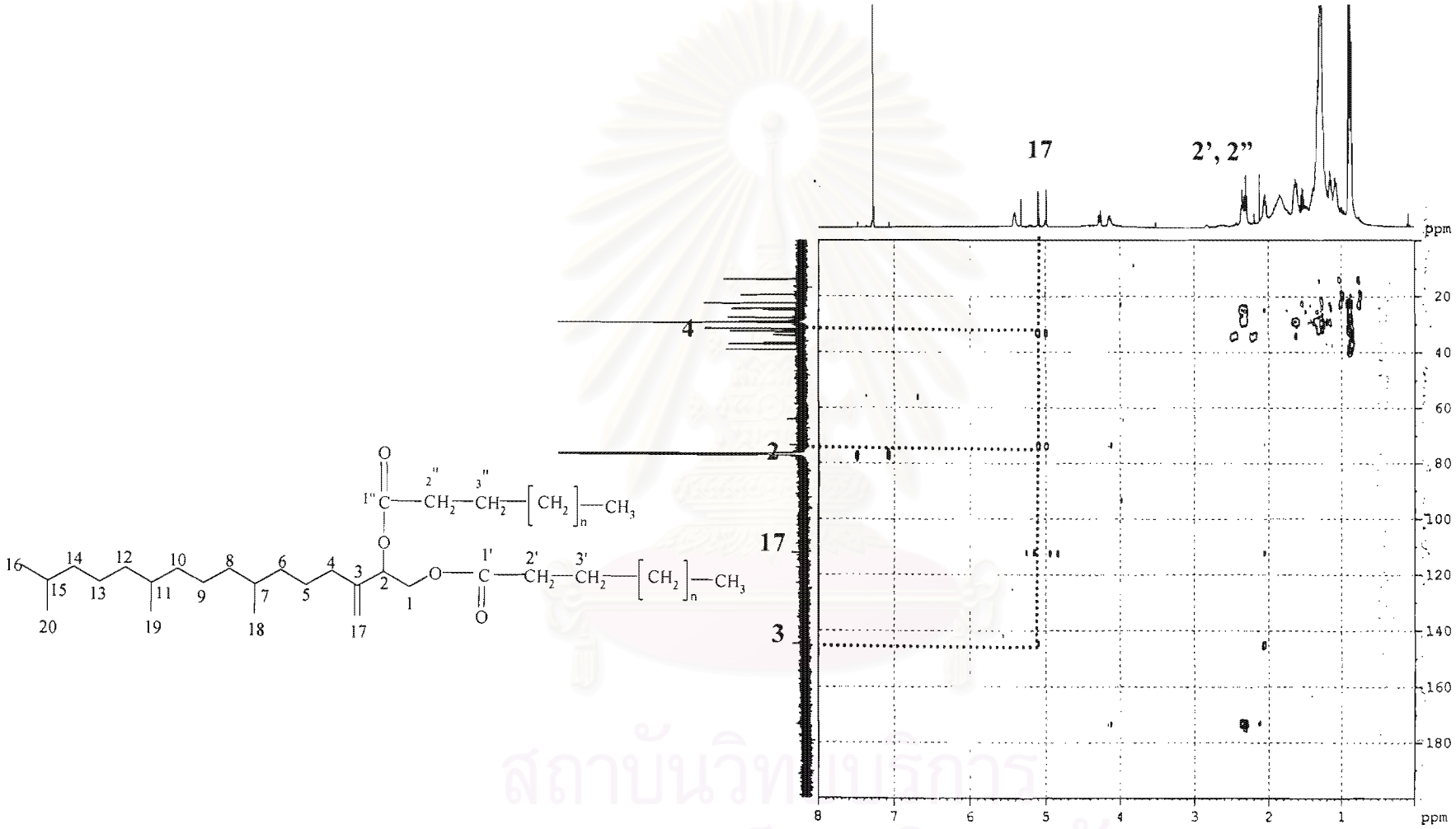


Figure 8a. The HMBC NMR spectrum of compound CC1.

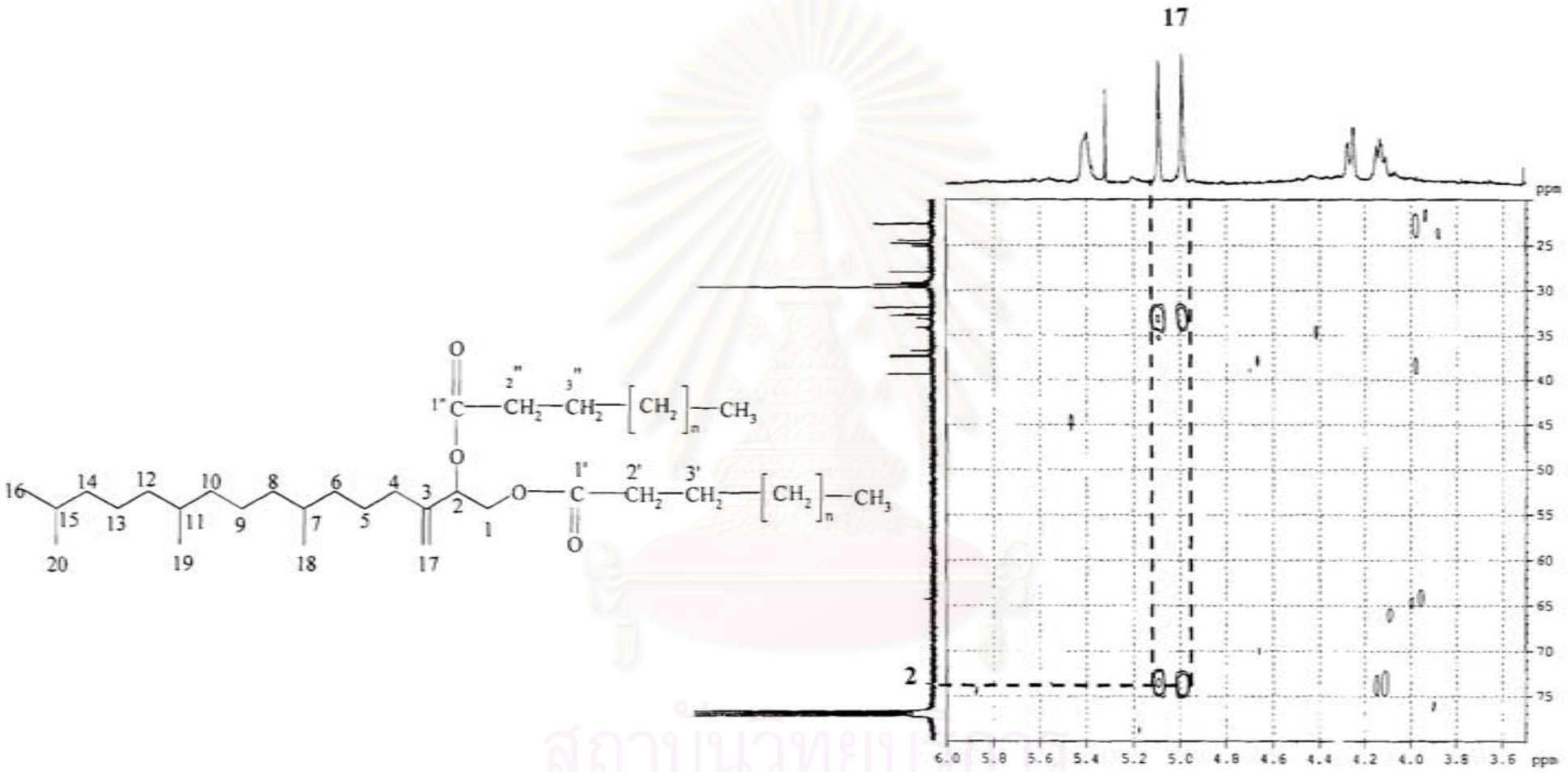


Figure 8b. The HMBC NMR spectrum of compound CC1 (expanded).

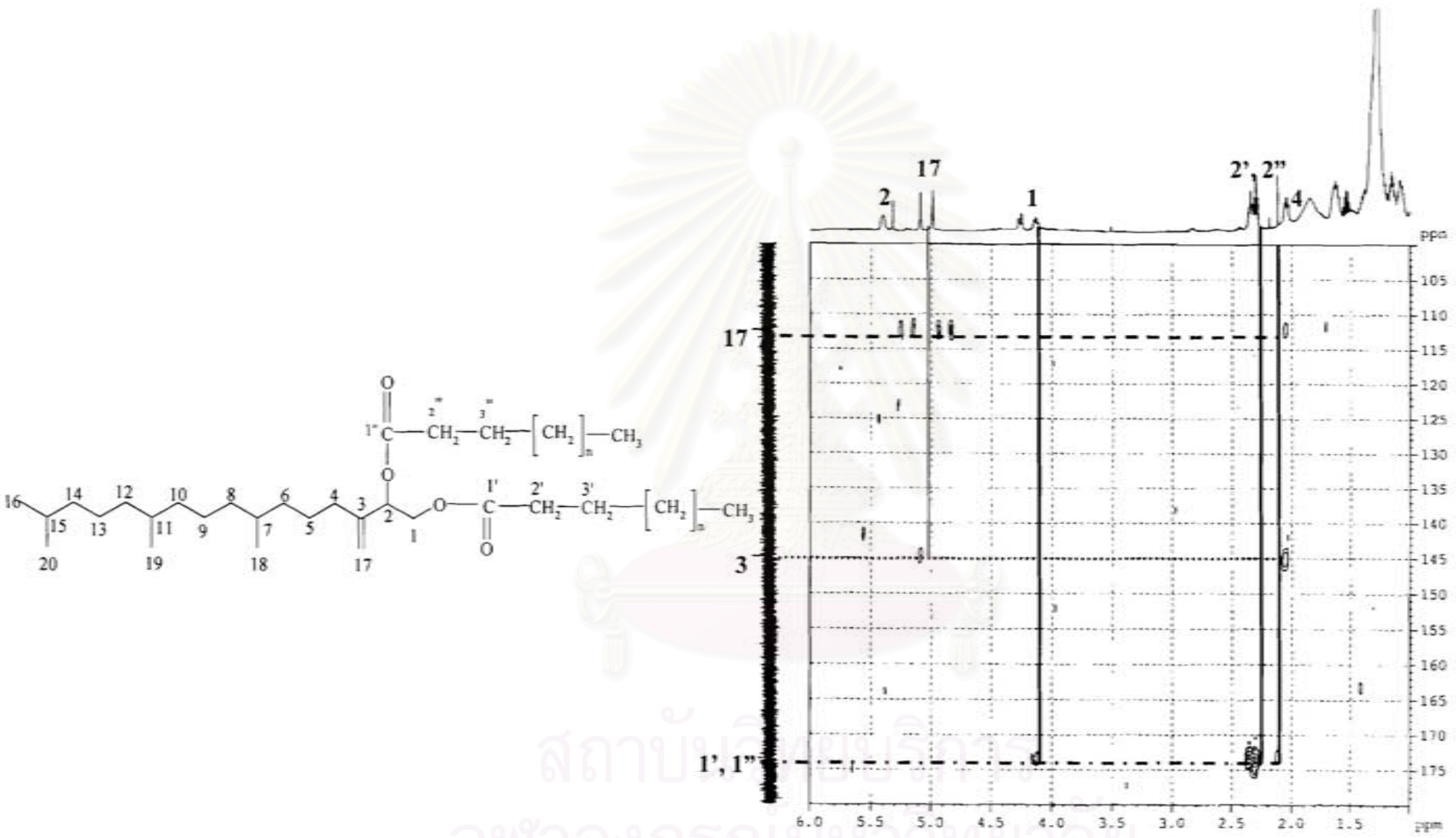


Figure 8c. The HMBC NMR spectrum of compound CC1 (expanded).

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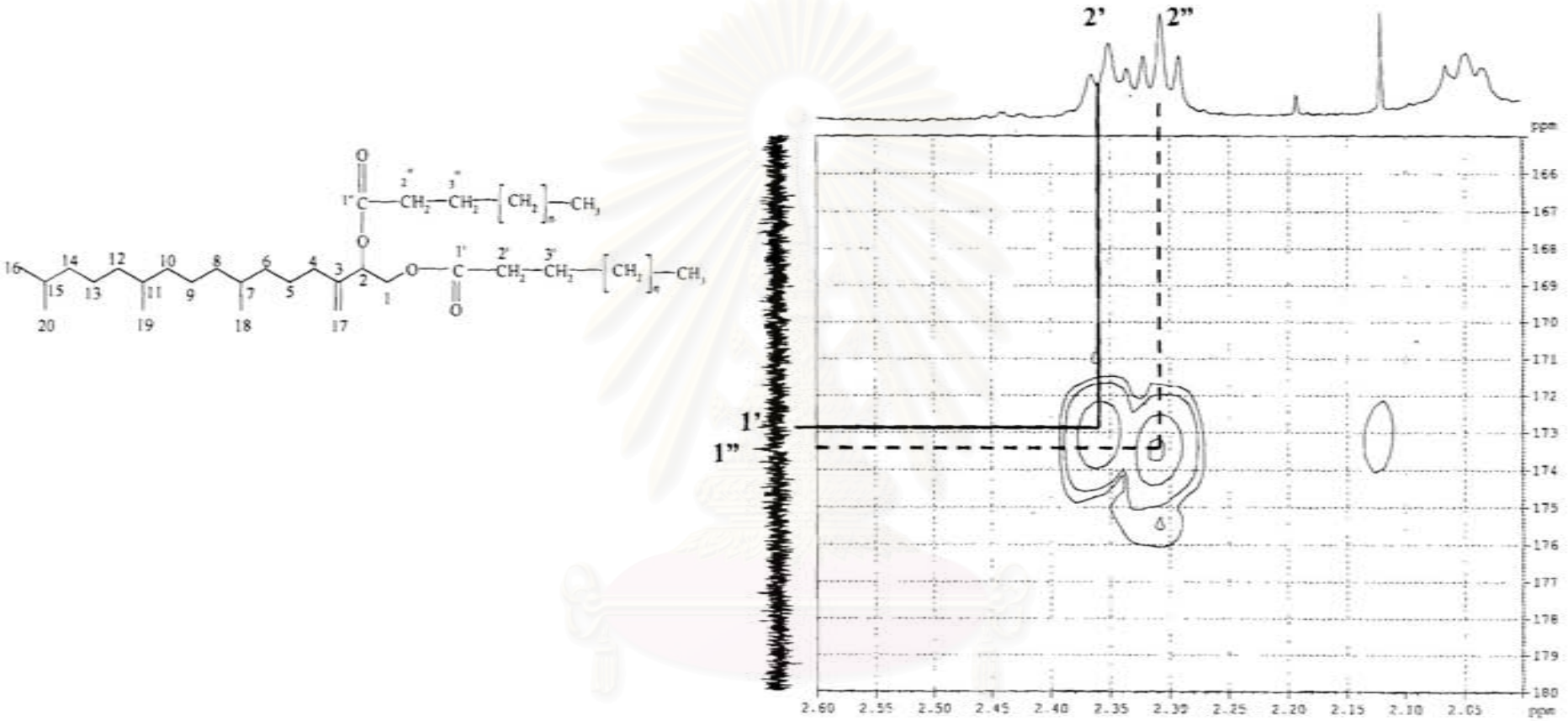


Figure 8d. The HMBC NMR spectrum of compound CC1 (expanded).

