การศึกษาทางพฤกษเคมีของใบดีหมี

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PHYTOCHEMICAL STUDY OF *CLEIDION SPICIFLORUM* (BURM. F.) MERR. LEAVES

Miss Supotchana Menkham

A Thesis Submitted in Partial Fulfillment of the Requirements

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จากการสกัดแยกสารเคมีจากใบดีหมี (*Cleidion spiciflorum* (Burm. f.) Merr.) สามารถแยกสารในกลุ่มฟลาโวนไกลโคไซด์ ได้ 2 ชนิด คือ acacetin-7-*O*-β-*D*-glucopyranoside (tilianin) และ diosmetin-7-*O*-β-*D*-glucopyranoside สารไตรเทอร์ปีนกลุ่ม lanostane 1 ชนิด คือ (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3β-ol สารไดเทอร์ปีน 1 ชนิด คือ *trans*-phytol และสารเฟนิลโพรพานอยด์ไกลโคไซด์ 1 ชนิด คือ *p*-propenylphenol-β-*D*-glucopyranoside การพิสูจน์เอกลักษณ์ของสารเหล่านี้ ทำโดยการวิเคราะห์ข้อมูล UV, IR, MS, 1-D และ 2-D NMR ร่วมกับการเปรียบเทียบกับค่าที่ได้มีรายงานไว้แล้ว

ภาควิชาเภสัชพฤกษศาสตร์	ลายมือชื่อนิสิต…….……..
สาขาวิชาเภสัชพฤกษศาสตร์	ลายมือชื่ออาจารย์ที่ปรึกษา……..
ปีการศึกษา 2544	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม……-……...

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KEY WORD : *CLEIDION SPICIFLORUM* / EUPHORBIACEAE / FLAVONE GLYCOSIDES / TRITERPENE / DITERPENE / PHENYLPROPANOID GLYCOSIDE

SUPOTCHANA MENKHAM : PHYTOCHEMICAL STUDY OF *CLEIDION SPICIFLORUM* BURM.F.) MERR. LEAVES. THESIS ADVISOR : ASST. PROF. RUTT SUTTISRI. PH.D., 172 pp. ISBN 974-031-064-8

From the leaves of *Cleidion spiciflorum* (Burm. f.) Merr., two flavone glycosides, acacetin-7-*O*-β-*D*-glucopyranoside (tilianin) and diosmetin-7-*O*-β-*D*-glucopyranoside, a lanostane triterpene, (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3β-ol, a diterpene, *trans*-phytol, and a phenylpropanoid glycoside, *p*-propenylphenol-β-*D*-glucopyranoside, were isolated. Identification of these compounds was accomplished by analysis of their UV, IR, MS, 1-D and 2-D NMR data, as well as comparison with reported values.

Department Pharmaceutical Botany Student's signature……..……..

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ABBREVIATIONS

br	=	broad
^{O}C	=	degree celsius
CC	=	column chromatography
$CDCl_3$	=	deuterated chloroform
$CHCl_3$	=	chloroform
cm	=	centimeter
^{13}C-NMR	=	Carbon-13 Nuclear Magnetic Resonance
COSY	=	Correlated Spectroscopy
δ	=	chemical shift
1-D	=	one dimensional
2-D	=	two dimensional
d	=	doublet
dd	=	doublet of doublets
DEPT	=	Distortionless Enhancement by Polarization Transfer
DMSO-d_6	=	deuterated dimethylsulfoxide
dq	=	doublet of quartets
EIMS	=	Electron Impact Mass Spectroscopy
EtOH	=	ethanol
eV	=	electron volt
g	=	gram
^{1}H-NMR	=	Proton Nuclear Magnetic Resonance
HETCOR	=	Heteronuclear Correlation Spectroscopy
HMBC	=	^{1}H-detected Heteronuclear Multiple Bond Coherence
HMQC	=	^{1}H-detected Heteronuclear Multiple Quantum Coherence
Hz	=	Hertz
IR	=	Infrared
J	=	coupling constant

KBr	=	potassium bromide
L	=	liter
λ_{max}	=	wavelength at maximum absorption (nm)
m	=	multiplet
m	=	meter
M^+	=	molecular ion
MeOH	=	methanol
mg	=	milligram
MHz	=	Megahertz
ml	=	milliliter
mm	=	millimeter
MS	=	Mass Spectrum
m/z	=	mass-to-charge ratio
ε	=	molar absorptivity
nm	=	nanometer
NMR	=	Nuclear Magnetic Resonance
ppm	=	part per million
q	=	quartet
rel. int.	=	relative intensity
s	=	singlet
sp.	=	species
t	=	triplet
TLC	=	Thin Layer Chromatography
UV	=	Ultraviolet
var.	=	variety
ν_{max}	=	wavenumber at maximum absorption

CHAPTER I

INTRODUCTION

BOTANICAL DESCRIPTION

Cleidion spiciflorum (Burm. f.) Merr. (synonym: *C. javanicum* Blume) (Figure 1) is a tree which belongs to the family Euphorbiaceae of the order Euphorbiales (Heywood, 1978). The plant can grow up to 10-20 m and is very commonly found in evergreen forest at low altitudes (up to 800 m). Its stem barks are grey-brown, thin and smooth. The leaves are simple, alternately arranged, up to 10-22 cm long and 3.5-8 cm wide. The shape of the leaf is elliptic-oblong to narrowly obovate, tapering or slightly pointed at both ends, with scattered, shallow but quite sharp teeth on the margin. The mature leaves are thin and completely smooth. The leaf stalks are long and slender, 3-10 cm in length, swollen at both ends and with glands at their tops.

The male and female flowers are usually on different trees. These flowers have no petals and no disc. The male ones are in dangling spike-like clusters at the leaf axils. The length of the inflorescences is up to 25 cm, with slender individual stalks. The sepals are globose, not overlapping, up to 0.7 cm long. The number of stamens are 35-80. They are inserted on raised receptacle with 4-cell anthers and slender connectives. The female flowers are solitary or in pairs at leaf axils with very long stalks that are thicker near the top. The number of the styles are 2-3. They are very long, up to 23 mm in fruit. The styles are joined at base and each has 2-3 stigmatic arms. The ovary is sparsely hairy.

The fruit of *C. spiciflorum* is glabrous, 1.5-2.8 cm in length with stalk (4-8 cm). It is green, usually strongly 2-lobed, rarely 1- or 3-lobed, with persistent styles of up to 3 cm. The outer layer is leathery, whereas the inside is whitish with thin chocolate brown inner layer. When ripe, it splits into 2-3 sections. The seeds are spherical and smooth (ลีนา, 2530; Gardner, Sidisunthorn and Anusarnsunthorn, 2000).

In the northern part of Thailand this plant is called “Di mi” or “Din mi” (Lampang), “Cha mafai” or “Ma dimi” (Northern) and “Soei-ka-chu” (Karen-Mae Hong Son), while in

Figure 1. *Cleidion spiciflorum* (Burm. f.) Merr. (from Gardner, Sidisunthorn and Anusarnsunthorn, 2000)

the southern part of the country it is called “Ka dao krachai” (Prachuap Khiri Khan), “kalai” or “Kamlai” (Surat Thani) and “Khat lai” (Ranong) (ส่วนพฤกษศาสตร์ป่าไม้ สำนักวิชาการป่าไม้ กรมป่าไม้, 2543).

ETHNOMEDICAL USES OF PLANTS IN THE FAMILY EUPHORBIACEAE

Croton sublyratus Kurz (Plau noi) is a tropical plant distributed throughout Southeast Asia (Tansakul and De-Eknamkul, 1998). In Thailand, the roots of Plau noi are used externally for scabies and in the treatment of leprosy and yaws while the stem barks are used as digestive and astringent. The leaves of this plant are applied to itch and also used as astringent, the flowers can be used to kill parasite, and the fruits are remedy for pus (นันทวัน และ อรนุช, 2539a). Plaunotol, the mucosal protective factor-enhancing antiulcer agent which is the active ingredient of the commercially available kelnac®, was originally found in the leaves of *C. sublyratus*.

Croton oblongifolius Roxb. (Plau yai), another *Croton* species widely distributed in Thailand, is often used with Plau noi. It has been used traditionally in many applications such as for dysmenorrhea, as a purgative and to treat dyspepsia and dysentery (Roengsumran *et al*., 1999).

Two other examples of the uses of plants in this genus are those of *Croton cumingii* Muell. Agr. and *Croton crassifolius* Geisel. The root of *C. cumingii* is antipyretic and antiemetic. In Thailand, both its bark and roots are used as a remedy for fever. The roots of *C. crassifolius* are carminative and is prescribed to cure inflamed and painful throat. When steeped in liquor, it is employed in the treatment of tuberculosis of the lymphatic glands and is also applied to contusions and wounds (Perry, 1980).

Several plants of the genus *Phyllanthus* have been popularly employed for the treatment of kidney and bladder calculi, diabetes, hepatitis and dysentery, and have been used against affections of the intestines (Obdulio *et al*., 1995). For example: the leaves and fruits of *Phyllanthus emblica* L. have been used as anti-inflammatory and antipyretic in subtropical and rural parts of China, India, Indonesia, and the Malay Peninsula (Ihantola-Vormisto *et al*., 1997). Decoction or tea made from the weed *Phyllanthus niruri* Thw. or *Phyllanthus amarus* Schum. is drunk as a diuretic to treat

kidney trouble, venereal disease, and gallstone. The stem and leaves are used as antipyretic and anti-infective. These plants are also mentioned as expectorant (especially for children's coughs), emmenagogue, antidiarrheic, and as a remedy for colic (นันทวัน และ อรนุช, 2539b; Perry, 1980).

In Malaysia, another *Phyllanthus* species, *Phyllanthus pulcher* Wall. is made into a decoction drunk to relieve stomachache, or used as an eyewash. Its leaves may be applied to aching teeth, or used in poultices applied to boils, swellings, ulcerated nose, stomach ache, or the abdomen to relieve intermittent fever (นันทวัน และ อรนุช, 2539b; Perry, 1980).

The genus *Euphorbia* is one of several large genera belonging to this plant family that can be found in Thailand. *Euphorbia antiquorum* L. is a native of Southeast Asia, and its roots have been used for the treatment of asthma and coughs. The stem of this plant has been used medicinally for the treatment of asthma, edema and as a purgative. Its latex is extremely purgative (นันทวัน และ อรนุช, 2539b). *Euphorbia sessiliflora* Roxb., indigenous to Thailand, has been used for the treatment of yaws and applied as a poultice to boils. Its latex is extremely caustic and poisonous (Sutthivaiyakit, Thapsut and Prachayasittikul, 2000).

In South China, the pulp of pounded *Ehorbia hirta* L. is smeared on a newborn baby's head to treat pustules. Its milky juice is dropped into eye as a remedy for conjunctivitis, ulcerated cornea, and other eye complaints. A decoction of the plant is administered to relieve convulsions, and as an expectorant. In Vietnam, it is used as antidysenteric, whereas in Thailand this plant is used to treat kidney and bladder calculi, dysentery and intestinal disorders (Perry, 1980).

Castor oil from the seed of *Ricinus communis* L. has long been known as purgative. In China, its crushed seeds also appear to be used as a remedy for many troubles, i. e. deafness, headache, lymphatic tuberculosis, skin affections, hemorrhage, edema, constipation, swellings and as a dressing for boils. A decoction made from these seeds is taken to cure hemorrhoids and the inside of the seed is administered to promote labor. In Philippines, the seeds are regarded as antirheumatic (Perry, 1980).

ETHNOMEDICAL USES OF *CLEIDION SPICIFLORUM*

In Thailand, the stem of *Cleidion spiciflorum* is used as analgesic and antipyretic. A decoction of its bark is drunk to cure stomachache. The seeds are laxative. However, the leaves of this plant have been found to be poisonous and a decoction of these leaves can cause abortion (นันทวัน และ อรนุช, 2539a; ลีนา, 2530).

Biological activities and chemical constituents of several genera of this plant family have been investigated. Terpenoids, steroids, flavonoids and other interesting groups of phytochemicals, some of which are very active, have been found. However, to the present, phytochemical study of the constituents of *C. speciflorum* has never been documented. Therefore, it is the objective of this investigation to study the nature of the chemical components in the leaves of this plant, which might add to our knowledge of this important plant family and provide valuable chemotaxonomic insight for future researches.

CHAPTER II

HISTORICAL

1. Botanical aspect of Euphorbiaceae

The family Euphorbiaceae, containing 321 genera and about 7,950 species (Mabberley, 1990) which are distributed in temperate, sub-tropical, and tropical areas, is a family of trees, shrubs, herbs or lianas. Some species are succulent. The plants are monoecious or dioecious with stems and leaves often with specialized cells or tubes of milky or colorless latex.

The leaves are usually simple and spirally arranged, sometimes opposite or whorled, with pinnate or palmate venation. Some species have large stipules to help in protecting terminal bud, whereas some may appear only as glands, or the stipules are completely absent.

The flowers are usually regular in basically cymose inflorescences at terminal or axillary position with or without involucral bracts. The perianths are usually inconspicuous, sometimes basally connate or absent.

The number of stamens is at least 5 (sometimes fewer or 1) and sometimes basally connate. The anthers usually have longitudinal slits. The nectary disk of discrete or united segments is sometimes present without or within the androecium.

The ovary is superior, (2-)3 carpelled, or 4-∞ carpelled, divided into several locules with distinct styles or bifid or more-branched style. Each locule has 1 or 2 ovules.

The fruit is often a capsular schizocarp or a drupe, samara or berry. The seeds often have caruncle around the micropyle and with straight or curved embryo embedded in copious oily endosperm, often with poisonous proteins (Mabberley, 1990).

As for economic uses of plants in this family, there are commercial products including rubber (*Hevea*), tung oil (*Aleurites*), castor oil (*Ricinus*), and cassava or tapioca (*Manihot*). Many species are grown ornamentally, especially from the genera *Euphorbia* (Poinsettia, etc.), Codiaeum (*Croton*) and *Phyllanthus* (Otaheite gooseberry)

2. Chemical constituents of euphorbiaceous plants

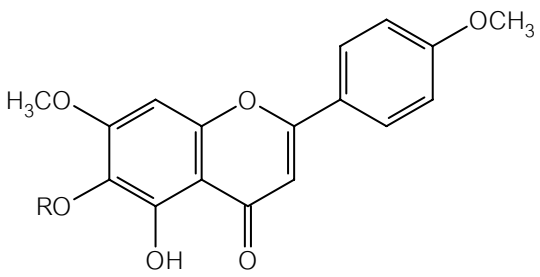
Plants in this family contain a wide range of chemical constituents, such as terpenoids, steroids, alkaloids, flavonoids and several other miscellaneous phytochemicals. The occurrence of flavone glycosides and triterpenoids, two classes of compounds found in the family Euphorbiaceae, can be summarized as follows.

2.1 Flavone glycosides of the family Euphorbiaceae

The flavone glycosides are the largest group of flavonoid glycosides. They are represented by approximately five hundred compounds which occur primarily in the families Labiatae, Compositae and Leguminosae (Harborne, 1994). However, only a limited number of this compound type have been reported as constituents of plants in the family Euphorbiaceae. These flavone glycosides are summarized in Table 1.

Table 1. Flavone glycosides isolated from plants in the family Euphorbiaceae

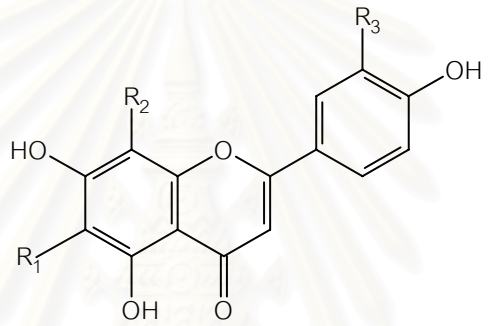
Compounds	Source	Plant part	Reference
7,4′-O-Dimethylscutellarein 6-O-β-D-glucopyranoside [1]	*Suregada multiflorum*	seed	Das and Chakravarty, 1993
7,4′-O-Dimethylscutellarein 6-neohesperidoside [2]	*Suregada multiflorum*	seed	Das and Chakravarty, 1993
7,4′-O-Dimethylscutellarein 6-sambubioside [3]	*Suregada multiflorum*	seed	Das and Chakravarty, 1993
Isoorientin [4]	*Glochidion zeylanicum*	leaf	Otsuka, Hirata and Shinzato, 2001
Luteolin 7,4′-dimethyl ether 3′-glucoside [5]	*Suregada multiflorum*	leaf	Parveen and Khan, 1987
Vitexin [6]	*Croton hovarum*	leaf	Krebs and Ramiarantsoa, 1997
	Glochidion zeylanicum	leaf	Otsuka, Hirata and Shinzato, 2001



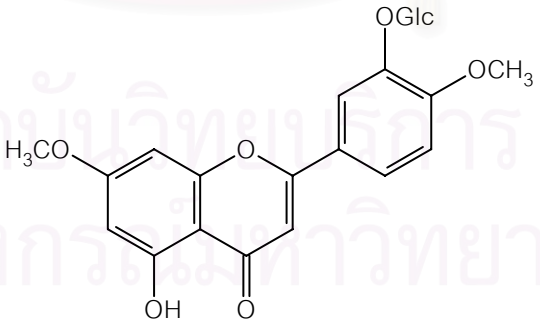
7,4′-O-Dimethylscutellarein 6-O-β-D-glucopyranoside [1] R = Glc

7,4′-O-Dimethylscutellarein 6-neohesperidoside [2] R = Glc^{2}-Rha

7,4′-O-Dimethylscutellarein 6-sambubioside [3] R = Glc^{2}-Xyl



	R_1	R_2	R_3
Isoorientin [4]	Glc	H	OH
Vitexin [6]	H	Glc	H



Luteolin 7,4′-dimethyl ether 3′-glucoside [5]

2.2 Triterpenoids of the family Euphorbiaceae

Previous phytochemical studies have indicated that terpenoids are abundant metabolites found form plants of this family. Some of these terpenoids displayed strong potential as candidates for drug development. A familiar example is the diterpenoid plaunotol, which is the active ingredient of a commercial drug named Kelnac®, a mucosal protective factor-enhancing antiulcer agent. The compound was originally found in the leaves of *Croton sublyratus* (Tansakul and De-Eknamkul, 1998). Another terpenoid, the lupane-type triterpene betulinic acid was isolated from the root bark of *Uapaca nitida* and exhibited significant antimalarial activity both *in vitro* and *in vivo*. (Steele *et al*., 1999). This compound is selectively cytotoxic against melanoma, neuroectodermal and malignant brain tumer cell lines (Zuco *et al*., 2002). Another study has demonstrated the compound as capable of inducing higher levels of apoptosis and cytotoxicity in low pH-adapted human melanoma cells than in normal cells (Schempp *et al*., 2002). Betulinic acid might therefore be useful as a cytotoxic agent in acidotic areas of tumours with minimal effect on normal tissues. In addition, this triterpenoid also showed other interesting activities such as antibacterial (Hess *et al*., 1995; Nick *et al*., 1995; Schuhly *et al*., 1999), antifungal (Hernandezperez *et al*., 1994), antiinflammatory (Recio *et al*., 1995; Mukherjee *et al*., 1997) and antispasmodic activity (Begum *et al*., 2000).

Other types of triterpenoids have also been reported as cytotoxic, for example, the triterpenes, cycloart-23-ene-3β,25-diol and cycloart-25-ene-3β,24-diol, isolated from *Euphorbia pulcherrima*, were cytotoxic against Ehrlich ascites tumor cells (Smith *et al*., 1996), whereas two other compounds, dihydroputranjivic acid and seco-3,4-taraxerone, displayed *in vitro* cytotoxic activity against Hep-G2 and A-431 human cancer cell lines and were potent inhibitors of topoisomerase II (Setzer *et al*., 2000).

The distribution of triterpenoids within the family Euphorbiaceae is summarized in Table 2.

Table 2. Distribution of triterpenoids in the family Euphorbiaceae

Compound	Source	Plant part	Reference
Acyclic-type			
Peplusol [7]	*Euphorbia peplus*	latex	Giner, Berkowitz and Andersson, 2000
(2*Z*, 6*Z*, 10*Z*, 14*E*, 18*E*, 22*E*)–Tetracosahexaen–1–ol [8]	*Phyllanthus niruri*	n.s.	Singh, 1989
Lanostane-type			
Acyclopeltenyl acetate [9]	*Macaranga peltata*	heartwood	Anjaneyulu and Reddy, 1981
24, 24-Dimethyllanosta-9(11), 25-dien-3-one [10]	*Bridelia tomentosa*	root	Boonyaratavej *et al*., 1990
Lanost–24–ene–3-cinnamoyl- 20–ol [11]	*Euphorbia antiquorum*	latex	Gewali *et al*., 1990
Lanost-25-en-3β-ol [12]	*Chamaesyce prostrata*	aerial part	Susana *et al*., 1999
Lanosterol [13]	*Euphorbia biglandulosa*	latex	Falsone and Schneider, 1985
	Euphorbia characias subsp. *characias*	latex	Fernandes-Ferreira, Novais and Pais, 1990
	Euphorbia lathyris	latex	Giner and Djerassi, 1995
	Euphorbia peplus	latex	Giner *et al*., 2000
	Euphorbia pulcherrima	n.s.	Sekula and Nes, 1980

Table 2. (continued)

Compound	Source	Plant part	Reference
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1967; 1968
24-Methyllanosta-9(11), 25-dien-3-one [14]	*Bridelia tomentosa*	root	Boonyaratavej *et al*., 1990
24-Methylenelanosterol [15]	*Euphorbia peplus*	latex	Giner *et al*., 2000
Mallotin [16]	*Mallotus stenanthus*	n.s.	Pal, Kulshreshtha and Rastogi, 1975
Cycloartane-type			
Cycloart-22-ene-3α, 25-diol [17]	*Euphorbia nicaeensis* subsp. *glareosa*	root	Oksuz *et al*., 1993
Cycloart-22-ene-3β, 25-diol [18]	*Euphorbia aleppica*	whole plant	Oksuz *et al*., 1996
	Euphorbia cyparissias	latex	Oksuz *et al*., 1994
Cycloart-23-ene-3β, 25-diol [19]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
	Euphorbia esula	n.s.	Shi and Jia, 1997
	Euphorbia myrsinites	n.s.	Oksuz *et al*., 1995
	Euphorbia petiolata	n.s.	Shi and Jia, 1997
	Euphorbia pulcherrima	leaf	Smith *et al*., 1996
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1967

Table 2. (continued)

Compound	Source	Plant part	Reference
Cycloart-23*Z*-en-3β, 25-diol [20]	*Euphorbia chamesyce*	whole plant	Tanaka *et al*., 1996
	Euphorbia sessiliflora	tuber	Sutthivaiyakit *et al*., 2000
Cycloart-24, 25-oxido-3β-ol [21]	*Euphorbia nicaeensis* subsp. *glareosa*	root	Oksuz *et al*., 1993
Cycloart-25-ene-3β,24-diol [22]	*Euphorbia aleppica*	whole plant	Oksuz *et al*., 1996
	Euphorbia cyparissias	latex	Oksuz *et al*., 1994
	Euphorbia nicaeensis subsp. *glareosa*	root	Oksuz *et al*., 1993
	Euphorbia sessiliflora	tuber	Sutthivaiyakit *et al*., 2000
	Euphorbia tortilis	n.s.	Anjaneyulu *et al*., 1993
	Euphorbia broteri	aerial part	Teresa *et al*., 1987
	Euphorbia pulcherrima	leaf	Smith *et al*., 1996
	Euphorbia myrsinites	n.s.	Oksuz *et al*., 1995
	Euphorbia trigona	stem	Anjaneyulu, Sambasiva and Connolly, 1985

Table 2. (continued)

Compound	Source	Plant part	Reference
Cycloart-3β, 24, 25-triol [23]	*Euphorbia petiolata*	tuber	Shi and Jia, 1997
	Euphorbia sessiliflora	tuber	Sutthivaiyakit *et al*., 2000
Cycloart–23–ene–3–acetate–25–ol [24]	*Sapium insigne*	root	Srivastava and Agnihotri, 1985
Cycloartenol [25]	*Euphorbia antiquorum*	latex	Anjaneyulu and Ravi, 1989
	Euphorbia biglandulosa	latex	Falsone and Schneider, 1985
	Euphorbia broteri	latex	Teresa *et al*., 1987
	Euphorbia caudicifolia	stem	Govardhan, Reddy and Sundararamaiah,
		latex	1984
	Euphorbia characias	latex	Warnaar, 1987
	Euphorbia characias	latex	Fernandes-Ferreira *et al*., 1990
	subsp. *characias*		
	Euphorbia cyparissias	latex	Oksuz *et al*., 1994
	Euphorbia lathyris	latex	Warnaar, 1987; Giner and Djerassi, 1995
	Euphorbia neriifolia	latex	Ilyas, Parveen and Amin, 1998
	Euphorbia peplus	latex	Giner *et al*., 2000

Table 2. (continued)

Compound	Source	Plant part	Reference
	Euphorbia petiolata	n.s.	Shi and Jia, 1997
	Euphorbia pulcherrima	latex	Warnaar, 1987
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1967; 1968
	Euphorbia segetalis	whole plant	Ferreira, Madureira and Ascenso, 1998
	Excoecaria agallocha	wood latex	Kawashima *et al*., 1971
Cycloartenyl acetate [26]	*Euphorbia broteri*	latex	Teresa *et al*., 1987
Cyclocaducinol [27]	*Euphorbia caducifolia*	latex	Afza *et al*., 1989
Cycloeuphordenol [28]	*Euphorbia tirucalli*	latex	Khan *et al*., 1988
Cyclolaudenol [29]	*Euphorbia aleppica*	whole plant	Oksuz *et al*., 1996.
	Euphorbia caudicifolia	latex	Govardhan *et al*., 1984
	Euphorbia myrsinites	n.s.	Oksuz *et al*., 1995
	Euphorbia nivalia	latex	Rao *et al*., 1986
Cyclolaudenone [30]	*Euphorbia caudicifolia*	stem	Govardhan *et al*., 1984
Cyclopeltenol [31]	*Macaranga peltata*	heartwood	Anjaneyulu and Reddy, 1981
Cyclopeltenyl acetate [32]	*Macaranga peltata*	heartwood	Anjaneyulu and Reddy, 1981
Cycloroylenol [33]	*Euphorbia royleana*	latex	Vijaya, Vimal and Dwipin, 1982

Table 2. (continued)

Compound	Source	Plant part	Reference
Cycloroylenyl acetate [34]	*Euphorbia royleana*	latex	Vijaya, Vimal and Dwipin, 1982
Dihydrocyclopeltenyl acetate [35]	*Macaranga peltata*	heartwood	Anjaneyulu and Reddy, 1981
Dihydrocycloroylenyl acetate [36]	*Euphorbia royleana*	latex	Vijaya, Vimal and Dwipin, 1982
24, 24-Dimethoxy-25, 26, 27-trisnorcycloartan-3β-ol [37]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
3-Epicyclolaudenol [38]	*Euphorbia caudicifolia*	latex	Govardhan *et al*., 1984
24 Epimeric cycloart-25-ene-3β, 24-diol [39]	*Euphorbia trigona*	stem	Anjaneyulu *et al*., 1985
Epimeric cycloartane-3β, 24, 25-triol [40]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
24, 25-Epoxycycloartanol [41]	*Euphorbia broteri*	latex	Teresa *et al*., 1987
	Euphorbia esula	n.s.	Shi and Jia, 1997
	Euphorbia petiolata	n.s.	Shi and Jia, 1997
3β-Hydroxycycloart-25-ene-24-hydroperoxide [42]	*Euphorbia cyparissias*	latex	Oksuz *et al*., 1994
3β-Hydroxycycloart-25-ene-24-one [43]	*Euphorbia aleppica*	whole plant	Oksuz *et al*., 1996
	Euphorbia broteri	aerial part	Teresa *et al*., 1987
	Euphorbia cyparissias	latex	Oksuz *et al*., 1994
	Euphorbia myrsinites	n.s.	Oksuz *et al*., 1995

Table 2. (continued)

Compound	Source	Plant part	Reference
	Euphorbia nicaeensis subsp. *glareosa*	root	Oksuz *et al*., 1993
Isocycloartenol [44]	*Euphorbia nivulia*	latex	Rao *et al*., 1986
	Euphorbia caudicifolia	stem	Govardhan *et al*., 1984
Isocyclopeltenyl acetate [45]	*Macaranga peltata*	heartwood	Anjaneyulu and Reddy, 1981
23, 25-O-Isopropylidene-cycloartanol [46]	*Euphorbia esula*	n.s.	Shi and Jia, 1997
24-Methylenecycloartanol [47]	*Euphorbia aleppica*	whole plant	Oksuz *et al*., 1996
	Euphorbia biglandulosa	latex	Falsone and Schneider, 1985
	Euphorbia broteri	latex	Teresa *et al*., 1987
	Euphorbia characias subsp. *characias*	latex	Fernandes-Ferreira *et al*., 1990
	Euphorbia cyparissias	latex	Oksuz *et al*., 1994
	Euphorbia nicaeensis subsp. *glareosa*	root	Oksuz *et al*., 1993
	Euphorbia myrsinites	n.s.	Oksuz *et al*., 1995
	Euphorbia peplus	latex	Giner *et al*., 2000

Table 2. (continued)

Compound	Source	Plant part	Reference
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1967; 1968
	Euphorbia segetalis	whole plant	Ferreira, Madureira and Ascenso, 1998
24-Methylenecycloartenyl acetate [48]	*Euphorbia nicaeensis* subsp. *glareosa*	root	Oksuz *et al*., 1993
	Euphorbia broteri	latex	Teresa *et al*., 1987
25-Methoxy-cycloart-23*E*-en-3β-ol [49]	*Euphorbia sessiliflora*	tuber	Sutthivaiyakit *et al*., 2000
Neriifolione [50]	*Euphorbia neriifolia*	latex	Ilyas *et al*., 1998
Wrightial [51]	*Euphorbia chamaesyce*	whole plant	Tanaka *et al*., 2000
Dammarane-type			
β-Anincanol [52]	*Euphorbia supina*	whole plant	Tanaka, Matsuda and Matsunaga, 1987
Dammara-20, 24-dien-3β-ol [53]	*Antidesma bunius*	stem	Hui and Sung, 1968
3β–Hydroxy–22, 23, 24, 25, 26, 27–hexanordammaran–2-one [54]	*Euphorbia supina*	whole plant	Tanaka *et al*., 1987

Table 2. (continued)

Compound	Source	Plant part	Reference
Tirucallane/Euphane-type			
Butyrospermol [55]	*Euphorbia broteri*	latex	Teresa *et al*., 1987
	Euphorbia chamaesyce	whole plant	Tanaka *et al*., 1994
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1968
Butyrospermyl acetate [56]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
Corollatadiol [57]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
	Euphorbia corollata	n.s.	Piatak and Reimann, 1972
Dihydroeuphol [58]	*Euphorbia royleana*	latex	Vijaya, Vimal and Dwipin, 1982
Dihydroeuphol acetate [59]	*Euphorbia royleana*	latex	Vijaya, Vimal and Dwipin, 1982
Dihydroroylenyl acetate [60]	*Euphorbia royleana*	latex	Vijaya, Vimal and Dwipin, 1982
Euphol [61]	*Euphorbia acrurensis*	latex	Macro *et al*., 1998
	Euphorbia antiquorum	latex	Anjaneyulu and Ramachandra Row, 1967; Anjaneyulu and Ravi, 1989
	Euphorbia broteri	latex	Teresa *et al*., 1987
	Euphorbia caracasana	n.s.	Morales Mendez, 1969
	Euphorbia kansui	root	Lin *et al*., 2000

Table 2. (continued)

Compound	Source	Plant part	Reference
	Euphorbia nicaeensis subsp. g*lareosa*	root	Oksuz *et al*., 1993
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1967; 1968
Euphol acetate [62]	*Euphorbia broteri*	latex	Teresa *et al*., 1987
	Euphorbia nicaeensis subsp. g*lareosa*	root	Oksuz *et al*., 1993
Euphol cinnamate [63]	*Euphorbia antiquorum*	latex	Anjaneyulu and Ravi, 1989
Euphorbinol [64]	*Euphorbia tirucalli*	stem	Rasool, Khan and Malik, 1989
Euphorbol [65]	*Euphorbia acrurensis*	latex	Macro *et al*., 1998
	Euphorbia antiquorum	latex	Anjaneyulu and Ravi, 1989
	Euphorbia cattimandoo	latex	Anjaneyulu and Ramachandra, 1967
	Euphorbia condylacarpa	root	Roshchin and Kir'galov, 1970
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1967; Ponsinet and Ourisson, 1968
Euphorbol acetate [66]	*Euphorbia antiquorum*	latex	Anjaneyulu and Ramachandra, 1967
	Euphorbia cattimandoo	latex	Anjaneyulu and Ramachandra, 1967

Table 2. (continued)

Compound	Source	Plant part	Reference
3α-Hydroxytirucalla-7,24*Z*-dien-26-oic acid [67]	*Celaenodendron mexicanum*	leaf	Camacho *et al*., 2000
Obtusifoliol [68]	*Euphorbia broteri*	atex	Teresa *et al*., 1987
3-Oxotirucalla-7,24*Z*-dien-26-oic acid [69]	*Celaenodendron mexicanum*	leaf	Camacho *et al*., 2000
Phyllantheol [70]	*Euphorbia acidus*	n.s.	Hui *et al*., 1976
	Phyllanthus engleri	n.s.	Hui *et al*., 1976
Tirucallol [71]	*Euphorbia kansui*	root	Lin *et al*., 2000
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1968
Lupanes			
3β-Acetoxy-30-*nor*-lupan-20-one [72]	*Claoxylon polot*	leaf, stem	Hui,Li and Lee, 1977
	Euphorbia maculata	whole plant	Matsunaga, Tanaka and Akagi, 1988
Betulin [73]	*Croton macrostachys*	stem bark, twig	Addae-Mensah *et al*., 1992b

Table 2. (continued)

Compound	Source	Plant part	Reference
	Croton megalocarpus	bark	Addae-Mensah *et al*., 1989
	Euphorbia broteri	aerial part	Teresa *et al*., 1987
	Euphorbia myrsinites	n.s.	Oksuz *et al*., 1995
	Euphorbia trigona	stem	Anjaneyulu *et al*., 1985
	Macaranga peltata	bark	Anjaneyulu and Reddy, 1981
	Phyllanthus flexuosus	stem bark	Tanaka and Matsunaga, 1988a; Tanaka, Matsuda and Matsunaga, 1993
Betulinic acid [74]	*Claoxylon polot*	leaf	Hui, Li and Lee, 1977
	Uapaca nitida	root bark	Steele *et al*., 1999
	Phyllanthus reticulatus	stem	Hui, Li and Wong, 1976
	Phyllanthus discoides	n.s.	Hui *et al*., 1976
Canaric acid [75]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
Epilupeol [76]	*Euphorbia cyparissias*	latex	Oksuz *et al*., 1994
Glochidiol [77]	*Glochidion* sp.	n.s.	Carpenter *et al*., 1980
	Glochidion eriocarpum	leaf	Hui and Li, 1976a
	Glochidion heyneanum	n.s.	Srivastava and Kulshreshtha, 1988

Table 2. (continued)

Compound	Source	Plant part	Reference
	Glochidion hohenackeri	root	Ganguly *et al*., 1968
	Glochidion macrophyllum	n.s.	Hui and Li, 1978
	Glochidion wrightii	leaf, stem	Hui and Fung, 1969
Glochidol [78]	*Glochidion eriocaepum*	stem	Hui and Li, 1976a
Glochidone [79]	*Euphorbia cyparissias*	latex	Oksuz *et al*., 1994
	Glochidion sp.	bark	Carpenter *et al*., 1980
	Glochidion eriocarpum	stem	Hui and Li, 1976
	Glochidion heyneanum	n.s.	Srivastava and Kulshreshtha, 1988
	Glochidion hohenackeri	root	Ganguly *et al*., 1968
	Glochidion macrophyllum	n.s.	Hui and Li, 1978
	Glochidion wrightii	leaf, stem	Hui and Fung, 1969
	Phyllanthus flexuosus	stem bark	Tanaka and Matsunaga, 1988a
	Phyllanthus watsonii	aerial part	Matsunaga *et al*., 1993
Glochidonol [80]	*Fluggea virosa*	stem	Hui *et al*., 1977
	Glochidion dasyphyllum	stem	Hui *et al*., 1970
	Glochidion eriocarpum	leaf	Hui and Li, 1976a

Table 2. (continued)

Compound	Source	Plant part	Reference
	Glochidion heyneanum	n.s.	Srivastava and Kulshreshtha, 1988
	Glochidion hongkongense	stem	Hui *et al*., 1970
	Glochidion macrophyllum	stem	Hui *et al*., 1970; Hui and Li, 1978
	Glochidion wrightii	stem	Hui and Fung, 1969; Carpenter *et al*., 1980
	Phyllanthus reticulatus	leaf, stem	Hui *et al*., 1976
	Phyllanthus watsonii	aerial part	Matsunaga *et al*., 1993
Glochilocudiol [81]	*Fluggea virosa*	stem	Hui *et al*., 1977
	Glochidion eriocarpum	stem	Hui and Li, 1976a
	Glochidion macrophyllum	n.s.	Hui and Li, 1978
	Glochidion multiloculare	n.s.	Hui and Li, 1978
3β-Hydroxy-30-*nor*-lupan-20-one [82]	*Claoxylon polot*	leaf, stem	Hui *et al*., 1977
	Euphorbia chamaesyce	seed	Tanaka *et al*., 1994
Lupan-3-one [83]	*Euphorbia cyparissias*	latex	Oksuz *et al*., 1994
20(29)-Lupene-1β-acetate,3α-ol [84]	*Glochidion* sp.	n.s.	Carpenter *et al*., 1980
20(29)-Lupene-1β-ol,3α-acetate [85]	*Glochidion* sp.	n.s.	Carpenter *et al*., 1980

Table 2. (continued)

Compound	Source	Plant part	Reference
20(29)-Lupene-1β,3α-diacetate [86]	*Glochidion* sp.	n.s.	Carpenter *et al*., 1980
20(29)-Lupene-1β,3β-diol [87]	*Glochidion dasyphyllum*	stem	Hui *et al*., 1970
	Glochidion eriocarpum	leaf	Hui and Li, 1976a
	Glochidion hongkongense	stem	Hui *et al*., 1970
	Glochidion macrophyllum	stem	Hui *et al*., 1970
	Phyllanthus watsonii	aerial part	Matsunaga *et al*., 1993
20(29)-Lupene-1,3-dione [88]	*Glochidion* sp.	bark	Carpenter *et al*., 1980
20(29)-Lupene-3β,15α-diol [89]	*Phyllanthus flexuosus*	stem bark	Tanaka *et al*., 1993
20(29)-Lupene-3α-23-diol [90]	*Glochidion eriocarpum*	stem	Hui and Li, 1976a
	Glochidion macrophyllum	stem	Hui and Lee, 1971
	Glochidion sp.	n.s.	Carpenter *et al*., 1980
20(29)-Lupene-3β-24,diol [91]	*Phyllanthus flexuosus*	stem bark	Tanaka, Tubesu and Matsunaga, 1988; Tanaka *et al*., 1993
20(29)-Lupene-1α, 3α, 23-triol [92]	*Glochidion* sp.	n.s.	Carpenter *et al*., 1980
20(30)-Lupene-3β, 29-diol [93]	*Euphorbia chamaesyce*	whole plant	Tanaka *et al*., 2000
Lupenone [94]	*Euphorbia segetalis*	whole plant	Ferreira, Madureira and Ascenso, 1998

Table 2. (continued)

Compound	Source	Plant part	Reference
	Glochidion eriocarpum	stem	Hui and Li, 1976a
	Glochidion wrightii	leaf, stem	Hui and Fung, 1969
	Phyllanthus distichus	n.s.	Hui *et al*., 1976
	Phyllanthus emblica	n.s.	Hui *et al*., 1976
Lupenyl acetate [95]	*Euphorbia maculata*	whole herb	Matsunaga *et al*., 1988
Lupeol [96]	*Croton macrostachys*	stem bark, twig	Addae-Mensah *et al*., 1992b
	Croton haumanianus	stem bark	Tchissamhou *et al*., 1990
	Croton megalocarpus	bark	Addae-Mensah *et al*., 1989
	Cnidosculus urens	n.s.	Bhattacharyya and Barros, 1986
	Euphorbia chamaesyce	seed	Tanaka *et al*., 1994
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1968
	Fluggea virosa	stem	Hui *et al*., 1977
	Glochidion eriocarpum	stem	Hui and Li, 1976a
	Glochidion puberum	leaf	Hui and Li, 1978
	Glochidion wrightii	leaf, stem	Hui and Fung, 1969

Table 2. (continued)