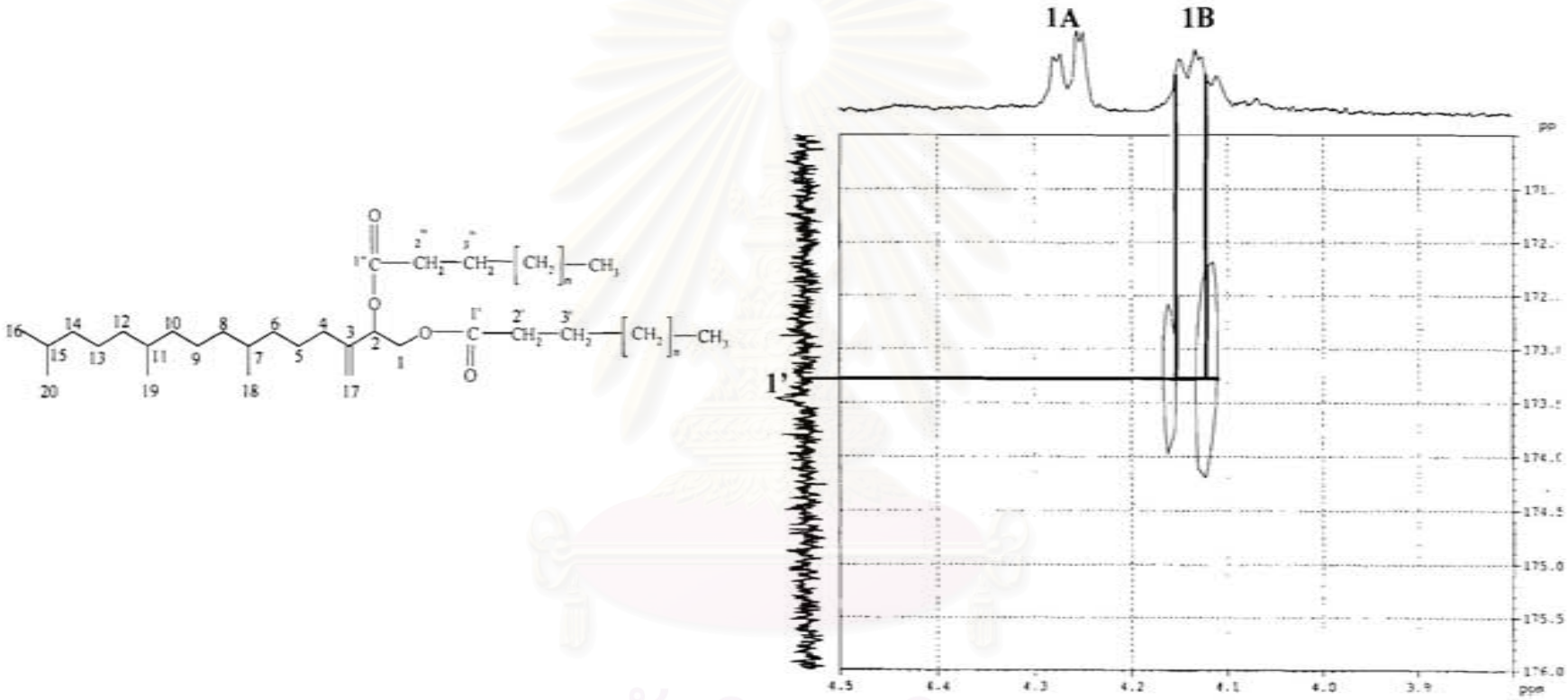


Figure 8e. The HMBC NMR spectrum of compound CC1 (expanded).

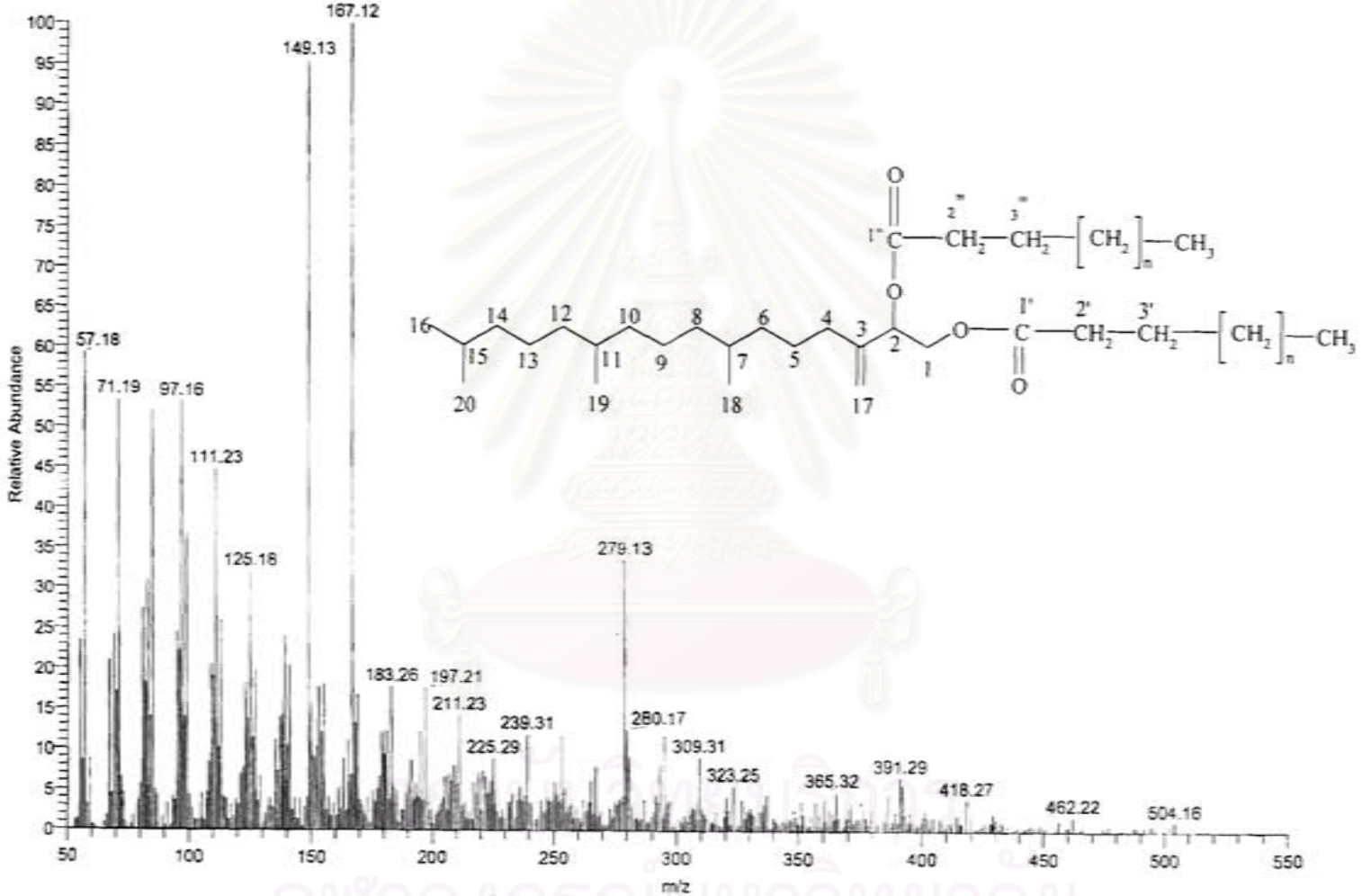


Figure 9. EIMS of compound CC1.

2. Identification of compound CC2

Compound CC2 was obtained as white amorphous powder (53.1 mg, 0.0106 % yield). The compound gave violet color to Liebermann-Burchard reagent, suggesting the presence of the triterpenoid nucleus. Its ^{1}H- and ^{13}C-NMR spectra gave evidences which suggested that it is a mixture of lupeol (CC2A) and another triterpenoid (CC2B).

In the ^{1}H-NMR spectrum (Figures 10a-10c), characteristic proton signals of lupeol were observed, including a downfield methyl singlet at δ 1.70 ppm (H-30) and a pair of broad singlets at δ 4.58 and 4.70 ppm (1H each, H-29). The carbinylic proton of lupeol (H-3) could be observed as a part of a two-proton multiplet at δ 3.21 ppm. This multiplet and the most downfield signal (*br s*) at δ 4.87 ppm implied the presence of a hydroxy substituent and a double bond, respectively, in the molecule of CC2B.

The ^{13}C-NMR spectrum (Figures 11a-11b) of CC2 showed four olefinic carbon signals at δ 109.3, 129.7, 142.8 and 151.0 ppm. The first and the last signals represented the double bond between C-20 and C-29 of lupeol, while the other two confirmed the unsaturation of CC2B. The DEPT experiments (Figures 12a-12c) and HMQC spectrum (Figures 13a-13b) were very helpful in ^{13}C-NMR assignments of each components of CC2. The carbon signals of CC2A, identical with lupeol, were first assigned, as shown in Table 12. The rest were therefore signals of CC2B, which included those of 8 methyl carbons at δ 14.6, 15.4, 16.1, 16.7, 25.3, 28.0, 29.2 and 31.3 ppm, 10 methylene carbons at δ 18.3, 21.1, 26.2, 27.5, 27.5, 33.3, 34.6, 37.4, 37.7, and 39.0 ppm, 5 methine carbons at δ 38.4, 51.2, 55.5, 79.0 and 129.7 ppm, and 7 quaternary carbons at δ 32.3, 34.4, 37.2, 38.9, 40.8, 43.3 and 142.8 ppm.

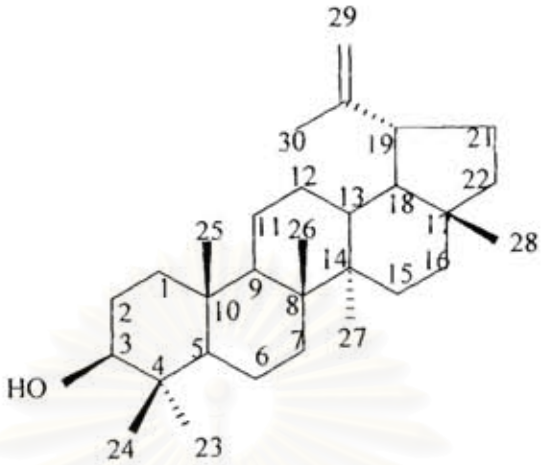
Comparison of ^{13}C-NMR data of CC2B with the reported data of germanicol (Gonzalez *et al.*, 1981), a C-18 unsaturated triterpenoid of the oleanane type, suggested that they were the same compound. This was also in accordance with the ^{1}H-NMR data. The ^{1}H-NMR assignments of CC2A and CC2B, as shown in Tables 12 and 13, respectively, were mainly based on analysis of the HMQC and

HMBC (Figures 14a-14e) spectra of CC2. The ^{13}C-NMR assignments of CC2A, compared with the reported data of lupeol (Menezes *et al.*, 1998), and of CC2B, with those of germanicol (Gonzalez *et al.*, 1981), are also shown in the two Tables.

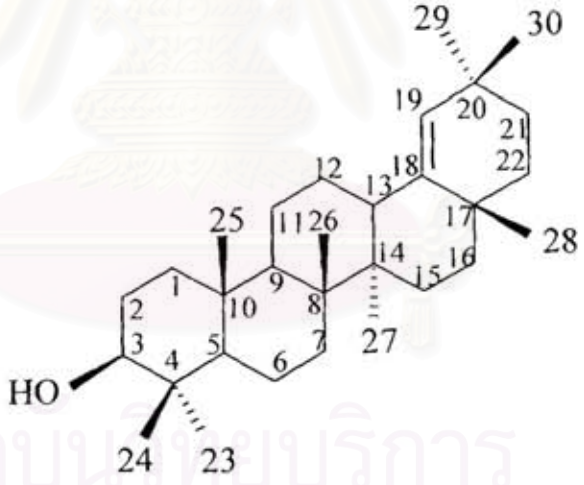
However, the ^{13}C-NMR assignments of germanicol and CC2B as shown in Table 13 are slightly different. This is due to the reversed chemical shift assignments for C-1 and C-13 of the two compounds. The signal assignments for C-1 (δ 39.0 ppm) and C-13 (δ 38.4 ppm) of CC2B were based on data obtained from the DEPT experiments which indicated those signals as belonging to a methylene and a methine carbon, respectively. The assignment for C-3 was also confirmed by the HMQC spectrum in which the correlation between the proton signal at δ 2.28 ppm, assigned for H-13 of CC2B, and the carbon signal at δ 38.4 ppm were observed.

The identification of CC2A and CC2B were also supported by the EIMS (Figure 15) of CC2 which showed the molecular ion peak at m/z 426, corresponding to the molecular formula of $C_{30}H_{50}O$. The base peak at m/z 189 and an intense fragment peak at m/z 218, were both indicative of the lupane-type triterpenoid (Budzikiewicz, Wilson and Djerassi, 1963; Ogunkoya, 1981). The former could also be considered as resulting from successive loss of a methyl group after the cleavage across the C ring of the oleanane skeleton. Mass fragmentation of CC2A and CC2B are shown in Schemes 5 and 6, respectively.

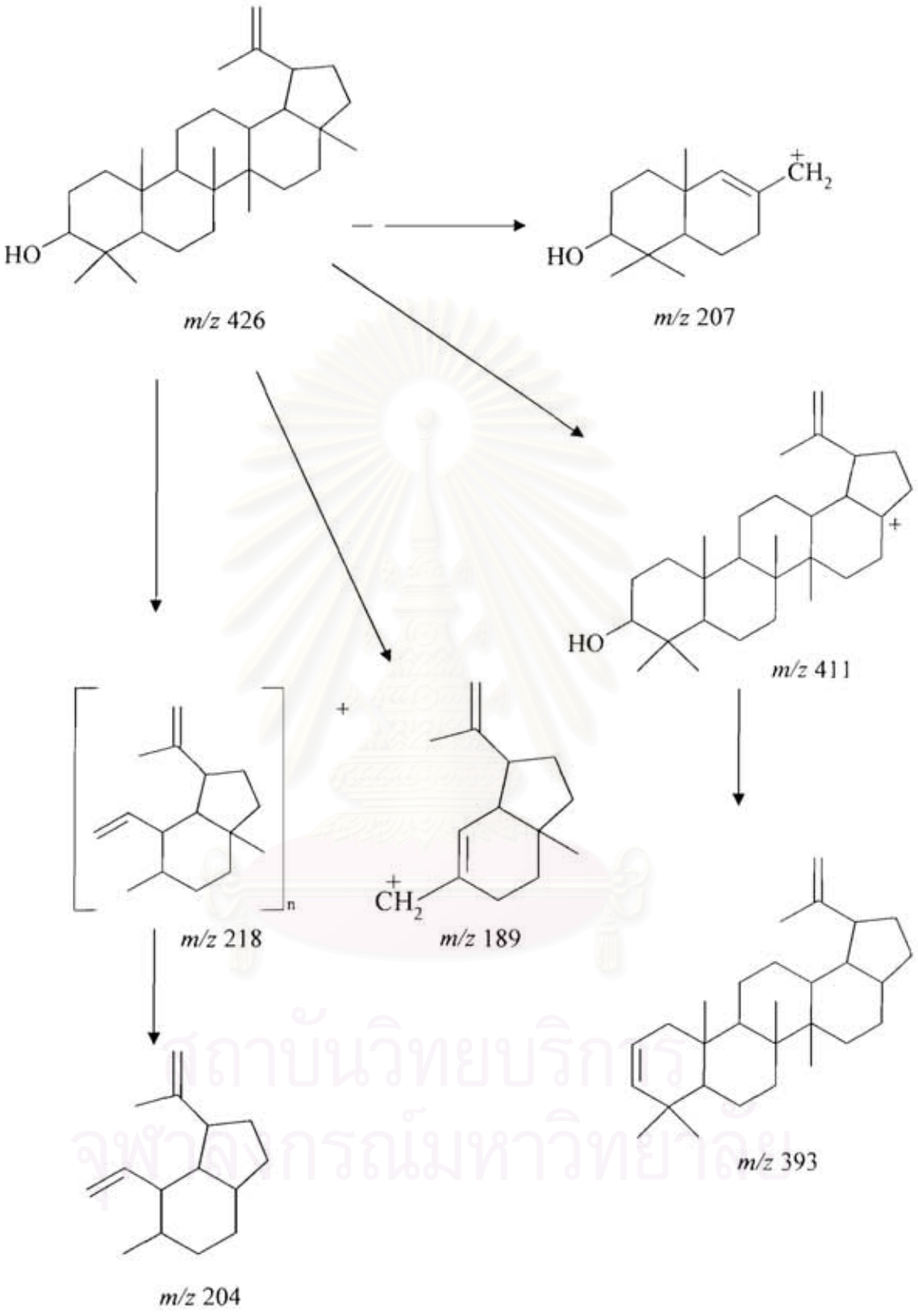
Therefore, it was concluded that compound CC2 is a mixture of two pentacyclic triterpenoids: the lupane-type lupeol (CC2A) and the oleanane-type germanicol (CC2B). These two triterpenoids have the same molecular formula of $C_{30}H_{50}O$. The ratio of the two components of CC2, as evident from the integration of peak areas, was found to be 1:1.



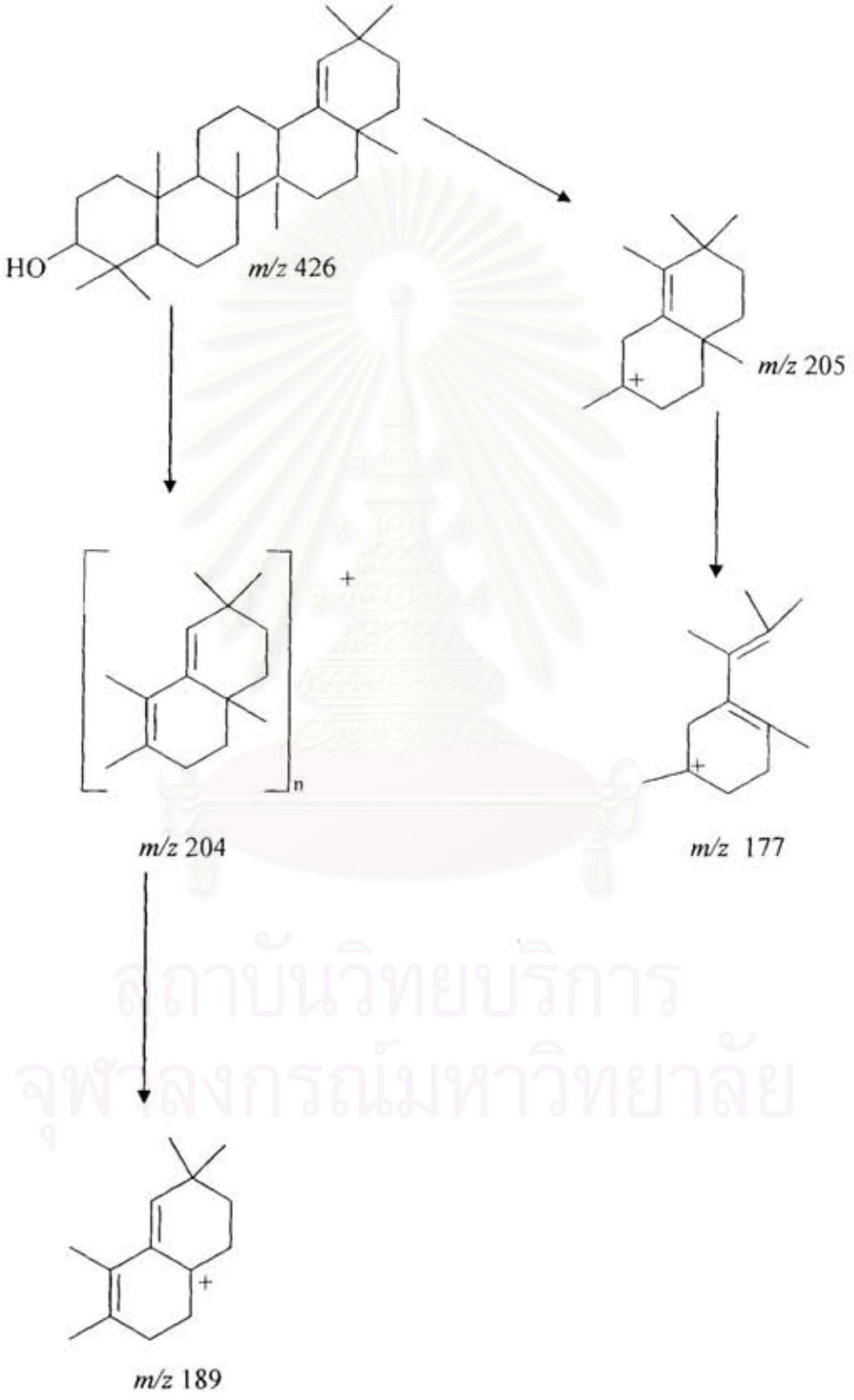
lupeol



germanicol



Scheme 5. Mass fragmentation of CC2A



Scheme 6. Mass fragmentation of CC2B

Table 12. ^{1}H and ^{13}C-NMR assignments of CC2A and reported ^{13}C-NMR assignment of lupeol (in $CDCl_3$).

Position	CC1		lupeol
	δ H	δ C	δ C
1		38.7	38.6
2		27.5	27.4
3	3.21 (*m*)	79.0	78.8
4		38.9	38.7
5		55.5	55.2
6		18.3	18.2
7		34.3	34.2
8		40.9	40.6
9		50.5	50.3
10		37.2	37.2
11		21.1	20.9
12		25.2	25.1
13		38.1	37.9
14		42.8	42.6
15		27.5	27.4
16		35.6	35.5
17		43.0	43.1
18		48.3	48.2
19	2.39 (*dd*, J = 11.1, 5.8)	48.0	47.8
20		151.0	150.7
21		29.9	29.7
22		40.0	39.8
23	0.98 (*s*)	28.0	27.9
24	0.78 (*s*)	15.4	15.4
25	0.84 (*s*)	16.1	15.9
26	1.04 (*s*)	16.0	15.8
27	0.96 (*s*)	14.6	14.4
28	0.80 (*s*)	18.0	18.1
29	4.58 (*br s*), 4.70 (*d*, J = 2.1)	109.3	109.2
30	1.70 (*br s*)	19.3	19.2

Table 13. ^{1}H and ^{13}C-NMR assignments of CC2B and reported ^{13}C-NMR assignment of germanicol (in $CDCl_3$).

Position	CC2B		germanicol
	δ H	δ C	δ C
1		39.0	38.5
2		27.4	27.4
3	3.21 (*m*)	79.0	79.0
4		38.9	39.0
5		55.5	55.7
6		18.3	18.3
7		34.6	34.7
8		40.8	40.8
9		51.2	51.3
10		37.2	37.3
11		20.9	21.2
12		26.2	26.2
13	2.28 (*d*, *J* = 12.5)	38.4	39.0
14		43.3	43.4
15		27.5	27.6
16		37.7	37.7
17		34.4	34.4
18		142.8	142.8
19	4.87 (*br s*, *J* = 11.1, 5.8)	129.7	129.8
20		32.3	32.3
21		33.3	33.4
22		37.4	37.4
23	0.99 (*s*)	28.0	28.0
24	0.78 (*s*)	15.4	15.4
25	0.89 (*s*)	16.1	16.1
26	1.09 (*s*)	16.7	16.7
27	0.75 (*s*)	14.6	14.6
28	1.03 (*s*)	25.3	25.3
29	0.95 (*s*)	31.3	31.3
30	0.95 (*s*)	29.2	29.2

Lupeol and germanicol can be found in a vaitety of plant sources. In *Caesalpinia*, lupeol has been isolated from the flower of *C. pulcherrima* and the leaves of *C. paraguariensis* (Mendes *et al.*, 2002, Rangasa *et al*, 2002, Kiem *et al.*, 2005), while germanicol has never been reported as a constituent of this plant genus. The toxicity of lupeol is very low (Patocka *et al.*, 2003), and it has been found to exhibit some interesting bioactivities including anti-inflammatory (Akihisa *et al.*, 1996; Raji *et al.*, 2000; Fernandez *et al.*, 2001; Mitaine-Offer *et* al., 2002; Hodges *et al.*, 2003) and antiarthritic activities (Kweifiookai and Carroll, 1993; Kweifiookai *et al.*, 1995; Geetha and Varalakshmi, 1998).

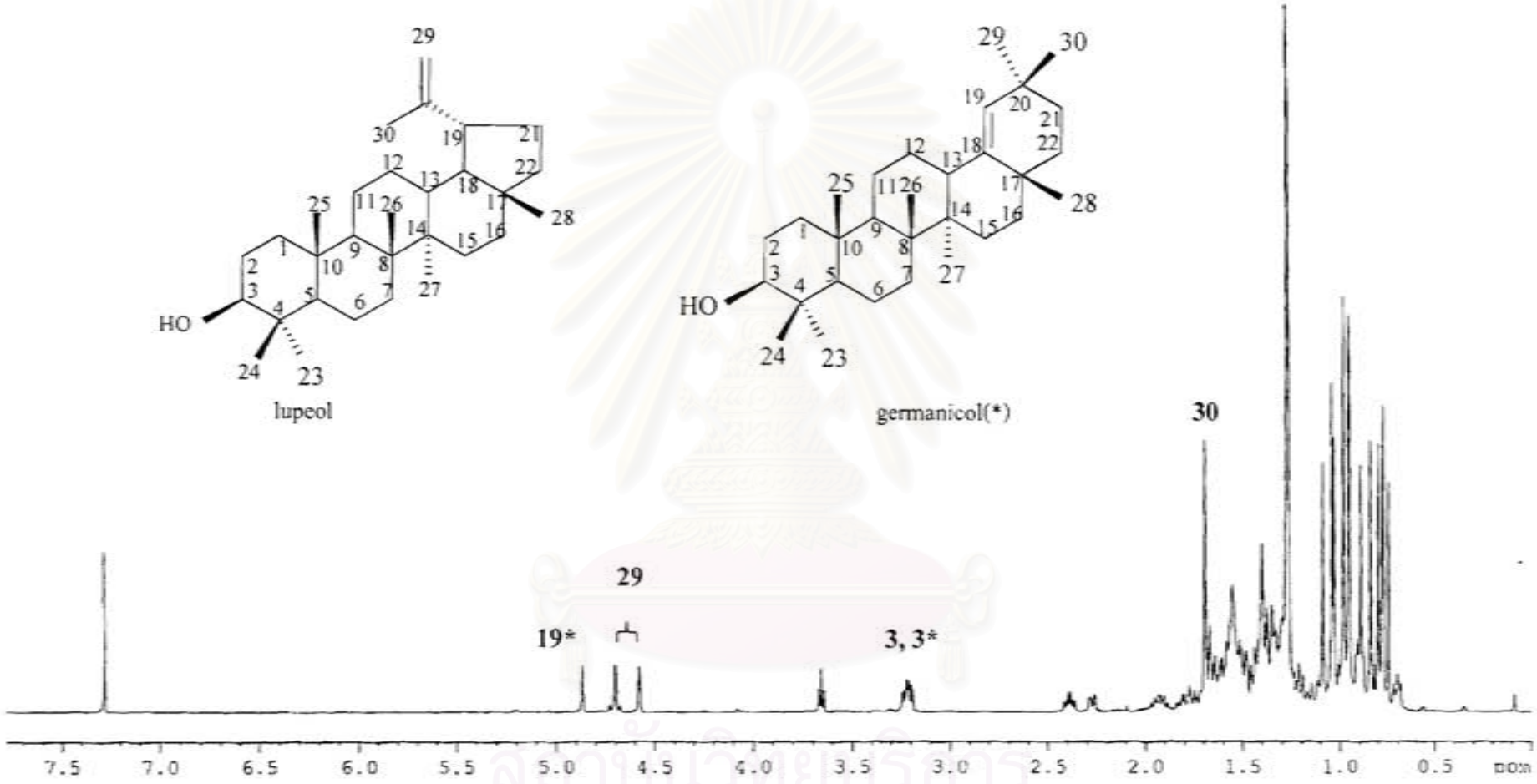


Figure 10a. The 500 MHz ^{1}H-NMR spectrum of compound CC2.