Compound	Source	Plant part	Reference
	Pera benensis	bark	Fournet *et al*., 1992
	Macaranga peltata	bark	Anjaneyulu and Reddy, 1981
	Mallotus repandus	leaf, stem	Hui and Li, 1977
	Phyllanthus distichus	n.s.	Hui *et al*., 1976
	Phyllanthus emblica	leaf, stem	Hui and Sung, 1968; Hui *et al*., 1976
	Phyllanthus flexuosus	stem bark	Tanaka and Matsunaga, 1988a
	Phyllanthus watsonii	aerial part	Matsunaga *et al*., 1993
Ocotillol-II [97]	*Phyllanthus flexuosus*	stem bark	Tanaka *et al*., 1993
1β, 2α, 3β-Trihydroxylup-20(29)-ene [98]	*Cephalomappa sinensis*	n.s.	Mei *et al*., 2001
Oleanane-type			
21α-Acetoxy-D: A-friedo-oleanan-3β-ol [99]	*Euphorbia tortilis*	n.s.	Anjaneyulu *et al*., 1993
3β-Acetoxyolean-12-en-28-oic acid [100]	*Drypetes molunduana*	n.s.	Wandji *et al*., 2000
	Securinega tinctoria	stem	Carvalho and Seita, 1993
3β-Acetoxy-*trans*-cinnamoyloxyl-olean-12-en-28-oic acid [101]	*Securinega tinctoria*	stem	Carvalho and Seita, 1993

Table 2. (continued)

Compound	Source	Plant part	Reference
α-Amyrin [102]	*Euphorbia characias* subsp. *characias*	latex	Fernandes-Ferreira *et al*., 1990
	Euphorbia paralias	latex	Breton *et al*., 1969
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1968
	Macaranga peltata	bark	Anjaneyulu and Reddy, 1981
	Mallotus repandus	leaf, stem	Hui and Li, 1977
β-Amyrin [103]	*Croton crassifolius*	root	Boonyarathanakornkit *et al*., 1988
	Croton hovarum	stem bark	Krebs and Ramiarantsoa, 1996
	Cnidosculus urens	n.s.	Bhattacharyya and Barros, 1986
	Euphorbia antiquorum	latex	Anjaneyulu and Ravi, 1989
	Euphorbia characias	latex	Warnaar, 1987
	Euphorbia pulcherrima	latex	Warnaar, 1987
	Euphorbia sp.	latex	Ponsinet and Ourisson, 1968
	Excoecaria agallocha	latex	Kawashima *et al*., 1971
	Glochidion heyneanum	n.s.	Srivastava and Kulshreshtha, 1988
	Macaranga peltata	bark	Anjaneyulu and Reddy, 1981

Table 2. (continued)

Compound	Source	Plant part	Reference
	Macaranga tanarius	stem	Markstadter *et al*., 2000
	Phyllanthus discoides	n.s.	Hui *et al*., 1976
	Phyllanthus flexuosus	stem bark	Tanaka and Matsunaga, 1988a
β-Amyrin acetate [104]	*Euphorbia antiquorum*	latex	Anjaneyulu and Ramachandra Row,1967
	Euphorbia maculata	whole plant	Matsunaga *et al*., 1988
β-Amyrin cinnamate [105]	*Cnidosculus urens*	n.s.	Bhattacharyya and Barros, 1986
δ-Amyrin formate [106]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1988b
δ-Amyrone [107]	*Excoecaria agallocha*	wood latex	Kawashima *et al*., 1971
Bayogenin acid [108]	*Drypetes molunduana*	n.s.	Wandji *et al*., 2000
3α-Benzoyloxy-D: A-friedo-oleanan-27,16α-lactone [109]	*Mallotus repandus*	stem	Sutthivaiyakit *et al*., 2001
3α, 21α-Diacetoxy-D: A-friedo-oleanane [110]	*Euphorbia tortilis*	n.s.	Anjaneyulu *et al*., 1993
3-Epi-β-Amyrin [111]	*Excoecaria agallocha*	latex	Kawashima *et al*., 1971
Epigermanicol [112]	*Euphorbia candelilla*	n.s.	Estrada, 1956
Epioleanolic acid [113]	*Celaenodendron mexicanum*	leaf	Camacho *et al*., 2000
Erythrodiol [114]	*Drypetes molunduana*	n.s.	Wandji *et al*., 2000

Table 2. (continued)

Compound	Source	Plant part	Reference
Germanicol [115]	*Cnidosculus urens*	n.s.	Bhattacharyya and Barros, 1986
Germanicol acetate [116]	*Cnidosculus urens*	n.s.	Bhattacharyya and Barros, 1986
	Euphorbia characias	latex	Warnaar, 1987
	Euphorbia lathyris	latex	Warnaar, 1987
	Euphorbia pulcherrima	latex	Warnaar, 1987
Geniculatin [117]	*Euphorbia geniculata*	aerial part	Tripathi and Tiwari, 1980
Glochidioside [118]	*Glochidion heyneanum*	aerial part	Srivastava and Kulshreshtha, 1986; 1988
Glochidioside N [119]	*Glochidion heyneanum*	aerial part	Srivastava and Kulshreshtha, 1986; 1988
Glochidioside Q [120]	*Glochidion heyneanum*	aerial part	Srivastava and Kulshreshtha, 1986; 1988
Hederagenin [121]	*Drypetes molunduana*	n.s.	Wandji *et al*., 2000
3α-Hydroxy-D: A-friedo-oleanan-27, 16α-lactone [122]	*Mallotus repandus*	stem	Sutthivaiyakit *et ai*., 2001
3β-Hydroxyolean-12-en-28-oic acid [123]	*Securinega tinctoria*	stem	Carvalho and Seita, 1993
3β-(*p*-Hydroxy-*trans*-cinnamoyloxy)olean-12-en-28-oic acid [124]	*Securinega tinctoria*	stem	Carvalho and Seita, 1993
Kamaladiol-3-acetate [125]	*Mallotus philippinensis*	stem bark	Nair and Rao, 1993

Table 2. (continued)

Compound	Source	Plant part	Reference
3-Keto-methylursolate [126]	*Euphorbia caudicifolia*	stem	Govardhan *et al*., 1984
26-Nor-D: A-friedo-olean-14-en-3β-ol [127]	*Phyllanthus watsonii*	aerial part	Matsunaga *et al*., 1993
26-Nor-D: A-friedo-olean-14-en-3-one [128]	*Phyllanthus watsonii*	aerial part	Matsunaga *et al*., 1993
9(11),12-Oleanadien-3β-ol [129]	*Phyllanthus flexuosus*	stem bark	Tanaka and Matsunaga, 1988a; Tanaka *et al*.,1988
11,13(18)-Oleanadien-3β-ol [130]	*Phyllanthus flexuosus*	stem bark	Tanaka and Matsunaga, 1988a; Tanaka *et al*.,1988
11,13(18)-Oleanadiene-3β,24-diol [131]	*Phyllanthus flexuosus*	stem bark	Tanaka *et al*., 1988; Tanaka *et al*.,1993
Olean-12-en-3β, 15α-diol [132]	*Phyllanthus flexuosus*	stem bark	Tanaka *et al*.,1988; Tanaka *et al*.,1993
Olean-12-en-3β, 24-diol [133]	*Phyllanthus flexuosus*	stem bark	Tanaka *et al*.,1988; Tanaka *et al*.,1993
Olean-12-en-3β, 9α-11α-triol [134]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1989b
Olean-12-en-3β, 15α, 24-triol [135]	*Phyllanthus flexuosus*	stem bark	Tanaka *et al*., 1988; Tanaka *et al*.,1993
Oleanolic acid [136]	*Croton lacciferus*	root	Bandara, Wimalasiri and Macleod, 1988
	Drypetes molunduana	n.s.	Wandji *et al*., 2000
	Euphorbia petiolata	n.s.	Shi and Jia, 1997
3-Oxo-D: A-friedo-oleanan-27, 16α-lactone [137]	*Mallotus repandus*	stem	Sutthivaiyakit *et ai*., 2001

Table 2. (continued)

Compound	Source	Plant part	Reference
3, 4-Seco-oleana-4(23), 18-dien-3-oic acid [138]	*Euphorbia chamaesyce*	seed	Tanaka *et al*., 1994
Taraxerane-type			
3β-acetoxy-D-friedoolean-14-en-28-oic acid [139]	*Croton lacciferus*	root	Bandara et al., 1988
Acetylaleuritolic acid [140]	*Croton cajucara*	bark	Maciel *et al*, 1998
	Croton crassifolius	root	Boonyarathanakornkit *et al*., 1988
	Croton megalocarpus	bark	Addae-Mansah *et al*., 1992a
	Croton oblongifolius	stem bark	Aiyar and Seshadri, 1971
	Maprounea africana	root	Pengsuparp *et al*., 1994; Chaudhuri *et al*., 1995
	Sapium pachystachys	n.s.	Siems *et al*., 1993
	Sapium rigidifolium	n.s.	Siems *et al*., 1993
Aleuritolic acid [141]	*Maprounea africana*	root	Pengsuparp *et al*., 1994; Chaudhuri *et al*., 1995
	Sapium baccatum	bark	Pradhan *et al*., 1984
Aleuritolic acid 3-*p*-hydroxybenzoate [142]	*Maprounea africana*	root	Chaudhuri *et al*., 1995

Table 2. (continued)

Compound	Source	Plant part	Reference
Aleuritolic acid 3-*p*-hydroxycinnamate [143]	*Maprounea membranacea*	bark	Beutler *et al*., 1995
Baccatin [144]	*Sapium baccatum*	n.s.	Saha *et al*., 1977
1β, 2α-Dihydroxyaleuritolic acid 2,3-bis-*p*-hydroxybenzoate [145]	*Maprounea africana*	root	Chaudhuri *et al*., 1995
Euphorginol [146]	*Euphorbia tirucalli*	stem	Rasool, Khan and Malik, 1989
1β-Hydroxyaleuritolic acid 3-*p*-hydroxybenzoate [147]	*Maprounea africana*	root	Beutler *et al*., 1995; Chaudhuri *et al*., 1995; Pengsuparp *et al*., 1994; 1995
2α-Hydroxyaleuritolic acid 2-*p*-hydroxybenzoate [148]	*Maprounea africana*	root	Beutler *et al*., 1995
	Maprounea membranacea	bark	Beutler *et al*., 1995
2α-Hydroxyaleuritolic acid 3-*p*-hydroxybenzoate [149]	*Maprounea africana*	root	Beutler *et al*., 1995; Chaudhuri *et al*., 1995
2α-Hydroxyaleuritolic acid 2, 3-bis-*p*-hydroxybenzoate [150]	*Maprounea africana*	root	Pengsuparp *et al*., 1994; Chaudhuri *et al*., 1995
3α-Hydroxyaleuritolic acid 2β-*p*-hydroxybenzoate [151]	*Maprounea africana*	root	Chaudhuri *et al*., 1995

Table 2. (continued)

Compound	Source	Plant part	Reference
7β-Hydroxymaprounic acid 3-*p*-hydroxybenzoate [152]	*Maprounea africana*	root	Chaudhuri *et al*., 1995
Isotaraxerol [153]	*Excoecaria agallocha*	leaf	Hui and Sung, 1968
	Macaranga tanarius	stem	Markstadter *et al*., 2000
11α,12α-Oxidotaraxerol [154]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1988b
	Euphorbia chamaesyce	seed	Tanaka *et al*., 1994
Sebiferenic acid [155]	*Sapium sebiferum*	bark	Pradhan *et al*., 1984
Taraxerol [156]	*Alchornea latifolia*	leaf	Setzer *et al*., 2000
	Croton caudatus	stem bark	Banerji, Nandi and Kundu, 1988
	Euphorbia antiquorum	root, stem bark	Anjaneyulu, Nageswara Rao and Ramachandra Row, 1967; Anjaneyulu and Ravi, 1989; Zhi-Da *et al*., 1989
	Macaranga tanarius	stem	Markstadter *et al*., 2000
	Sapium discolor	leaf, stem	Hui and Sung, 1968
Taraxerone [157]	*Alchornea latifolia*	leaf	Setzer *et al*., 2000

Table 2. (continued)

Compound	Source	Plant part	Reference
	Croton caudatus	stem bark	Banerji *et al*., 1988
	Euphorbia antiquorum	stem	Anjaneyulu, Nageswara Rao and Ramachandra Row, 1967; Anjaneyulu and Ravi, 1989
	Macaranga tanarius	stem	Markstadter *et al*., 2000
Taraxeryl acetate [158]	*Croton caudatus*	stem bark	Banerji *et al*., 1988
	Euphorbia maculata	whole herb	Matsunaga *et al*., 1988
3,4-Seco-4(23),14-taraxeradien-3-oic acid [159]	*Euphorbia broteri*	aerial part	Teresa *et al*., 1987
Multiflorane-type			
3β-Acetoxymultiflor-8-en-7-one [160]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b
3β-Hydroxymultiflor-8-en-7-one [161]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b
	Euphorbia chamaesyce	whole plant	Tanaka *et al*., 1996
3β-Hydroxymultiflor-8-en-16-one [162]	*Antidesma menasu*	aerial part	Rizvi *et al*., 1980
16α-Hydroxymultiflor-8-en-3-one [163]	*Antidesma menasu*	aerial part	Rizvi *et al*., 1980
Isomultiflorenol [164]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b

Table 2. (continued)

Compound	Source	Plant part	Reference
Multiflorenol [165]	*Suregada multiflorum*	leaf	Talapatra *et al*., 1989
Glutinane-type			
Alnusenol [166]	*Euphorbia cyparissias*	n.s.	Oksuz *et al*., 1994
	Euphorbia chamaesyce	whole plant	Tanaka *et al*., 1996
	Euphorbia segetalis	whole plant	Ferreira *et al*., 1998
5-Glutinen-3β-acetate [167]	*Euphorbia maculata*	*whole plant*	Matsunaga *et al*., 1988
5-Glutinen-3β-ol [168]	*Euphorbia cyparissias*	n.s.	Oksuz *et al*., 1994
Glutinone [169]	*Euphorbia cyparissias*	n.s.	Oksuz *et al*., 1994
Glut-5-ene-3α-methylbutyrate [170]	*Euphorbia cyparissias*	latex	Oksuz *et al*., 1994
Friedelane-type			
3β-Acetoxy-29-friedelanol [171]	*Euphorbia antiquorum*	n.s.	Anjaneyulu and Ravi, 1989
29-Acetoxy-3β-friedelanol [172]	*Euphorbia antiquorum*	n.s.	Anjaneyulu and Ravi, 1989
3β-Acetoxyfriedelan-30-ol [173]	*Euphorbia antiquorum*	stem	Anjaneyulu and Ravi, 1989
30-Acetoxyfriedelan-3β-ol [174]	*Euphorbia antiquorum*	stem	Anjaneyulu and Ravi, 1989

Table 2. (continued)

Compound	Source	Plant part	Reference
Antidesmanol [175]	*Euphorbia antiquorum*	n.s.	Anjaneyulu and Ravi, 1989
3β,29-Diacetoxyfriedelane [176]	*Euphorbia antiquorum*	n.s.	Anjaneyulu and Ravi, 1989
Dihydroputranjivic acid [177]	*Alchornea latifolia*	leaf	Setzer *et al*., 2000
Drypemolundein B [178]	*Drypetes molunduana*	n.s.	Wandji *et al*., 2000
Epifriedelinol [179]	*Alchornea latifolia*	leaf	Setzer *et al*., 2000
	Euphorbia antiquorum	stem bark	Anjaneyulu *et al*., 1967; Anjaneyulu amd Ravi, 1989
	Phyllanthus watsonii	aerial part	Matsunaga *et al*., 1993
	Euphorbia antiquorum	stem	Anjaneyulu amd Ravi, 1989
	Fluggea virosa	stem	Hui *et al*., 1977
	Glochidion macrophyllum	leaf, stem	Hui and Li, 1978
	Glochidion puberum	leaf	Hui and Li, 1978
	Glochidion wrightii	leaf, stem	Hui and Fung, 1969
	Mallotus hookerianus	leaf, stem	Hui and Li, 1976b
	Phyllanthus reticulatus	leaf, stem	Hui *et al*., 1976
Friedelan-3β, 30-diol [180]	*Euphorbia antiquorum*	stem	Anjaneyulu amd Ravi, 1989

Table 2. (continued)

Compound	Source	Plant part	Reference
Friedelan-3β, 30-diacetate [181]	*Euphorbia antiquorum*	stem	Anjaneyulu amd Ravi, 1989
Friedelane-3, 7-dione [182]	*Drypetes molunduana*	n.s.	Wandji *et al*., 2000
Friedelin [183]	*Alchornea latifolia*	leaf	Setzer *et al*., 2000
	Antidesma bunius	leaf	Hui and Sung, 1968
	Celaenodendron mexicanum	leaf	Camacho *et al*., 2000
	Celaenodendron mexicanum	seed	Castaneda *et al*., 1992
	Claoxylon polot	leaf, stem	Hui *et al*., 1977
	Croton hovarum	bark	Krebs and Ramiarantsoa, 1996
	Euphorbia segetalis	whole plant	Ferreira *et al*., 1998
	Fluggea microcarpa	trunk bark	Hui *et al*., 1977
	Glochidion puberum	leaf	Hui and Li, 1978
	Glochidion wrightii	leaf, stem	Hui and Fung, 1969
	Macaranga tanarius	stem	Markstadter *et al*., 2000
	Mallotus hookerianus	leaf, stem	Hui and Li, 1976b
	Mallotus philippinensis	stem bark	Nair and Rao, 1993
	Mallotus repandus	leaf, stem	Hui and Li, 1977

Table 2. (continued)

Compound	Source	Plant part	Reference
	Phyllanthus flexuosus	stem bark	Tanaka and Matsunaga, 1988a
	Phyllanthus reticulatus	leaf, stem	Hui *et al*., 1976
	Phyllanthus watsonii	aerial part	Matsunaga *et al*., 1993
Friedelinol [184]	*Euphorbia antiquorum*	stem	Anjaneyulu *et al*., 1967; Anjaneyulu amd Ravi, 1989
	Fluggea microcarpa	trunk bark	Hui *et al*., 1977
	Fluggea virosa	leaf, stem	Hui *et al*., 1977
3β-Hydroxyfriedelan-16-one [185]	*Celaenodendron mexicanum*	seed, leaf	Castaneda *et al*., 1992; Camacho *et al*., 2000
21α-Hydroxyfriedelen-3-one [186]	*Phyllanthus reticulatus*	leaf, stem	Hui *et al*., 1976
21α-Hydroxy-4(23)-friedelen-3-one [187]	*Phyllanthus reticulatus*	leaf, stem	Hui *et al*., 1976
Maytensifolin B [188]	*Celaenodendron mexicanum*	leaf	Camacho *et al*., 2000
Ursane-type			
3β-Benzoyl-13α-ursan-28,12β-olide [189]	*Mallotus repandus*	leaf, stem	Hui and Li, 1977
3β-28-Dihydroxy-12-ursen-27-oic acid [190]	*Mallotus hookerianus*	leaf, stem	Hui and Li, 1976b

Table 2. (continued)

Compound	Source	Plant part	Reference
2α-Hydroxymaprounic acid 2,3-bis-*p*-hydroxybenzoate [191]	*Maprounea africana*	bark	Mansukh *et al*., 1983
3α-Hydroxy-13α-ursan-28,12β-olide [192]	*Mallotus repandus*	leaf, stem	Hui and Li, 1977
	Mallotus repandus	stem, root bark	Huang, Wang and Lin, 1999
3β-Hydroxy-13α-ursan-28,12β-olide [193]	*Mallotus repandus*	leaf, stem	Hui and Li, 1977
3α-Hydroxy-13α-ursan-12β, 28-olide 3-benzoate [194]	*Mallotus repandus*	stem, root bark	Huang, Wang and Lin, 1999
3α-Hydroxy-28β-methoxy-13α-ursan-28,12β-epoxide 3-benzoate [195]	*Mallotus repandus*	stem, root bark	Huang, Wang and Lin, 1999
3α-Hydroxy-13α-ursan-28-oic acid [196]	*Mallotus repandus*	stem	Huang, Wang and Lin, 1999
		root bark	
3-Keto-methyl ester-12-ursen-28-oic acid [197]	*Euphorbia caducifolia*	stem	Govardhan *et al*., 1984
Maprounic acid [198]	*Maprounea africana*	bark	Mansukh *et al*., 1983
Maprounic acid *p*-hydroxybenzoate [199]	*Maprounea africana*	bark	Mansukh *et al*., 1983
Neoilexonol [200]	*Euphorbia maculata*	whole plant	Matsunaga *et al*., 1988

Table 2. (continued)

Compound	Source	Plant part	Reference
3-Oxo-13α-ursan-28,12β-olide [201]	*Mallotus repandus*	stem, root bark	Huang, Wang and Lin, 1999
3-Oxoquinovic acid [202]	*Mallotus hookerianus*	leaf, stem	Hui and Li, 1976b
9(11),12-Ursadien-3β-ol [203]	*Euphorbia maculata*	whole herb	Matsunaga *et al*., 1988
Ursolic acid [204]	*Croton sparsiflorus*	leaf, stem	Satish and Bhakum, 1972
	Euphorbia paralias	latex	Breton *et al*., 1969
	Mallotus repandus	leaf, stem, root bark	Hui and Li, 1977 Huang, Wang and Lin, 1999
Ursolic benzoate [205]	*Mallotus repandus*	leaf, stem	Hui and Li, 1977
Hopane-type			
17β-21β-Epoxy-3β-hopanol [206]	*Euphorbia supina*	whole plant	Tanaka *et al*., 1990
Hopenol B [207]	*Euphorbia supina*	whole plant	Matsunaga and Morita, 1983
	Euphorbia lathyris	latex	Giner and Djerassi, 1995
Hopenone B [208]	*Euphorbia cyparissias*	n.s.	Starratt, 1969.
21αH-Hop-22(29)-en-3β, 30-diol [209]	*Mallotus repandus*	stem	Hui and Li, 1977

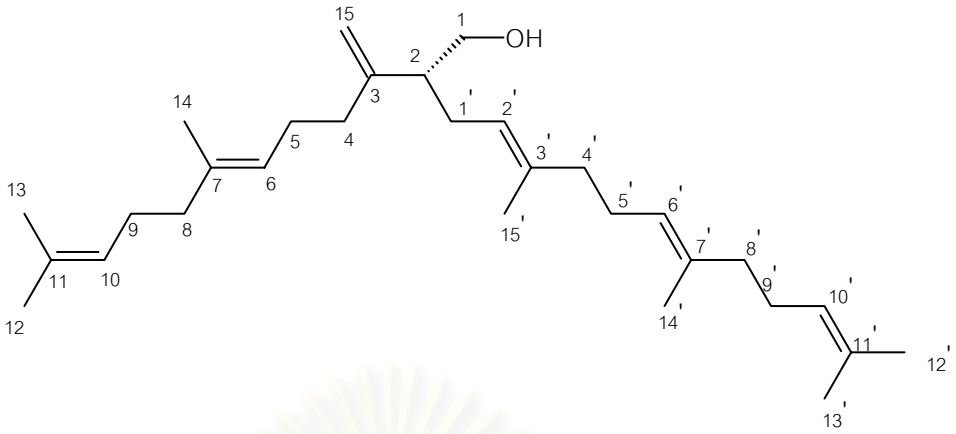
Table 2. (continued)

Compound	Source	Plant part	Reference
Moretenol [210]	*Euphorbia trigona*	stem	Anjaneyulu *et al*., 1985
	Mallotus nepalensis	leaf	Sil *et al*., 1980
	Sapium sebiferum	root bark	Kouno *et al*., 1983
Moretenone [211]	*Mallotus nepalensis*	leaf	Sil, Som and Dutta, 1980
	Sapium sebiferum	root bark	Kouno *et al*., 1983
21αH-29-Nor-3-22-hopanedione [212]	*Mallotus paniculatus*	stem	Hui and Li, 1976b
Sebiferic acid [213]	*Sapium sebiferum*	bark	Pradhan and Khastgir, 1973; Pradhan *et al*., 1984
Fernane-type			
7,9(11)-Fernadien-3β-ol [214]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1988b
Fern-8-en-3β-ol [215]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991a
Neospirosupinanetrione [216]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991a
Neospirosupinanonediol [217]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991a
3, 4-Seco-8β H-ferna-4(23), 9(11)-dien-3-oic acid [218]	*Euphorbia chamaesyce*	whole plant	Tanaka *et al*., 1996
	Euphorbia sp.	n.s.	Wada *et al*., 1998
3, 4-Seco-8β H-ferna-4(23), 9(11)-dien-3-ol [219]	*Euphorbia* sp.	whole plant	Wada *et al*., 1998

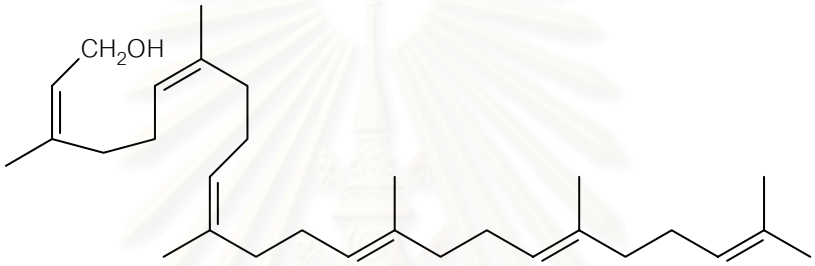
Table 2. (continued)

Compound	Source	Plant part	Reference
Spirosupinanonediol [220]	*Euphorbia supina*	whole plant	Matsunaga *et al*., 1984; Tanaka and Matsunaga, 1991a
Supinenolone A [221]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1989a
Supinenolone B [222]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1989a
Supinenolone C [223]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1989a
Supinenolone D [224]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b
Supinenolone E [225]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b
Supinenolone E acetate [226]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b
Adianane-type			
Espinendiol A [227]	*Euphorbia supina*	n.s.	Tanaka, Matsunaga and Ishida, 1989
Espinendiol B [228]	*Euphorbia supina*	n.s.	Tanaka, Matsunaga and Ishida, 1989
Espinenoxide [229]	*Euphorbia supina*	n.s.	Tanaka, Matsunaga and Ishida, 1989
Trinorisoespinenoxide [230]	*Euphorbia supina*	whole plant	Tanaka and Matsunaga, 1991b
	Euphorbia supina	n.s.	Tanaka *et al*., 1989
Ring cleaved Tetratriterpenoid			
Dumsin [231]	*Croton jatrophoides*	root bark	Kubo *et al*., 1990

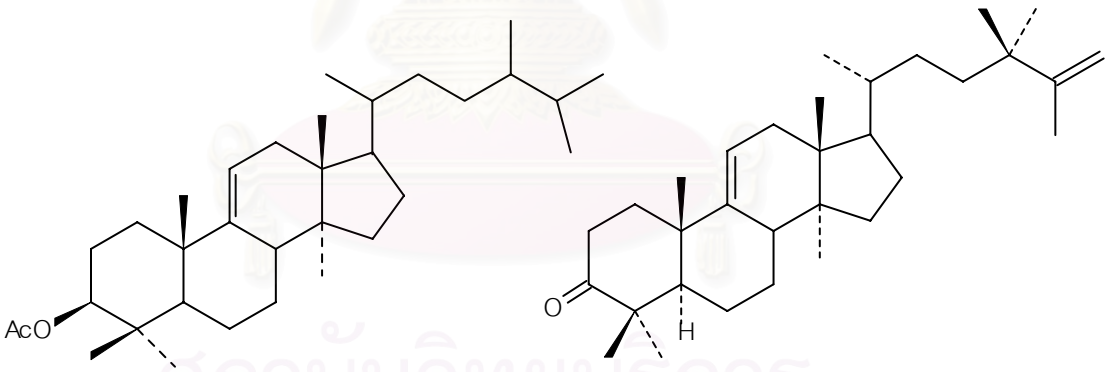
n.s. = not specified



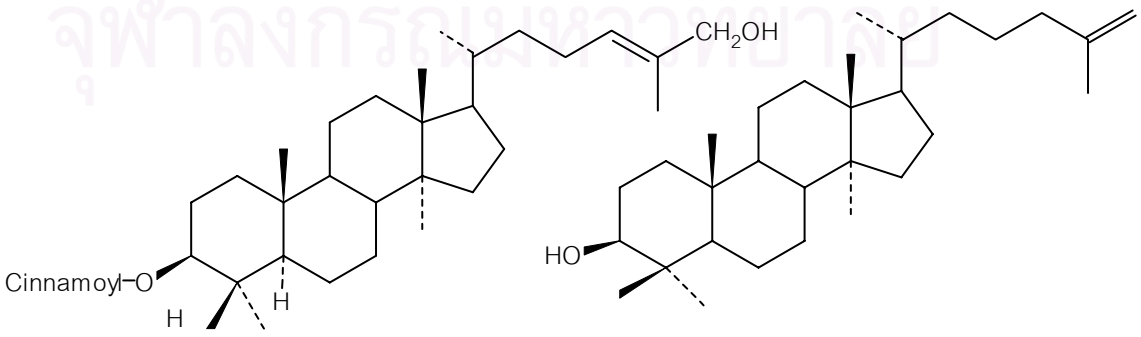
Peplusol [7]



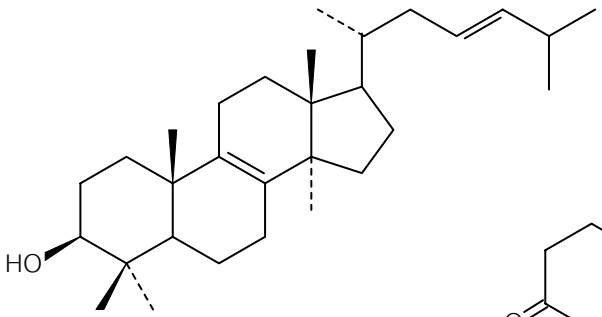
(2*Z*, 6*Z*, 10*Z*, 14*E*, 18*E*, 22*E*)–Tetracosahexaen–1–ol [8]



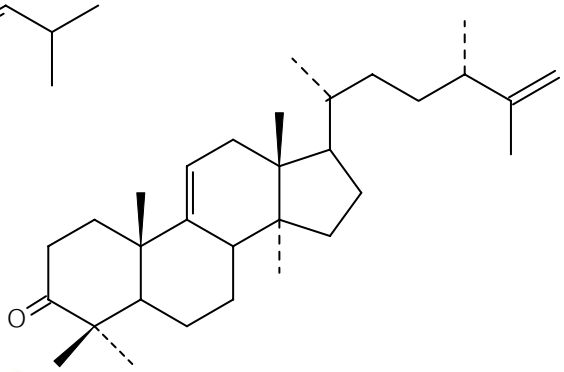
Acyclopeltenyl acetate [9] 24, 24-Dimethyllanosta-9(11), 25-dien-3-one [10]



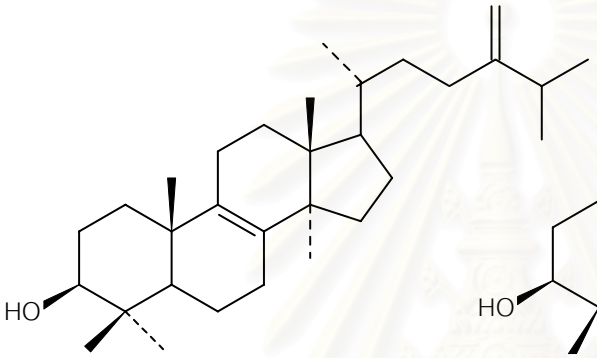
Lanost-24-ene-3-cinnamoyl-20*E*-ol [11] Lanost-25-en–3β-ol [12]



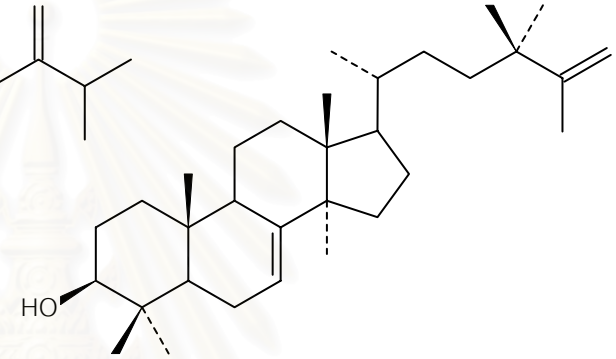
Lanosterol [13]



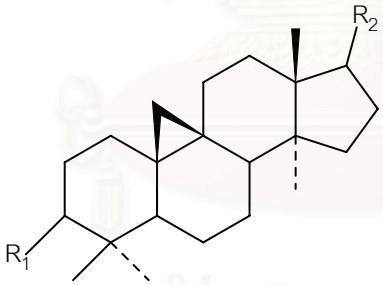
24-Methyllanosta-9(11), 25-dien-3-one [14]

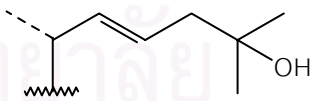
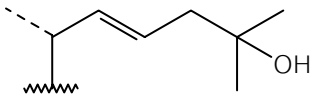
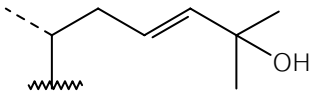


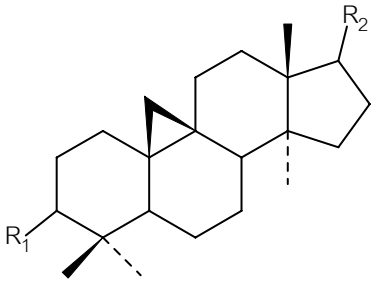
24-methylenelanosterol [15]

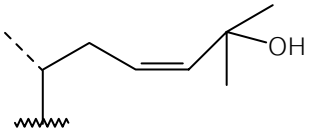
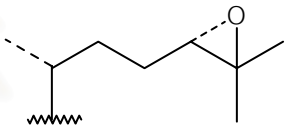
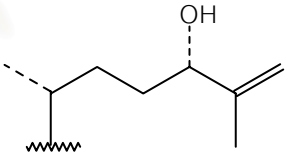
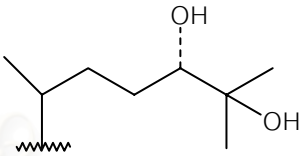
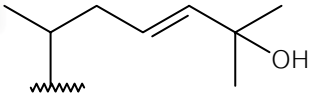
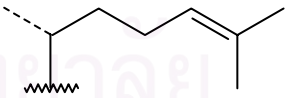
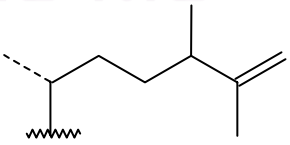
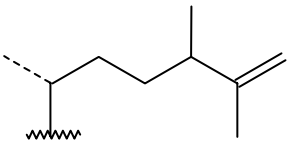


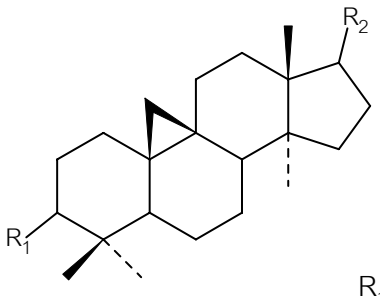
Mallotin [16]

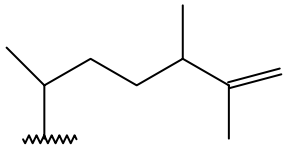
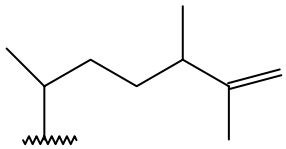
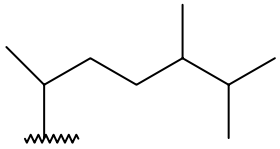
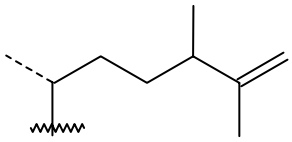
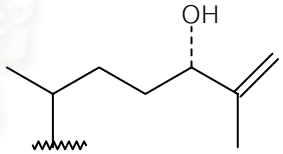
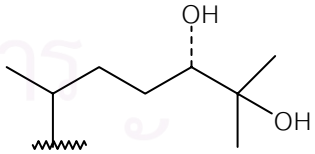
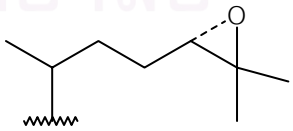
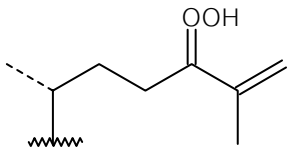


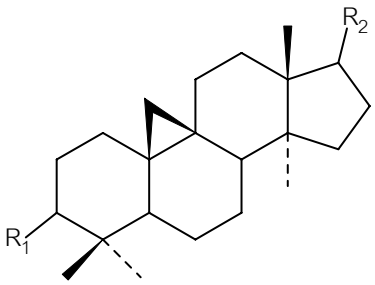
		R_1	R_2
Cycloart-22-ene-3α, 25-diol	[17]	αOH	
Cycloart-22-ene-3β, 25-diol	[18]	βOH	
Cycloart-23-ene-3β, 25-diol	[19]	βOH	

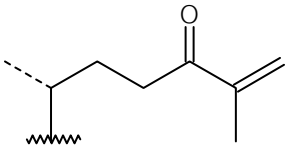
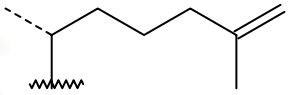
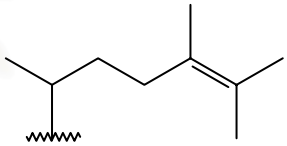
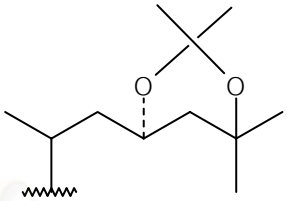
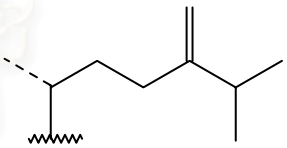
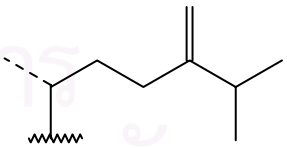
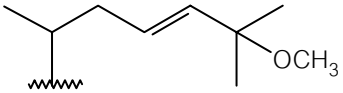
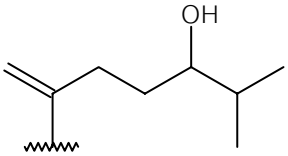
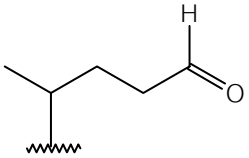


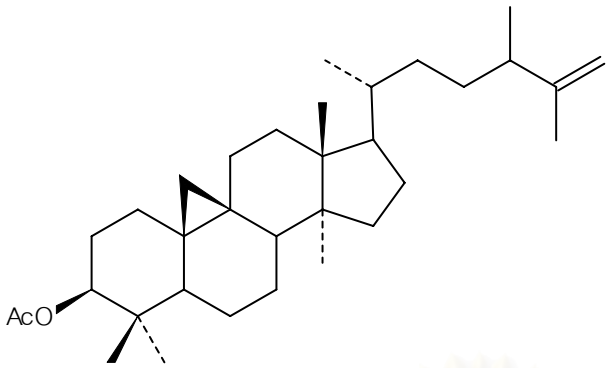
	R_1	R_2
Cycloart-23*Z*-ene-3β, 25-diol [20]	βOH	
Cycloart-24, 25-oxido-3β-ol [21]	βOH	
Cycloart-25-ene-3β,24-diol [22]	βOH	
Cycloart-3β, 24, 25-triol [23]	βOH	
Cycloart-23-ene-3-acetate-25-ol [24]	βOAc	
Cycloartenol [25]	βOH	
Cyclolaudenol [29]	βOH	
Cyclolaudenone [30]	=O	



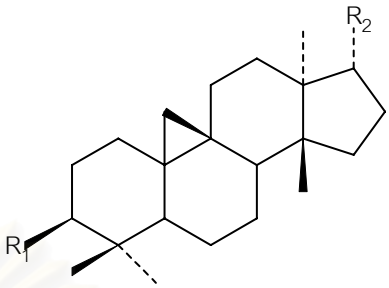
	R_1	R_2
Cyclopeltenol [31]	βOH	
Cyclopeltenyl acetate [32]	βOAc	
Dihydrocyclopeltenyl acetate [35]	βOAc	
3-Epicyclolaudenol [38]	αOH	
24 Epimeric cycloart-25-ene-3β, 24-diol [39]	βOH	
Epimeric cycloartane-3β, 24, 25-triol [40]	βOH	
24, 25-Epoxycycloartanol [41]	βOH	
3β-Hydroxycycloart-25-ene-24-hydroperoxide [42]	βOH	



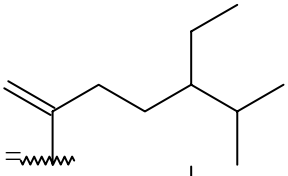
		R_1	R_2
3β-Hydroxycycloart-25-ene-24-one	[43]	βOH	
Isocycloartenol	[44]	βOH	
Isocyclopeltenyl acetate	[45]	βOH	
23, 25-O-Isopropylidene-cycloartanol	[46]	βOH	
24-Methylenecycloartanol	[47]	βOH	
24-Methylenecycloartenyl acetate	[48]	βOAc	
25-Methoxy-cycloart-23*E*-en-3β-ol	[49]	βOH	
Neriifolione	[50]	=O	
Wrightial	[51]	βOH	



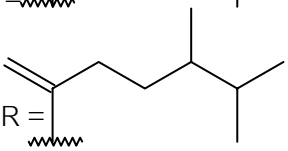
Cycloartenyl acetate [26]