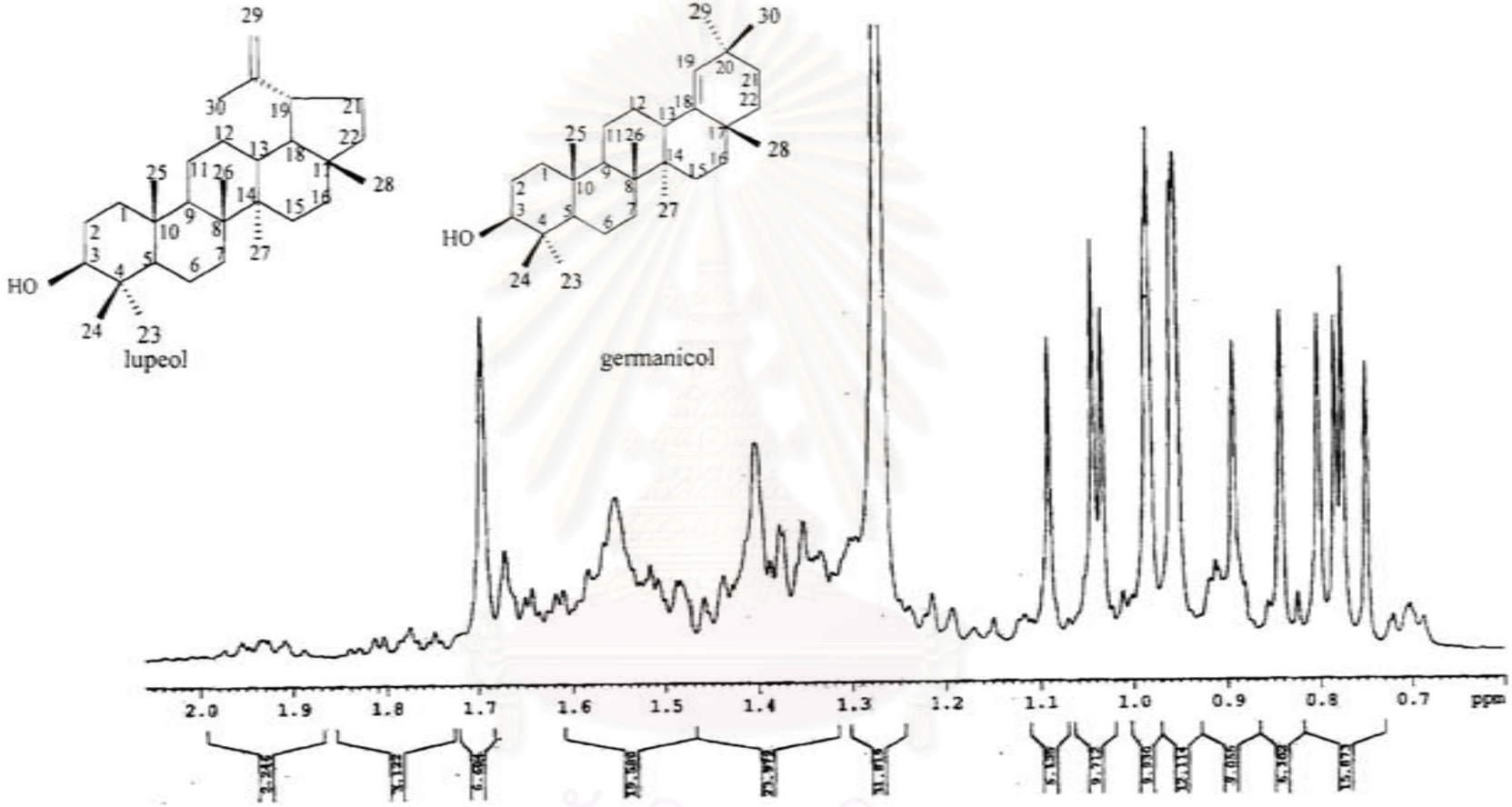


Figure 10b. The 500 MHz ^{1}H-NMR spectrum of compound CC2 (expanded).

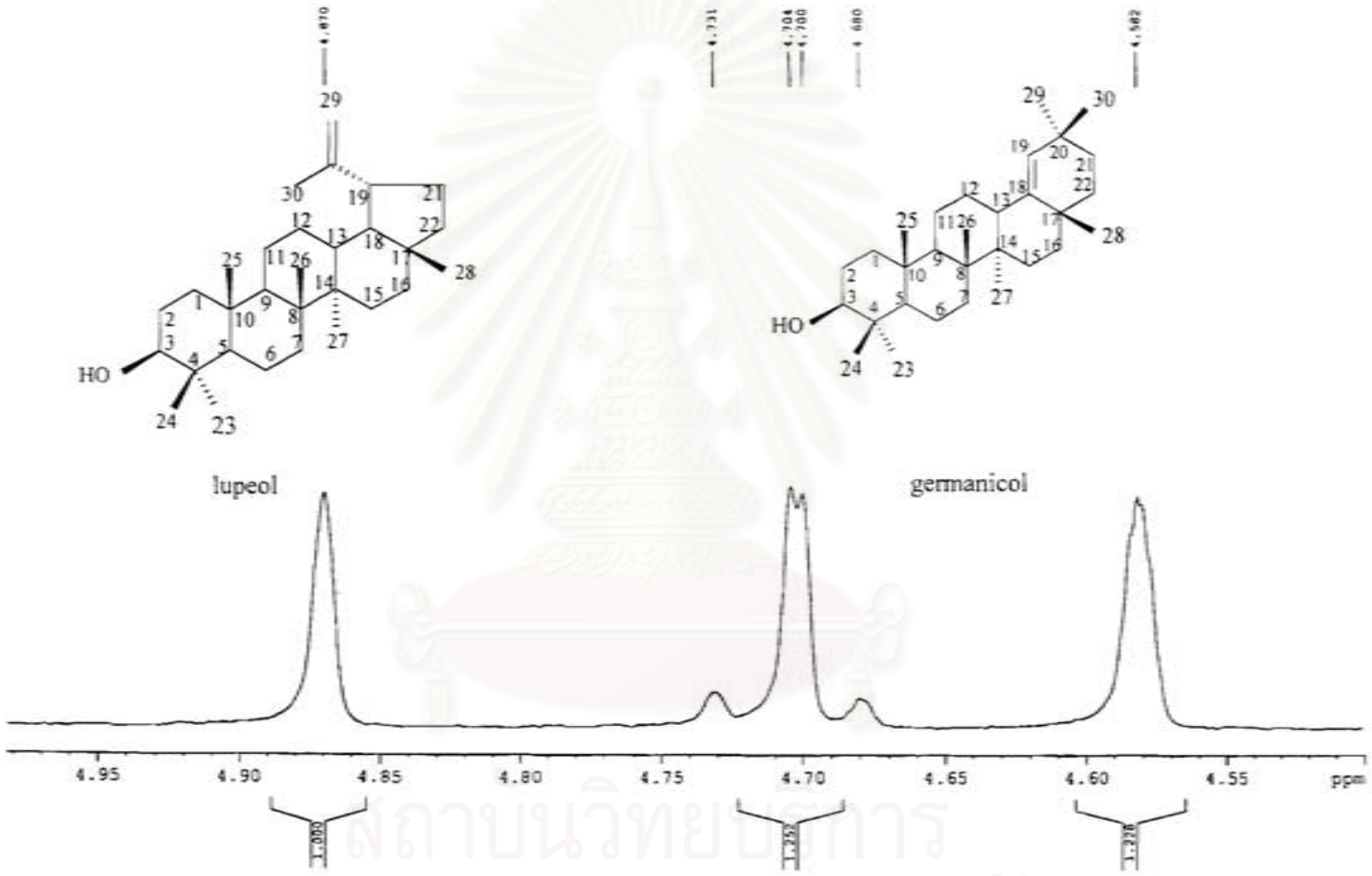


Figure 10c. The 500 MHz ^{1}H-NMR spectrum of compound CC2 (expanded).

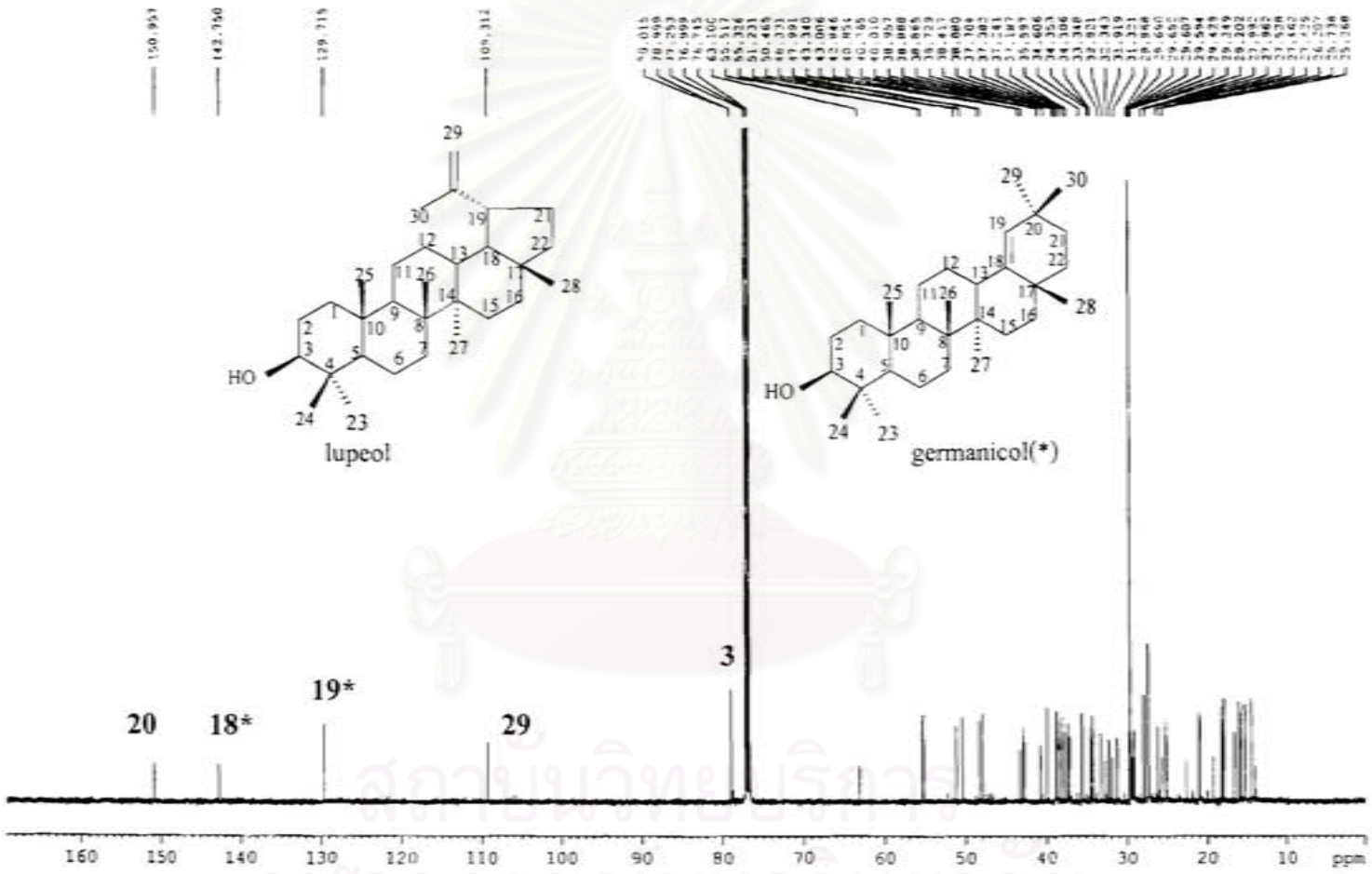


Figure 11a. The 125MHz ^{13}C-NMR spectrum of compound CC2.