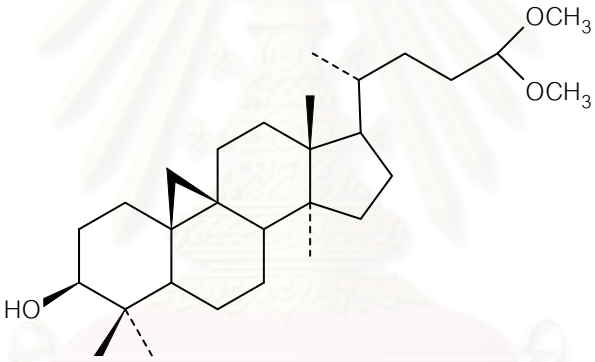


Cyclocaducinol [27] R =

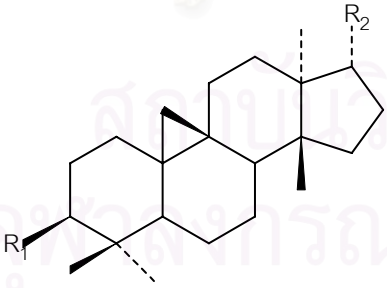


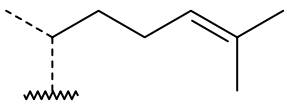
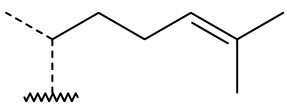
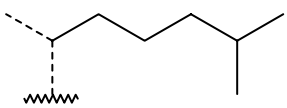
Cycloeuphordenol [28] R =

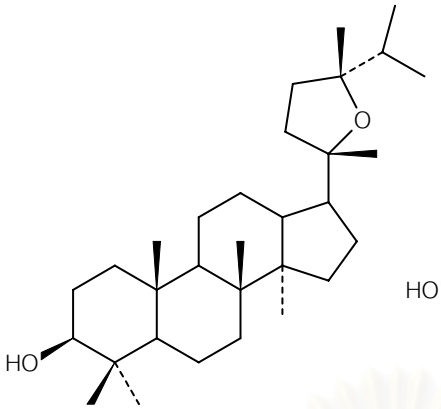




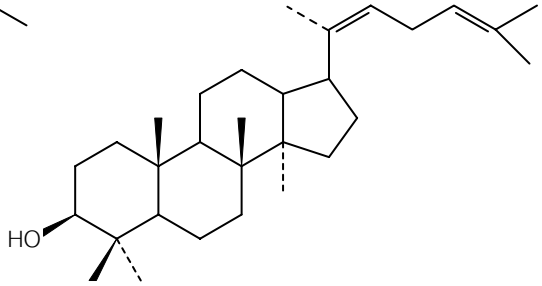
24, 24-Dimethoxy-25, 26, 27-trisnorcycloartan-3β-ol [37]



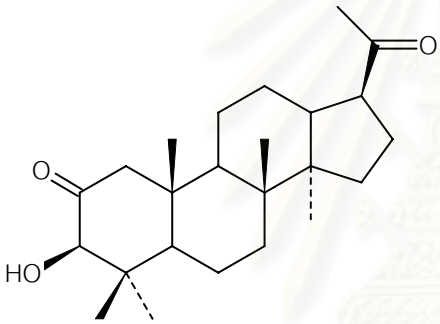
		R_1	R_2
Cycloroylenol	[33]	OH	
Cycloroylenyl acetate	[34]	OAc	
Dihydrocycloroylenyl acetate	[36]	OAc	



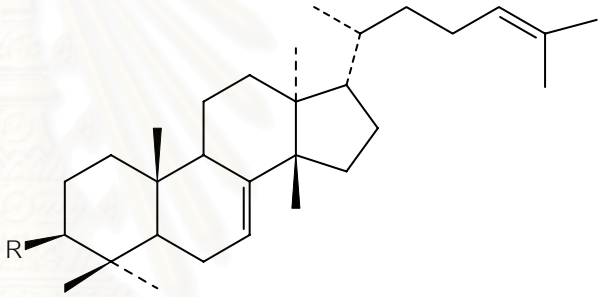
β-Anincanol [52]



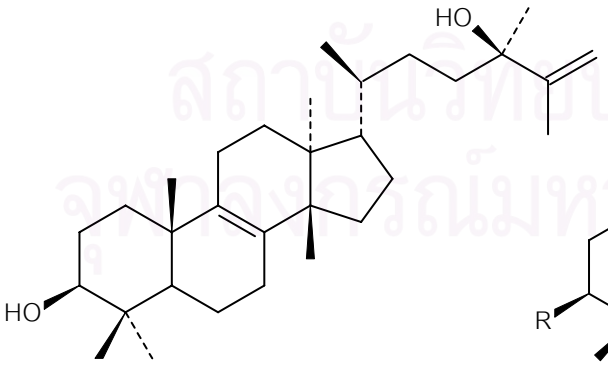
Dammara-20, 24-dien-3β-ol [53]



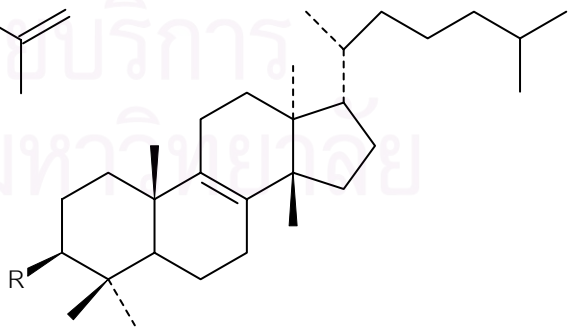
3β-Hydroxy-22, 23, 24, 25, 26, 27
-hexanordammaran-2-one [54]



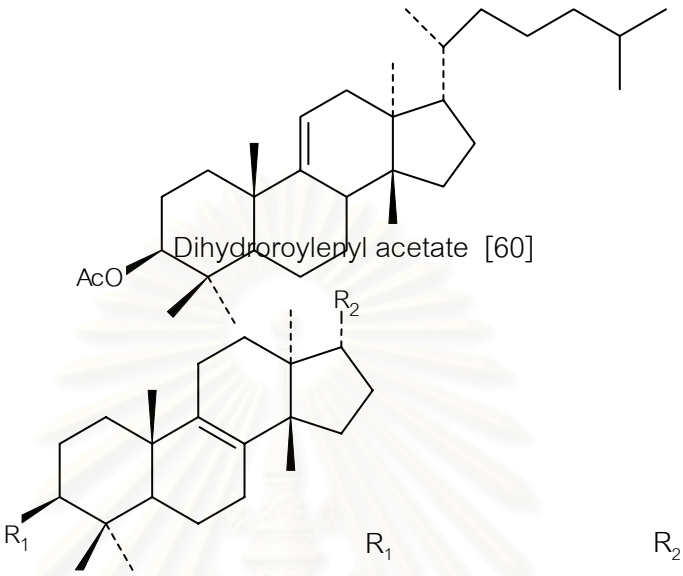
Butyrospermol [55] R = OH
Butyrospermyl acetate [56] R = OAc



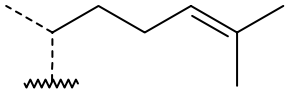
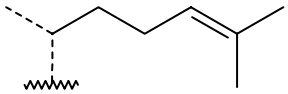
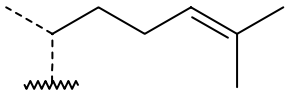
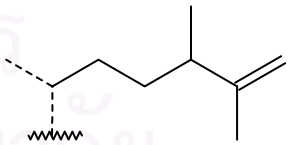
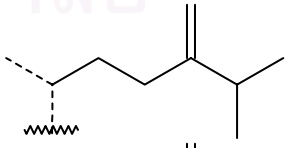
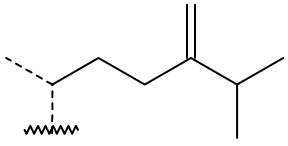
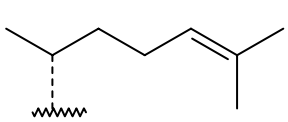
Corollatadiol [57]

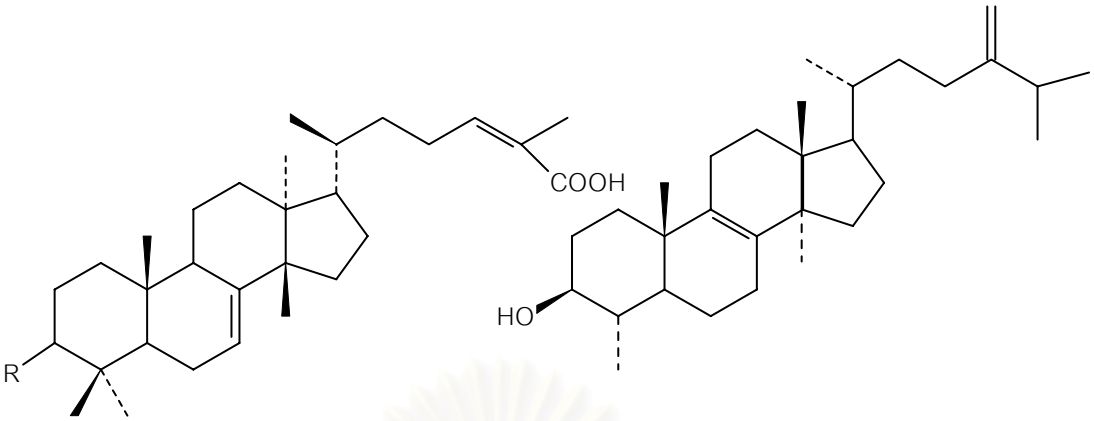


Dihydroeuphol [58] R = OH
Dihydroeuphol acetate [59] R = OAc



Dihydroroylenyl acetate [60]

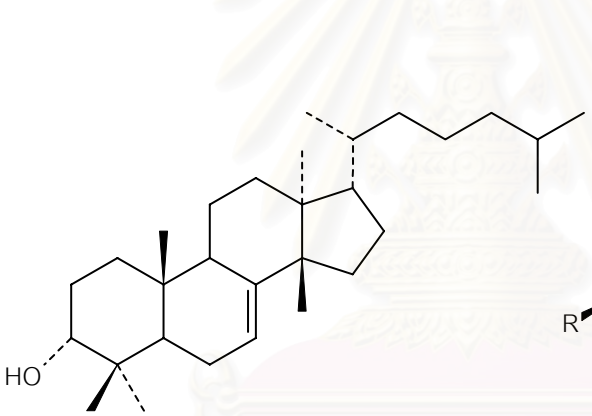
	R_1	R_2
Euphol [61]	OH	
Euphol acetate [62]	OAc	
Euphol cinnamate [63]	O-cinnamoyl	
Euphorbinol [64]	OH	
Euphorbol [65]	OH	
Euphorbol acetate [66]	OAc	
Tirucallol [71]	OH	



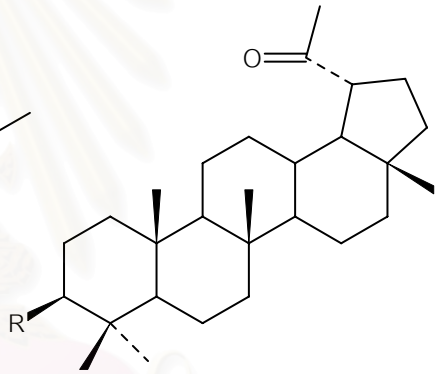
Obtusifoliol [68]

3α-Hydroxytirucalla-7,24*Z*-dien-26-oic acid [67] R = αOH

3-Oxotirucalla-7,24*Z*-dien-26-oic acid [69] R = =O

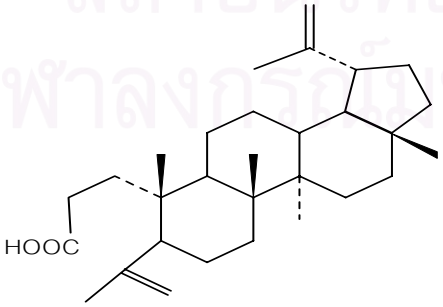


Phyllantheol [70]

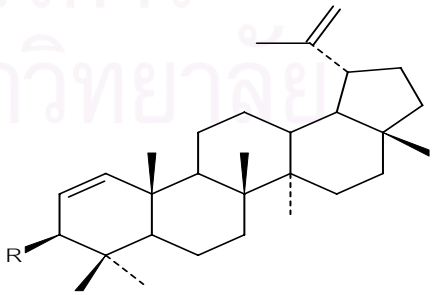


3β-Acetoxy-30-*nor*-lupan-20-one [72] R = OAc

3β-Hydroxy-30-*nor*-lupan-20-one [82] R = OH

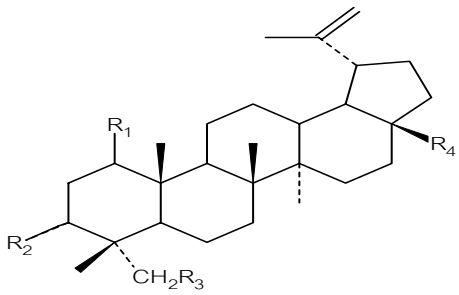


Canaric acid [75]

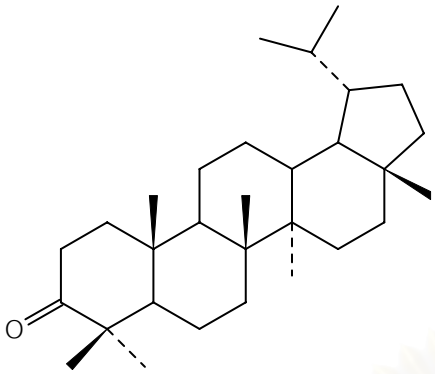


Glochidol [78] R = OH

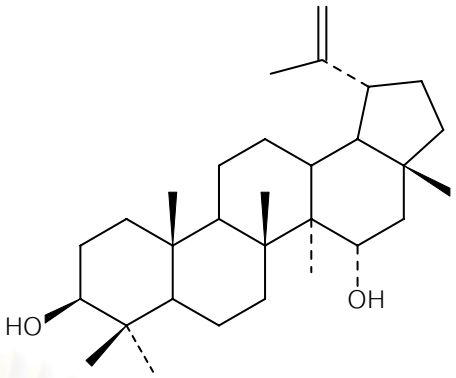
Glochidone [79] R = =O



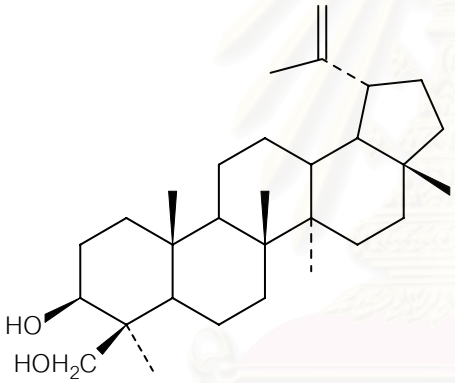
	R_1	R_2	R_3	R_4
Betulin [73]	H	βOH	H	CH_2OH
Betulinic acid [74]	H	βOH	H	COOH
Epilupeol [76]	H	αOH	H	CH_3
Glochidiol [77]	βOH	αOH	H	CH_3
Glochidonol [80]	βOH	=O	H	CH_3
Glochilocudiol [81]	αOH	βOH	H	CH_3
20(29)-Lupene-1β-acetate-3α-ol [84]	βOAc	αOH	H	CH_3
20(29)-Lupene-1β-ol-3α-acetate [85]	βOH	αOAc	H	CH_3
20(29)-Lupene-1β,3α-diacetate [86]	βOAc	αOAc	H	CH_3
20(29)-Lupene-1β,3β-diol [87]	βOH	βOH	H	CH_3
20(29)-Lupene-1,3-dione [88]	=O	=O	H	CH_3
20(29)-Lupene-3α,23-diol [90]	H	αOH	OH	CH_3
20(29)-Lupene-1α, 3α, 23-triol [92]	αOH	αOH	OH	CH_3
Lupenone [94]	H	=O	H	CH_3
Lupeol [96]	H	βOH	H	CH_3



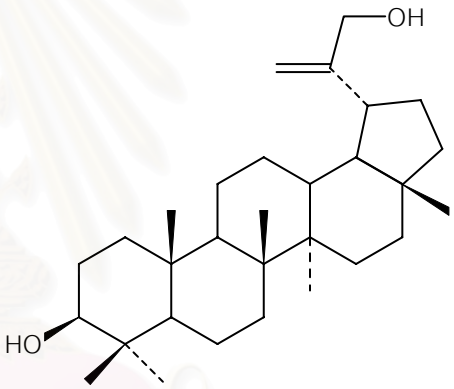
Lupan-3-one [83]



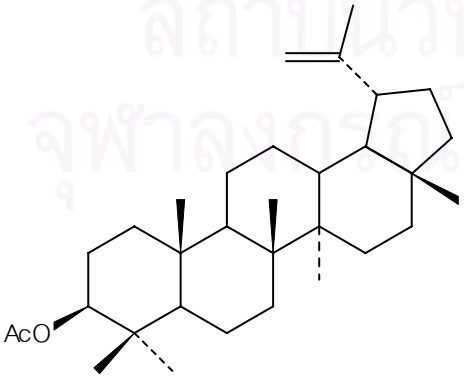
20(29)-Lupene-3β,15α-diol [89]



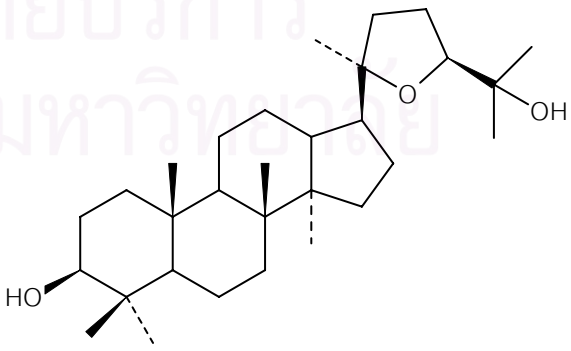
20(29)-Lupene-3α, 24-diol [91]



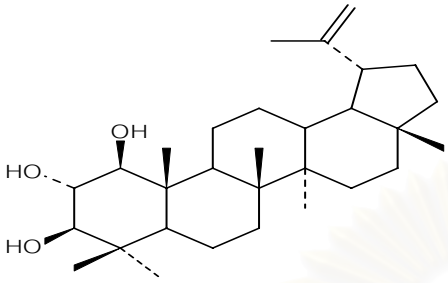
20(30)-Lupene-3β, 29-diol [93]

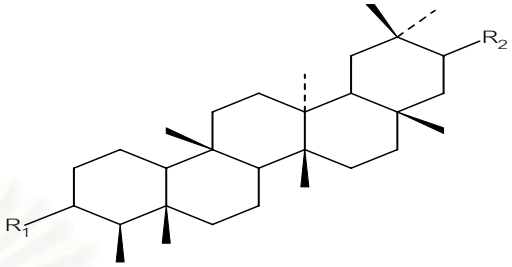


Lupenyl acetate [95]



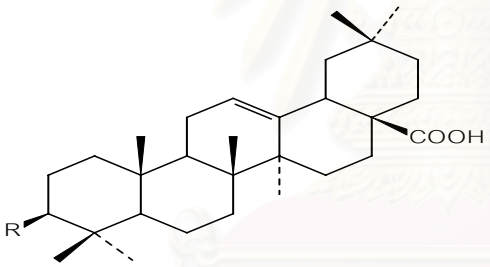
Ocotillol-II [97]

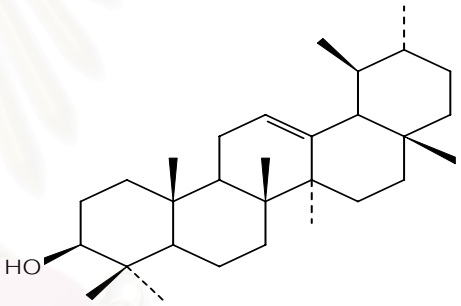




1β, 2α, 3β-Trihydroxylup-20(29)-ene [98]

	R_1	R_2
21α-Acetoxy-D: A-friedo-oleanan-3β-ol [99]	βOH	αAc
3α, 21α-Diacetoxy-D: A-friedo-oleanane [110]	αAc	αAc

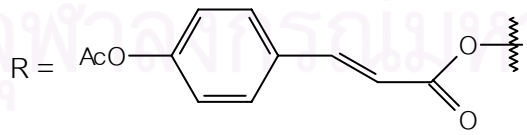




α-Amyrin [102]

3β-Acetoxyolean-12-en-28-oic acid [100] R = OAc

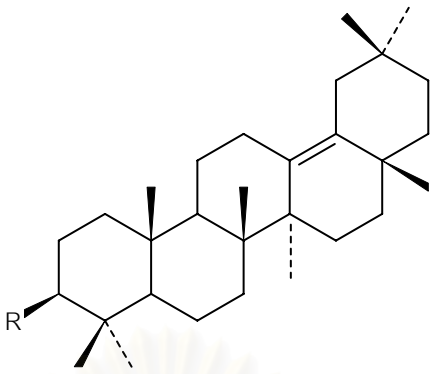
3β-(*p*-Acetoxy-*trans*-cinnamoyloxyl-olean-12-en-28-oic acid [101]



3β-Hydroxyolean-12-en-28-oic acid [123] R = OH

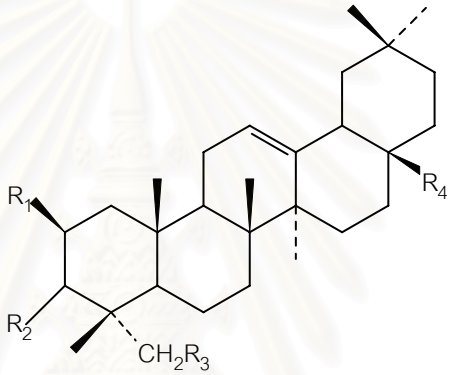
3β-(*p*-Hydroxy-*trans*-cinnamoyloxy)olean-12-en-28-oic acid [124]

R = O-*p*-hydroxy-*trans*-cinnamoyl

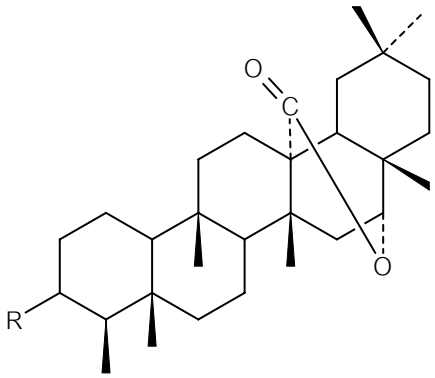


δ-Amyrin formate [106] R = O-formyl

δ-Amyrone [107] R = =O



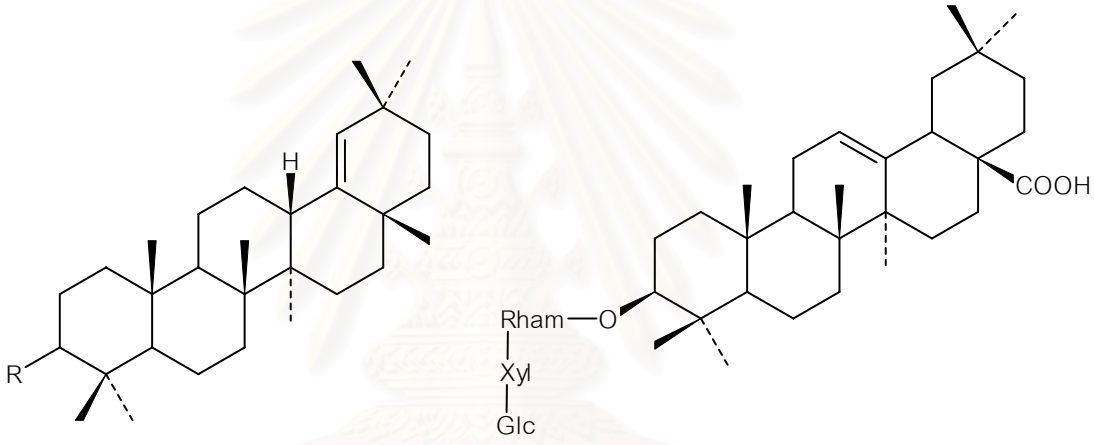
		R_1	R_2	R_3	R_4
β-Amyrin	[103]	H	βOH	H	CH_3
β-Amyrin acetate	[104]	H	βOAc	H	CH_3
β-Amyrin cinnamate	[105]	H	βO-cinnamoyl	H	CH_3
Bayogenin acid	[108]	OH	βOH	OH	COOH
3-Epi-β-amyrin	[111]	H	αOH	H	CH_3
Epioleanolic acid	[113]	H	αOH	H	COOH
Erythrodiol	[114]	H	βOH	H	CH_2OH
Hederagenin	[121]	H	βOH	OH	COOH
Oleanolic acid	[136]	H	βOH	H	COOH



3α-Benzoyloxy-D: A-friedo-oleanan-27, 16α-lactone [109] R = O-benzoyl

3α-Hydroxy-D: A-friedo-oleanan-27, 16α-lactone [122] R = OH

3-Oxo-D: A-friedo-oleanan-27, 16α-lactone [137] R = =O

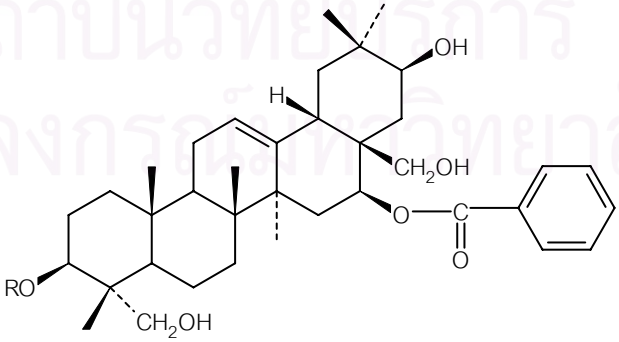


Epigermanicol [112] R = αOH

Germanicol [115] R = βOH

Germanicol acetate [116] R = βOAc

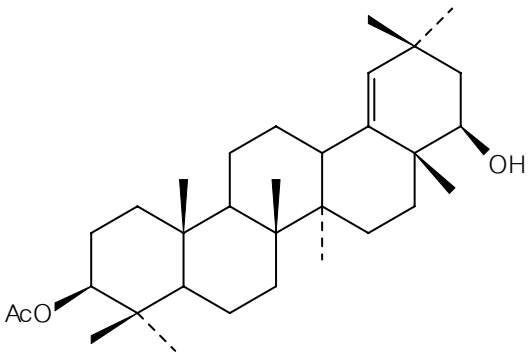
Geniculatin [117]

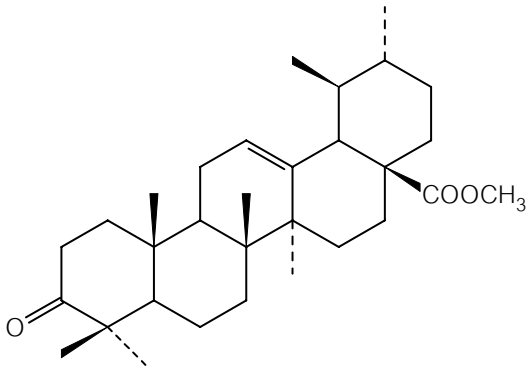


Glochidioside [118] Glc-(1→3)-Glc

Glochidioside N [119] Glc

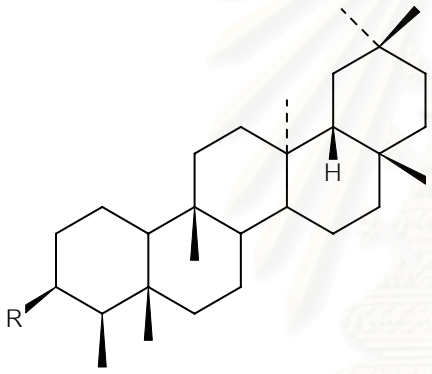
Glochidioside Q [120] Glc-(1→2)-Glc

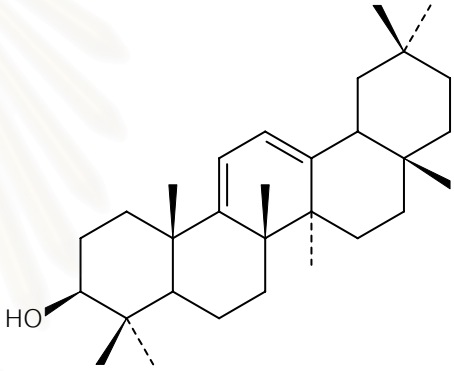




Kamaladiol-3-acetate [125]

3-Keto-methylursolate [126]

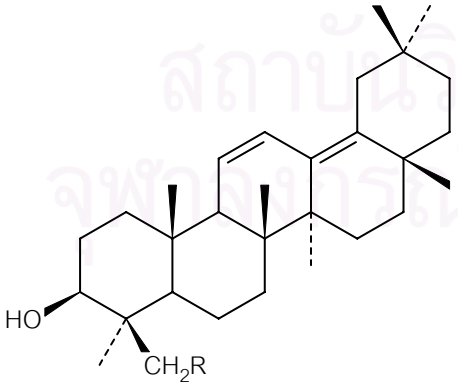


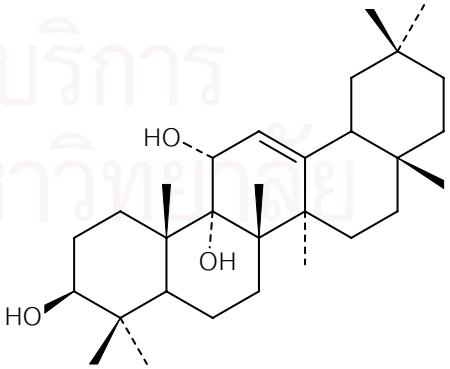


26-nor-D: A-friedo-olean-14-en-3β-ol [127] R = OH

26-nor-D: A-friedo-olean-14-en-3-one [128] R = =O

9(11),12-Oleanadien-3β-ol [129]

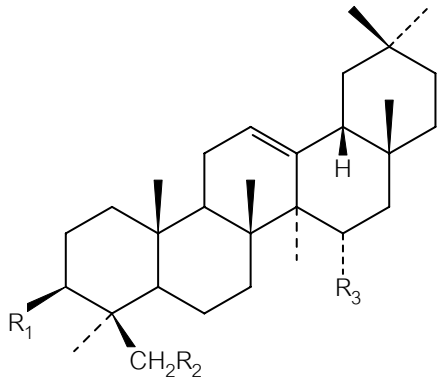




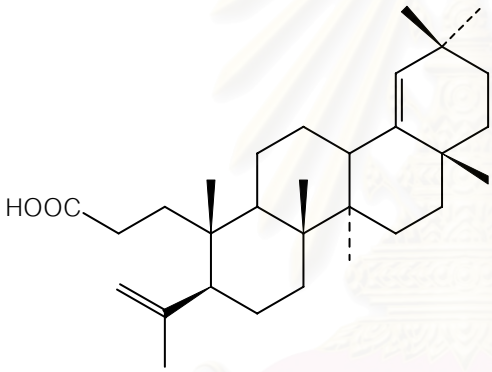
11,13(18)-Oleanadien-3β-ol [130] R = H

11,13(18)-Oleanadiene-3β,24-diol [131] R = OH

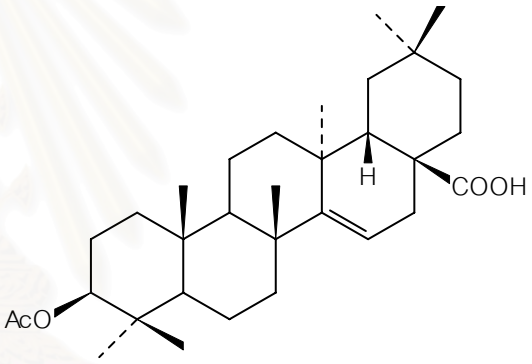
Olean-12-en-3β,9α,11α-triol [134]



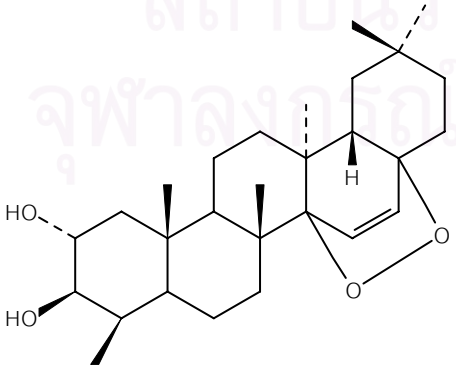
	R_1	R_2	R_3
Olean-12-en-3β,15α-diol [132]	OH	H	OH
Olean-12-en-3β,24-diol [133]	OH	OH	H
Olean-12-en-3β,15α,24-triol [135]	OH	OH	OH



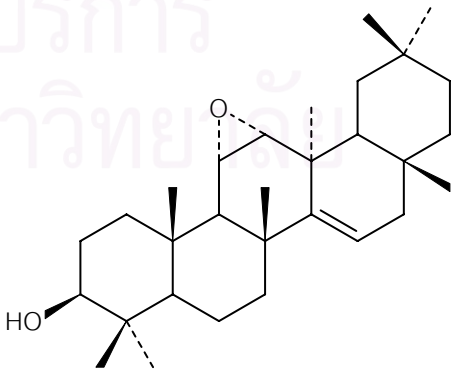
3,4-Seco-oleana-4(23),18-dien-3-oic acid [138]



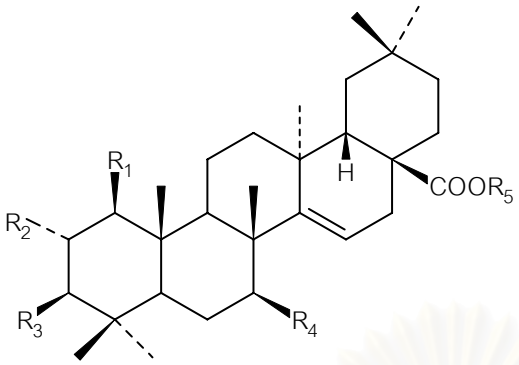
3β-Acetoxy-D-friedoolean-14-en-28-oic acid [139]



Baccatin [144]



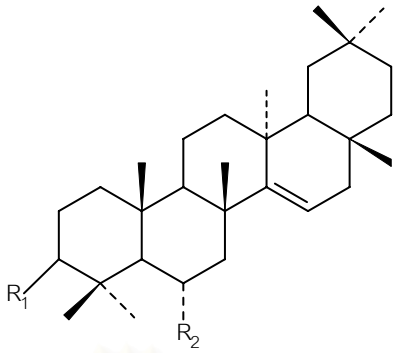
11α,12α-Oxidotaraxerol [154]



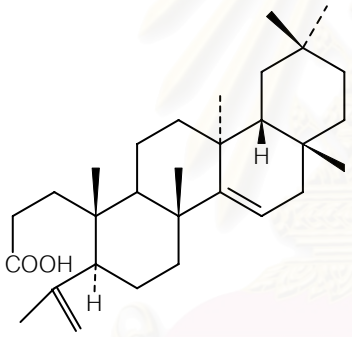
A = O-*p*-hydroxybenzoyl

B = O-*p*-hydroxycinnamoyl

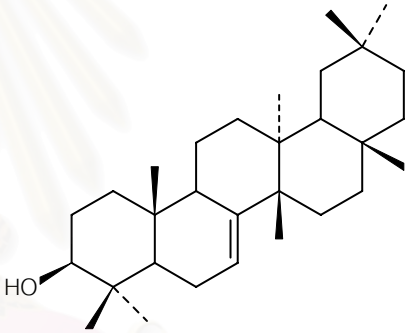
	R_1	R_2	R_3	R_4
Acetylaleuritolic acid [140]	H	H	OAc	H
Aleuritolic acid [141]	H	H	OH	H
Aleuritolic acid 3-*p*-hydroxybenzoate [142]	H	H	A	H
Aleuritolic acid 3-*p*-hydroxycinnamate [143]	H	H	B	H
1β, 2α-Dihydroxyaleuritolic acid 2,3-bis-*p*-hydroxybenzoate [145]	OH	A	A	H
1β-Hydroxyaleuritolic acid 3-*p*-hydroxybenzoate [147]	OH	H	A	H
2α-Hydroxyaleuritolic acid 2-*p*-hydroxybenzoate [148]	H	A	OH	H
2α-Hydroxyaleuritolic acid 3-*p*-hydroxybenzoate [149]	H	OH	A	H
2α-Hydroxyaleuritolic acid 2, 3-bis-*p*-hydroxybenzoate [150]	H	A	A	H
3α-Hydroxyaleuritolic acid 2β-*p*-hydroxybenzoate [151]	H	A	αOH	H
7β-Hydroxymaprounic acid 3-*p*-hydroxybenzoate [152]	H	H	A	OH
Sebiferenic acid [155]	H	OH	OH	H



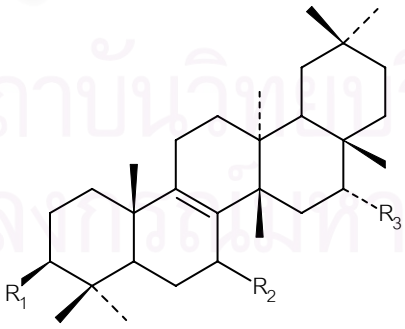
		R_1	R_2
Euphorginol	[146]	H	OH
Isotaraxerol	[153]	αOH	H
Taraxerol	[156]	βOH	H
Taraxerone	[157]	=O	H
Taraxeryl acetate	[158]	βOAc	H



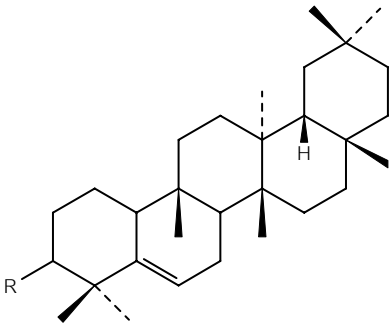
3,4-Seco-4(23),14-taraxeradien-3-oic acid [159]



Multiflorenol [165]



		R_1	R_2	R_3
3β-Acetoxymultiflor-8-en-7-one	[160]	OAc	=O	H
3β-Hydroxymultiflor-8-en-7-one	[161]	OH	=O	H
3β-Hydroxymultiflor-8-en-16-one	[162]	OH	H	=O
16α-Hydroxymultiflor-8-en-3-one	[163]	=O	H	OH
Isomultiflorenol	[164]	OH	H	H



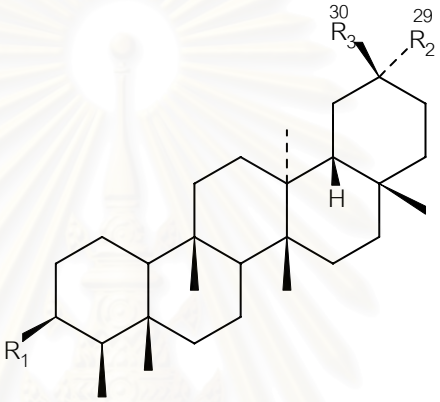
Alnusenol [166] R = αOH

5-Glutinen-3β-acetate [167] R = βOAc

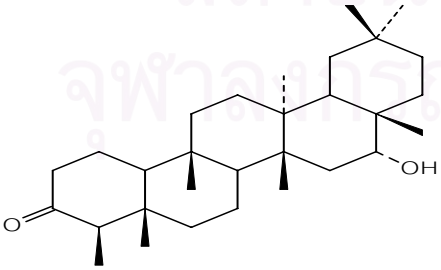
5-Glutinen-3β-ol [168] R = βOH

Glutinone [169] R = =O

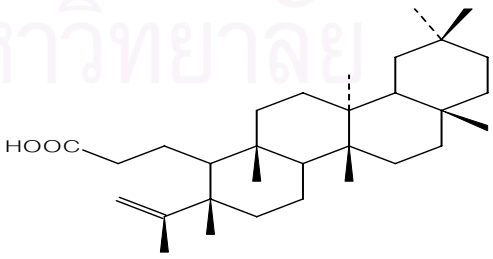
Glut-5-ene-3α-methylbutyrate [170] R = O-methylbutyl



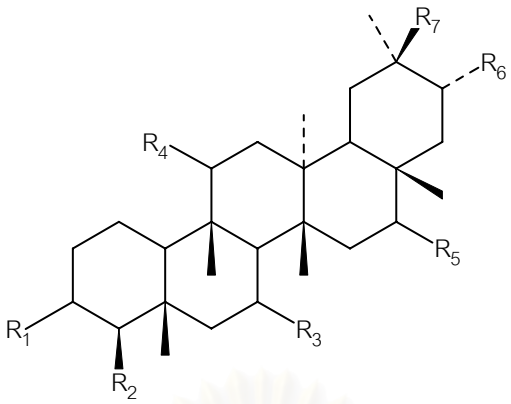
		R_1	R_2	R_3
3β-Acetoxy-29-friedelanol	[171]	OAc	CH_2OH	CH_3
29-Acetoxy-3β-friedelanol	[172]	OH	CH_2OAc	CH_3
3β-Acetoxyfriedelan-30-ol	[173]	OAc	CH_3	CH_2OH
30-Acetoxyfriedelan-3β-ol	[174]	OH	CH_3	CH_2OAc
3β,29-Diacetoxyfriedelane	[176]	OAc	CH_2OAc	CH_3



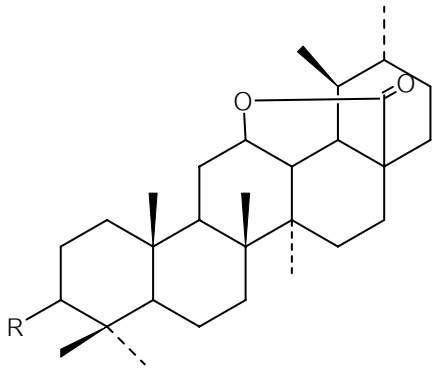
Antidesmanol [175]



Dihydroputranjivic acid [177]



	R_1	R_2	R_3	R_4	R_5	R_6	R_7
Drypemolundein B [178]	=O	CH_3	H	=O	H	H	CH_3
Epifriedelinol [179]	βOH	CH_3	H	H	H	H	CH_3
Friedelan 3β, 30-diol [180]	βOH	CH_3	H	H	H	H	CH_2OH
Friedelan 3β, 30-diacetate [181]	βOAc	CH_3	H	H	H	H	OAc
Friedelane-3, 7-dione [182]	=O	CH_3	=O	H	H	H	CH_3
Friedelin [183]	=O	CH_3	H	H	H	H	CH_3
Friedelinol [184]	αOH	CH_3	H	H	H	H	CH_3
3β-Hydroxyfriedelan-16-one [185]	βOH	CH_3	H	H	=O	H	CH_3
21α-Hydroxyfriedelen-3-one [186]	=O	CH_3	H	H	H	OH	CH_3
21α-Hydroxy-4(23)-friedelen-3-one [187]	=O	$=CH_2$	H	H	H	OH	CH_3
Maytensifolin B [188]	=O	CH_3	H	H	=O	H	CH_3



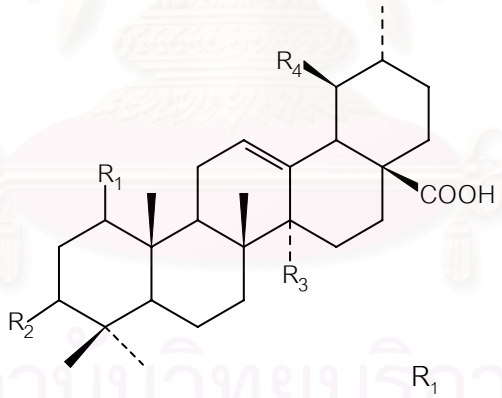
3β-Benzoyl-13α-ursan-28,12β-olide [189] R = βO-benzoyl

3α-Hydroxy-13α-ursan-28,12β-olide [192] R = αOH

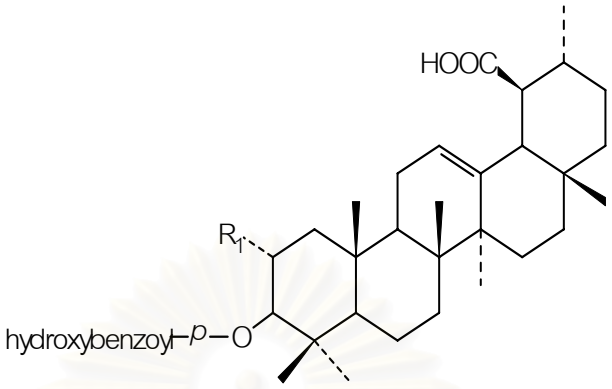
3β-Hydroxy-13α-ursan-28,12β-olide [193] R = βOH

3α-Hydroxy-13α-ursan-28,12β-olide 3-*p*-hydroxylbenzoate [194]
R = αO-hydroxybenzoyl

3-Oxo-13α-ursan-28,12β-olide [201] R = =O

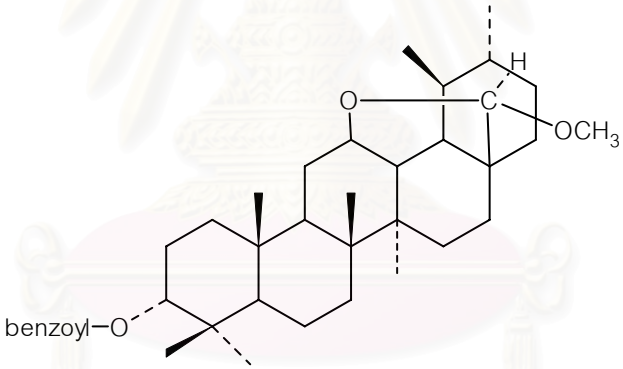


		R_1	R_2	R_3	R_4
3β-28-Dihydroxy-12-ursen-27-oic acid	[190]	H	βOH	COOH	CH_3
3-Keto-methyl ester-12-ursen-28-oic acid	[197]	CO_2CH_3	=O	CH_3	CH_3
Maprounic acid	[198]	H	βOH	CH_3	CH_2OH
3-Oxoquinovic acid	[202]	H	=O	COOH	CH_3

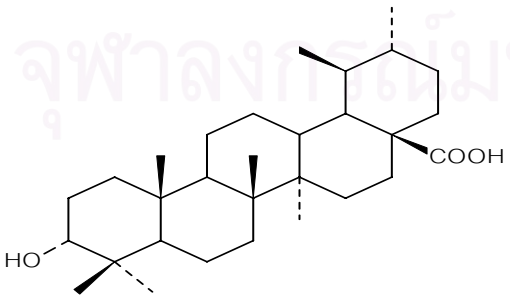


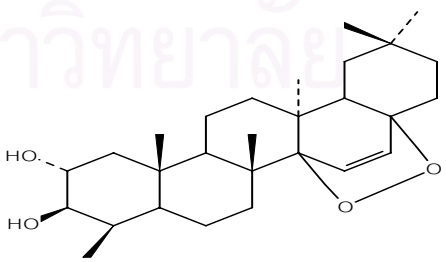
2α-hydroxymaprounic acid 2,3-bis-*p*-hydroxybenzoate [191] R = O-methylbenzoyl

Maprounic acid *p*-hydroxybenzoate [199] R = H

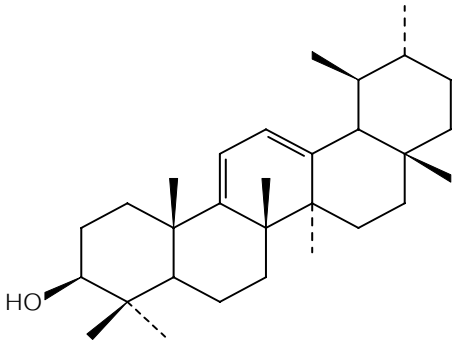


3α-Hydroxy-28β-methoxy-13α- ursan-12β,28-epoxide 3-benzoate [195]

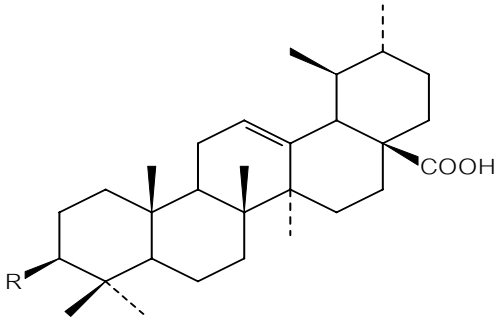




3α-Hydroxy-13α-ursan-28-oic acid [196] Neoilexonol [200]

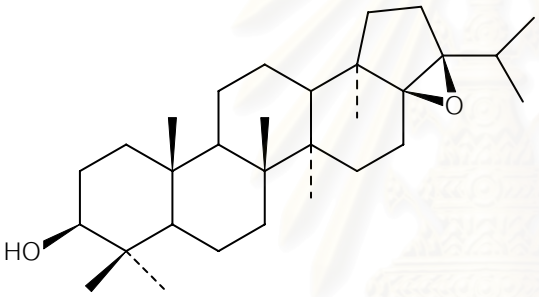


9(11),12-Ursadien-3β-ol [203]

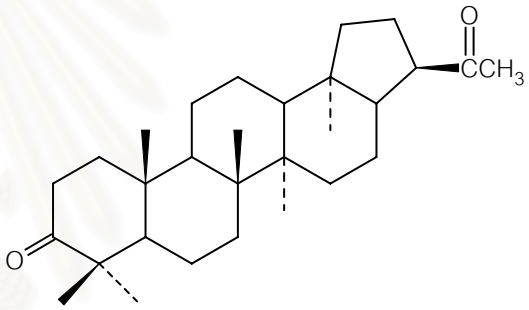


Ursolic acid [204] R = OH

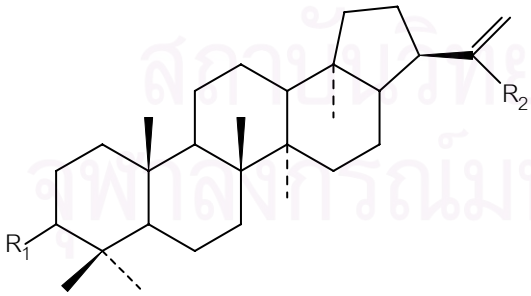
Ursolic benzoate [205] R = O-benzoyl

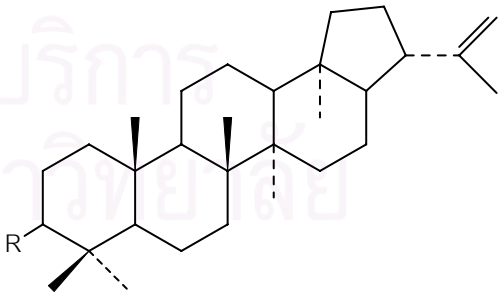


17β,21β-Epoxy-3β-hopanol [206]



21αH-29-Nor-3,22-hopanedione [212]

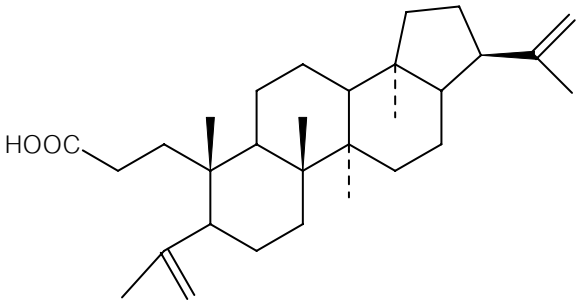




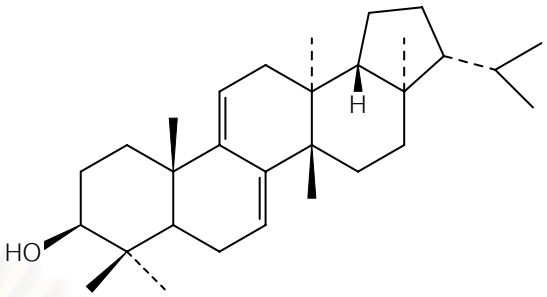
	R_1	R_2
21αH-Hop-22(29)-en -3β, 30-diol [209]	βOH	OH
Moretenol [210]	βOH	CH_3
Moretenone [211]	=O	CH_3

Hopenol B [207] R = βOH

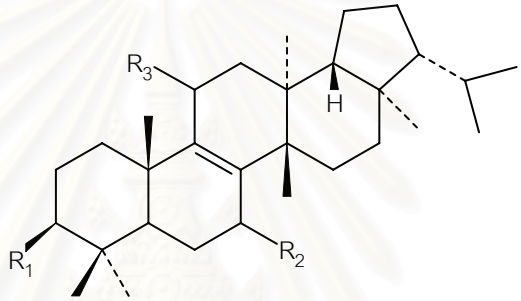
Hopenone B [208] R = =O



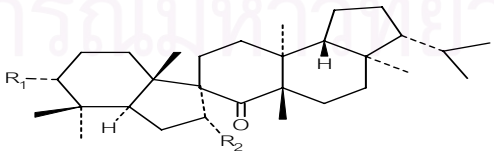
Sebiferic acid [213]



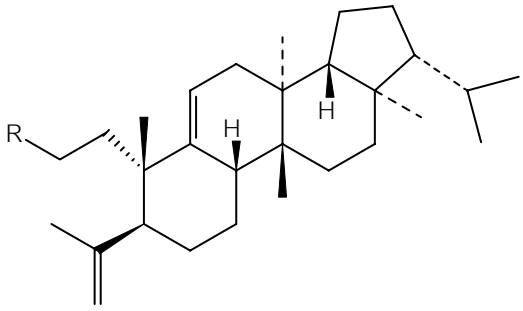
7,9(11)-Fernadien-3β-ol [214]



		R_1	R_2	R_3
Fern-8-en-3β-ol	[215]	OH	H	H
Supinenolone A	[221]	OH	αOH	=O
Supinenolone B	[222]	OH	=O	βOH
Supinenolone C	[223]	OH	=O	=O
Supinenolone D	[224]	=O	=O	=O
Supinenolone E	[225]	OH	=O	H
Supinenolone E acetate	[226]	OAc	=O	H

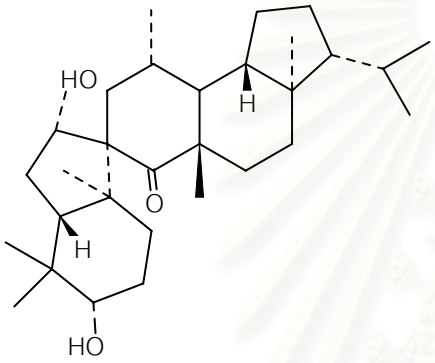


		R_1	R_2
Neospirosupinanetrione	[216]	=O	=O
Neospirosupinanonediol	[217]	OH	OH

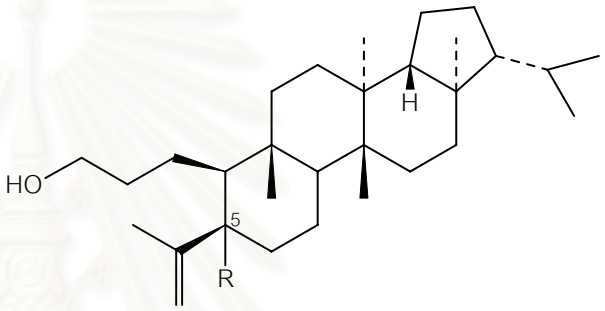


3, 4-Seco-8β H-ferna-4(23), 9(11)-dien-3-oic acid [218] R = COOH

3, 4-Seco-8β H-ferna-4(23), 9(11)-dien-3-ol [219] R = OH

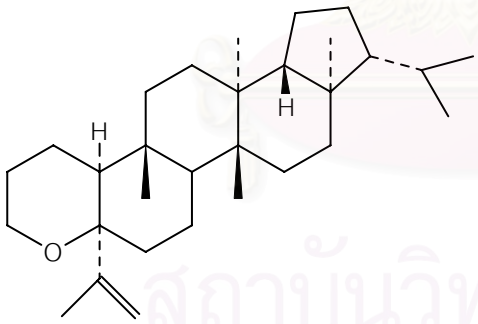


Spirosupinanonediol [220]

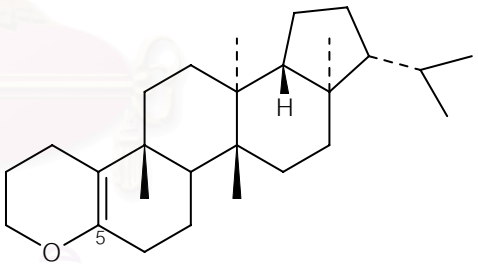


Espinendiol A [227] R = αOH

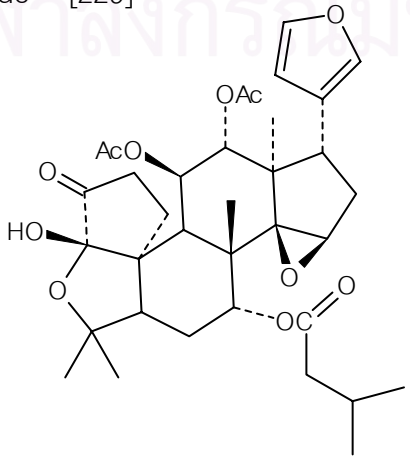
Espinendiol B [228] R = βOH



Espinenoxide [229]



Trinorisoespinenoxide [230]



Dumsin [231]

CHAPTER III

EXPERIMENTAL

Source of Plant Material

The leaves of *Cleidion spiciflorum* (Burm. f.) Merr. were collected from Doi Phukha National Park, Nan Province, Thailand, in May 2000. The plant was identified by comparison with literature and the herbarium specimen was deposited in the herbarium of the Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University.

General Techniques

1. Chromatographic Techniques

   1.1 Thin Layer Chromatography (TLC)

   Technique : one way ascending

   Stationary phase : TLC aluminium sheets silica gel 60F 254, layer thickness 0.2 mm

   Solvent systems : Various solvent systems depending on materials.

   Distance : 10 cm

   Temperature : 28 – 35 ^{O}C (room temperature)

   Detection : 1) UV light (254 and 365 nm)

   : 2) 10% sulfuric acid in ethanol and heating at 110 ^{O}C

   1.2 Column Chromatography (CC)

   Column : Flat bottom glass column (various diameter)

   Stationary phase : 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 : - 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.

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

Technique : Long and short column chromatography, quick column chromatography

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 TLC plate was then sprayed with 10% sulfuric acid in ethanol and heated at 110 ^{O}C. Fractions of similar chromatographic pattern were combined.

1.3 Gel Filtration Chromatography

Gel filter : Sephadex LH-20 (Sigma)

Packing method : Gel filter was suspended in the eluent and left standing to swell for 24 hours prior to use. It was then poured into the column and allowed to set tightly.

Sample loading : The sample was dissolved in a small volume of the eluent and applied on top of the column.

2. Spectroscopy

2.1 Ultraviolet (UV) Absorption Spectra

UV spectra (in methanol) were obtained on a Milton Roy Spectronic 3000 Array Spectrometer (Pharmaceutical Research Equipment Center, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

2.2 Infrared (IR) Absorption Spectra

IR spectra (KBr disc and thin film) were obtained on a Perkin Elmer Infrared Spectrophotometer Model 283 (Pharmaceutical Research Equipment Center, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

2.3 Mass Spectra (MS)

The electron impact mass spectra (EIMS) were obtained on a Fisons VG Trio 2000 quadrupole mass spectrometer (Department of Chemistry, Faculty of Science, Chulalongkorn University) operating at 70 eV.

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

The ^{1}H and ^{13}C NMR spectra were obtained either on a JEOL JNM–A500 (Alpha series) 500 MHz NMR spectrometer (Scientific and Technological Research Equipment Center, Chulalongkorn University) or a Bruker Avance DPX–300 300 MHz NMR spectrometer (Faculty of Pharmaceutical Sciences, Chulalongkorn University).

NMR solvents used in this study were deuterated dimethylsulfoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$). Chemical shifts were reported in ppm scale using the chemical shift of the solvent as the reference signal.

3. Melting Points

Melting points were obtained on a Gallenkamp Melting Point Apparatus Model MFB 595 (Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University). The melting points were uncorrected.

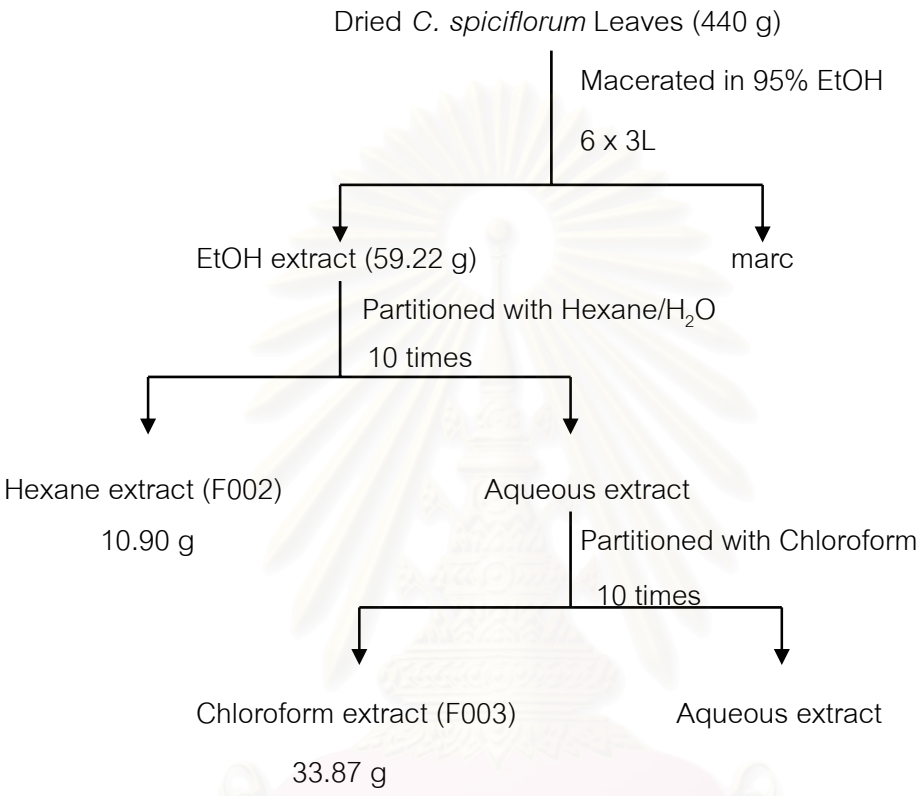
4. Solvents

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

Extraction

The dried leaves of *Cleidion spiciflorum* (440 g) were blended into small pieces, macerated six times in 95% ethanol (3 liters 3 days each) and then filtered. The filtrate of each batch was combined and concentrated to remove ethanol under reduced pressure to yield 59.22 g of dried crude extract (13.46% of dried weight). The ethanol extract (F001) was partitioned (10 times) with 1 liter of hexane and chloroform, respectively. Each fraction was evaporated to dryness under reduced pressure to give

10.90 g of the hexane extract (F002, 2.48% of dried weight) and 33.87 g of the chloroform extract (F003, 7.70% of dried weight).



Scheme 1. Extraction of *Cleidion spiciflorum* leaves

Isolation

1. Fractionation of the hexane extract

The hexane extract (F002, 10.90 g) was subjected to silica gel short column chromatography using hexane – chloroform (6:1) as the eluent. One hundred and forty-five 30-ml fractions were collected and combined according to their TLC pattern into six major fractions, CS1 – CS6 (Table 3). From fraction CS5 and CS6, colorless needle crystals (255 mg) were obtained from acetone and shown to be a mixture of common plant sterols by TLC comparison.

Table 3. Combined fractions from the hexane extract, F002

Fraction	Number of eluates	Weight (g)
CS1	1 - 18	0.08
CS2	19 - 30	0.01
CS3	31 - 63	0.46
CS4	64 - 113	1.72
CS5	114 - 137	0.71
CS6	138 - 145	7.76

Fraction CS4 was separated by column chromatography using silica gel (100 g, 3.0x31 cm) with hexane - chloroform (2:1) as the solvent system. The sample (1.72 g) was dissolved in a small volume of the eluent and loaded on the top of the column, then eluted by the solvent mixture. The fractional volume was about 20 ml. All eluates were collected and combined following TLC examination, with hexane - chloroform (2:1) as the developing solvent system. Fraction CS4 was further separated into five fractions (CS7-CS11) as shown in Table 4.

Fraction CS11, recrystallized in acetone as colorless needles (20 mg, 0.0045%), was shown to be a mixture of common plant sterols by TLC comparison.

Table 4. Combined fractions from CS4

Fraction	Number of eluates	Weight (g)
CS7	1 - 17	0.06
CS8	18 - 30	0.55
CS9	31 - 34	0.13
CS10	35 - 74	0.43
CS11	75 - 116	0.07

1.1 Isolation of compounds CLS 1 and CLS 2

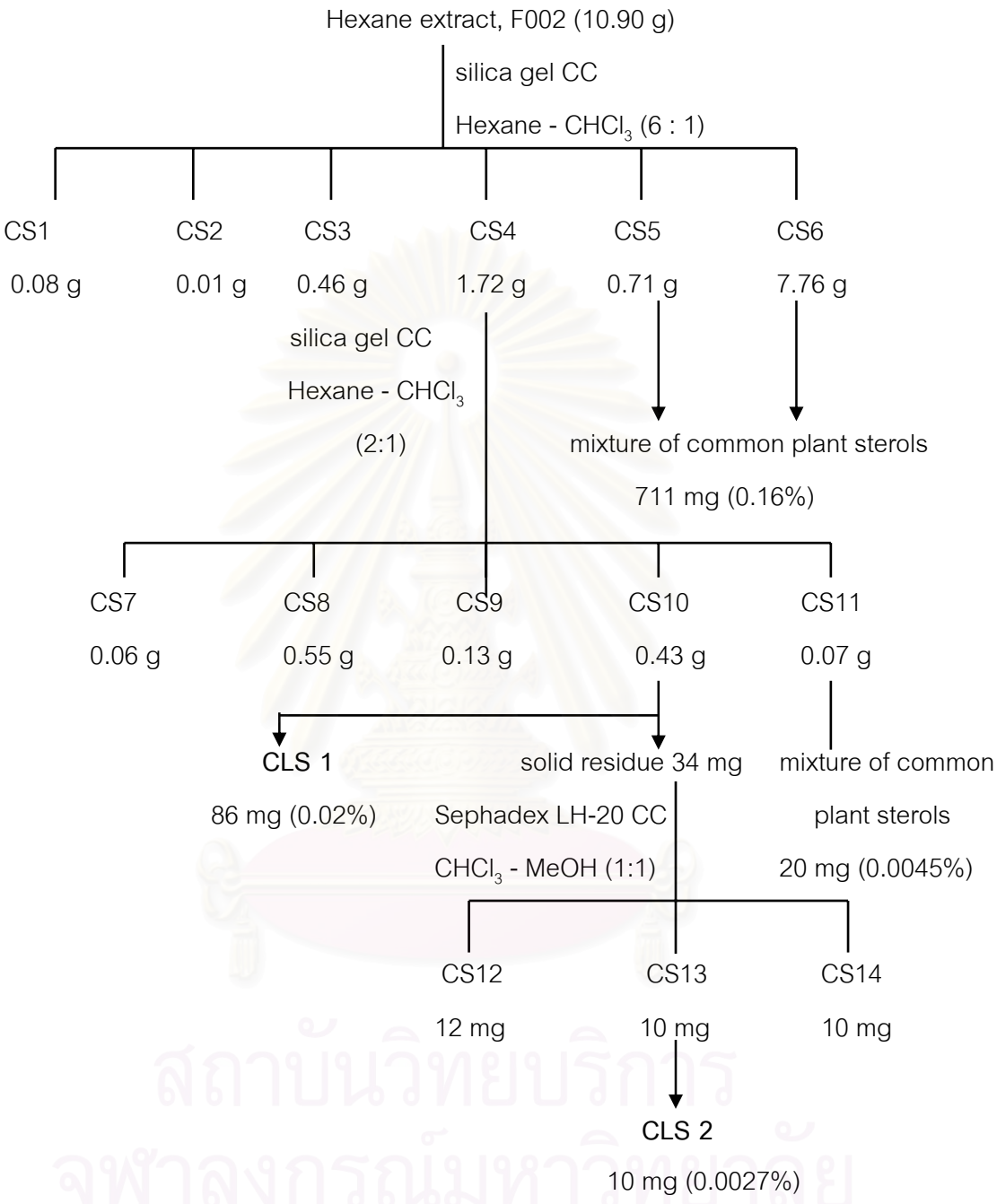
Fraction CS10 displayed two major orange-red spots on TLC plate after detected. Dissolved in methanol, it could be separated into 2 parts: solid residue and supernatant. The supernatant liquid was evaporated to yield compound CLS 1 as a yellow oil (86 mg, 0.02%). The solid residue (34 mg) was further separated by gel filtration chromatography on a Sephadex LH-20 column using chloroform - methanol (1:1). Elution was performed utilizing the as an eluent. Each 10 ml fraction was collected and compared by TLC, using hexane – chloroform (1:2) as the developing solvent system. Forty fractions were combined into three major fractions (CS12-CS14) as shown in Table 5.

Table 5. Combined fractions from CS10

Fraction	Number of eluates	Weight (mg)
CS12	1 - 10	12
CS13	11 - 25	10
CS14	26 - 40	10

Fraction CS13 appeared as one orange-red spot on TLC. It was therefore recrystallized in methanol to give compound CLS 2 as colorless needles (10 mg, 0.0027%).

The fractionation of the hexane extract is summarized in scheme 2.



Scheme 2. Isolation of the hexane extract (F002)

2. Fractionation of the chloroform extract

The chloroform extract (33.87 g) was subjected on quick column chromatography using a sintered glass filter column of silica gel (350 g), eluted in a polarity gradient manner with chloroform and added methanol as the solvent. Each 250-ml eluate was examined by TLC, using chloroform - methanol (9:1) as the developing system. A total of seventy fractions were collected and combined into six major ones (CS15–CS20). The solvents used and the fractions collected in this initial separation are summarized in Table 6.

Table 6. Combined fractions from quick column chromatography of chloroform extract, F003.

Fraction	Number of eluates	$CHCl_3$: MeOH Ratio	Weight (g)
CS15	1 - 10	18 : 1	0.67
CS16	11 - 15	9 : 1	1.39
CS17	16 – 31	17 : 3	3.52
CS18	32 – 43	17 : 3	3.27
CS19	44 – 52	4 : 1	9.13
CS20	53 - 70	0 : 1	1.11

2.1 Isolation of compound CLS 3

Fraction CS 18, which displayed interesting TLC profile, was selected for further investigation. The sample (3.27 g) was rechromatographed on a silica gel column (130 g, 1.5x20 cm) using chloroform – methanol (9:1) as an eluent. Sixty fractions (25-ml) were collected and combined according to the TLC pattern into six major fractions (CS21-CS26) as shown in Table 7.

Table 7. Combined fractions from CS18

Fraction	Number of eluates	Weight (g)
CS21	1 - 10	0.05
CS22	11 - 13	0.02
CS23	14 - 26	0.21
CS24	27 – 32	0.13
CS25	33 – 45	0.09
CS26	46 – 60	1.85

Fraction CS25, which appeared as a yellow spot on TLC, was recrystallized in methanol to give 86 mg of compound CLS 3 as a yellow powder (0.02% yield).

2.2 Isolation of compound CLS 4

Fraction CS26 (1.86 g), displaying two major TLC spots, was further separated on gel filtration chromatography using a Sephadex LH-20 column (2.2 cmx120 cm). Elution was performed utilizing methanol as the solvent system. Thirty fractions (15-ml each) were collected and compared by TLC, developing with chloroform-methanol (9:1) and were combined into three major ones (CS27-CS29) as shown in Table 8.

Table 8.Combined fractions from CS26

Fraction	Number of eluates	Weight (g)
CS27	1 - 11	1.11
CS28	12 - 16	0.46
CS29	17 - 30	0.27

Fraction CS28 displayed one red-orange spot on TLC upon detection with 10% sulfuric acid. Colorless amorphous powder (460 mg, 0.11%) was collected and designated as compound CLS4 from this fraction.

2.3 Isolation of compound CLS 5

Another fraction obtained from the previous column (Table 8) which was selected for further isolation was fraction CS29. The sample (0.27 g) was put through a silica gel column (50 g, 3.0x10 cm), eluted with chloroform - methanol (9:1). The volume of each collected fraction was 10 ml. TLC comparison, using the eluent as the developing solvent, led to the combination of these 44 fractions into three major ones (CS30-CS32), as shown in Table 9.

Table 9. Combined fractions from CS29

Fraction	Number of eluates	Weight (mg)
CS30	1 - 15	110
CS31	16 - 18	30
CS32	19 - 44	110

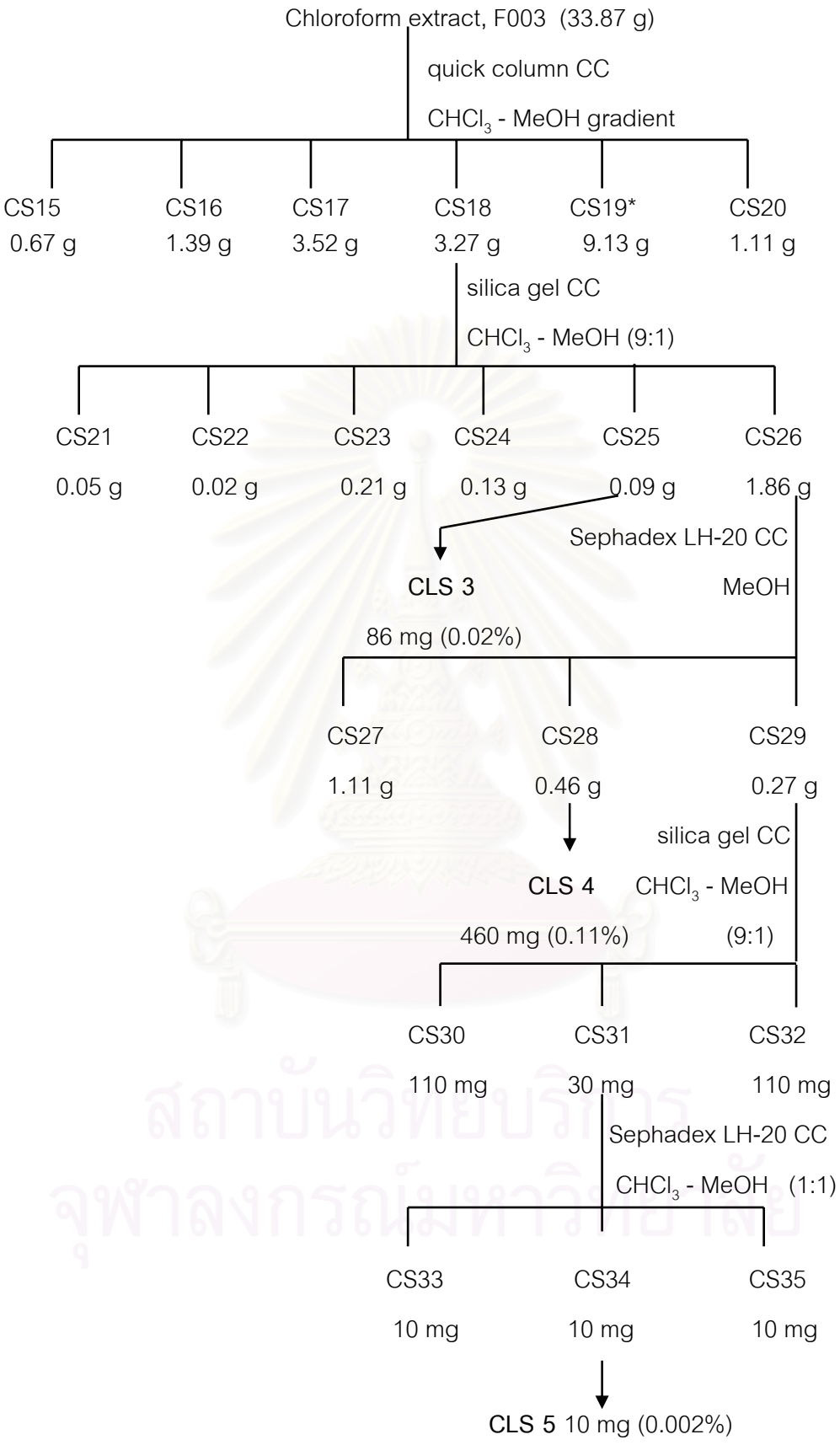
Fraction CS31 (30 mg), which displayed (interesting)promising spots upon TLC investigation, was submitted for further separation on a Sephadex LH-20 column, utilizing chloroform-methanol (1:1) as the solvent system. The separation was monitored by TLC, using chloroform - methanol (9:1) as the developing solvent system. Thirty 10-ml fractions were combined into three major fractions (CS33-CS35), as shown in Table 10.

Table 10. Combined fractions from CS31

Fraction	Number of eluates	Weight (mg)
CS33	1 - 9	10
CS34	10 - 18	10
CS35	19 - 30	10

From fraction CS34, 10 mg of yellow powder, designated as compound CLS5 (0.002% yield), was collected.

The fractionation of the chloroform extract is summarized in scheme 3.



Scheme 3. Isolation of the chloroform extract (F003)

2.4 Isolation of compound CLS 2 from the chloroform extract

Another fraction obtained from the chloroform extract (F003) which was also further investigated was the fraction CS19. The whole fraction (9.13 g) was subjected to silica gel column chromatography, employing chloroform - methanol (9:1) as both the eluent and the developing solvent system for the TLC. One hundred fractions (50-ml) were collected and combined according to their TLC profiles into three major fractions (CS36-CS38), as shown in Table 11.

Table 11. Combined fractions from CS19

Fraction	Number of eluates	Weight (g)
CS36	1 - 31	0.08
CS37	32 - 70	0.62
CS38	71 - 100	7.90

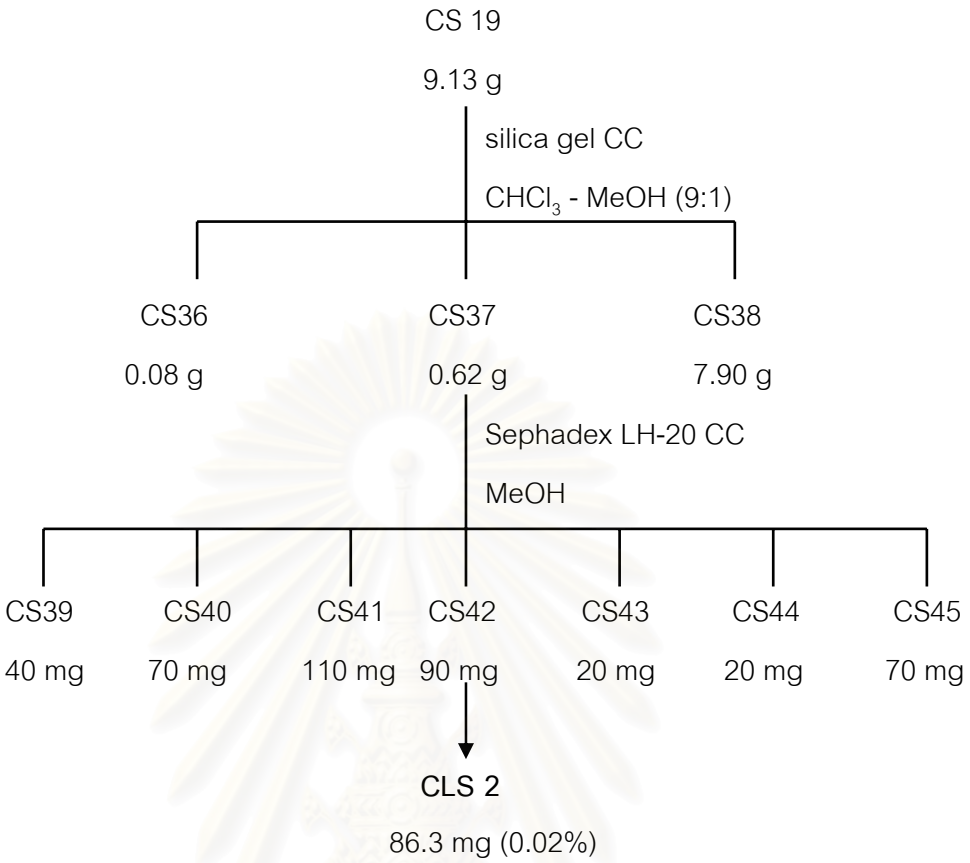
Fraction CS37 (0.62 g) was further purified by Sephadex LH-20 column, eluted with methanol. Each 10 ml fraction was inspected, using chloroform - methanol (9:1) as the developing solvent system for TLC. Forty-three fractions were collected and later pooled into seven major fractions (CS39-CS45), as shown in table 12.

Table 12. Combined fractions from CS37

Fraction	Number of eluates	Weight (mg)
CS39	1 - 8	40
CS40	9 - 12	70
CS41	13 - 16	110
CS42	17 – 22	90
CS43	23 – 27	20
CS45	28 – 43	90

Fraction CS42 was crystallized in methanol to give colorless needles (86.3 mg, 0.02%), of compound CLS 2.

The fractionation of fraction CS 19 is summarized in scheme 3.



Scheme 4. Isolation of fraction CS 19

Characterization of the isolated compounds

1. **Compound CLS 1**

Appearance : Light yellow oil

Solubility : Miscible in chloroform, acetone and methanol

EIMS *m/z* (% relative intensity) : 296(1), 279(1), 197(1), 196(4), 152(2), 137(5), 126(12), 123(43), 111(10), 109(8), 99(5), 95(15), 85(12), 83(18), 81(28), 71(100), 69(23) and 57(25) (Figure 2, page 85)

IR ν_{max} (thin film) cm^{-1} : 3400 (OH), 3019, 2928, 2869, 1521, 1467, 1424 1380, 1211, 1017, 928, 849 (Figure 3, page 86)

^{1}H-NMR (δ ppm, 500 MHz $CDCl_3$) (Figure 7, page 90)

0.82 (6H, *d*, *J* = 6.7 Hz), 0.84 (6H, *d*, *J* = 6.7 Hz), 1.50 (1H, *septet*, *J* = 6.7 Hz), 1.64 (3H, *s*), 1.96 (2H, *m*), 4.13 (2H, *d*, *J* = 6.7 Hz) and 5.39 (1H, *t*, *J* = 6.7 Hz)

^{13}C-NMR (δ ppm, 125 MHz, $CDCl_3$) (Figure 4, page 87)

16.2 (*q*), 19.7 (*q*), 19.7 (*q*,), 22.6 (*q*), 22.7 (*q*), 24.5 (*t*), 24.8 (*t*), 25.1 (*t*), 28.0 (*d*), 32.7 (*d*), 32.8 (*d*), 36.7 (*t*), 37.3 (*t*), 37.3 (*t*), 37.4 (*t*), 39.3 (*t*), 39.9 (*t*), 59.4 (*t*), 123.1 (*d*) and 140.3 (*s*).