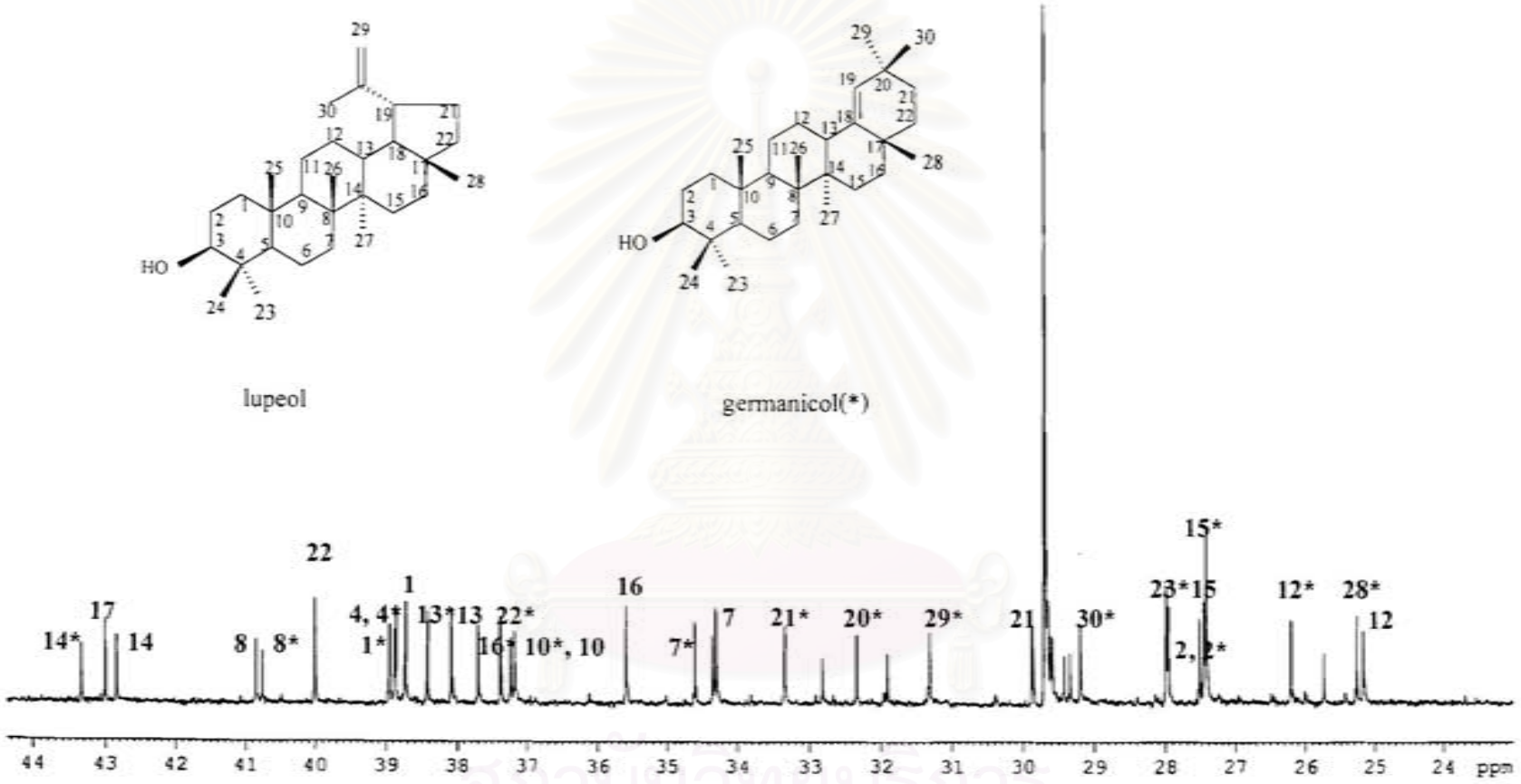


Figure 11b. The 125MHz ^{13}C-NMR spectrum of compound CC2 (expanded).

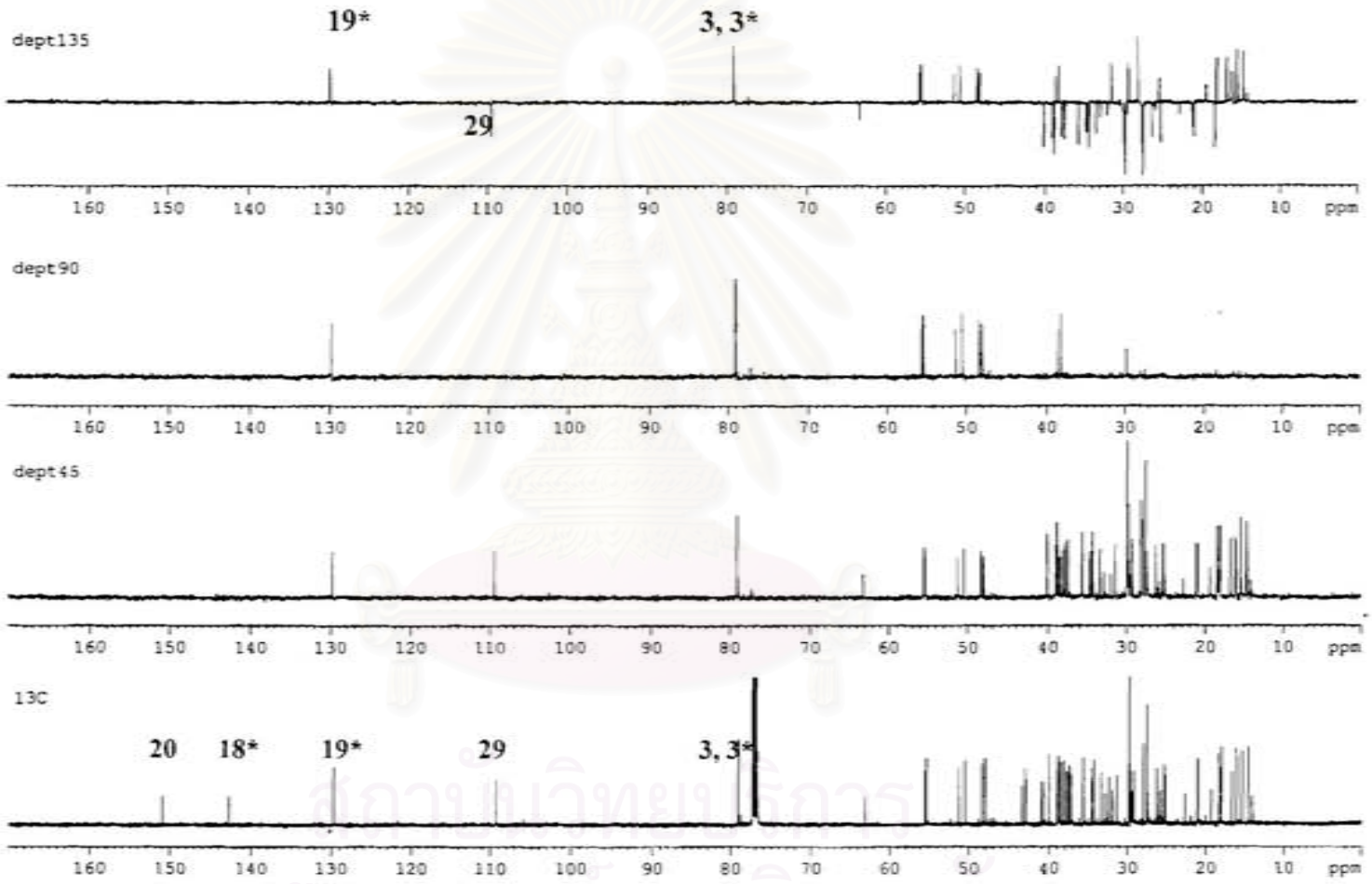


Figure 12a. The 125 MHz ^{13}C-DEPT NMR spectrum of compound CC2.

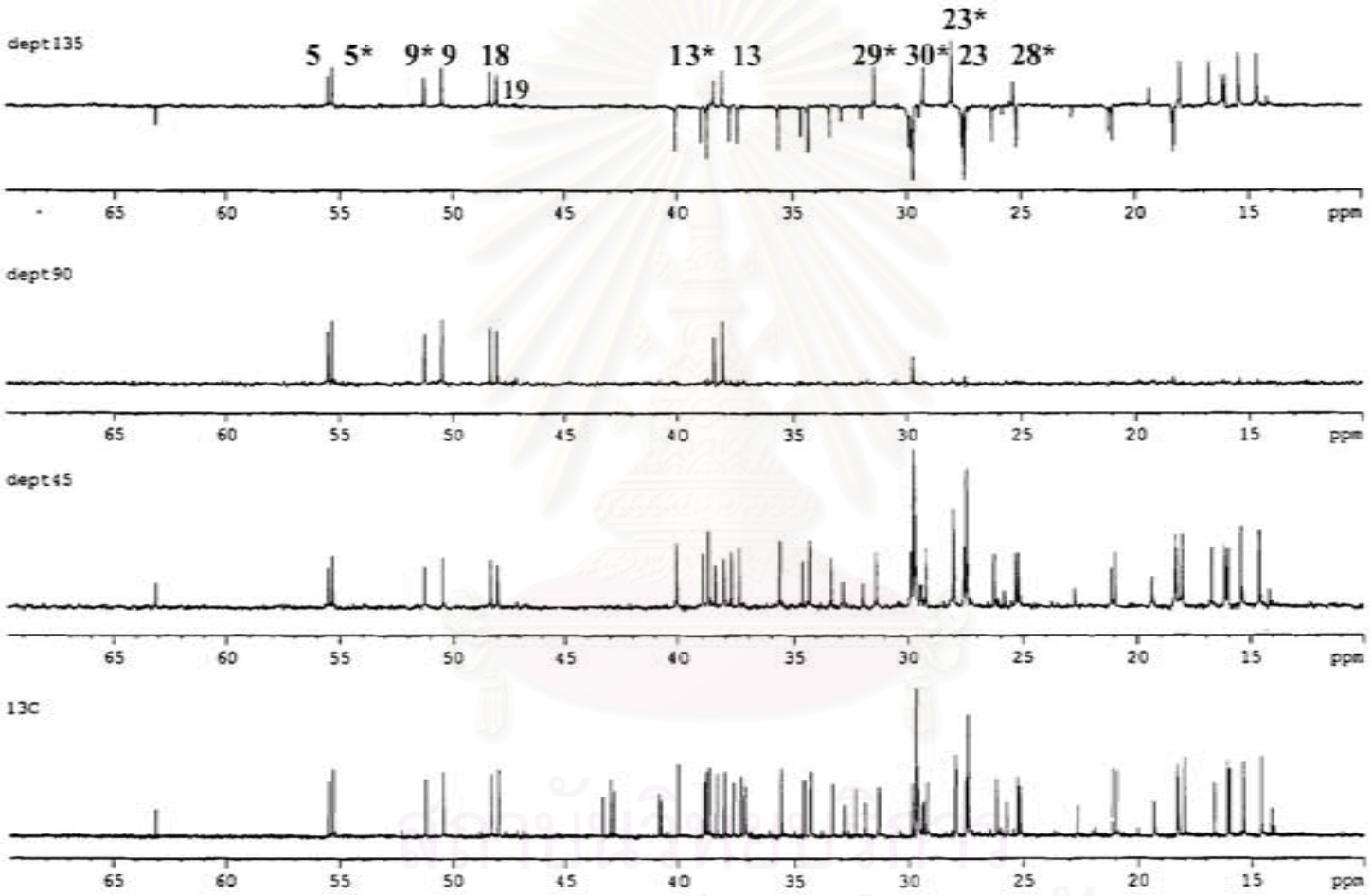


Figure 12b. The 125 MHz ^{13}C-DEPT NMR spectrum of compound CC2 (expanded).

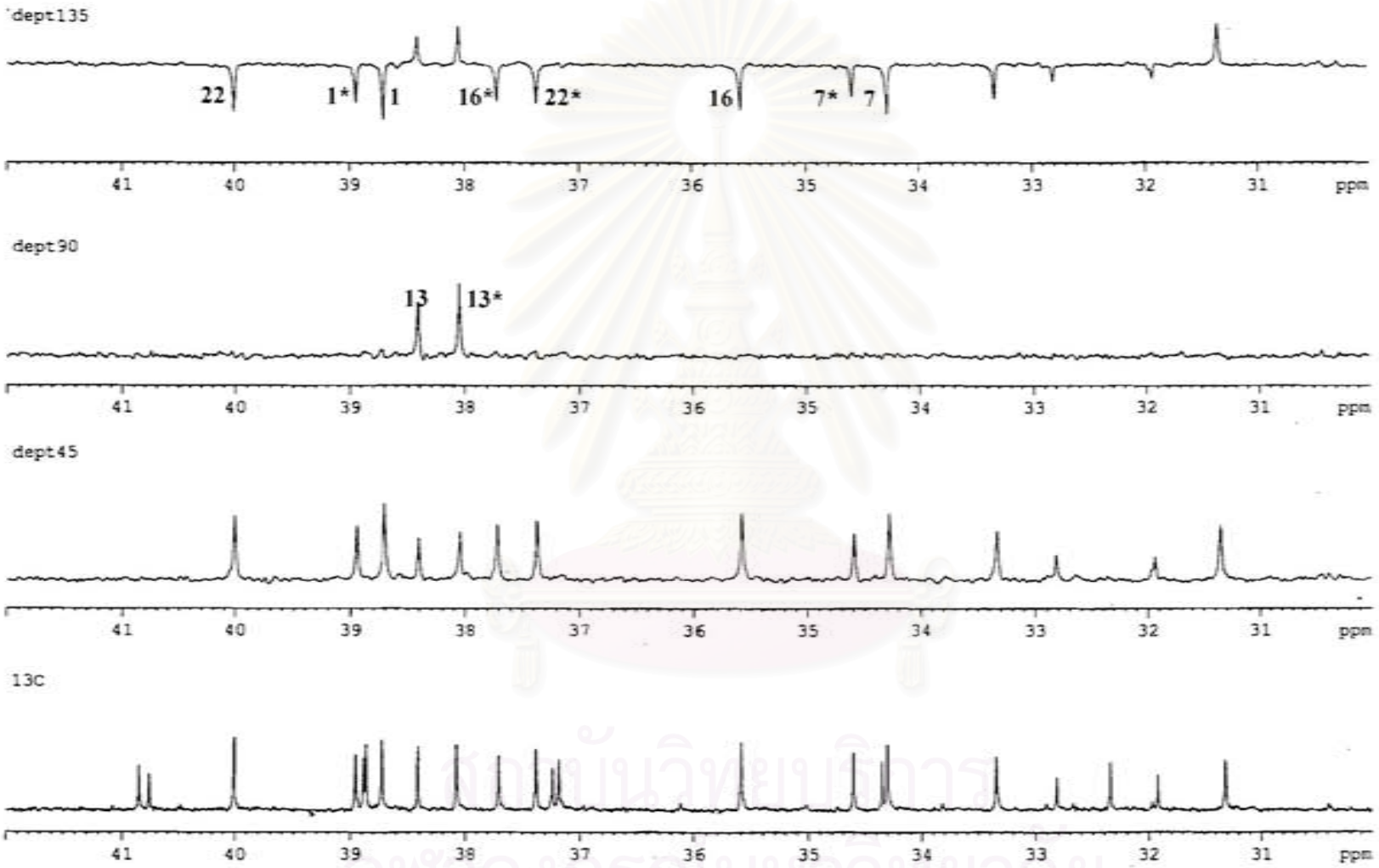


Figure 12c. The 125 MHz ^{13}C-DEPT NMR spectrum of compound CC2 (expanded).