2. **Compound CLS 2**

Appearance : colorless needles (methanol)

Solubility : Miscible in hexane, chloroform and acetone

Melting Point : 162-163 ^{o}C

EIMS *m/z* (% relative intensity) : 440(10), 439(10), 425(18), 407(10), 314(25), 313 (100), 283(10), 274 (18), 259 (12), 246 (10), 173 (12), 119 (32), 109 (48), 95 (75), 83 (64) and 69 (53) (Figure 11, page 99)

IR ν_{max} (thin flim) cm^{-1} : 3414 (OH), 2933, 2870, 1635, 1617, 1450, 1380 1369, 1096, 1045, 886 and 621 (Figure 12, page 100)

^{1}H-NMR (δ ppm, 500 MHz, $CDCl_3$) (Figure 13, page 101)

0.64 (3H, *s*), 0.71 (3H, *s*), 0.79 (3H, *s*), 0.85 (3H, *d*, *J* = 6.1 Hz), 0.96 (3H, *s*), 0.97 (3H, *d*, *J* = 7.0 Hz), 1.02 (3H, *s*), 1.62 (3H, *s*), 3.20 (1H, *dd*, *J* = 11.6, 4.3 Hz), 4.65 (2H, *br s*) and 5.20 (1H, *d*, *J* = 5.8 Hz)

^{13}C-NMR (δ ppm, 125 MHz, $CDCl_3$)(Figure 15a, page 101; Figure 15b, page 102)

14.4 (*q*), 15.7 (*q*), 18.4 (*q*), 18.5 (*q*), 18.6 (*q*), 20.2 (*q*), 21.4 (*t*), 22.3 (*q*), 27.8 (*t*,), 28.0 (*t*), 28.1 (*t*), 28.2 (*q*), 31.5 (*t*), 33.9 (*t*), 34.0 (*t*), 36.0 (*d*), 36.1 (*t*), 37.1 (*t*), 39.1 (*s*), 39.4 (*s*), 41.6 (*d*), 41.8 (*d*), 44.2 (*s*), 47.0 (*s*), 50.9 (*d*), 52.5 (*d*), 78.9 (*d*), 109.3 (*t*), 114.9 (*d*), 148.5 (*s*) and 150.2 (*s*)

3. Compound CLS 3

Appearance : Yellow amorphous powder (chloroform)

Solubility : Misible in methanol

Melting Point : 259-262 ^{o}C

EIMS *m/z* (% relative intensity) : 446(4), 264(3), 236(3), 181(3),139(6), 125(17), 111(42), 97(100), 83(85), 71(52), 69(48) and 57 (46) (Figure 20, page 118)

UV λ_{max} nm (log ε), in MeOH : 253(1.084), 267(1.053) and 343(1.133) (Figure 22, page 120)

IR ν_{max} (KBr) cm^{-1} : 3413 (OH), 2925, 1635,1616, 1509, 1234, 1076, 1041, 632 and 618 (Figure 21, page 119)

^{1}H-NMR (δ ppm, 300 MHz, $CDCl_3$) (Figure 26, page 124)

3.26 - 3.43 (4H, *m*), 3.71 (2H, *d*, *J* = 1.2 Hz), 3.86 (3H, *s*), 5.06 (1H, *d*, *J* = 7.1 Hz), 6.45 (1H, *br s*) 6.84 (1H, *br s*), 6.84 (1H, *br s*), 6.91 (1H, *s*), 7.12 (2H, *d*, *J* = 8.7 Hz), 8.05 (2H, *d*, *J* = 8.7 Hz) and 12.91 (1H, *br s*)

^{13}C-NMR (δ ppm, 75 MHz, $CDCl_3$) (Figure 23, page 121)

55.7 (*q*), 60.8 (*t*), 69.8 (*d*), 73.3 (*d*), 77.3 (*d*), 76.6 (*d*), 95.1 (*d*), 99.8 (*d*), 100.2 (*d*), 103.9 (*d*), 105.5 (*s*), 114.8 (*d*), 122.8 (*s*), 128.5 (*d*), 157.1 (*s*), 161.2 (*s*), 162.6 (*s*), 163.2 (*s*), 164.0 (*s*) and 182.1 (*s*)

4. Compound CLS 4

Appearance : White amorphous powder (methanol)

Solubility : Soluble in methanol

Melting Point : 169 - 173 ^{o}C

EIMS *m/z* (% relative intensity) : 296(4), 269(3), 268(5), 267(20), 255(2), 238(2), 224(3), 210(5), 176(4), 168(6), 134(70), 116(12), 112(25), 111(13), 99(15), 98(100), 84(68), 71(30), 74(53), 75(23), 57(47) (Figure 29, page 131)

IR ν_{max} (KBr) cm^{-1} : 3292 (OH), 2934, 2869, 1455, 1371, 1097, 1043, 888 (Figure 30, page 132)

^{1}H-NMR (δ ppm, 300 MHz, $CDCl_3$) (Figure 34, page 136)

1.81 (3H, *d*, *J* = 6.3 Hz), 3.15-3.20 (4H, *m),* 3.68 (1H, *d*, *J* = 7.7 Hz) 4.81 (1H, *d*, *J* = 7.2 Hz), 6.13 (1H, *dq*, *J* = 15.9, 6.3 Hz), 6.34 (1H, *d*, *J* = 15.9 Hz), 6.94 (2H, *d*, *J* = 8.5 Hz) and 7.28 (2H, *d*, *J* = 8.5 Hz)

^{13}C-NMR (δ ppm, 75 MHz, $CDCl_3$) (Figure 31, page 133)

18.4 (*q*), 60.9 (*t*), 69.9 (*d*), 73.4 (*d*), 76.7 (*d*), 77.1 (*d*), 100.5 (*d*), 116.3 (*d*), 123.5 (*d*), 126.6 (*d*), 130.2 (*d*), 131.2 (*s*) and 156.3 (*s*).

5. Compound CLS 5

Appearance : Yellow amorphous powder (chloroform)

Solubility : Soluble in methanol

Melting Point : 249 - 253 ^{o}C

EIMS *m/z* (% relative intensity) : 462(2), 429(2), 327(11), 285(12), 267(31), 239(8), 210(10), 134(19), 112(15), 98(100), 84(82) and 74(70) (Figure 38, page 144)

UV λ_{max} nm (log ε), in MeOH : 252(0.532) and 342(0.391) (Figure 40, page 146)

IR ν_{max} (KBr) cm^{-1} : 3413 (OH), 2922, 1638, 1616, 1494, 1261, 1073 and 621 (Figure 39, page 145)

^{1}H-NMR (δ ppm, 300 MHz, $CDCl_3$) (Figure 41, page 147)

3.17 - 3.70 (6H, *m*), 3.86 (*s*), 5.07 (1H, *d, J* = 6.7 Hz), 6.44 (1H, *s*), 6.81 (1H, *br s*) 6.83 (1H, *br s*), 7.10 (1H, *d*, *J* = 8.4 Hz), 7.45 (1H, *br s*), 7.57 (1H, *br d*, *J* = 8.4 Hz) and 12.94 (1H, *br s*)

^{13}C-NMR (δ ppm, 75 MHz, $CDCl_3$) (Figure 42, page 148)

56.0 (*q*), 60.8 (*t*), 69.8 (*d*), 73.3 (*d*), 76.6 (*d*), 77.4 (*d*), 95.0 (*d*), 99.8 (*d*), 100.1 (*d*), 104.0 (*d*), 105.6 (*s*), 112.4 (*d*), 113.3 (*d*), 119.1 (*d*), 123.1 (*s*), 147.0 (*s*), 151.5 (*s*), 157.2 (*s*), 161.3 (*s*), 163.2 (*s*), 164.3 (*s*) and 182.2 (*s*)

CHAPTER IV

RESULTS AND DISCUSSION

Chromatographic separation of the ethanol leaf extract of *Cleidion spiciflorum* (Burm. f.) Merr. led to the isolation of five chemical constituents. The identification of these compounds was based on spectroscopic data (UV, IR, NMR and mass spectra) and also confirmed by comparison with those of previously reported in the literature. The details can be discussed as follows.

1. Identification of *trans*-phytol (compound CLS 1)

Compound CLS 1 was obtained as light yellow oil (86 mg, 0.02% yield) from the fraction CS4. The EIMS spectrum of this compound (Figure 2) showed a molecular ion peak at *m/z* 296, which corresponded to the molecular formula of $C_{20}H_{40}O$. A mass fragment peak at *m/z* 279 was indicative of the loss of a hydroxyl group. The presence of the alcohol functionality in the molecule was confirmed by an IR absorption peak at 3400 cm^{-1} (Figure 3).

The ^{13}C NMR spectrum of CLS 1 (Figure 4) showed 20 carbon signals, suggestive of a diterpenoid structure. The DEPT (Figure 5) and ^{1}H-^{13}C HETCOR (Figure 6) experiments were employed to classify these signals into those of a quaternary carbon at δ 140.3, four methine carbons at δ 28.0, 32.7, 32.8, and 123.1 ppm, ten methylene carbons at δ 24.5, 24.8, 25.1, 36.7, 37.3, 37.3, 37.4, 39.3, 39.9 and 59.4 ppm, and five methyl carbons at δ 16.2, 19.7, 19.7, 22.6 and 22.7 ppm. The two most downfield carbon chemical shifts at δ 123.1 and 140.3 ppm represents the trisubstituted double bond between C-2 and C-3 of *trans*-phytol.

The ^{1}H- (Figure 7) and ^{1}H-^{1}H COSY NMR spectra (Figure 8) exhibited signals for four methyl doublets at δ 0.82 (H_3-18 and H_3-19) and 0.84 ppm (H_3-16 and H_3-17). The most downfield methyl singlet at δ 1.64 ppm belongs to Me-20 which is substituted on a double bond. The equivalent methylene protons at position 1 of this compound

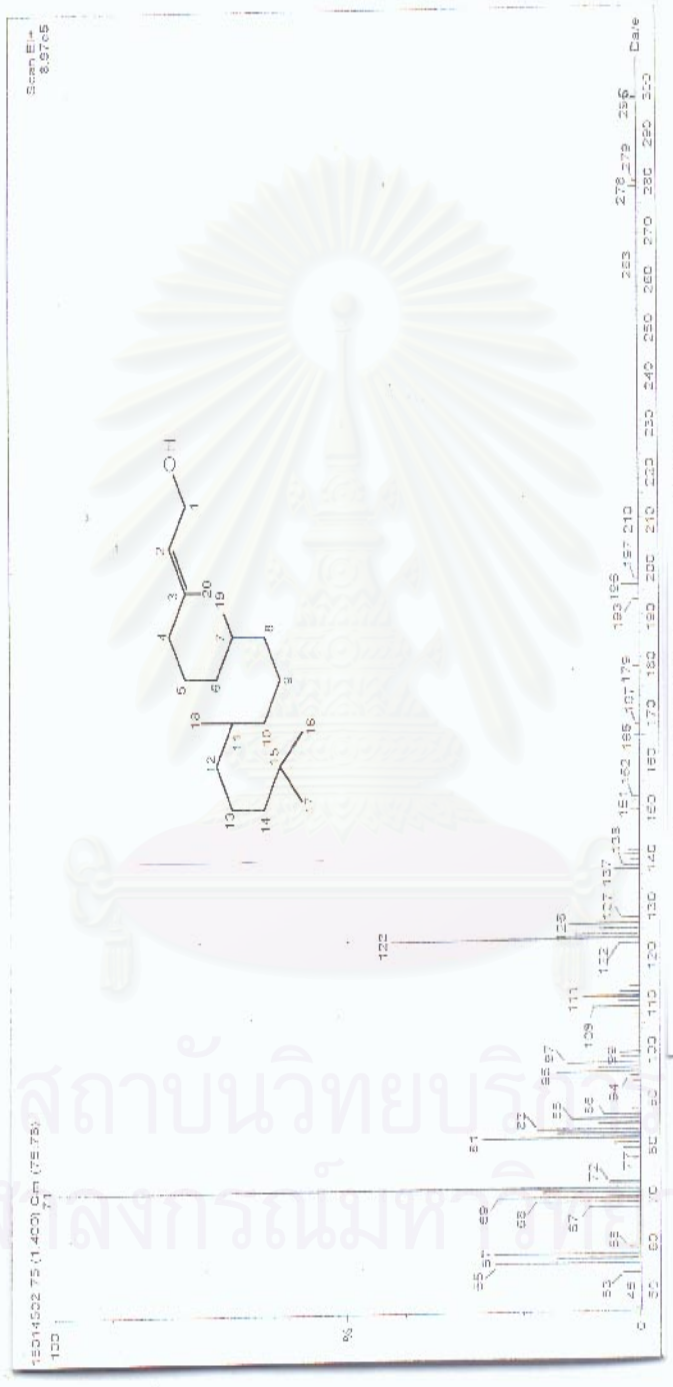


Figure 2. EIMS of compound CLS 1

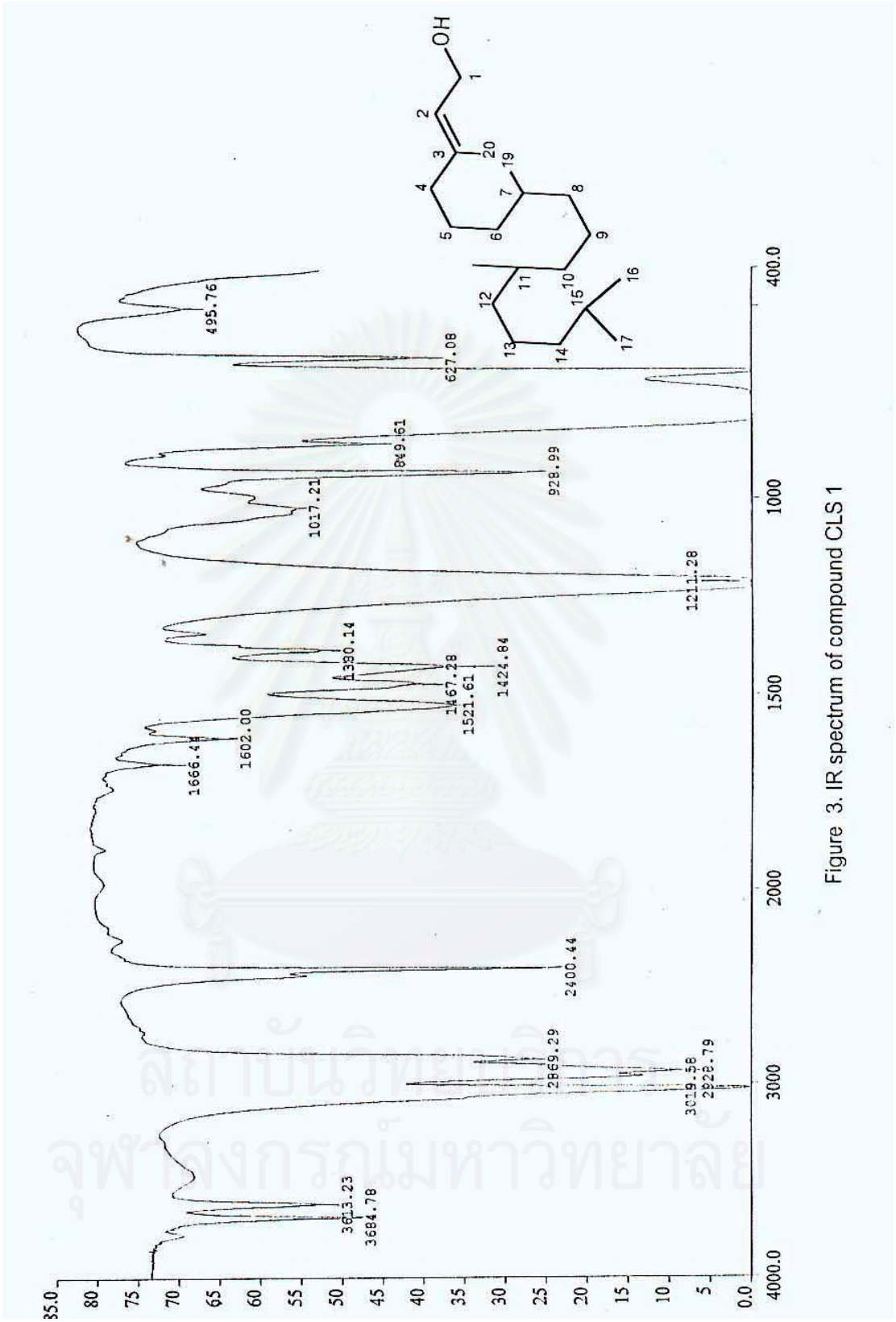


Figure 3. IR spectrum of compound CLS 1

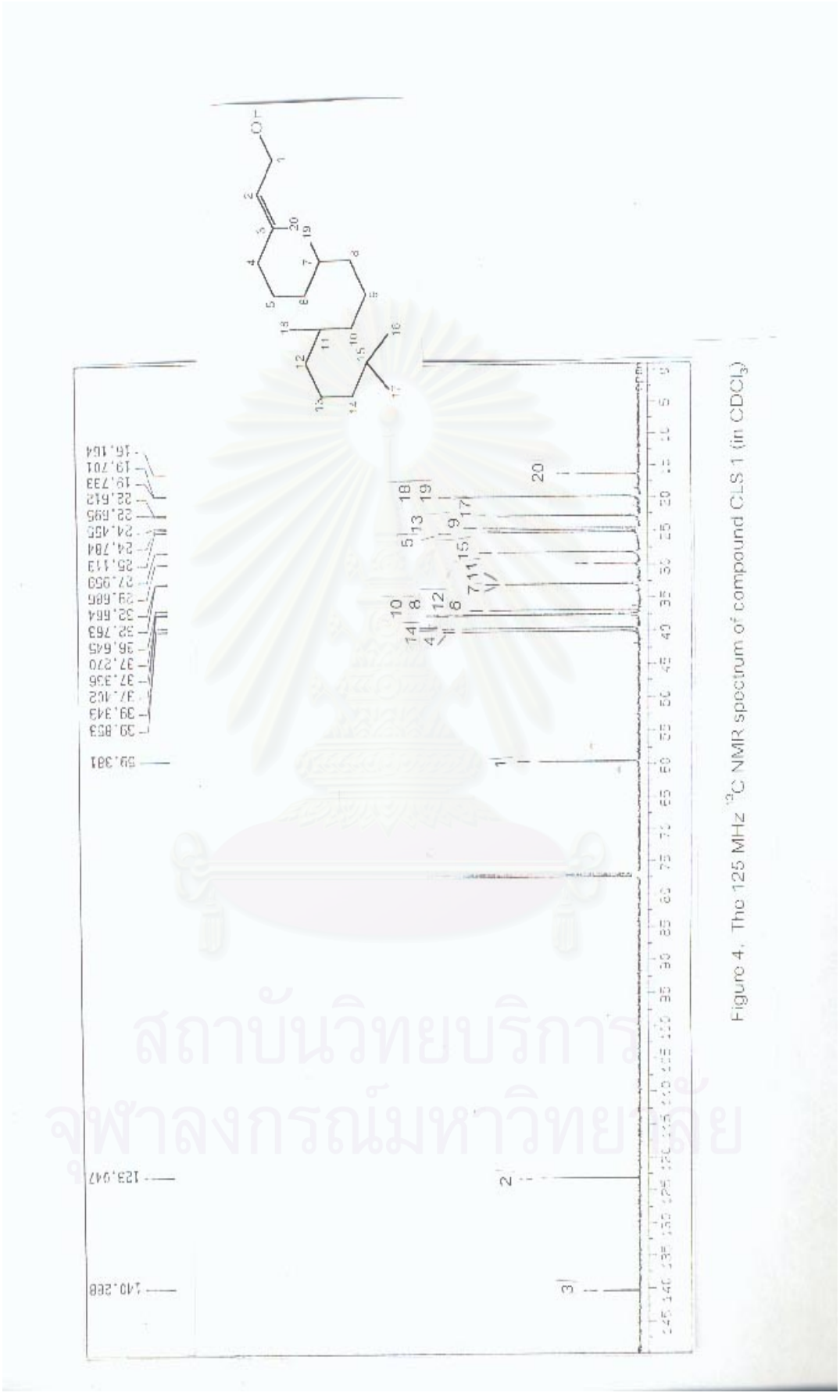


Figure 4. The 125 MHz ^{13}C NMR spectrum of compound CLS 1 (in $CDCl_3$)

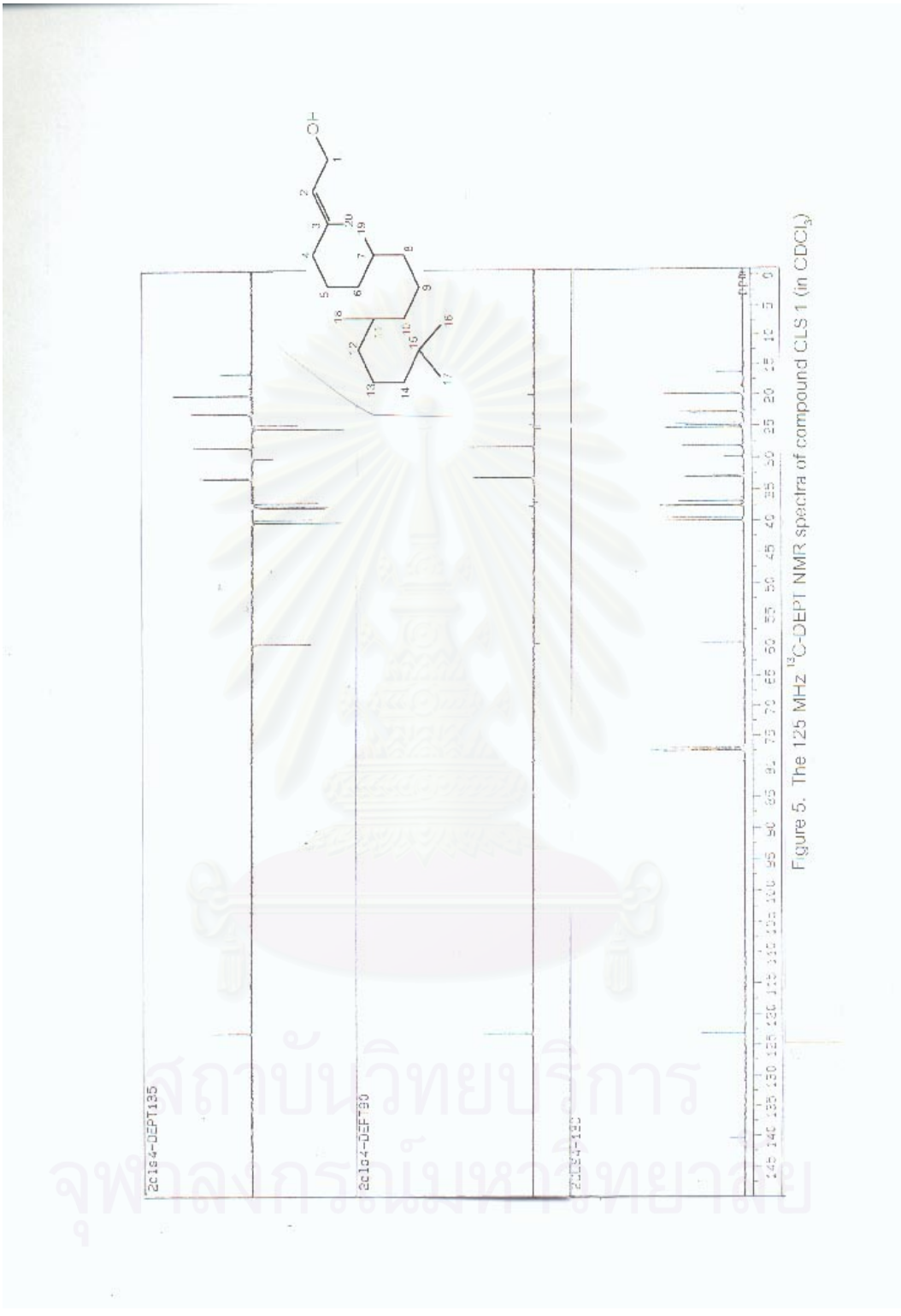


Figure 5. The 125 MHz ^{13}C-DEPT NMR spectra of compound CLS 1 (in $CDCl_3$)

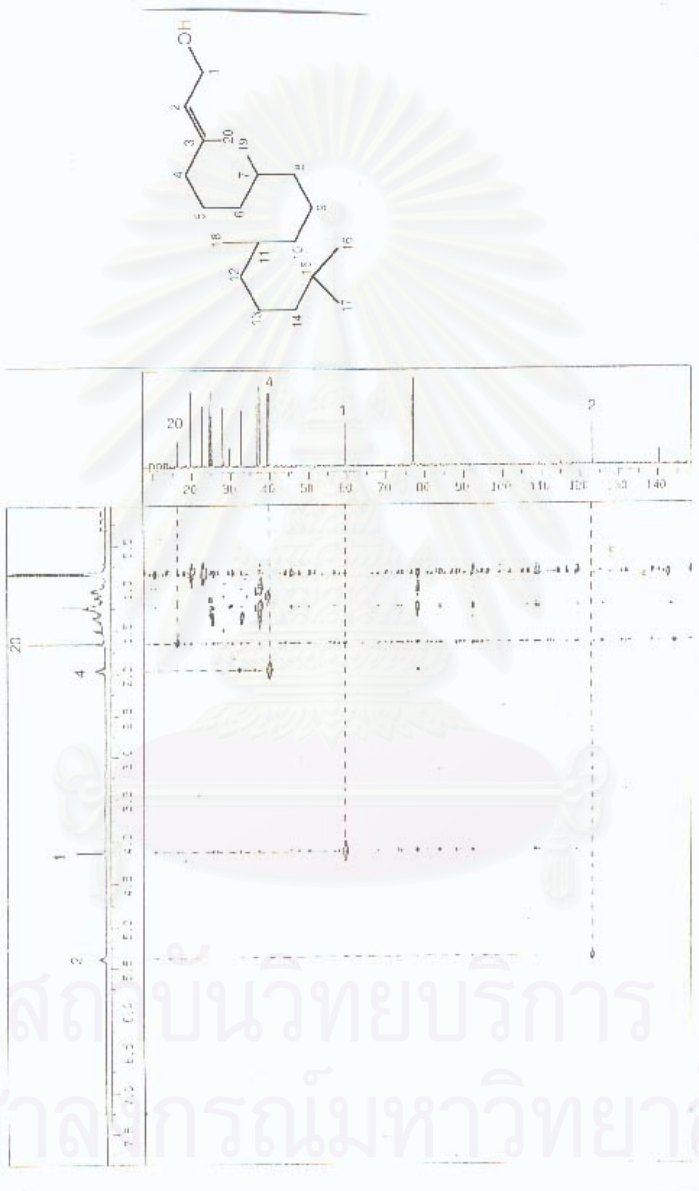


Figure 6. The 500 MHz ^{1}H-^{13}C HETCOR spectrum of compound CLS 1 (in $CDCl_3$)

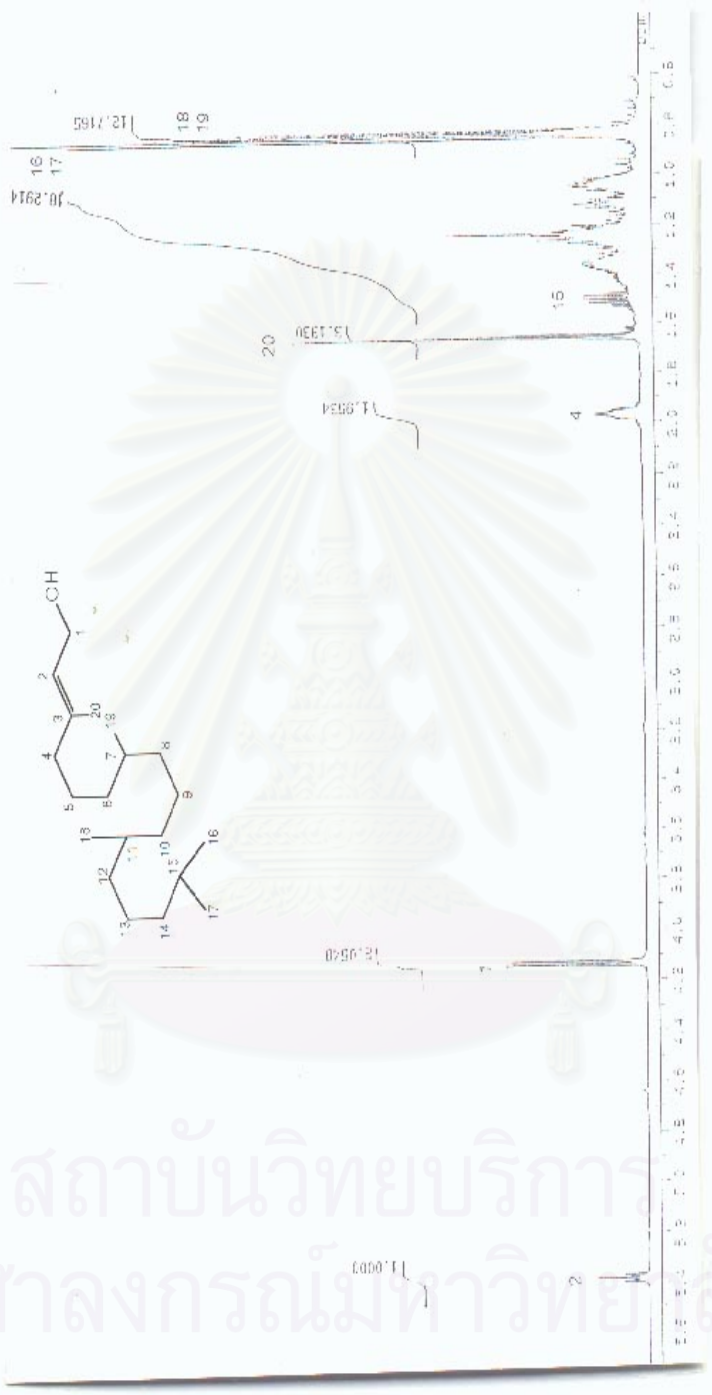
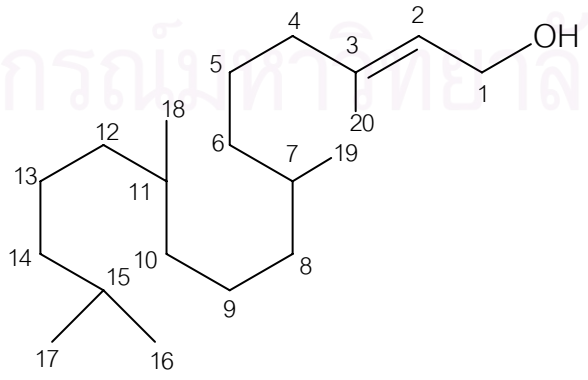


Figure 7. The 500 MHz ^{1}H NMR spectrum of compound CLS 1 (in $CDCl_3$)

Figure 8. The 500 MHz ^{1}H-^{1}H COSY spectrum of compound CLS 1 (in $CDCl_3$)

appeared as doublet at δ 4.13 ppm (*J* = 6.7 Hz) and had a COSY cross peak with the H-2 olefinic methine proton at δ 5.39 ppm.

The identication of CLS 1 was done chiefly by comparison of the carbon chemical shifts of this compound with *trans*-phytol (Sims and Pettus, 1976; Hasan, Burdi and Ahmad, 1991), as shown in table 13. The NMR assignments of CLS 1 were also confirmed by the HMBC experiment (Figure 9). The Me-18 proton signal at δ 0.82 ppm displayed three-bond correlations with C-10 (δ 37.4 ppm) and C-12 (δ 37.3 ppm), confirming its position as attached at C-11 (δ 32.8 ppm). Similarly, cross peaks could be observed between Me-19 proton signal and equivalent carbon signals of C-6 and C-8. Both gem-dimethyl Me-16 and Me-17 displayed three-bond correlation with each other and also with C-14 (δ 39.3 ppm) and C-17 (δ 22.6 ppm), establishing their positions as at one end of the chain. Correlations could also be observed between H_3-20 signal at δ 1.64 ppm and C-2 (δ 123.1 ppm), C-3 (140.3 ppm) and C-4 (δ 39.9 ppm), placing this methyl at position 3. At another end of this linear molecule, cross peak between the hydroxy-substituted methylene protons signal at δ 4.13 ppm and C-3 (δ 140.3 ppm) could also be observed, while the vicinal olefinic H-2 signal (δ 5.39 ppm) produced cross peaks with C-4 (δ 39.9 ppm), and C-20 (δ 16.2 ppm). Major HMBC correlations in the structure of compound CLS 1 can be summarized as shown in Figure 10. Compound CLS 1 was therefore assigned as the known linear diterpenoid structure of *trans*-phytol. This compound has been reported as exhibiting cytotoxic activity (Sung *et al*., 1999). Plaunotol, the antiulcer constituent of *Croton sublyratus*, is another linear diterpenoid found in the same plant family, Euphorbiaceae.



trans-Phytol

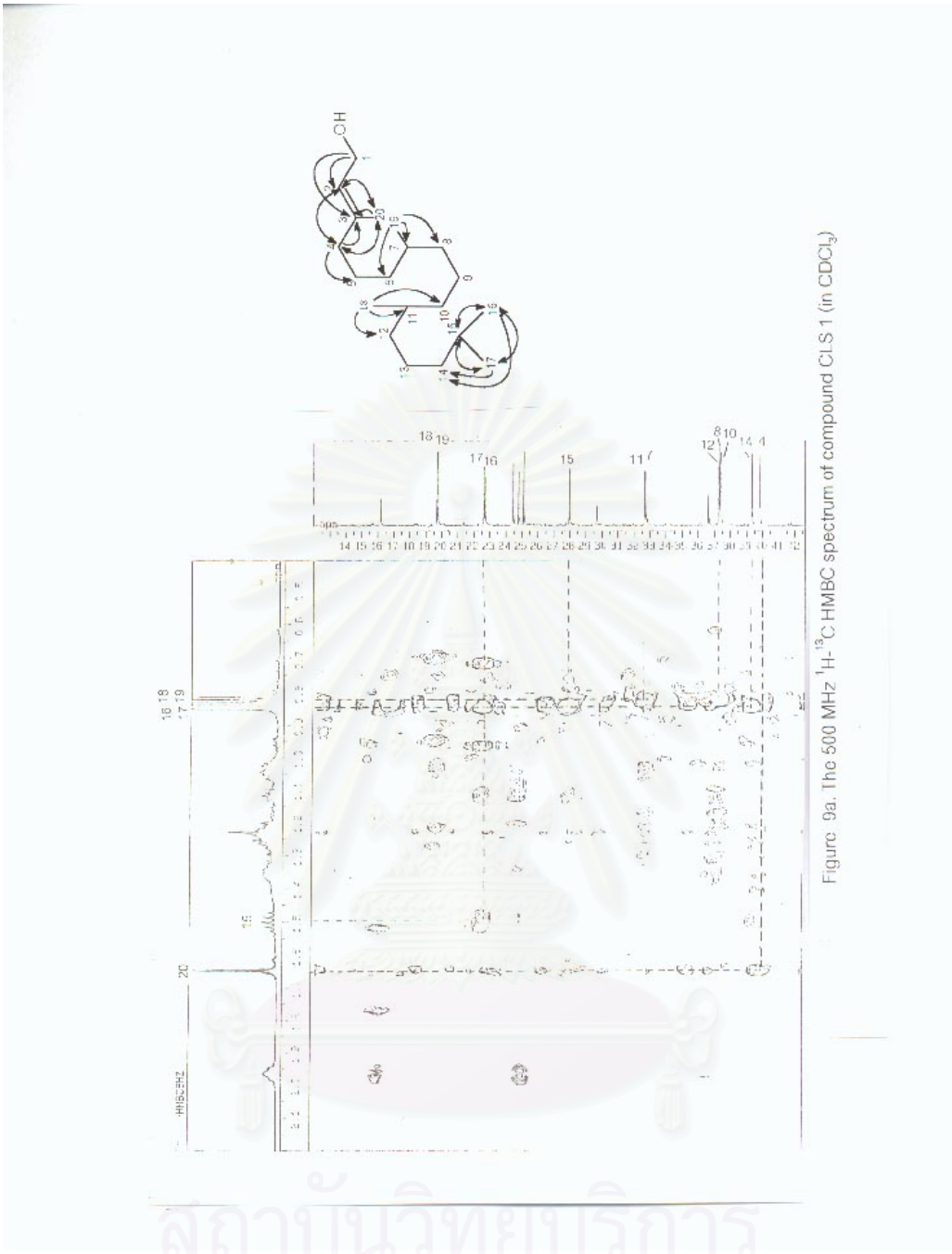


Figure 9a. The 500 MHz ^{1}H- ^{13}C HMBC spectrum of compound CLS 1 (in $CDCl_3$)

Figure 9b. The 500 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 1 (expanded)

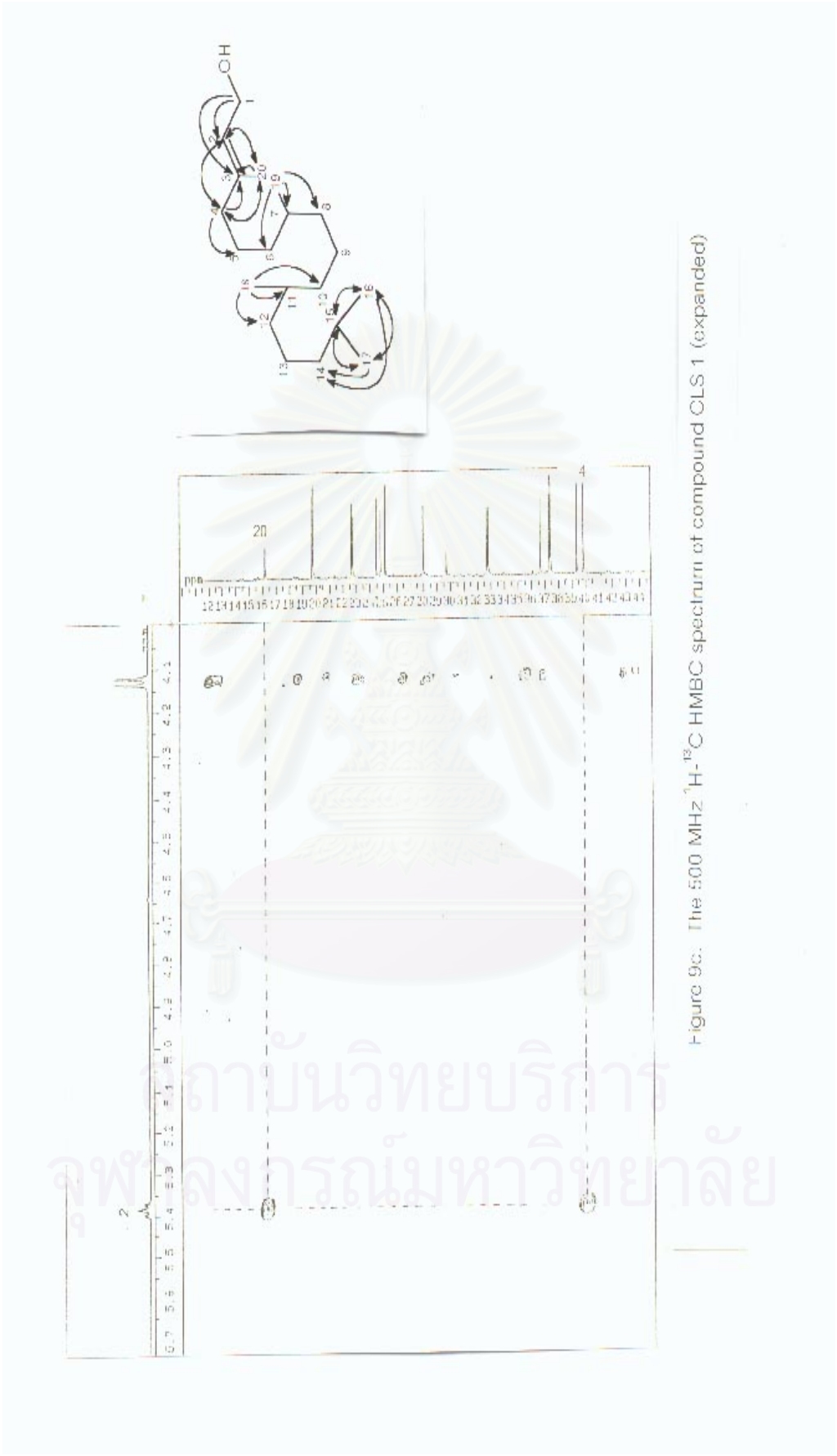


Figure 9c. The 500 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 1 (expanded)

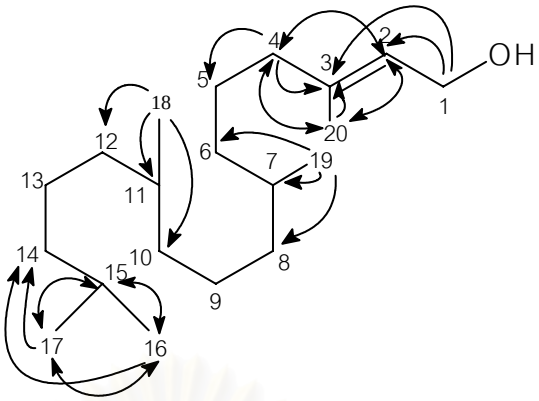


Figure 10. Major HMBC correlations of CLS 1

Table 13. Comparison of ^{13}C NMR data of *trans*-phytol (in $CDCl_3$) (Hasan, Burdi and Ahmad, 1991) and compound CLS 1 (in $CDCl_3$)

Carbon	Chemical shift (δ) ppm	
	Literature value	CLS 1
1	59.5	59.4
2	123.2	123.1
3	140.4	140.3
4	40.0	39.9
5	25.2	25.1
6	36.7	36.7
7	32.7	32.8
8	37.4	37.3
9	24.5	24.5
10	37.5	37.4
11	32.8	32.7
12	37.3	37.3
13	24.8	24.8
14	39.4	39.3
15	28.0	28.0
16	22.7	22.7
17	22.6	22.6
18	19.8	19.7
19	19.7	19.7
20	16.2	16.2

Table 14. ^{1}H and ^{13}C NMR data of *trans*-phytol (compound CLS 1)

Position	δ_C	δ_H	HMBC correlations
1	59.4	4.13, *d*, *J* = 6.7 Hz	C-2, C-3
2	123.1	5.39, *t*, *J* = 6.7 Hz	C-4, C-20
3	140.3	-	
4	39.9	1.96, *m*	C-2, C-3, C-5, C-20
5	25.1	1.00-1.44, *m*	
6	36.7	1.00-1.44, *m*	
7	32.8	1.00-1.44, *m*	
8	37.3	1.00-1.44, *m*	
9	24.5	1.00-1.44, *m*	
10	37.4	1.00-1.44, *m*	
11	32.7	1.00-1.44, *m*	
12	37.3	1.00-1.44, *m*	
13	24.8	1.00-1.44, *m*	
14	39.3	1.00-1.44, *m*	
15	28.0	1.50, *septet*, *J* = 6.7 Hz	C-16, C-17
16	22.7	0.84, *d*, *J* = 6.7 Hz	C-14, C-15, C-17
17	22.6	0.84, *d*, *J* = 6.7 Hz	C-14, C-15, C-16
18	19.7	0.82, *d*, *J* = 6.7 Hz	C-10, C-11, C-12
19	19.7	0.82, *d*, *J* = 6.7 Hz	C-6, C-7, C-8
20	16.2	1.64, *s*	C-2, C-3, C-4

2. Identification of (24*S*)-24-methyl–5α-lanosta-9(11),25-dien-3β-ol (compound CLS 2)

Compound CLS 2 was recrystallized as colorless needles (10 mg, 0.0027% yield) from methanol. The molecular formula of $C_{31}H_{52}O$ was suggested for this compound based on its EIMS (Figure 11) molecular ion peak at m/z 440. Successive losses of methyl and hydroxy groups produced the mass fragment peaks at *m/z* 425 and 407, respectively. The base peak at *m/z* 313 was the result of the loss of C_9H_{19} side chain. The presence of hydroxy groups in the molecule was also confirmed by a very intense IR absorption band at 3414 cm^{-1} (Figure 12). The IR spectrum also indicated the presence of geminal dimethyl groups in this molecule as a pair of absorption bands at 1380 and 1369 cm^{-1}.

The ^{1}H (Figure 13) and COSY (Figure 14) NMR spectra of CLS 2 displayed signals for eight methyl groups, five of which were tertiary methyls at δ 0.64, 0.71, 0.79, 0.96 and 1.02 ppm assignable to H_3-18, H_3-30, H_3-29, H_3-28 and H_3-19, respectively. Two secondary methyl resonances appeared as signals at δ 0.85 (*d*, *J* = 6.1 Hz, H_3-21) and 0.97 ppm (*d*, *J* = 7.0 Hz, H_3-31), and one vinylic methyl group at δ 1.62 ppm (H_3-27). The most downfield signal in the spectrum at δ 5.20 ppm (*d*, *J* = 5.8 Hz) belongs to the H-11 vinylic methine proton. A broad singlet signifying exomethylene protons appeared at δ 4.65 ppm. The hydroxy-substituted methine proton at position 3 appeared as a doublet of doublet (*J* = 11.6, 4.3 Hz) at δ 3.20 ppm.

The ^{13}C NMR spectrum of CLS 2 (Figure 15) exhibited 31 carbon signals, suggestive of a triterpenoid structure. DEPT (Figure 16) and HMQC (Figure 17a-17c) experiments were employed to classify these signals into those of eight methyl carbons at δ 14.4 (C-18), 15.7 (C-29),18.4 (C-21), 18.5 (C-30), 18.6 (C-27), 20.2 (C-31), 22.3 (C-19) and 28.2 (C-28) ppm, ten methylene carbons at δ 21.4 (C-6), 27.8 (C-2), 28.0 (C-7), 28.1 (C-16), 31.5 (C-23), 33.9 (C-15), 34.0 (C-22), 36.1 (C-1), 37.1 (C-12) and 109.3 ppm (the exomethylene C-26), seven methine carbons at δ 36.0 (C-20), 41.6 (C-24), 41.8 (C-8), 50.9 (C-17), 52.5 (C-5), 78.9 (C-3) and 114.9 (C-11) ppm, and, lastly, six quaternary carbons at δ 39.1 (C-4), 39.4 (C-10), 44.2 (C-13), 47.0 (C-14) ppm, including the two olefinic carbons at δ 148.5 and 150.2 ppm assignable to C-9 and C-25,

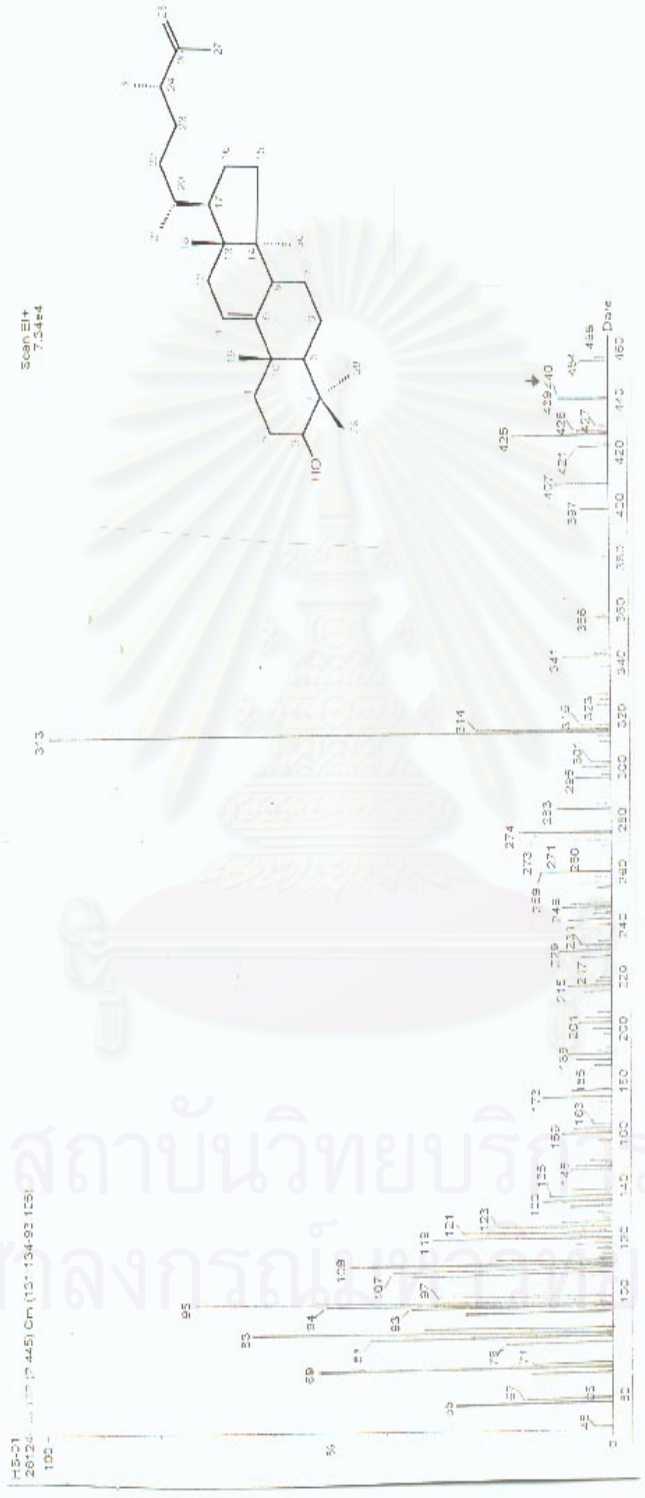


Figure 11. EIMS of compound CLS 2

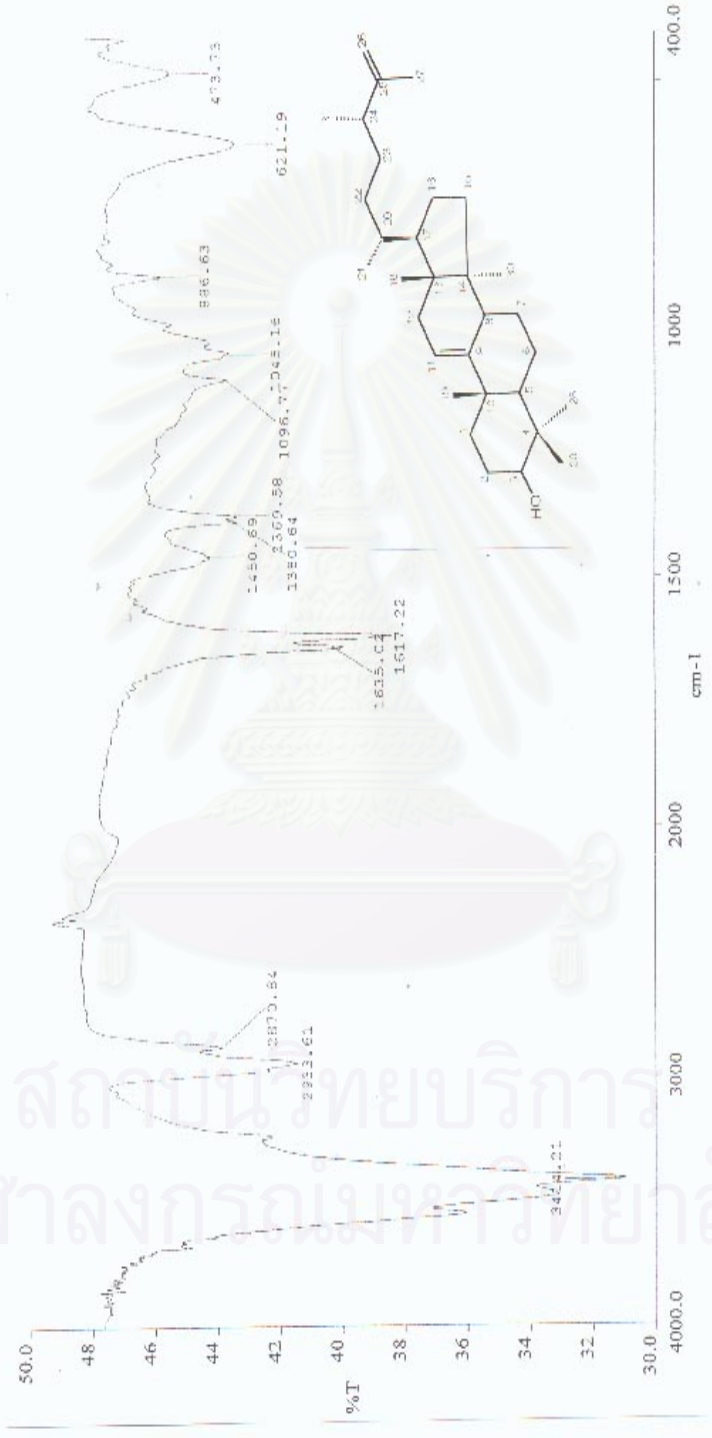


Figure 12. IR spectrum of compound CLS 2

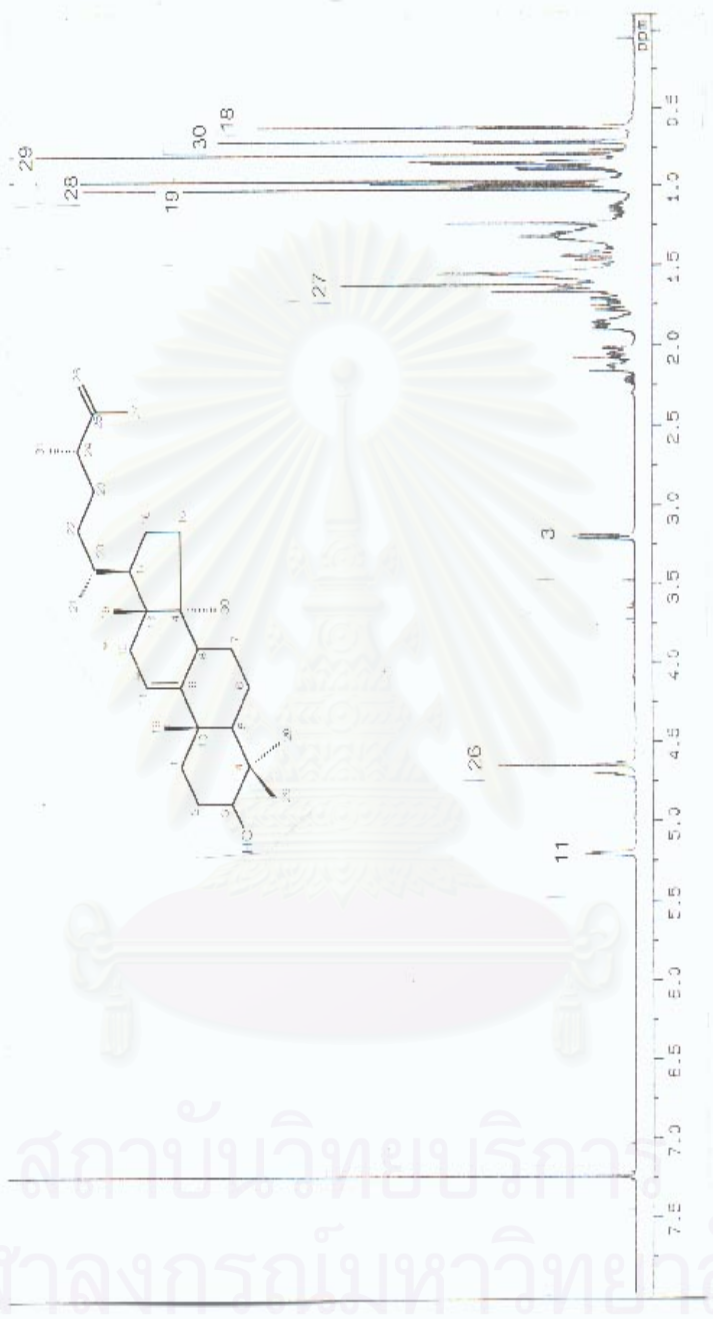


Figure 13. The 500 MHz ^{1}H NMR spectrum of compound CI S 2 (in $CDCl_3$)

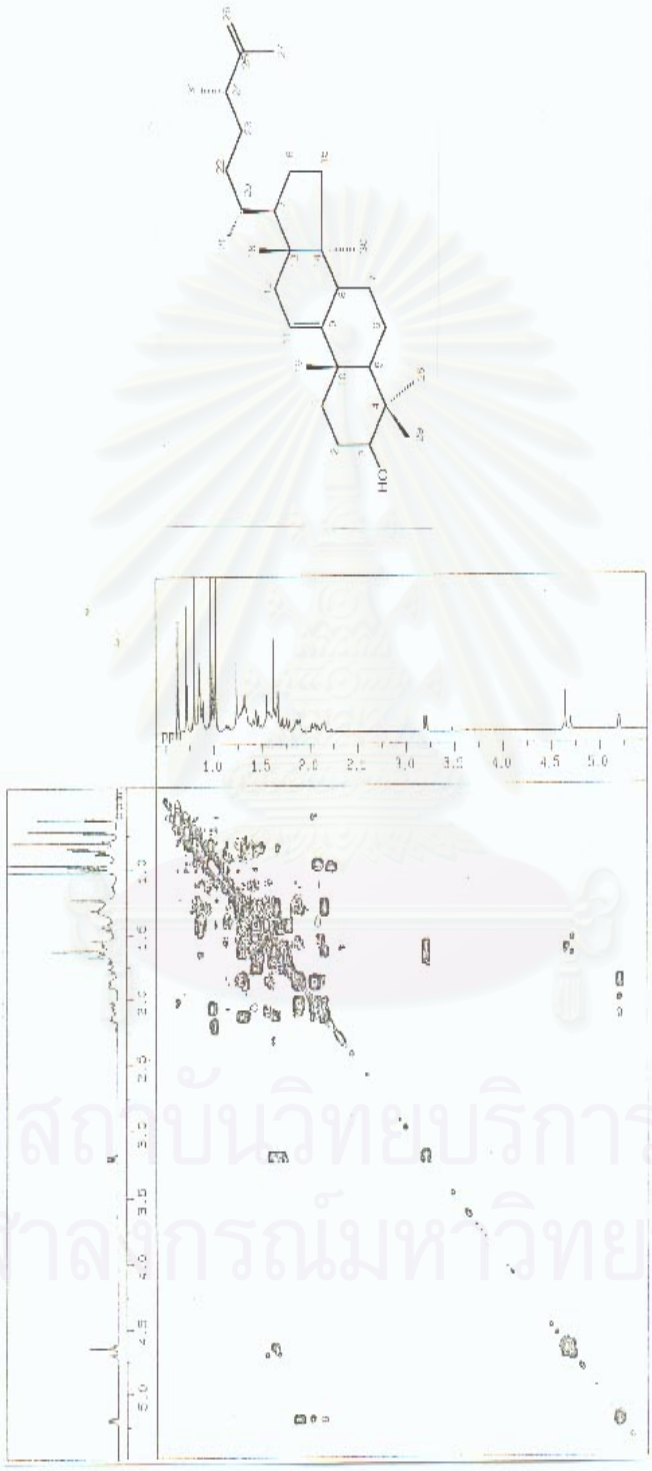


Figure 14. The 500 MHz ^{1}H-^{1}H COSY spectrum of compound CI S 2 (in $CDCl_3$)

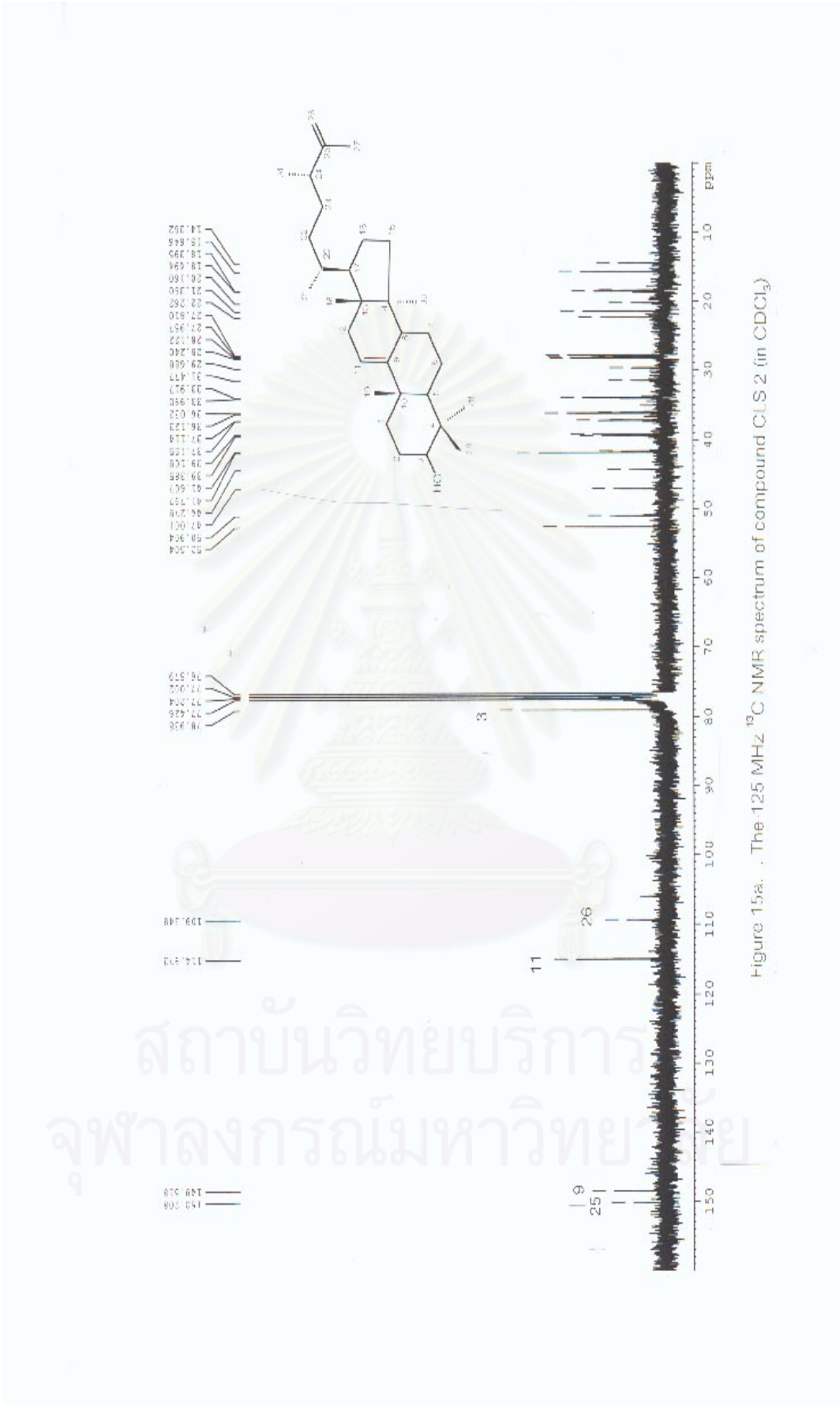


Figure 15a. . The 125 MHz ^{13}C NMR spectrum of compound CLS 2 (in $CDCl_3$)

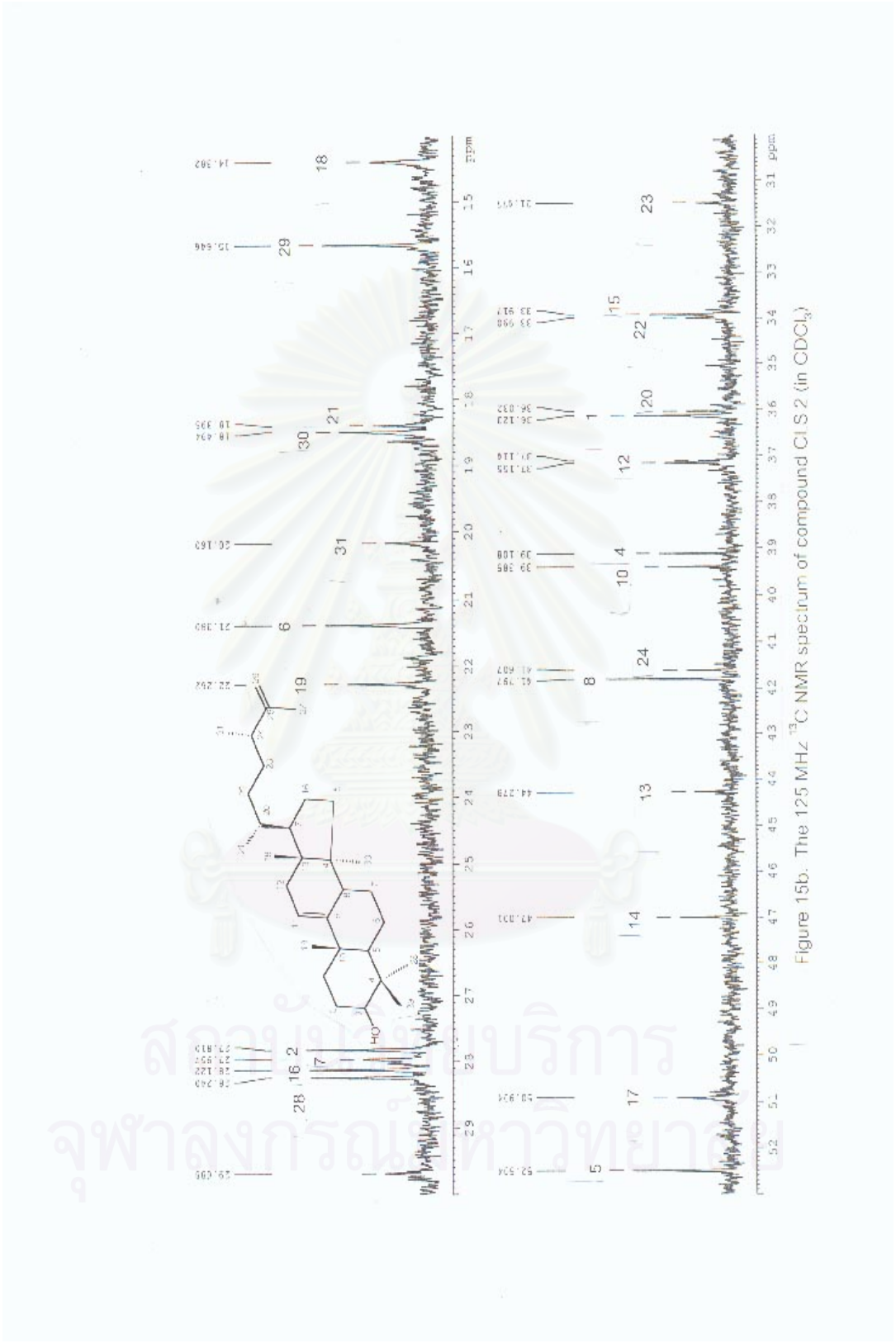


Figure 15b. The 125 MHz ^{13}C NMR spectrum of compound CI S 2 (in $CDCl_3$)

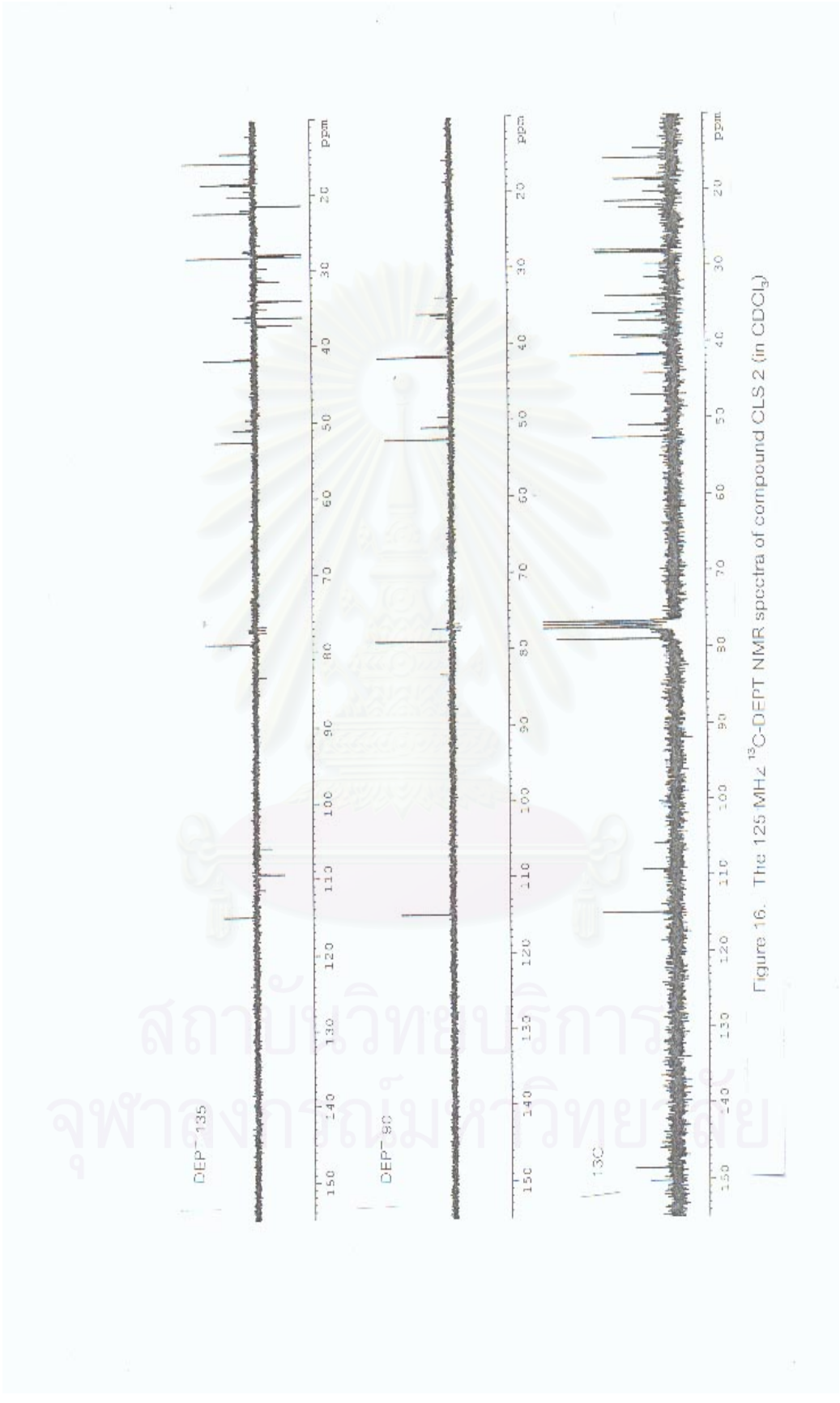


Figure 16. The 125 MHz ^{13}C-DEPT NMR spectra of compound CLS 2 (in $CDCl_3$)

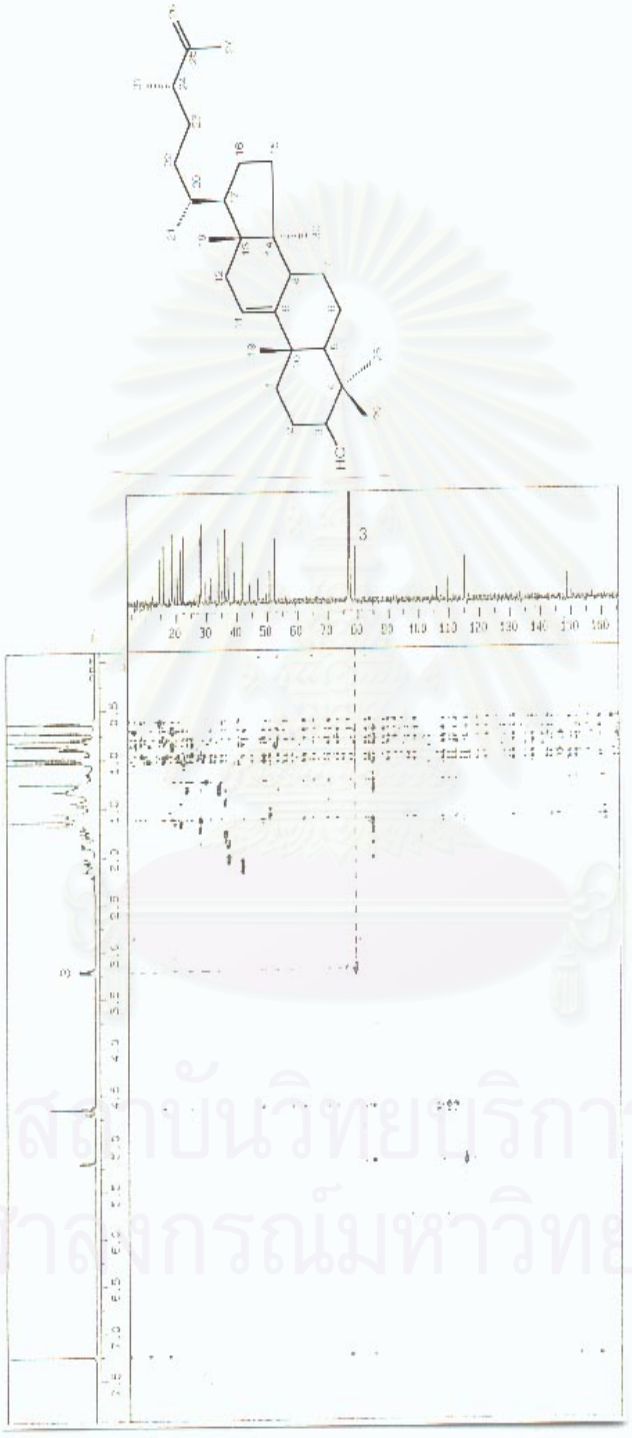


Figure 17a. The 500 MHz ^{1}H-^{13}C HMQC spectrum of compound CLS 2 (in $CDCl_3$)

Figure 17b. The 500 MHz ^{1}H-^{13}C HMQC spectrum of compound CLS 2 (expanded)

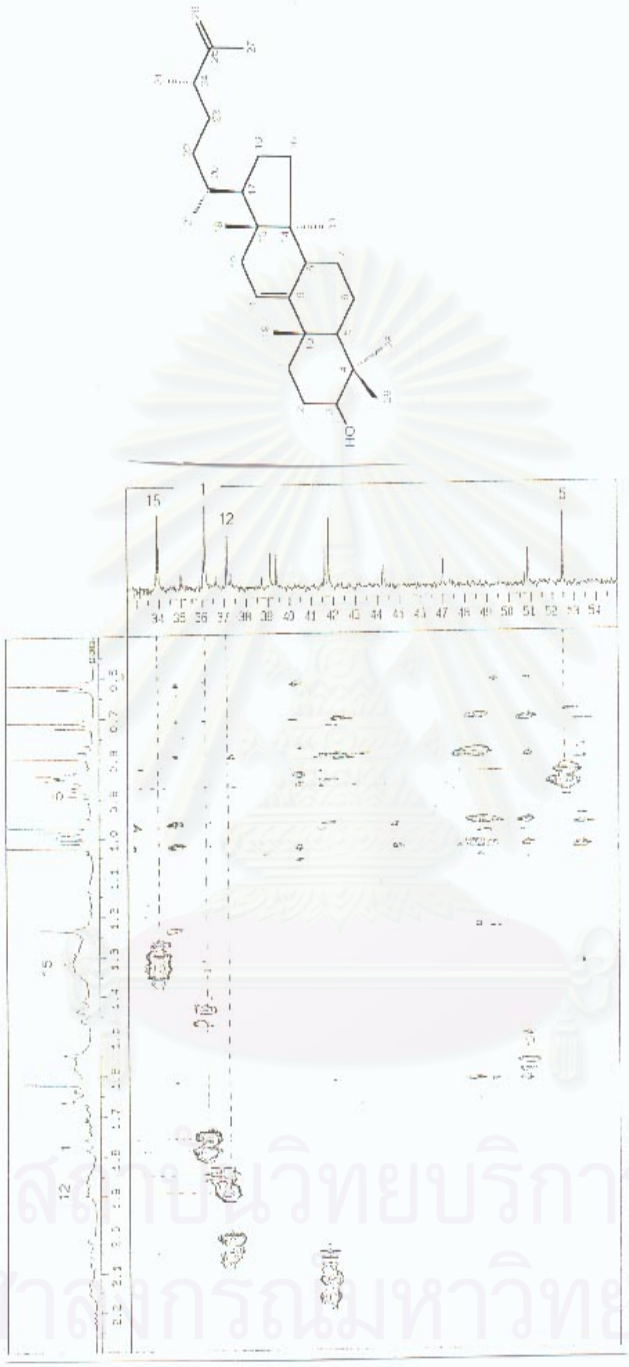


Figure 17c. The 500 MHz ^{1}H-^{13}C HMQC spectrum of compound CLS 2 (expanded)

respectively. These data indicated the presence of two double bonds in the structure: one trisubstituted double bond and one disubstituted exomethylene group.

Judging from the above data, compound CLS 2 should be a triterpenoid having the lanostane basic structure with an additional methyl group. This structure consists of two major partial structures: a cyclopentanoperhydrophenanthrene ring similar to those of steroids, but with 5 tertiary methyls (two of which are gem-dimethyls at position 4 of ring A) and a C_8-C_9 side chain with secondary and/or tertiary methyls. ^{1}H-^{13}C HMBC experiment (Figure 18a-18d) was performed in order to confirm this structure and the positions of the substituents.

In the 4-ring partial structure, correlations could be observed between Me-18 protons at δ 0.62 ppm and C-12 (δ 37.1 ppm), C-13 (δ 44.2 ppm), C-14 (δ 47.0 ppm) and C-17 (δ 50.9 ppm), while Me-19 protons signal at δ 1.02 ppm displayed cross peaks with C-1 (δ 36.1 ppm), C-5 (δ 52.5 ppm), C-10 (δ 39.4 ppm) and the olifinic C-9 (δ 148.5 ppm). The Me-30 protons, adjacent to Me-18, gave cross peaks between its signal at δ 0.71 ppm and those signals of C-8 (δ 41.8 ppm), C-13, C-14 and C-15 (δ 33.9 ppm). The gem-dimethyls at position 4 of ring A (Me-28 and Me-29) produced peaks with the carbon signals of each other, the hydroxy-substituted C-3 (δ 78.9 ppm) and C-5. The position of the trisubstituted double bond between positions 9 and 11 was established by the long-range coupling between the H-11 olefinic methine proton (δ 5.20 ppm, *d*, *J* = 5.8 Hz) and C-8, C-10, C-12 and C-13.

As for the rest of the molecule, one tertiary methyl, two secondary methyls and an exomethylene group could be found in the side chain. The HMBC cross peaks were observed between Me-21 proton signal at δ 0.85 ppm and C-17, C-20 (δ 36.0 ppm) and C-22 (δ 34.0 ppm). The tertiary Me-27 at the end of the side chain displayed correlations between its proton signal (δ 0.97 ppm) and C-24 (δ 41.6 ppm) and the two olefinic C-25 (δ 150.2 ppm) and C-26 (δ 109.3 ppm). The position of this exo-methylene moiety was also confirmed by cross peaks between H_2-26 (δ 4.65 ppm, *br s*) and C-24 and C-27 (δ 18.6 ppm). And, finally, the position of the additional methyl group (Me-31) was established as at position 24 through the observed HMBC cross peaks of this methyl protons and C-23 (δ 31.5 ppm), C-24 and C-25.