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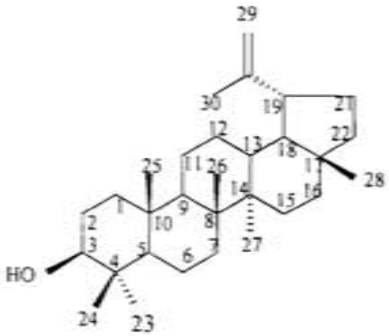
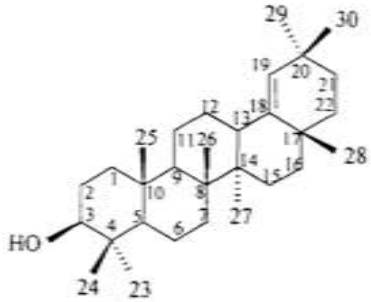


lupeol



germanicol

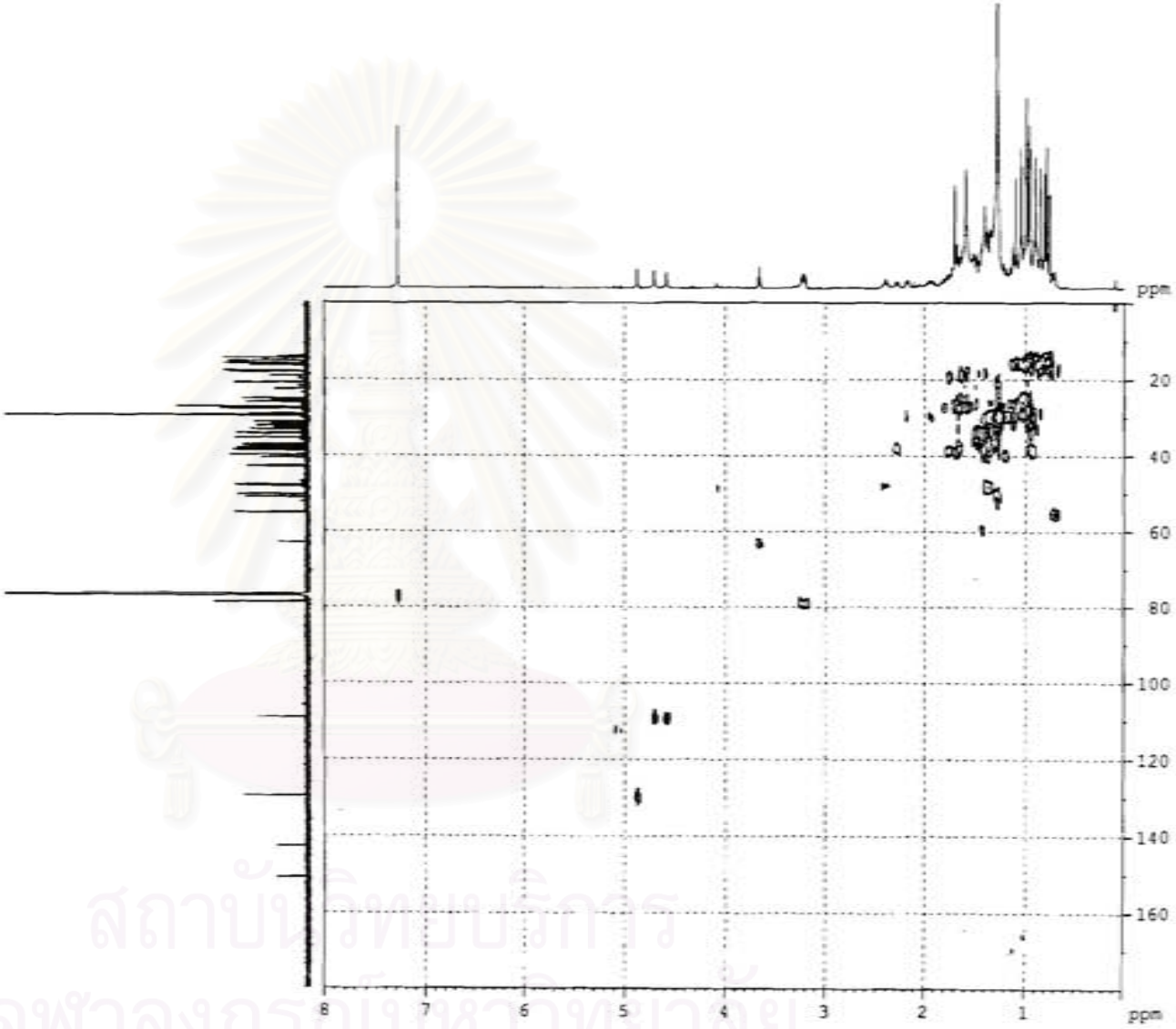
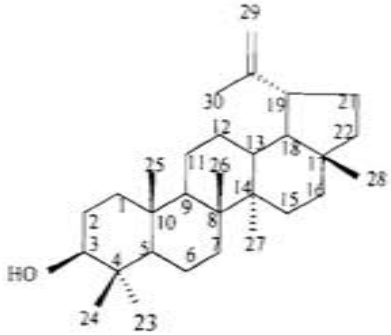
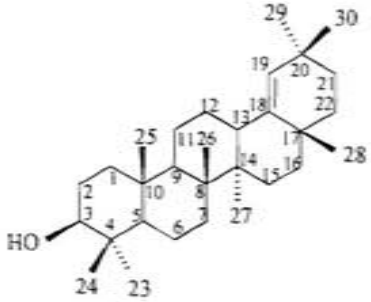


Figure 13a. The ^{1}H-^{13}C HMQC NMR spectrum of compound CC2.



lupeol



germanicol

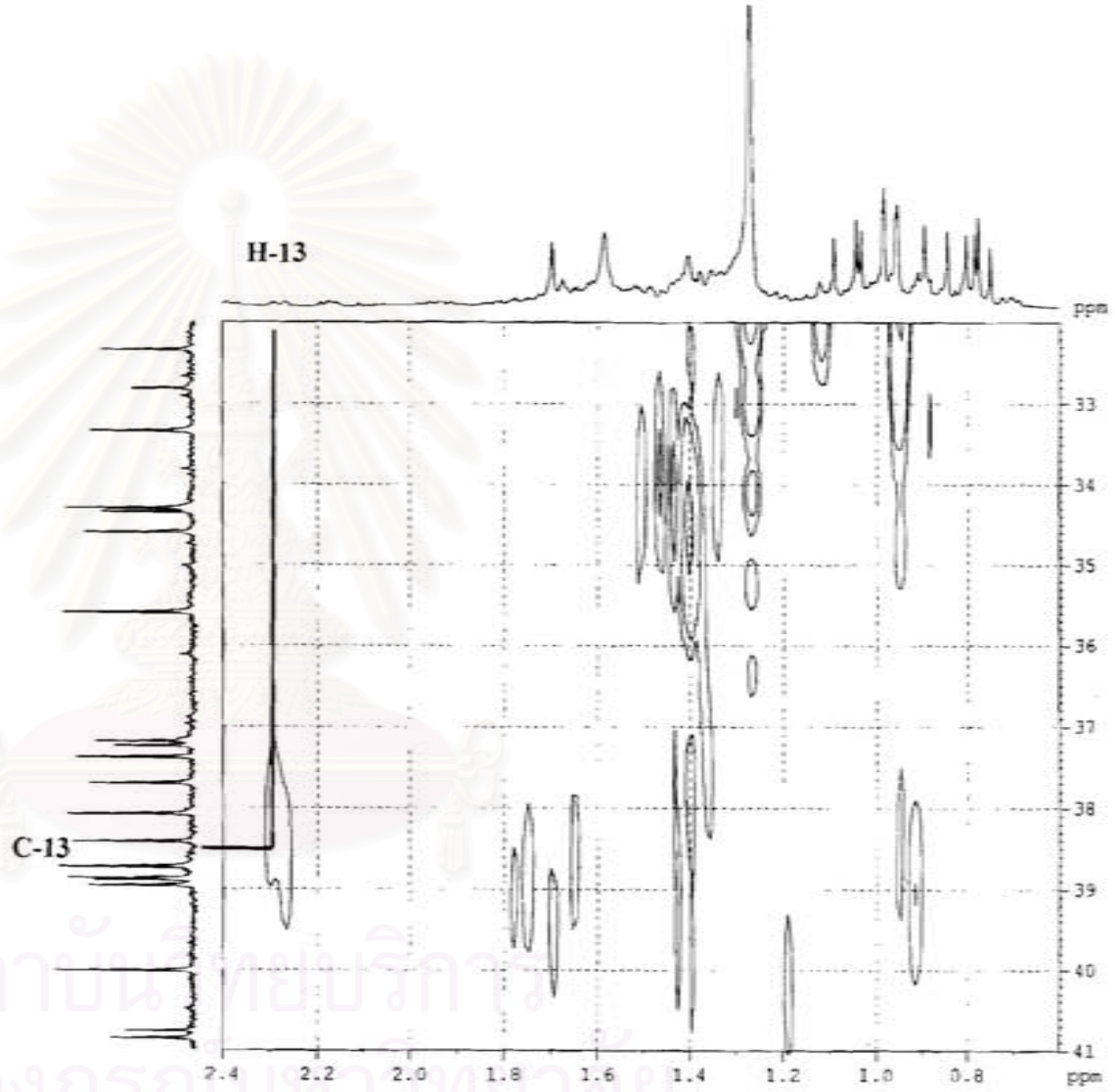


Figure 13b. The ^{1}H-^{13}C HMQC NMR spectrum of compound CC2 (expanded).

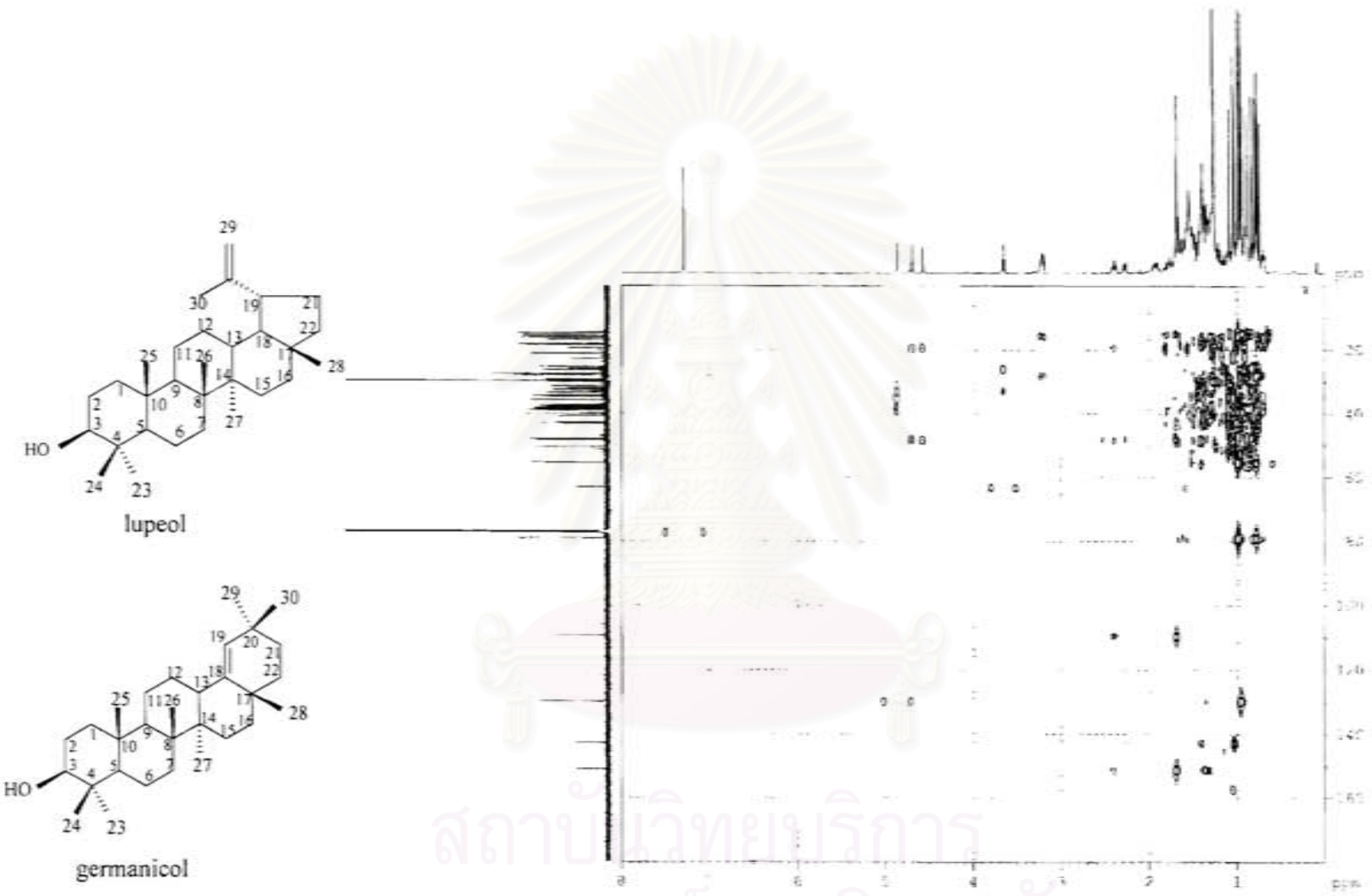


Figure 14a. The HMBC NMR spectrum of compound CC2.

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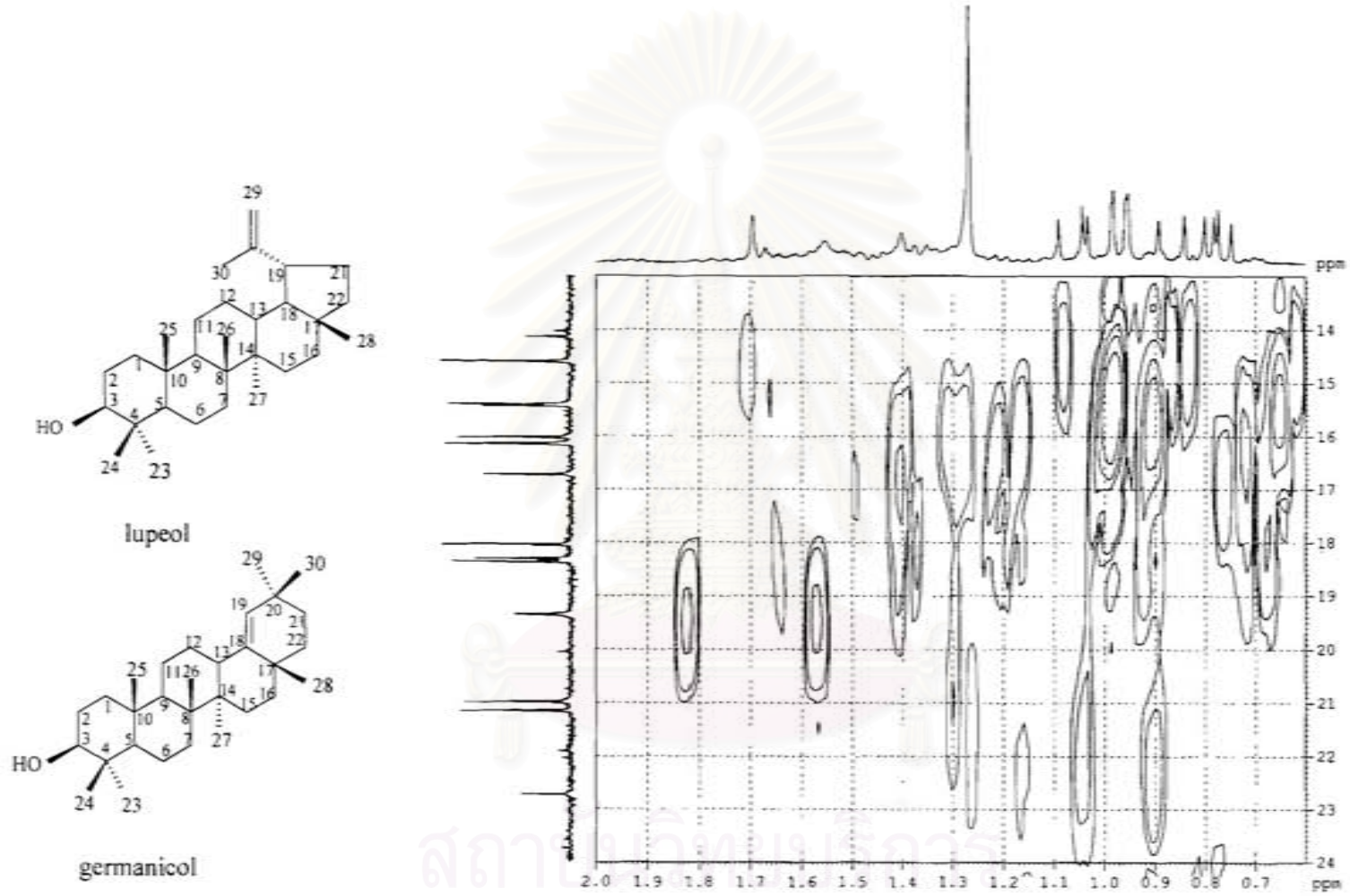


Figure 14b. The HMBC NMR spectrum of compound CC2 (expanded).

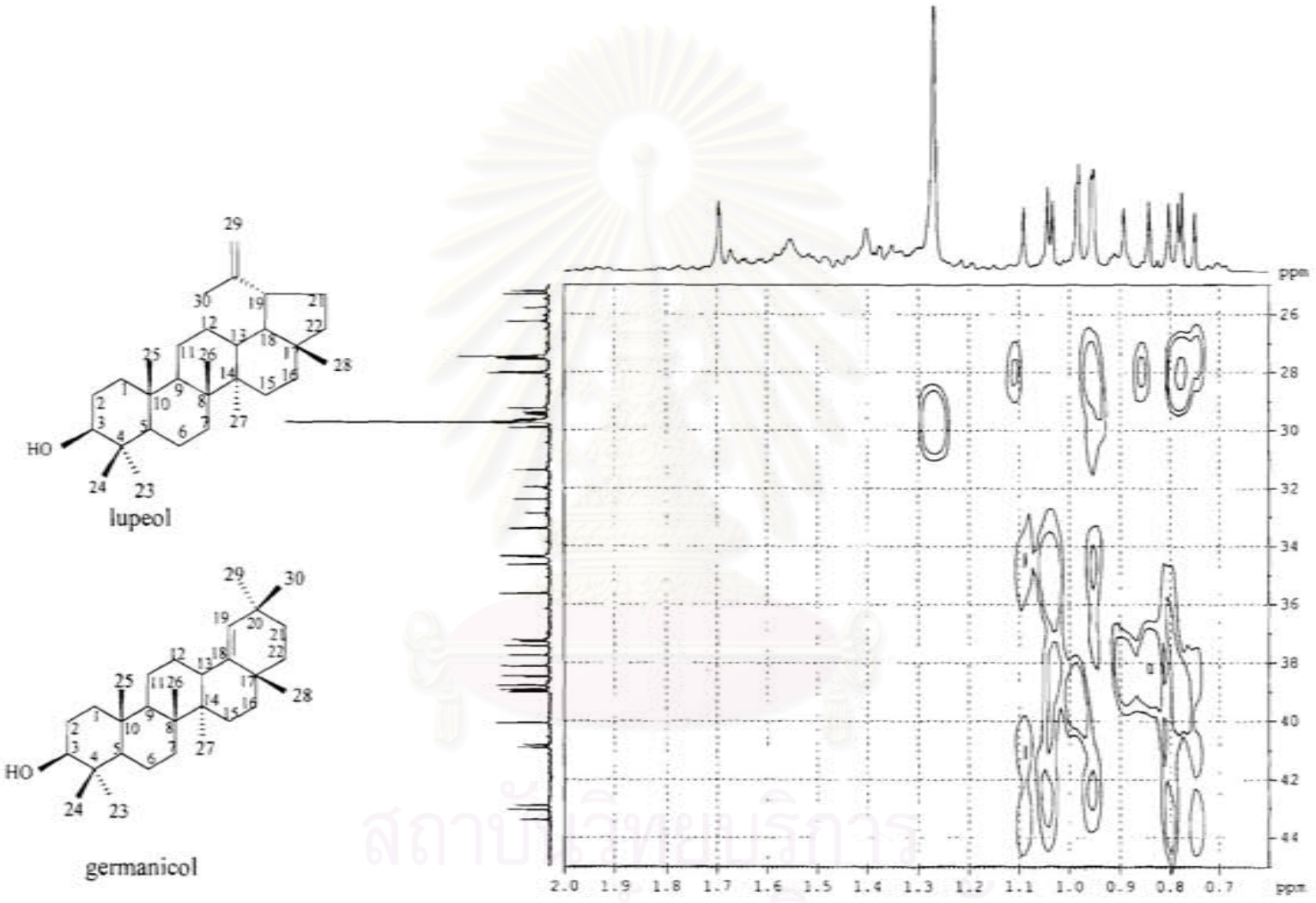


Figure 14c. The HMBC NMR spectrum of compound CC2 (expanded).

107

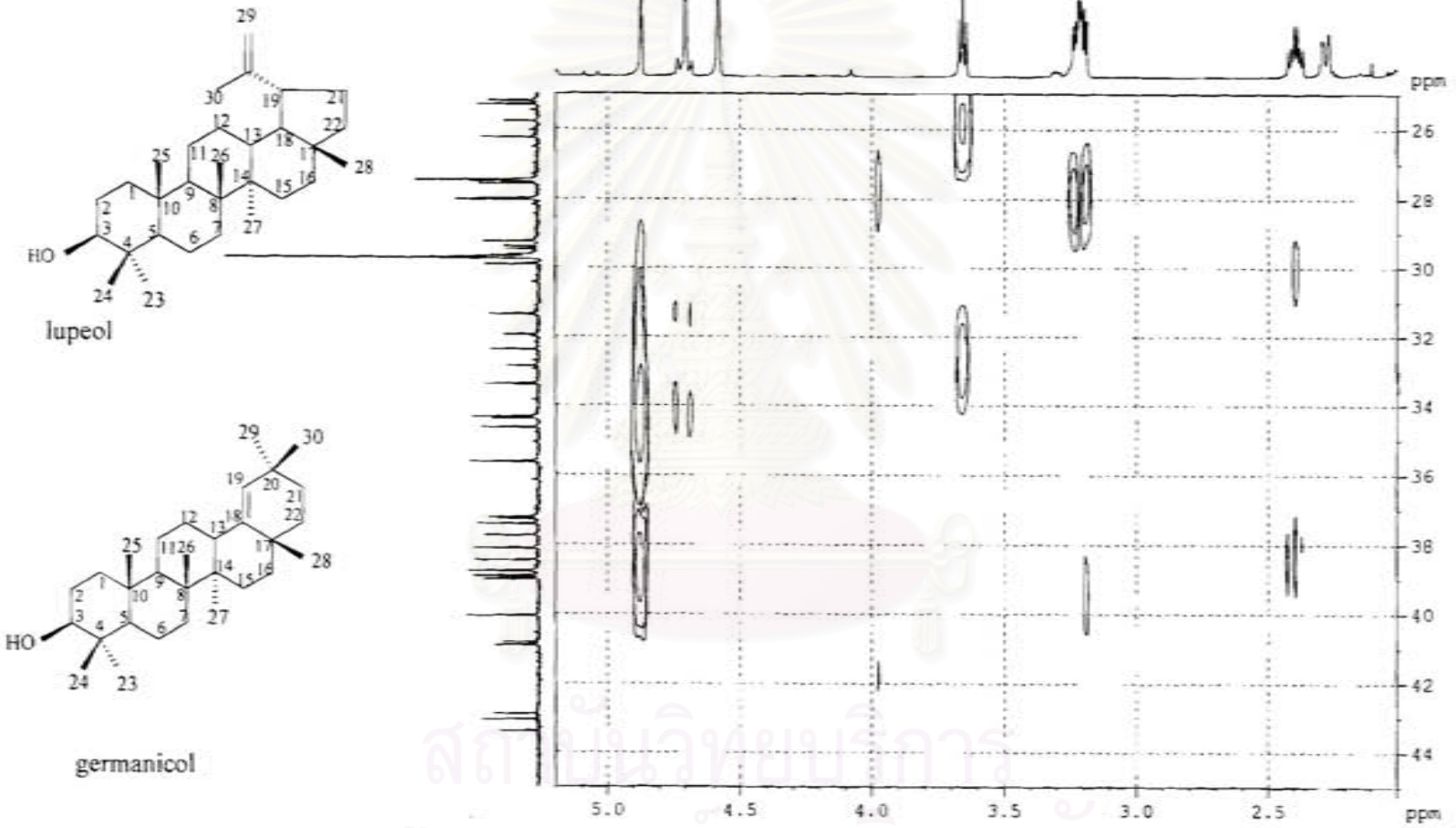


Figure 14e. The HMBC NMR spectrum of compound CC2 (expanded).