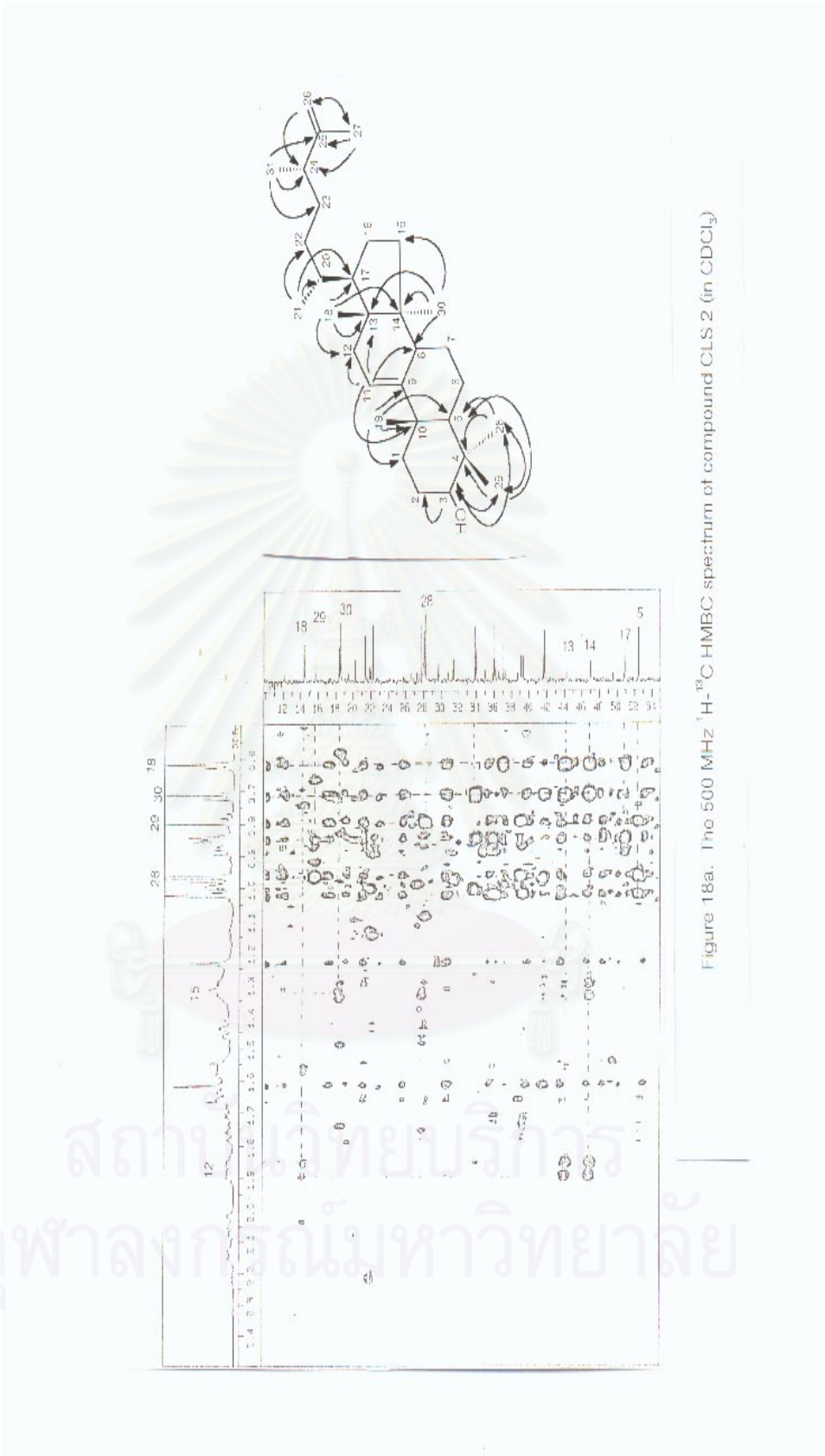


Figure 18a. The 500 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 2 (in $CDCl_3$)

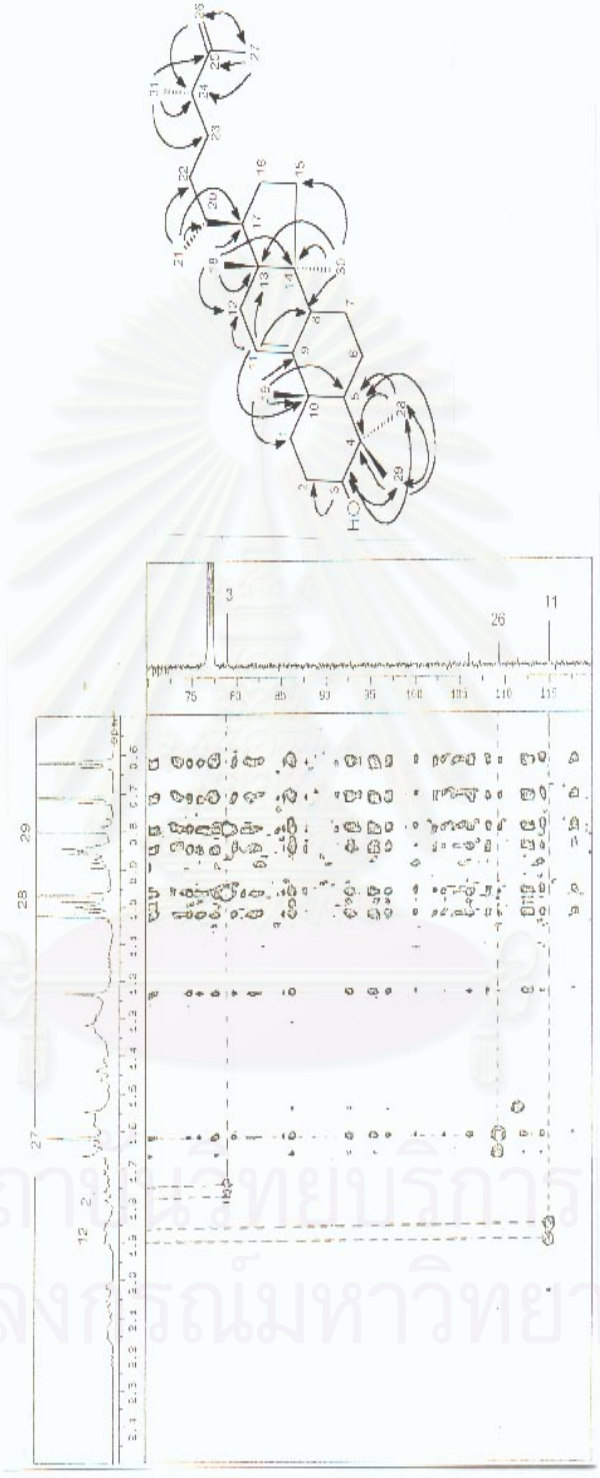


Figure 18b. The 500 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 2 (expanded)

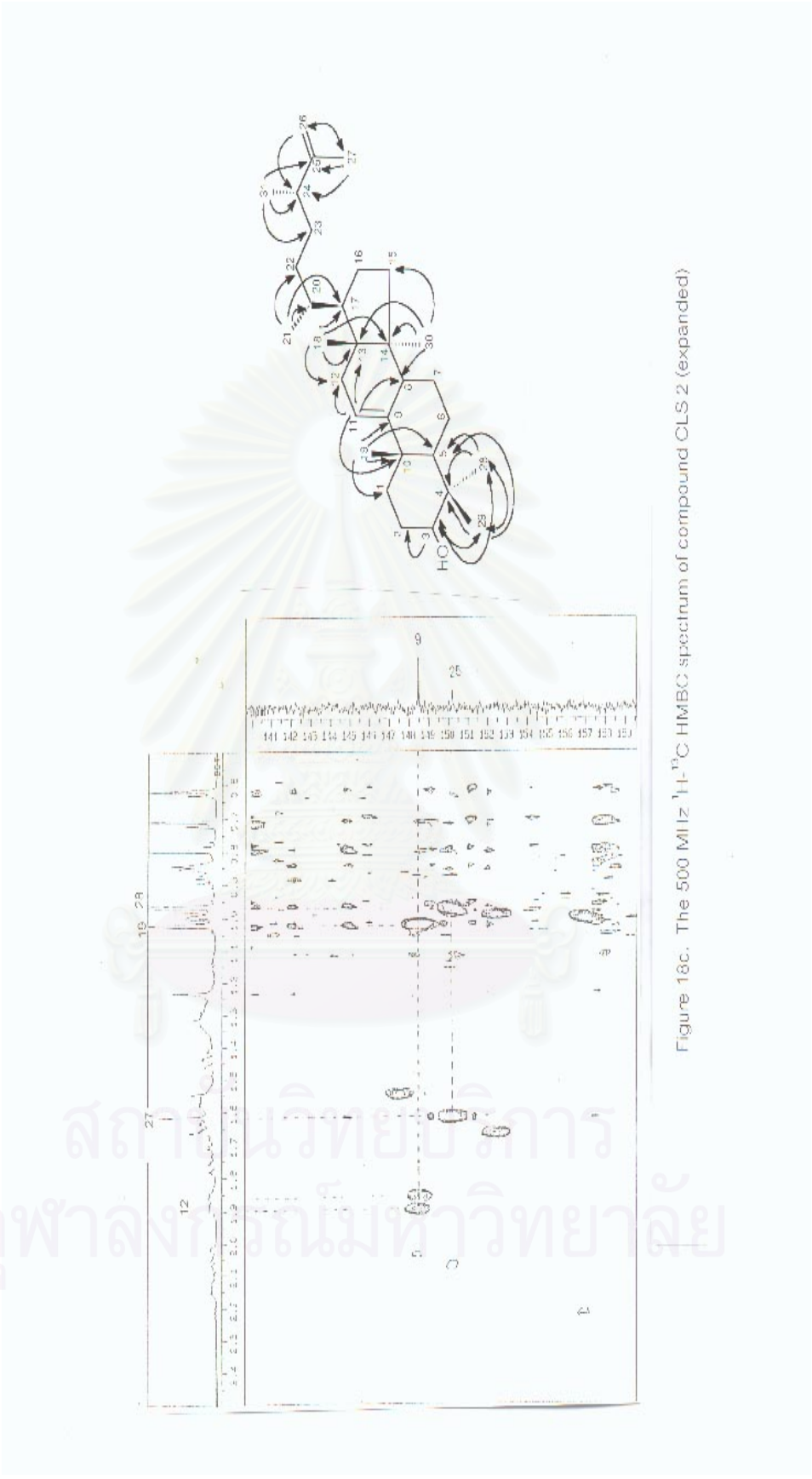


Figure 18c. The 500 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 2 (expanded)

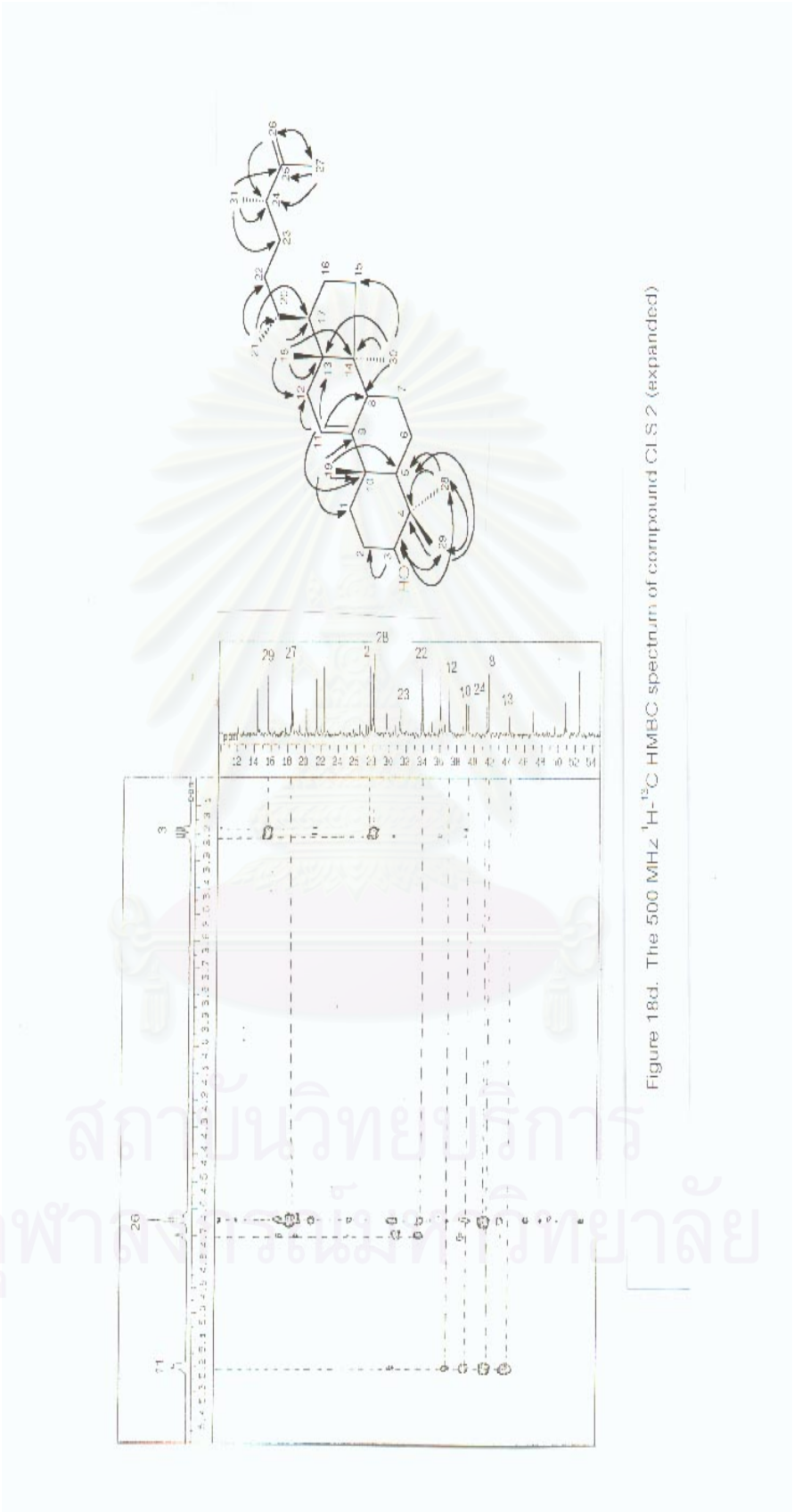


Figure 18d. The 500 MHz ^{1}H-^{13}C HMBC spectrum of compound CI S 2 (expanded)

The orientation of the 3-hydroxy and 24 methyl groups was determined to be β and *s*, respectively, by comparison of the related chemical shifts with those of previously reported (Chakravarty *et al*., 1996). Therefore, compound CLS 2 was identified as (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3β-ol and comparison with (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3-yl acetate (Chakravarty *et al*., 1996)(Table 15). The complete ^{1}H- and ^{13}C-NMR chemical shift assignments of this compound were shown in Table 16.

This is the first report of (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3β-ol as a constituent of plant in the family Euphorbiaceae. The compound has previously been isolated from two different plant families: Yano *et al*. (1992) first discovered this triterpenoid from an extract of the stem and branches of *Neolitsea aciculata* (family Lauraceae), and, later, Chakravarty *et al*. (1996) isolated it from the overground part of *Glycosmis arborea* (family Rutaceae).

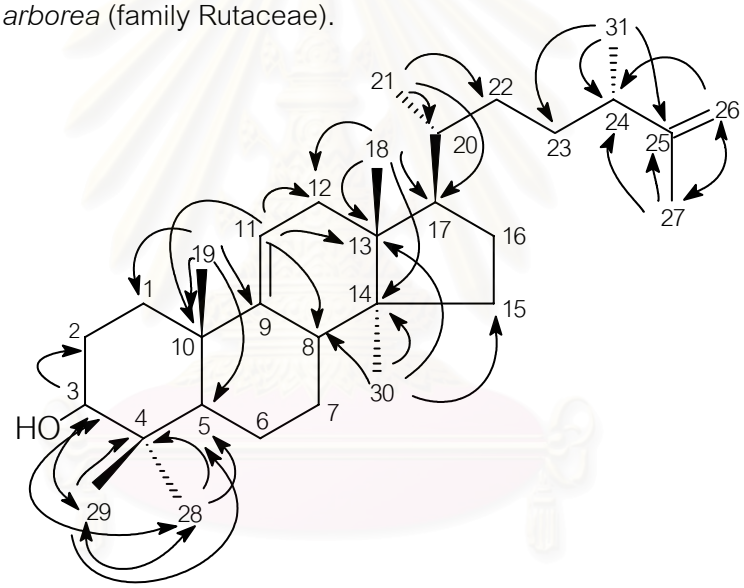
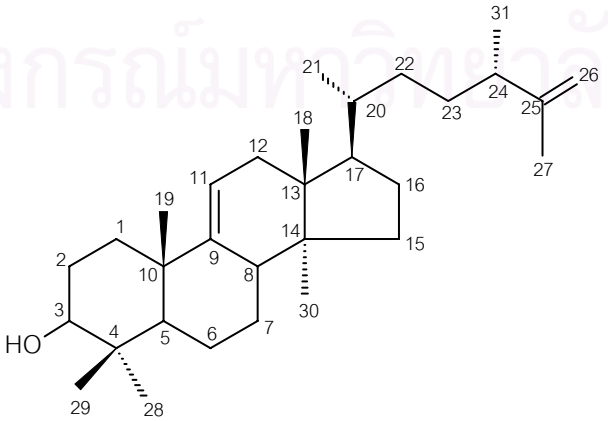


Figure 20. Major HMBC correlations of CLS 2



(24*S*)-24-Methyl-5α-lanosta-9(11), 25-dien-3β-ol

Table 15. Comparison of ^{13}C NMR data of (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3-yl acetate (in $CDCl_3$) (Chakravarty *et al.*, 1996) and compound CLS 2 (in $CDCl_3$)

Carbon	Chemical shift (δ) ppm	
	Literature value	Compound CLS 2
1	35.8	36.1
2	24.2	27.8
3	80.9	78.9
4	38.0	39.1
5	52.5	52.5
6	21.2	21.4
7	28.0	28.0
8	41.8	41.8
9	148.1	148.5
10	39.3	39.4
11	115.2	114.9
12	37.1	37.1
13	44.3	44.2
14	47.0	47.0
15	33.9	33.9
16	28.0	28.1
17	50.9	50.9
18	14.1	14.4
19	22.3	22.3
20	36.1	36.0
21	18.4	18.4
22	34.0	34.0
23	31.5	31.5
24	41.6	41.6
25	150.2	150.2
26	109.4	109.3
27	18.6	18.6
28	28.2	28.2
29	16.8	15.7
30	18.5	18.5
31	20.2	20.2

Table 16. ^{1}H and ^{13}C NMR data of (24*S*)-24-methyl-5α-lanosta-9(11), 25-dien-3β-ol) (compound CLS 2)

Position	δ_C	δ_H	HMBC correlations
1	36.1	1.10-2.30, *m*	
2	27.8	1.10-2.30, *m*	
3	78.9	3.20, *dd*, *J* = 11.6, 4.3 Hz	C-2, C-28, C-29
4	39.1	-	
5	52.5	1.10-2.30, *m*	
6	21.4	1.10-2.30, *m*	
7	28.0	1.10-2.30, *m*	
8	41.8	1.10-2.30, *m*	
9	148.5	-	
10	39.4	-	
11	114.9	5.20, *d*, *J* = 5.8 HZ	C-8, C-10, C-12, C-13
12	37.1	1.10-2.30, *m*	
13	44.2	-	
14	47.0	-	
15	33.9	1.10-2.30, *m*	
16	28.1	1.10-2.30, *m*	
17	50.9	1.10-2.30, *m*	
18	14.4	0.64, *s*	C-12, C-13, C-14, C-17
19	22.3	1.02, *s*	C-1, C-5, C-9, C-10
20	36.0	1.10-2.30, *m*	
21	18.4	0.85, *d*, *J* = 6.1 Hz	C-17, C-20, C22
22	34.0	1.10-2.30, *m*	
23	31.5	1.10-2.30, *m*	
24	41.6	1.10-2.30, *m*	
25	150.2	-	
26	109.3	4.65, *br s*	C24, C-27
27	18.6	1.62, *s*	C-24, C-25, C-26
28	28.2	0.96, *s*	C-3, C-4, C-5, C-29
29	15.7	0.79, *s*	C-3, C-4, C-5, C-28
30	18.5	0.71, *s*	C-8, C-13, C-14, C-15
31	20.2	0.97, *d*, *J* = 7.02 Hz	C23, C-24, C-25

3. Identification of tilianin (compound CLS 3)

Compound CLS 3 was crystallized as yellow powder from chloroform (86 mg, 0.02% yield). The EI mass spectrum of compound CLS 3 (Figure 20) showed the molecular ion $[M]^+$ peak at *m/z* 446, corresponding to $C_{22}H_{22}O_{10}$. Its IR spectrum (Figure 21) revealed absorption bands at 3413 and 1635 cm^{-1}, suggesting the presence of hydroxyl groups and chelated carbonyl, respectively, whereas the UV absorptions at 253, 267 and 343 nm (Figure 22) suggested a flavone structure (Markham, 1982).

The ^{13}C NMR spectrum of CLS 3 (Figure 23) exhibited 22 signals. DEPT (Figure 24) and ^{1}H-^{13}C HMQC experiment (Figure 25) were useful in classifying these signals into those of one methoxyl carbon at δ 55.7 ppm (4′-OCH_3), seven methine carbons at δ 95.1 (C-8), 99.8 (C-6), 104.0 (C-3), 114.8 (C-3′ and C-5′), and 128.7 ppm (C-2′ and C-6′), and eight quaternary carbons at δ 105.6 (C-10), 122.9 (C-1′), 157.1 (C-9), 161.2 (C-5), 162.6 (C-4′), 163.2 (C-7), 164.0 (C-2) and 182.1 (C-4) ppm. Six carbon signals at δ 60.8, 69.8, 73.3, 76.6, 77.3 and 100.2 ppm were reminiscent of a β -glucopyranosyl unit while the other sixteen carbon signals could be identified as those of the flavonoid aglycone portion possessing hydroxyl and methoxyl substituents.

The ^{1}H NMR spectrum of CLS 3 (Figure 26) showed the most downfield signal at δ 12.91 ppm which could be attributed to a chelated C-5 hydroxyl group. The characteristic flavone H-3 signal appeared as a sharp singlet at δ 6.91 ppm. The substitution pattern of the aromatic A-ring was determined as *meta* from the two aromatic proton signals at δ 6.45 and 6.84 ppm, both appeared as broad singlets, which could be assigned to H-6 and H-8, respectively.

For the B-ring, the spectrum showed a pair of *ortho*-coupled doublets (J = 8.7 Hz) at δ 8.05 (H-2′ and H-6′) and 7.12 ppm (H-3′ and H-5′), characteristic of a para-substituted benzene ring. It also exhibited one methoxyl signal (δ 3.86 ppm) which substituted at C-4′ of this ring.

The coupling constant (J = 7.1 Hz) of the anomeric proton signal at δ 5.06 ppm indicated the configuration of the glycosidic linkage as β. The only hydroxyl group available for the sugar attachment is that of position 7. This was further confirmed by

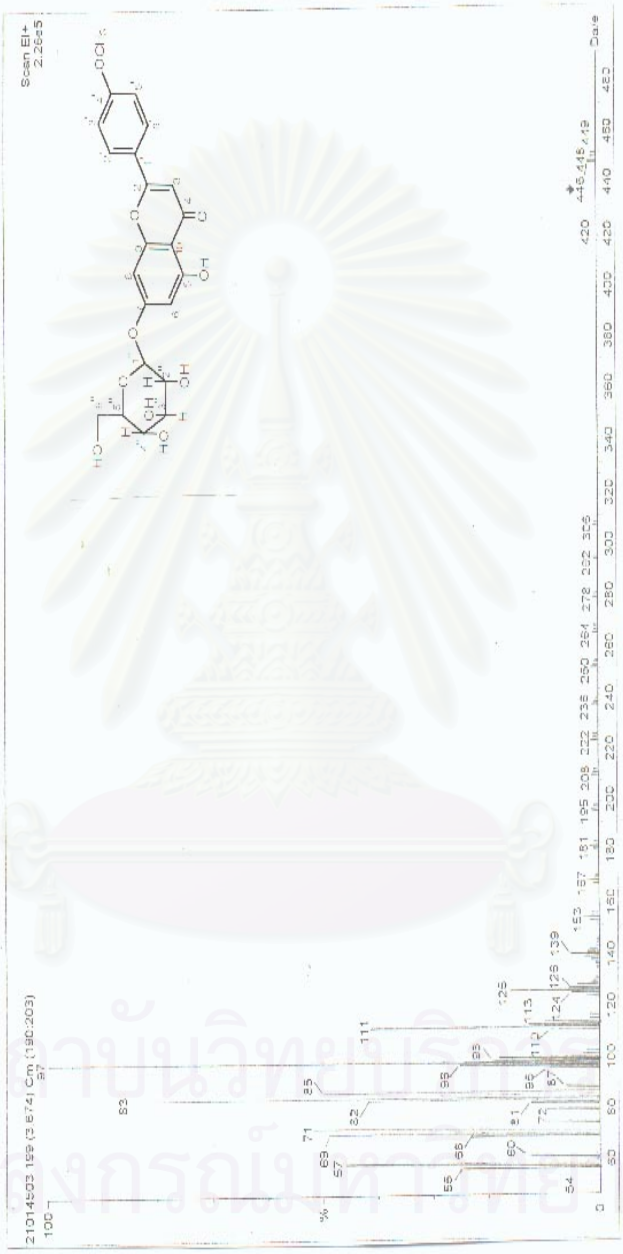


Figure 20. EIMS of compound CLS 3

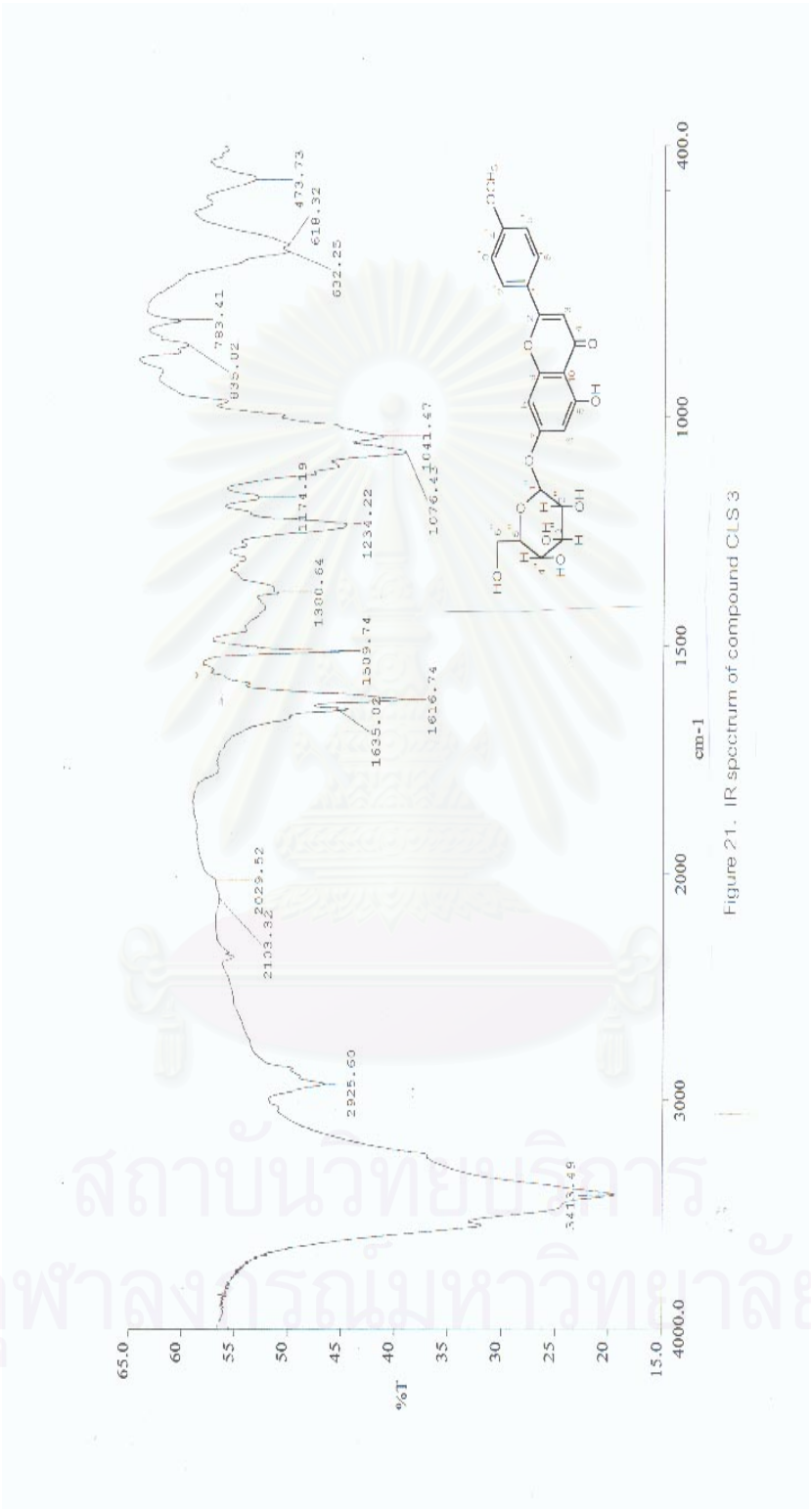


Figure 21. IR spectrum of compound CLS 3

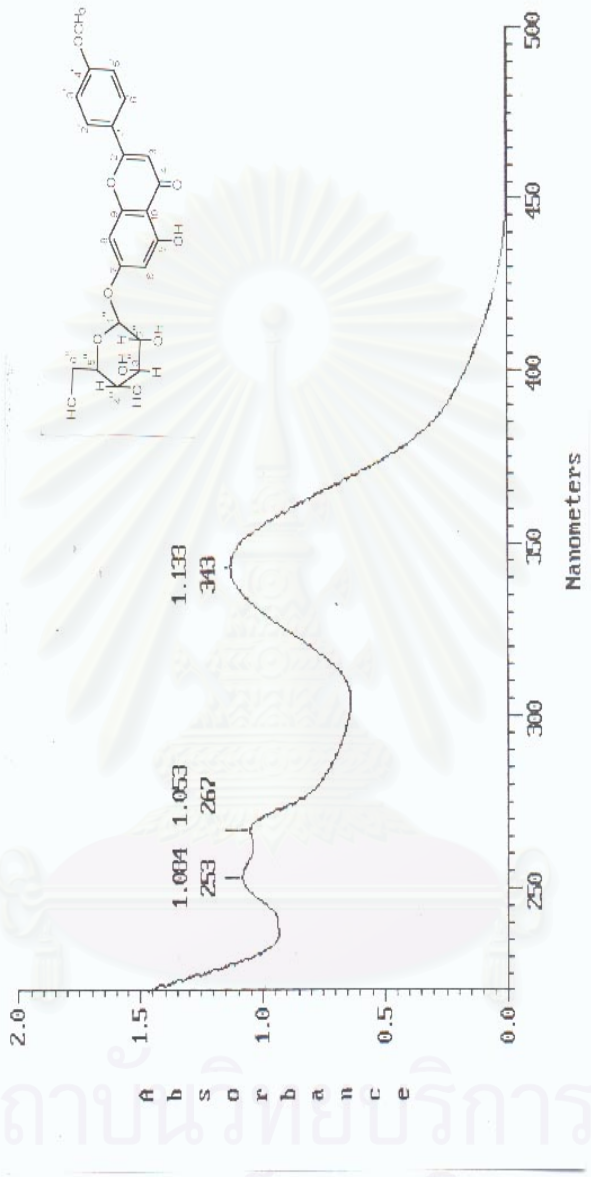


Figure 22. UV spectrum of compound CI S.3

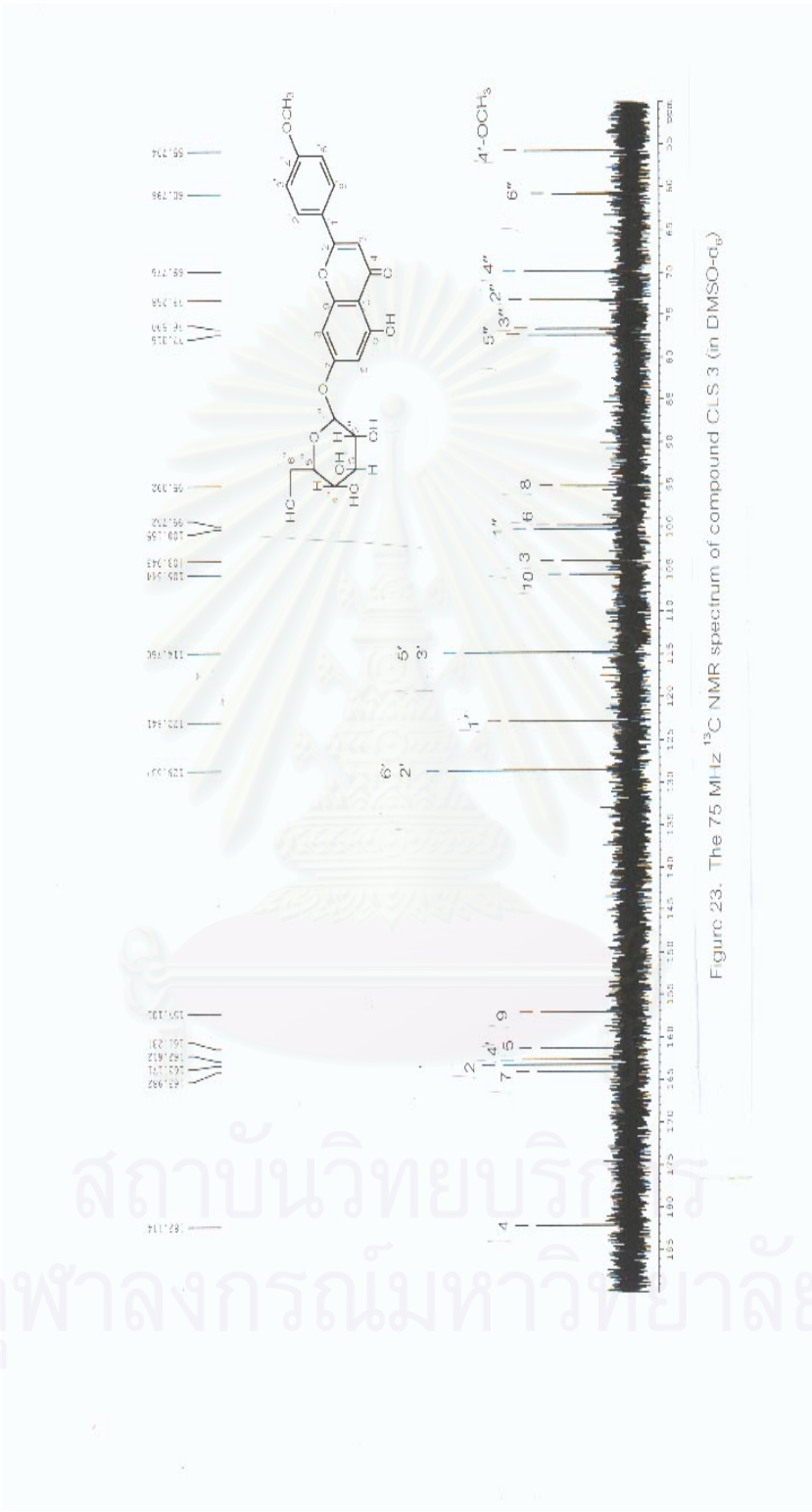


Figure 23. The 75 MHz ^{13}C NMR spectrum of compound CLS 3 (in DMSO-d_6)

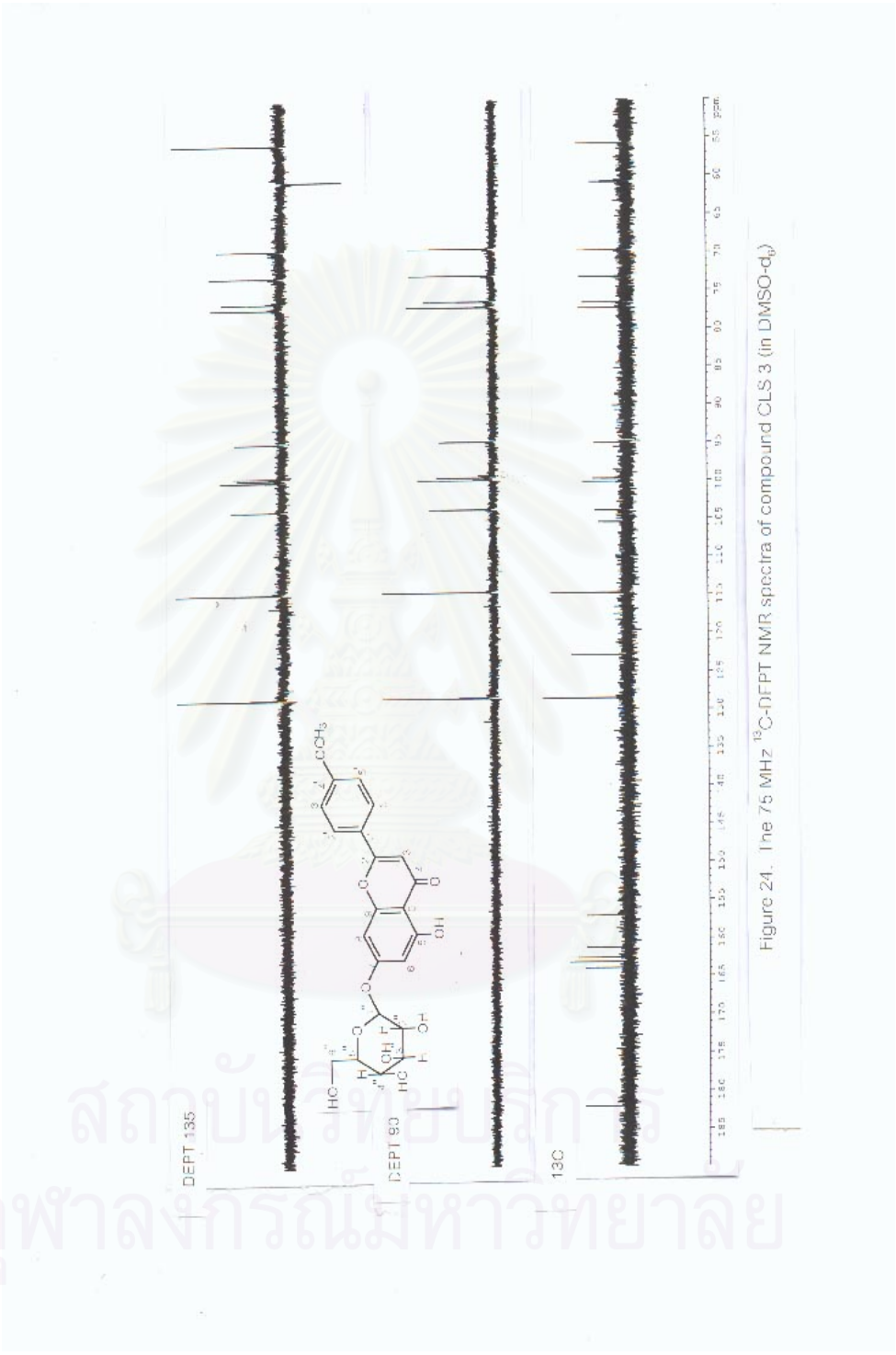


Figure 24. The 75 MHz ^{13}C-DEPT NMR spectra of compound CLS 3 (in DMSO-d_6)

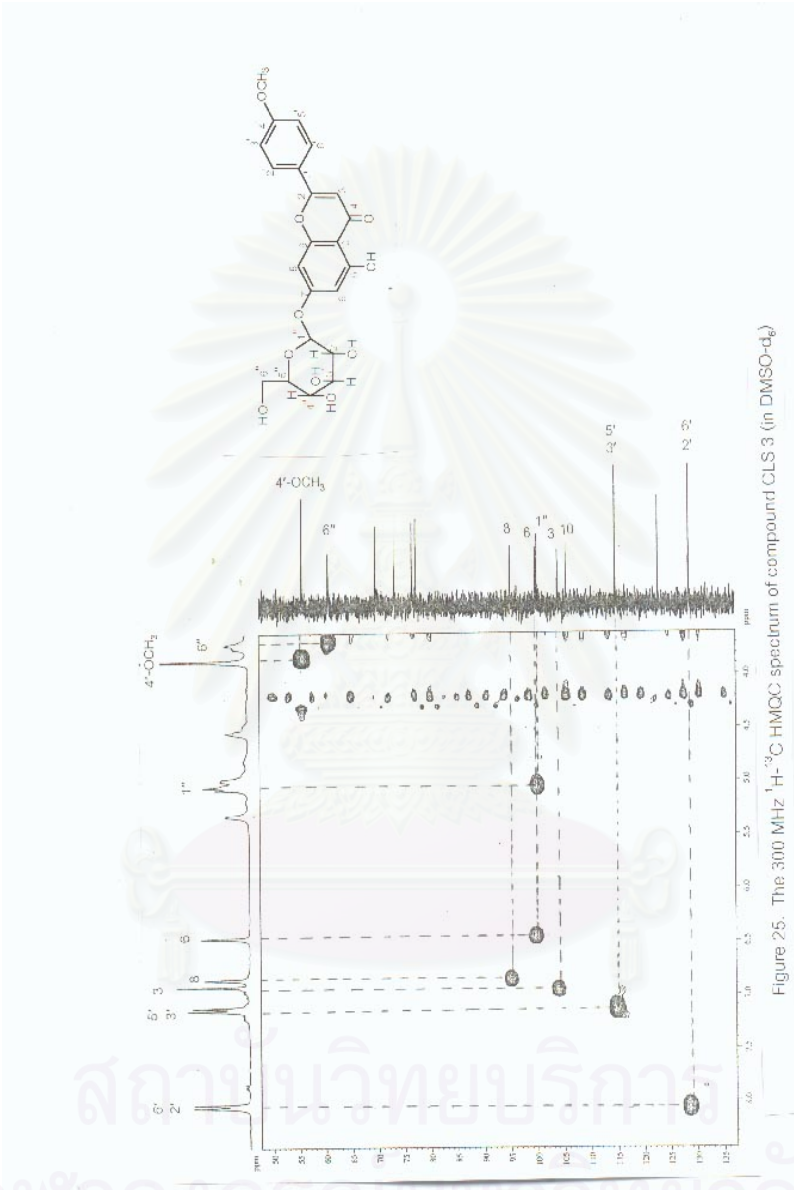


Figure 25. The 300 MHz ^{1}H-^{13}C HMQC spectrum of compound CLS 3 (in DMSO-d_6)

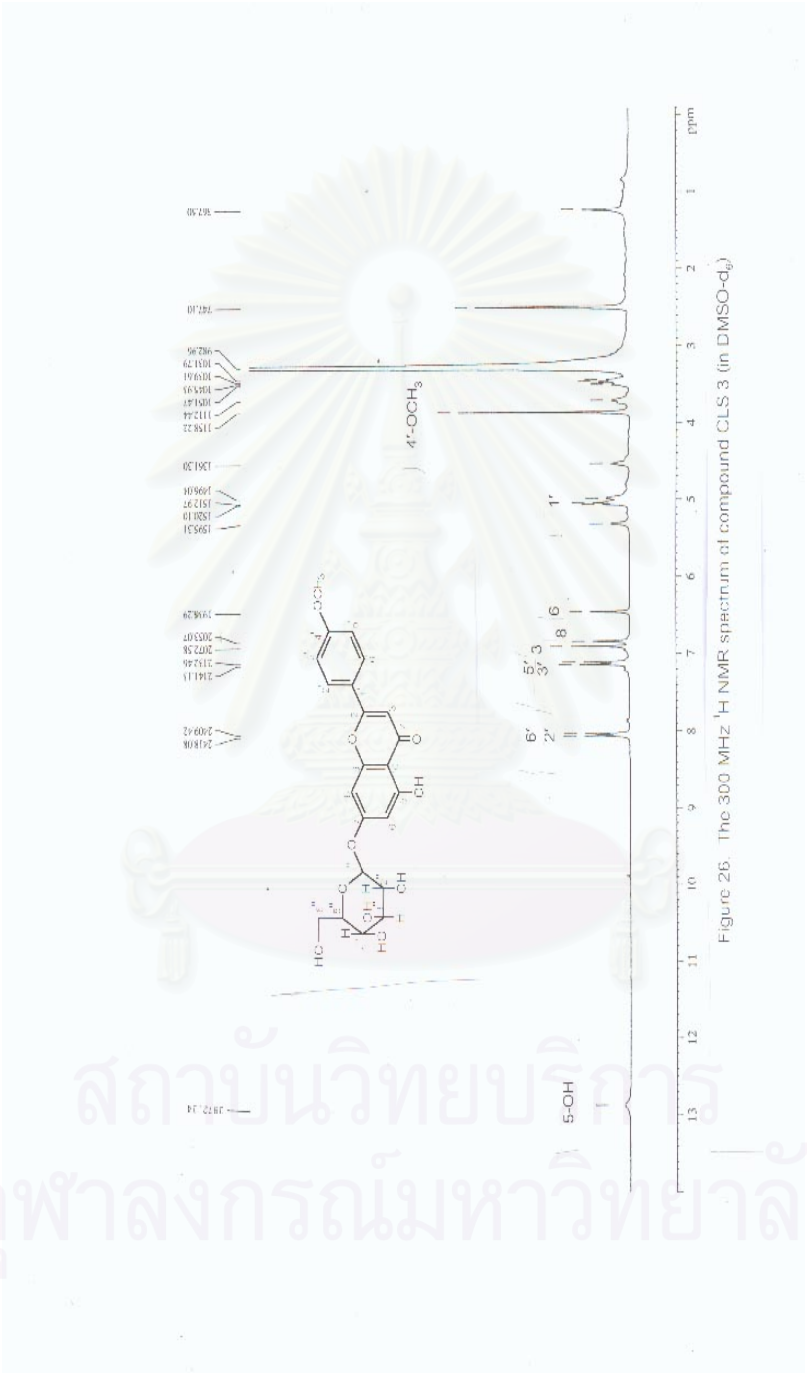


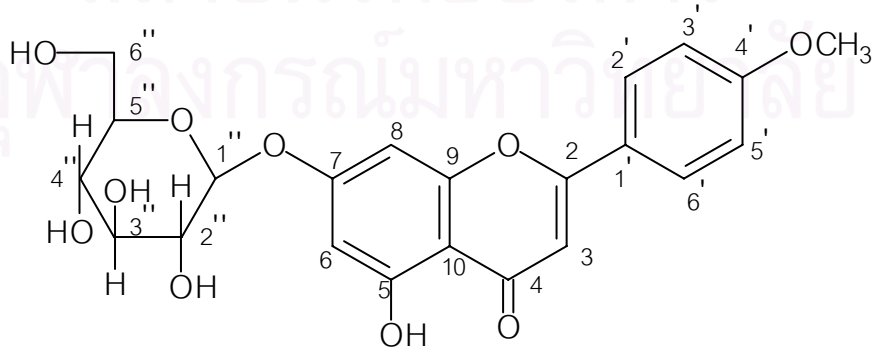
Figure 26. The 300 MHz ^{1}H NMR spectrum of compound CLS 3 (in DMSO-d_6)

^{1}H-^{13}C HMBC experiment (Figure 27a-27b), in which the anomeric proton signal of glucose (δ 5.06 ppm, *d*, *J* = 7.1 Hz, H-1″) displayed three-bond correlation with C-7 (δ 164.0 ppm) of the flavonoid aglycone.