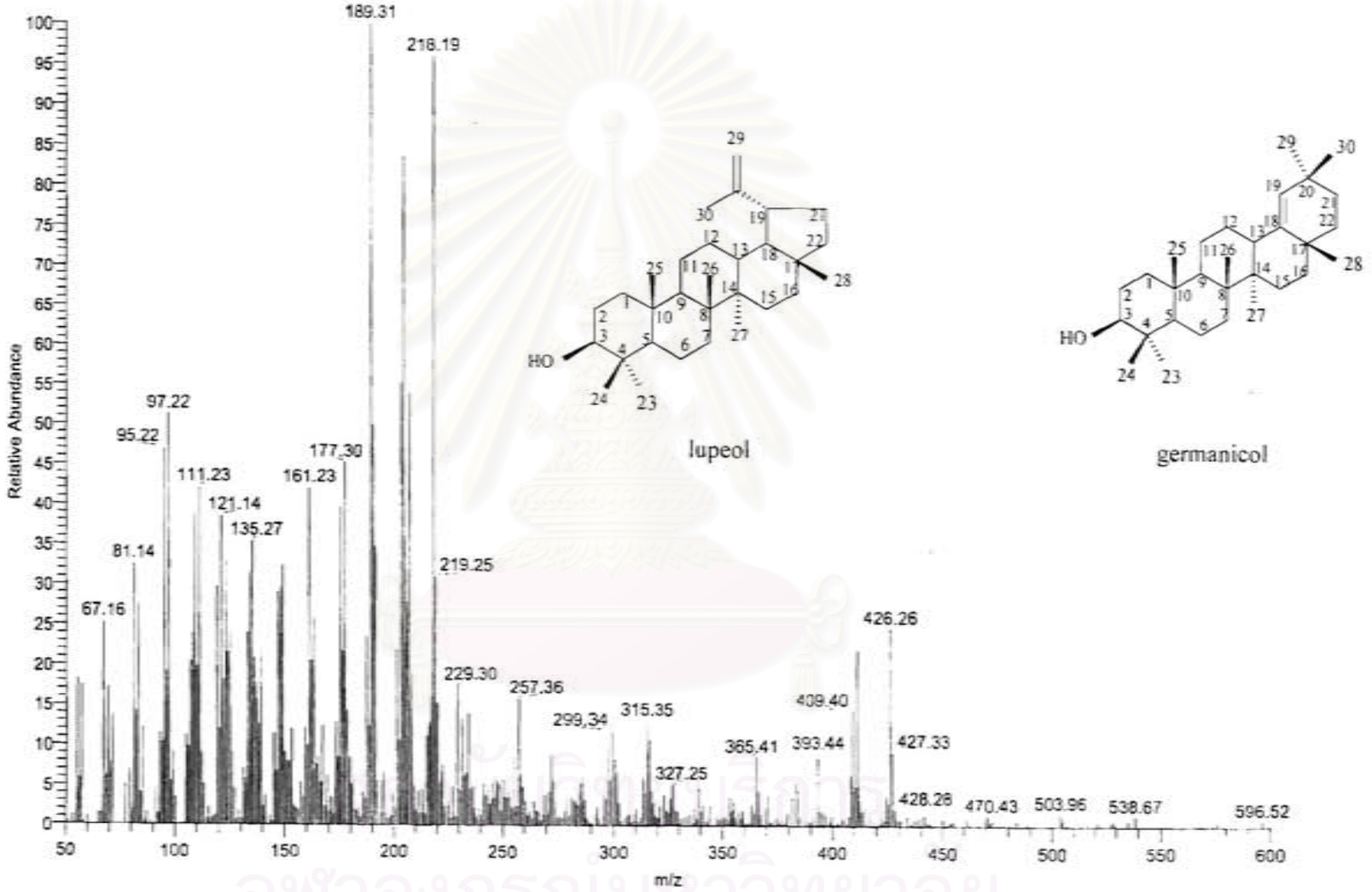


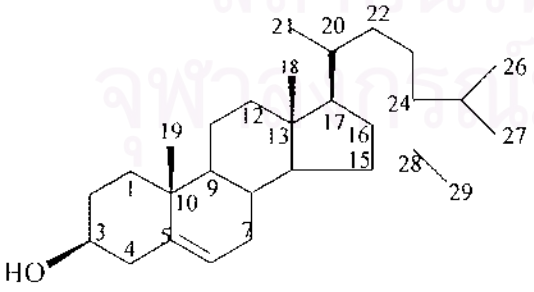
Figure 15. EIMS of compound CC2

3. Identification of compound CC3

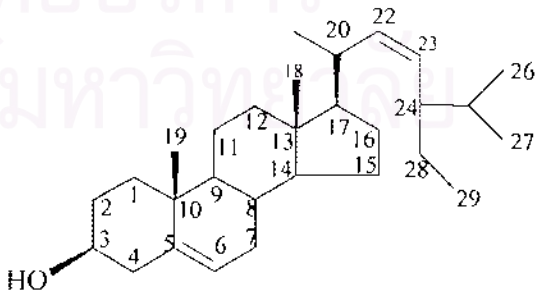
Compound CC3 was obtained as colorless needles (103.5 mg, 0.0207% yield). The compound gave violet-red color to Liebermann-Burchard reagent, suggesting the presence of the steroid nucleus. The ^{1}H-NMR spectrum (Figure 16) gave evidences which suggested that CC3 is a mixture of *β*-sitosterol (CC3A) and stigmasterol (CC3B). A singlet at δ 5.33 ppm was assignable to H-6 of both *β*-sitosterol and stigmasterol, while two signals at δ 5.00 and 5.15 ppm were attributable to H-22 and H-23 of stigmasterol, respectively. A multiplet at δ 3.50 ppm was attributable to the methine proton of hydroxy-substituted position 3. The ratio of CC2A and CC2B in the mixture, as deduced from the integration of peak areas, was found to be 4 : 1.

In the ^{13}C-NMR spectrum (Figures 17a-17b), 29 carbon signals of *β*-stiosterol were evident, while the signals of stigmasterol could hardly be observed. However, the signals for C-22 and C-23 of stigmasterol were observable at δ 138.1 and 129.2 ppm, respectively.

Therefore, it was concluded that CC3 is a mixture of *β*-sitosterol and stigmasterol, both of which are common phytosterols widely distributed in the plant kingdom. Comparison of ^{13}C-NMR data of CC3A and CC3B with the reported data of *β*-sitosterol and stigmasterol (Rubinstein *et al.*, 1976), respectively, is shown in Table 14. The structure of *β*-sitosterol and stigmasterol are shown below.



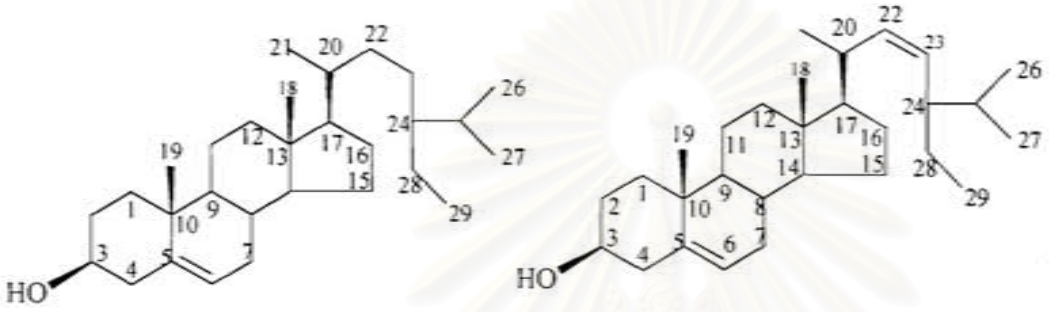
β-sitosterol



stigmasterol

Table 14. ^{13}C-NMR assi nments of CC3 and reported dada of β-sitosterol and stigmasterol (in $CDCl_3$).

Position	δ C			
	CC3A	CC3B	β-sitosterol	stigmasterol
1	37.3	37.3	37.2	37.2
2	31.8	31.8	31.7	31.7
3	71.8	71.8	71.7	71.8
4	42.4	42.4	42.3	42.4
5	140.6	140.6	140.8	140.8
6	121.6	121.6	121.7	121.7
7	32.0	32.0	31.9	32.0
8	32.0	32.0	31.9	32.0
9	50.2	50.2	50.1	50.2
10	36.6	36.6	36.5	36.6
11	21.2	21.2	21.1	21.1
12	39.9	39.9	39.8	39.7
13	42.4	42.4	42.3	42.4
14	56.8	56.8	56.8	56.9
15	24.4	24.4	24.3	24.4
16	28.4	29.0	28.2	29.0
17	56.1	56.1	56.0	56.1
18	12.0	12.1	11.9	12.1
19	19.5	19.5	19.4	19.4
20	36.2	40.6	36.1	40.5
21	18.9	21.2	18.8	21.1
22	34.1	138.1	33.9	138.0
23	26.2	129.2	26.1	129.3
24	45.9	51.3	45.8	51.3
25	29.3	32.0	29.1	32.0
26	19.9	21.2	19.8	21.3
27	19.2	19.2	19.0	19.0
28	23.2	25.5	23.1	25.4
29	12.0	12.4	11.9	12.3



β- sitosterol

stigmasterol

Figure 16. The 300 MHz ^{1}H-NMR spectrum of compound CC3.

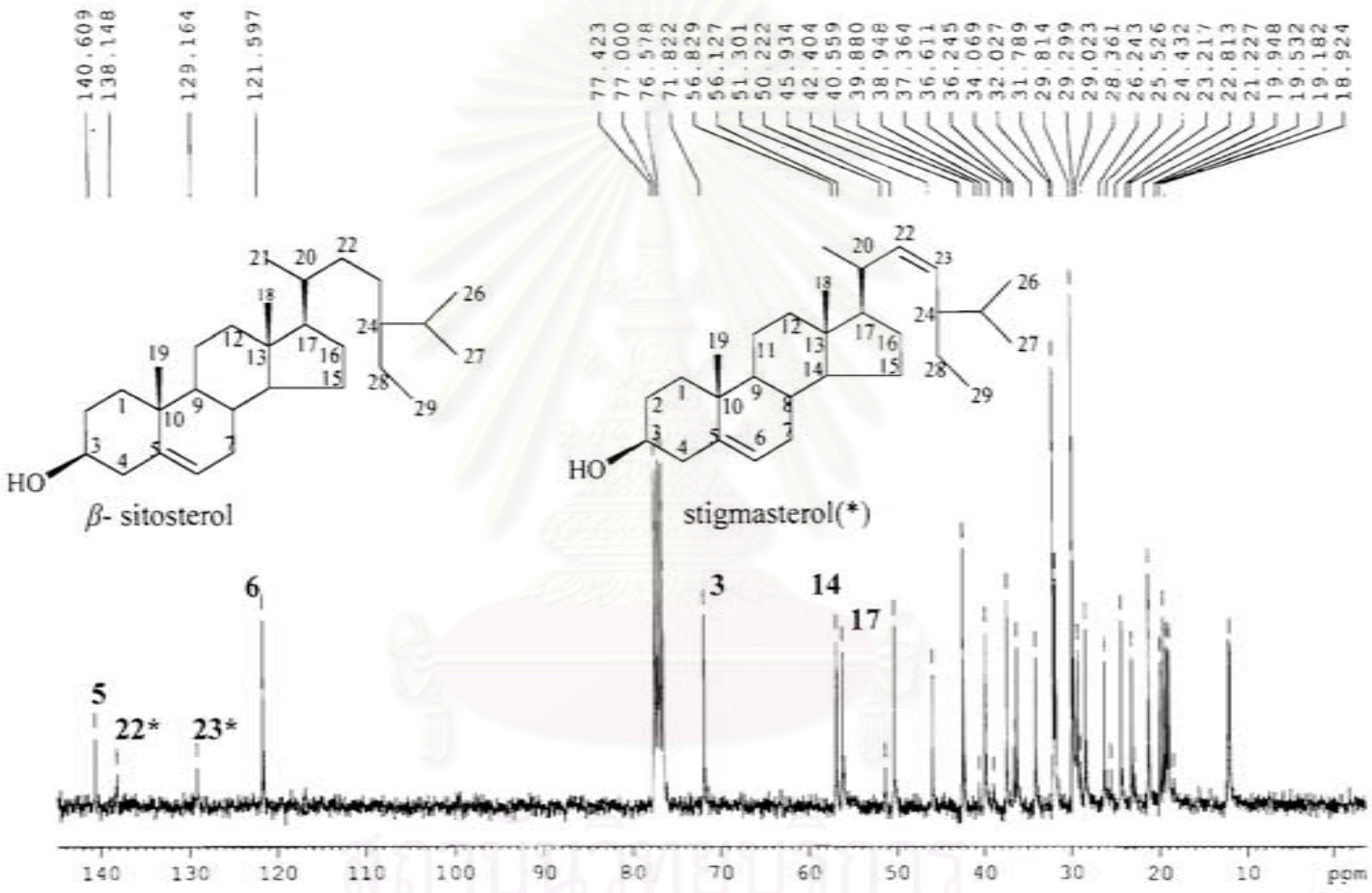


Figure 17a. The 125 MHz ^{13}C-NMR spectrum of compound CC3.

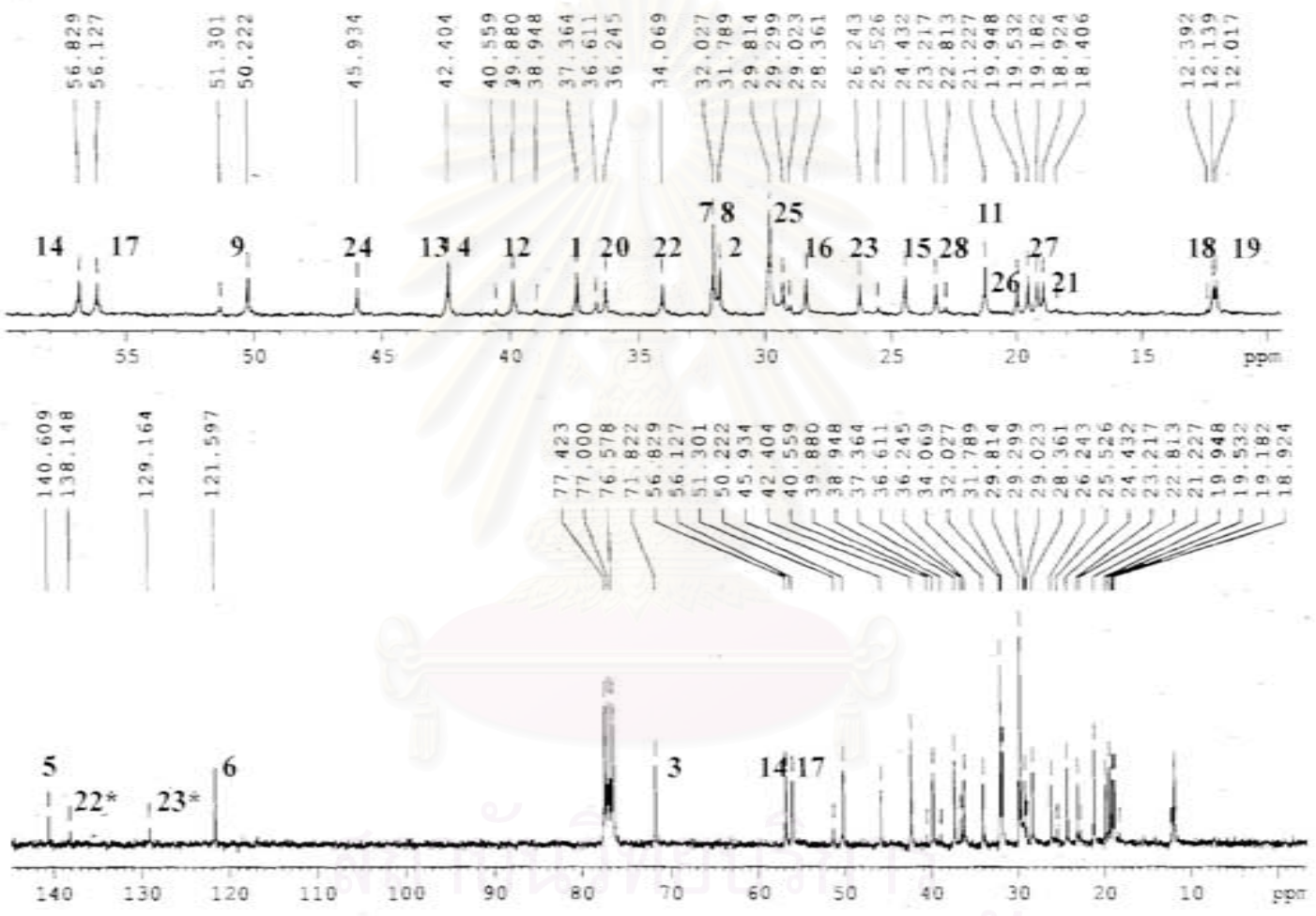


Figure 17b. The 125 MHz ^{13}C-NMR spectrum of compound CC3 (expanded).

CHAPTER V

CONCLUSION

Investigation of the leaves of *Caesalpinia coriaria* led to the isolation of a diester of an acyclic diterpenoid, 7,11,15-trimethyl-3-methylene-hexadecan-1,2-diol and a triterpenoids mixture of the lupane-type lupeol and the oleanane-type germanicol together with a mixture of two steroids, β-sitosterol and stigmasterol. The identification of the isolated compounds were mainly based on their spectroscopic data.

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VITA

Miss Chaithaya Saengngoen was born on October 3 rd, 1975 in Phitsanulok, Thailand. She graduated with Bachelor's degree of Science in Pharmacy in 1999 from the Faculty of Pharmacy, Chiangmai University, Chiangmai, Thailand.

She is presently working as a pharmacist in Department of Community Pharmacy Bangkrathum Hospital, Phitsanulok.