The HMBC experiment was also useful in comfirming the aglycone structure. Correlations could be observed between aromatic proton at position 6 (δ 6.45 ppm) and C-8 (δ 95.1 ppm) and C-10 (δ 105.5 ppm), whereas the H-8 signal (δ 6.84 ppm) showed correlations to C-6 (δ 99.8 ppm), C-9 (δ 157.1 ppm) and C-10. Another olefinic proton signal at δ 6.91 ppm (H-3) displayed HMBC cross peaks with C-1′ (δ 122.8 ppm), C-2 (δ 163.2 ppm), C-4 (δ 182.1 ppm) and C-10 (δ 105.5 ppm).

The signal of the equivalent aromatic protons in ring B at δ 7.12 ppm (H-3′ and H-5′) showed long-range coupling with C-1′ (δ 122.8 ppm), while another aromatic proton signal at δ 8.05 ppm (H-2′ and H-6′) showed three-bond coupling with C-4′ (δ 162.6 ppm) and C-2. The methoxyl protons at δ 3.86 ppm exhibited long-range coupling with C-4′ (δ 162.6 ppm), confirming its position in the structure. Major HMBC correlations in the structure of CLS 3 can be summarized as shown in Figure 30.

Therefore, the flavonoid aglycone was identified as 5,7-dihydroxy-4′-methoxyflavone (acacetin) and compound CLS 3 is tilianin (acacetin-7-*O*-β-D-glucopyranoside) (Figure 31), confirmed by comparison with literature value (Agrawal, 1989). This flavone glycoside was isolated from the leaves of *Tilia japonica* (Tiliaceae) (Farkas, Major and Vermes, 1964). The same compound isolated from the herb *Saussurae stella* (Family Compositae) was shown to be antioxidant (Zheng *et al*., 1997). However, this is the first report of tilianin from *Cleidion spiciflorum*.



Tilianin

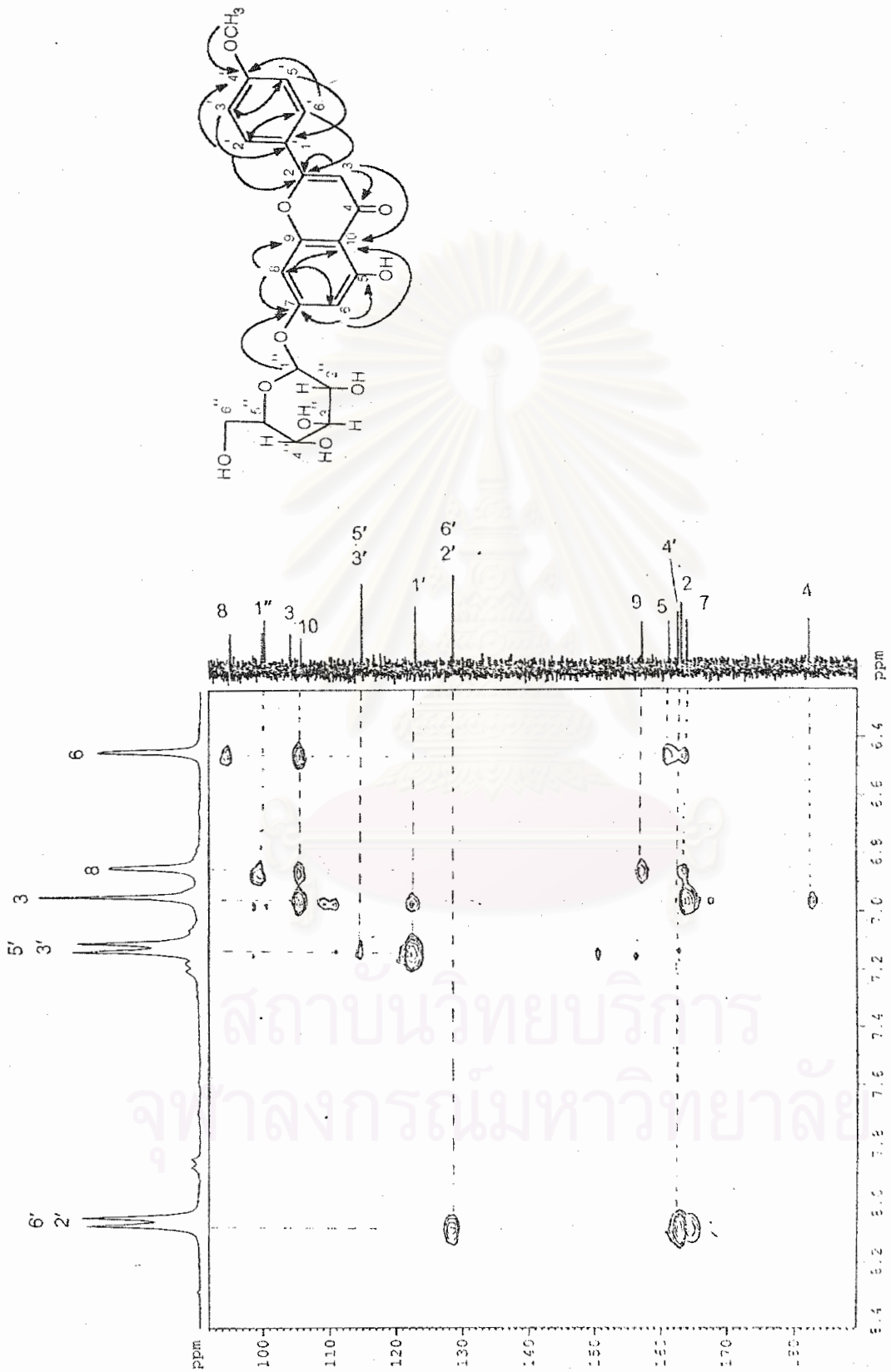


Figure 27a. The 300 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 3 (in DMSO-d_6)

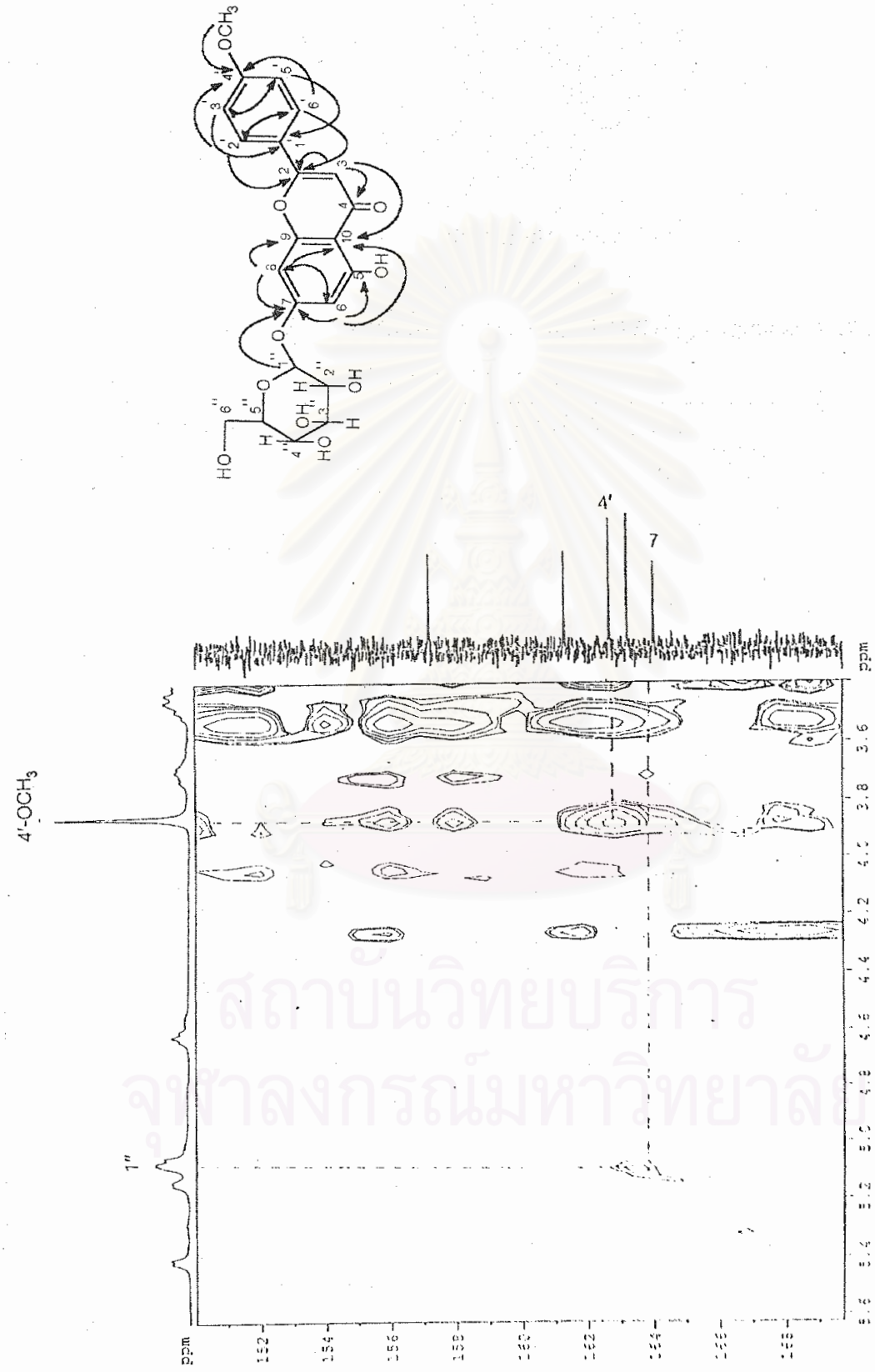


Figure 27b. The 300 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 3 (expanded)

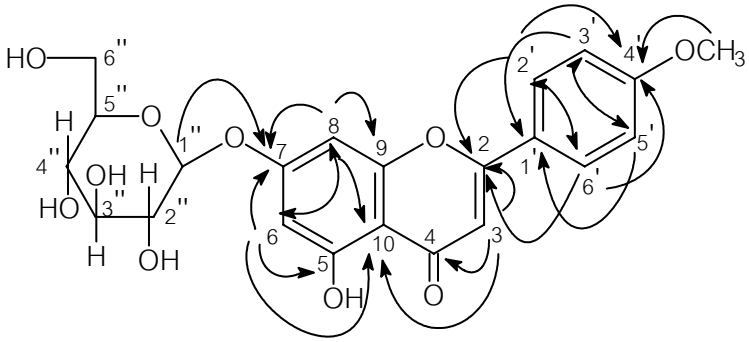


Figure 30. Major HMBC correlations of CLS 3

Table 17. Comparison of the ^{13}C NMR data of tilianin (in DMSO-d_6) (Agrawal, 1989: 318, 321) and compound CLS 3 (in DMSO-d_6)

Carbon	Chemical shift (δ) ppm	
	Literature value	Compound CLS 3
2	162.8	163.2
3	103.6	103.9
4	181.8	182.1
5	162.3	161.2
6	99.4	99.8
7	163.6	164.0
8	94.3	95.1
9	156.8	157.1
10	105.2	105.5
1′	122.5	122.8
2′	128.2	128.5
3′	114.5	114.8
4′	160.9	162.6
5′	114.5	114.8
6′	128.2	128.5
1″	99.8	100.2
2″	73.0	73.3
3″	77.0	76.6
4″	69.5	69.8
5″	76.3	77.3
6″	60.5	60.8

Table 18. ^{1}H and ^{13}C NMR data of tilianin (compound CLS 3)

Position	δ_C	δ_H	HMBC correlations
2	163.2	-	
3	103.9	6.91, *s*	C-2, C-4, C-10
4	182.1	-	
5	161.2	-	
6	99.8	6.45, *br s*	C-5, C-7, C-8, C-10
7	164.0	-	
8	95.1	6.84, *br s*	C-6, C-7, C-9, C-10
9	157.1	-	
10	105.5	-	
1′	122.8	-	
2′	128.5	8.05, *d*, *J* = 8.7 Hz	C-2, C-4′, C-6′
3′	114.8	7.12, *d*, *J* = 8.7 Hz	C-1′, C-5′
4′	162.6	-	
5′	114.8	7.12, *d*, *J* = 8.7 Hz	C-1′, C-3′
6′	128.5	8.05, *d*, *J* = 8.7 Hz	C-2, C-2′, C-4′
4′-OCH_3	55.7	3.86, *s*	C-4′
5-OH	-	12.91, *br s*	
1″	100.2	5.06, *d*, *J* = 7.1 Hz	C-7
2″	73.3	3.26-3.71, *m*	
3″	76.6	3.26-3.71, *m*	
4″	69.8	3.26-3.71, *m*	
5″	77.3	3.26-3.71, *m*	
6″	60.8	3.26-3.71, *m*	

4. Identification of *p*-propenylphenol β-*D*-glucopyranoside (compound CLS 4)

Compound CLS 4, obtained as white amorphous powder from methanol, has a melting point of 169 - 173 °C. The EI-MS of compound CLS 4 exhibited a molecular ion peak at *m/z* 296 (Figure 29), consistent with a molecular formula of $C_{15}H_{20}O_6$. The fragment ion peak at m/z 116 could be attributed to the loss of a sugar moiety ($C_6H_{12}O_6$). Its IR spectrum (Figure 30) exhibited broad absorption band for O-H stretching at 3292 cm^{-1}, also suggested hydroxyl group(s) as part of the structure.

Of the fifteen carbon signals in the ^{13}C-NMR spectrum of CLS 4 (Figure 31), six (δ 60.9, 69.9, 73.4, 76.7, 77.1 and 100.5 ppm) belong to a β-glucopyranosyl unit. DEPT (Figure 32) and ^{1}H-^{13}C HETCOR experiment (Figure 33) were performed to identify these signals as those of two quaternary carbons at δ 131.2 (C-1) and 156.3 ppm (C-4), one methylene carbon at δ 60.9 ppm (C-6′), eleven methine carbons at δ 69.9 (C-4′), 73.4 (C-2′), 76.7 (C-3′), 77.1 (C-5′), 100.5 (C-1′), 116.3 (C-3 and C-5), 123.5 (C-8), 126.6 (C-2 and C-6) and 130.2 ppm (C-7), and one methyl carbon at δ 18.4 ppm (C-9).

The ^{1}H-NMR (Figure 34) and ^{1}H-^{1}H COSY spectrum (Figure 35) of CLS 4 exhibited a doublet signal of one methyl group at δ 1.81 ppm (*d*, *J* = 6.3 Hz, H_3-9)coupled to the more upfield signal of the two *trans* olefinic proton signals at δ 6.34 ppm (*d*, *J* = 15.9 Hz, H-7) and 6.13 ppm (*dq*, *J* = 15.9, 6.3 Hz, H-8). A pair of doublets (*J* = 8.5 Hz) at δ 7.28 and 6.94 ppm, each signal integrated for 2 protons at the position 2,6 and 3,5, respectively, were assignable to the aromatic protons of the para-substituted benzene ring. The β-anomeric proton of a glucose moiety appeared as a doublet at δ 4.81 ppm (*J* = 7.2 Hz, H-1′).

The aglycone of CLS 4 was assigned as the phenolic structure of *p*-anol (*p*-propenylphenol). ^{1}H-^{13}C HMBC experiment (Figure 36a-36b) was performed in order to confirm the whole structure. Correlations could be observed between methyl protons of position 9 at δ 1.81 ppm and C-8 (δ 123.5 ppm) and C-7 (δ 130.2 ppm), while H-8 signal showed two-bond coupling with both C-7 and C-9 (δ 18.1 ppm), and also displayed three-bond correlation with the aromatic C-1 (δ 131.2 ppm). The anomeric proton at δ 4.81 ppm showed long-range coupling with C-4 (δ 156.4 ppm) of the aglycone structure, indicating the site of glycosidic linkage. Major HMBC correlations in the structure of CLS 4 can be summarized as shown in Figure 37.

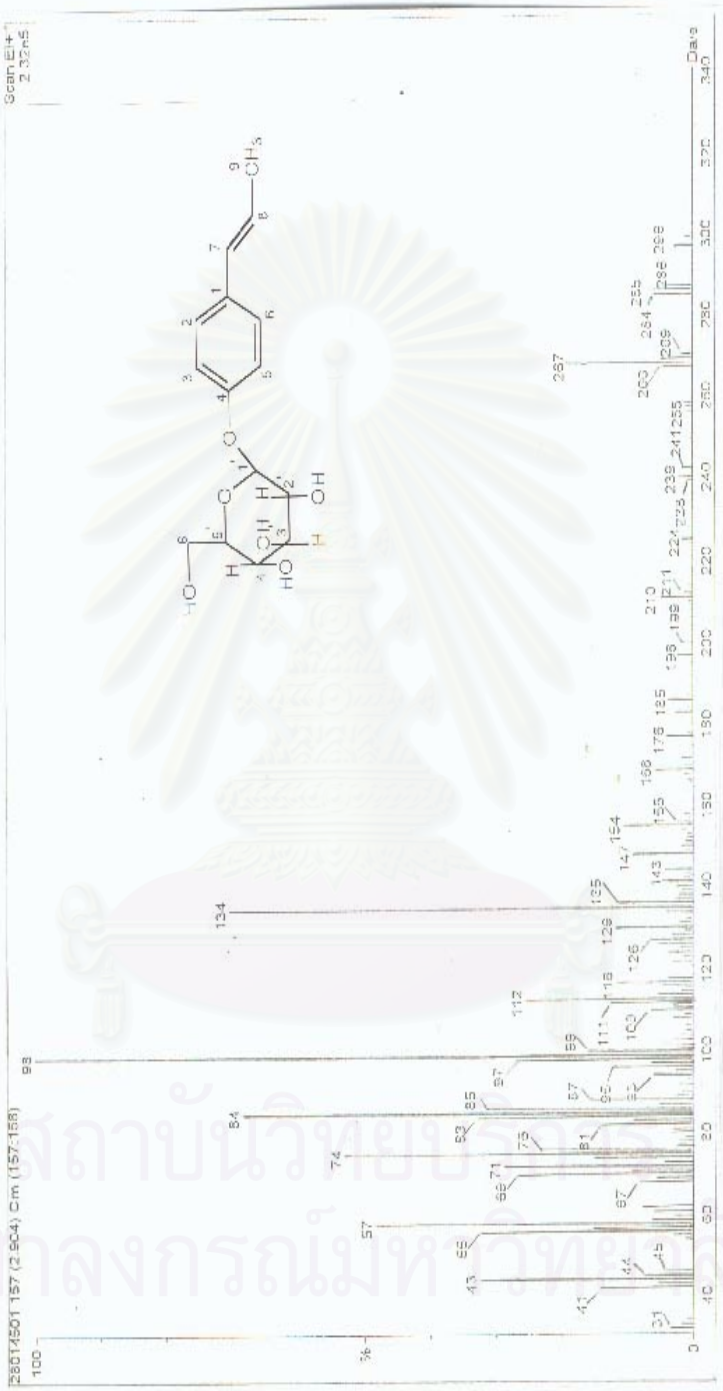


Figure 29. EIMS of compound CLS 4 (in DMSO-d_6)

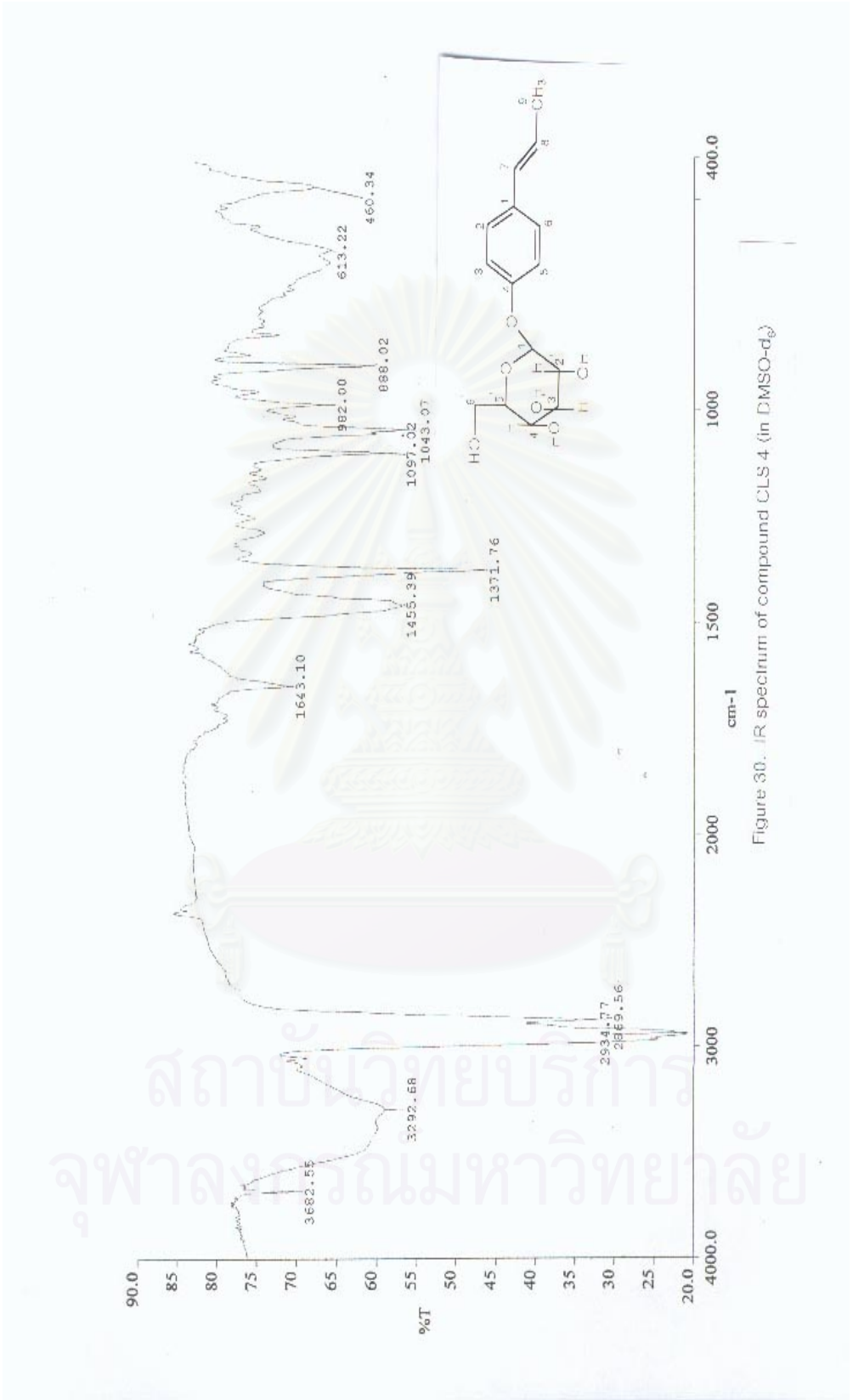


Figure 30. IR spectrum of compound CLS 4 (in DMSO-d_6)

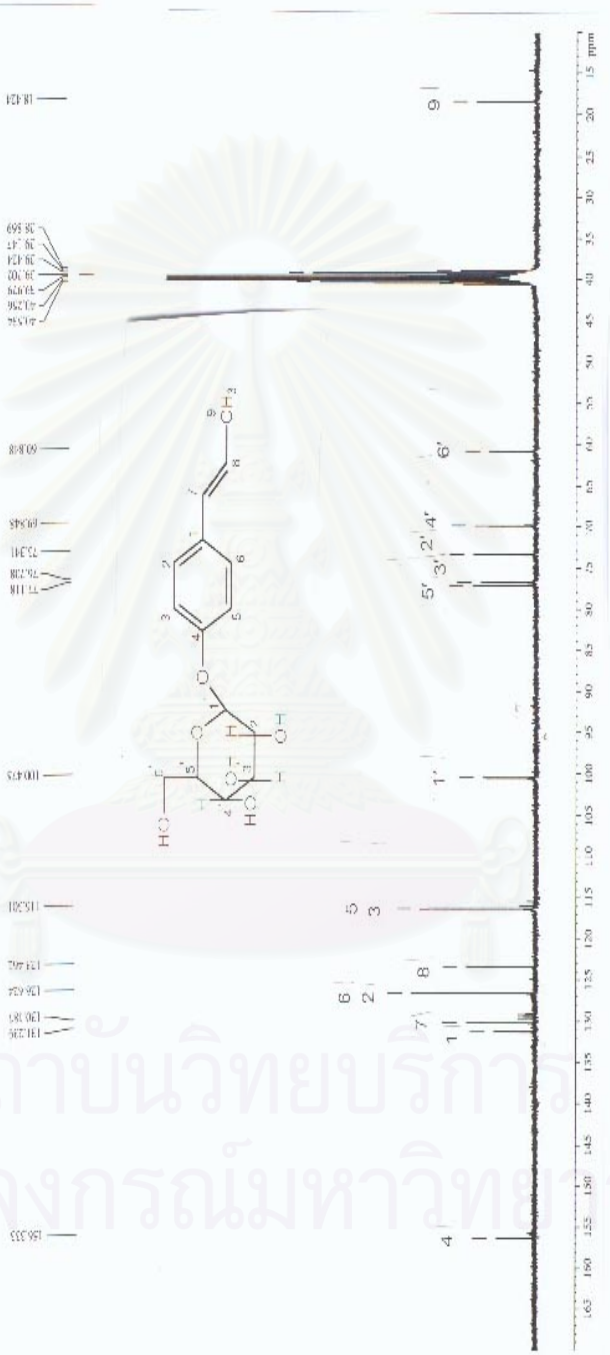


Figure 31. The 75 MHz ^{13}C NMR spectrum of compound CLS 4 (in DMSO-d_6)

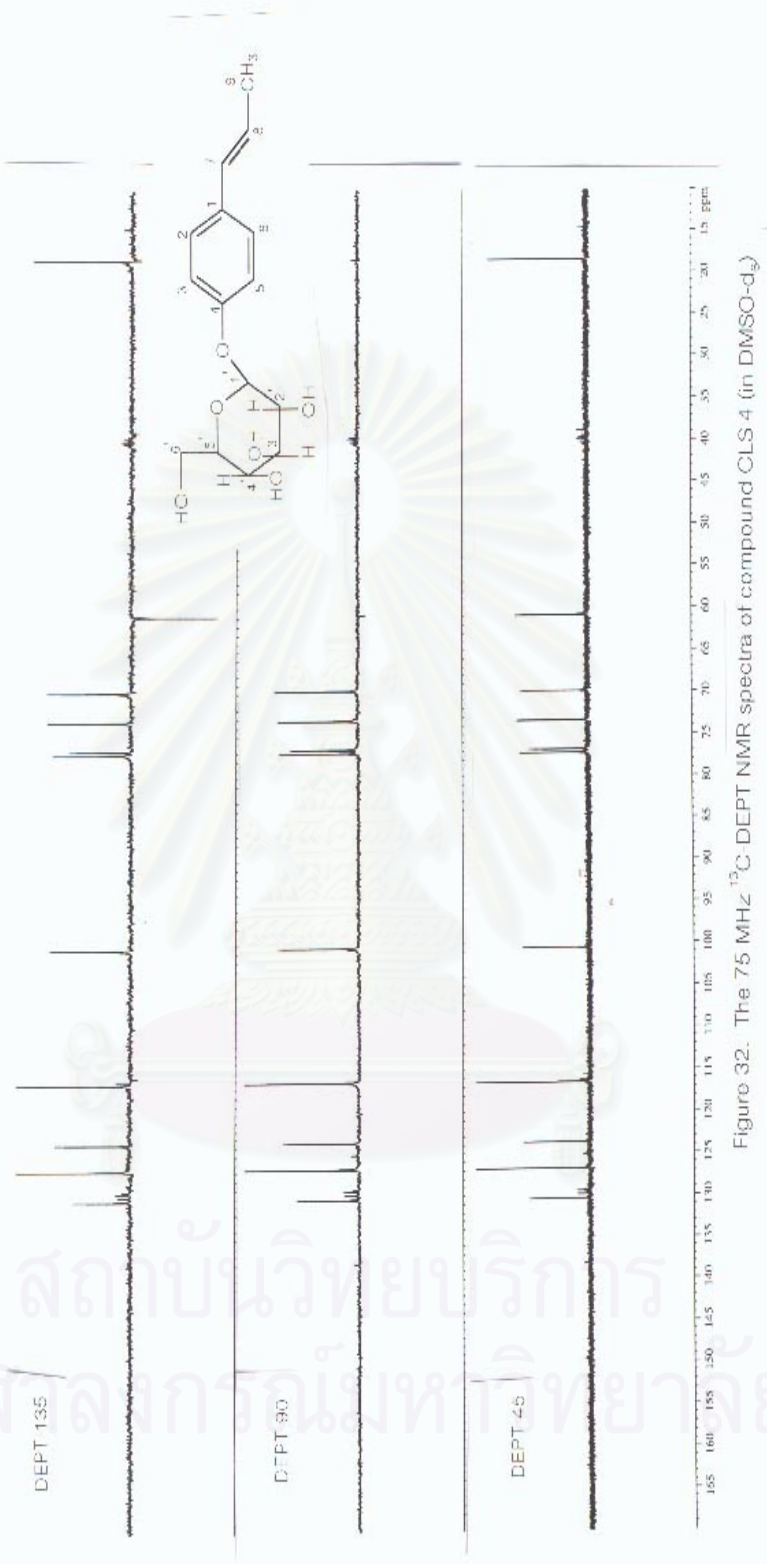


Figure 32. The 75 MHz ^{13}C DEPT NMR spectra of compound CLS 4 (in DMSO-d_6)

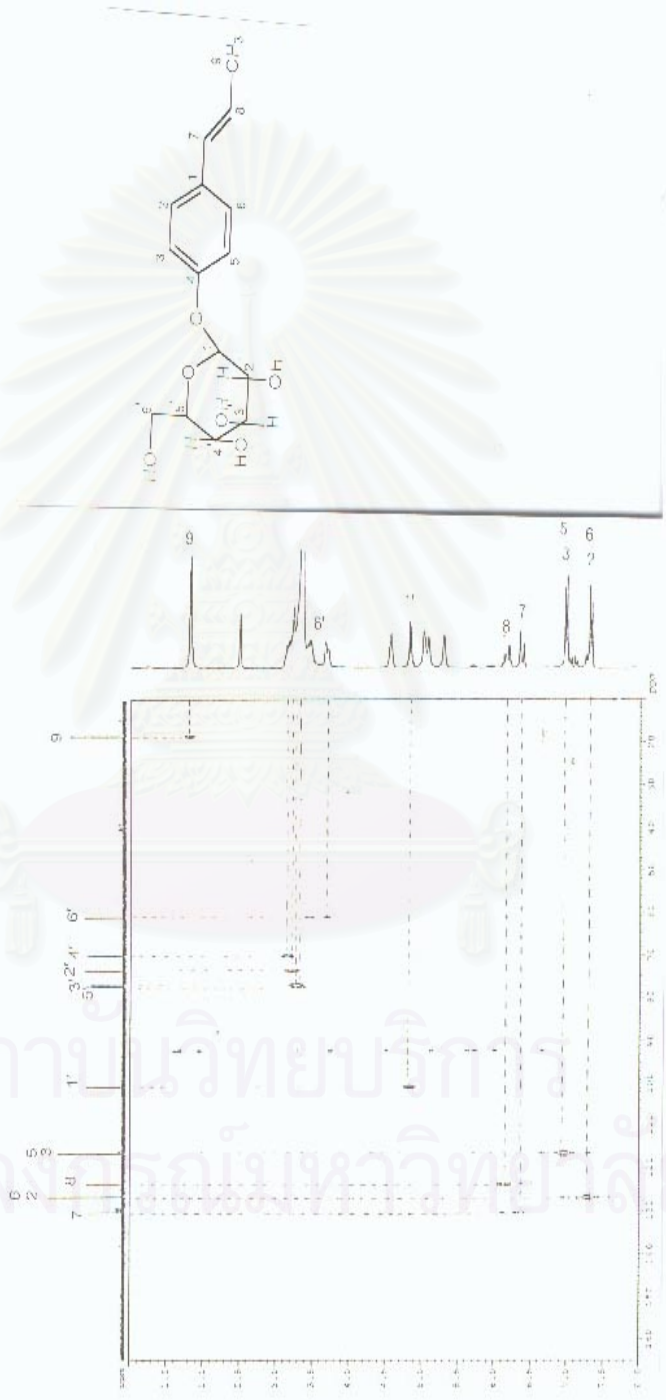


Figure 33. The 300 MHz ^{1}H-^{13}C HETCOR spectrum of compound CLS 4 (in DMSO-d_6)

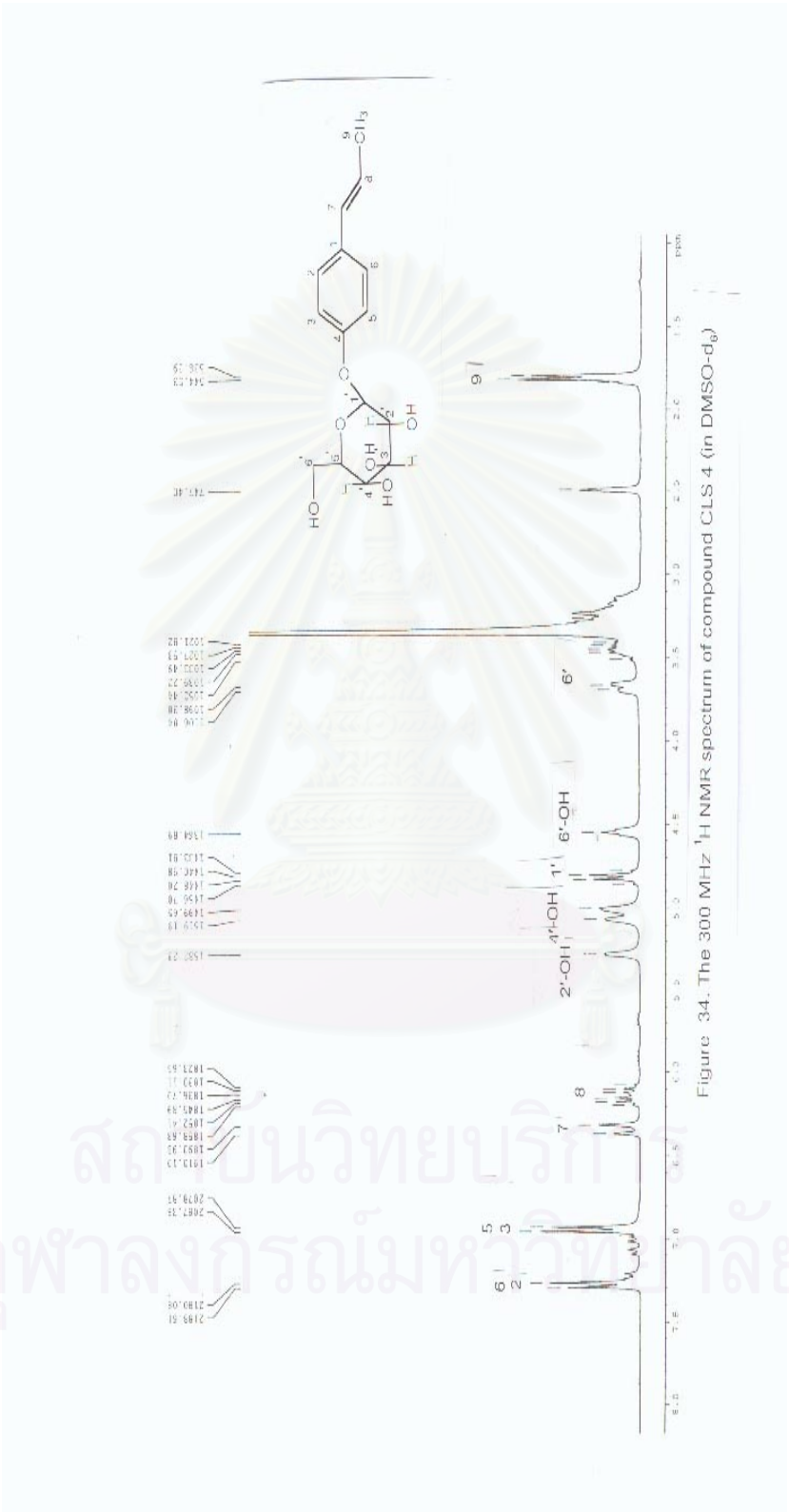


Figure 34. The 300 MHz ^{1}H NMR spectrum of compound CLS 4 (in DMSO-d_6)

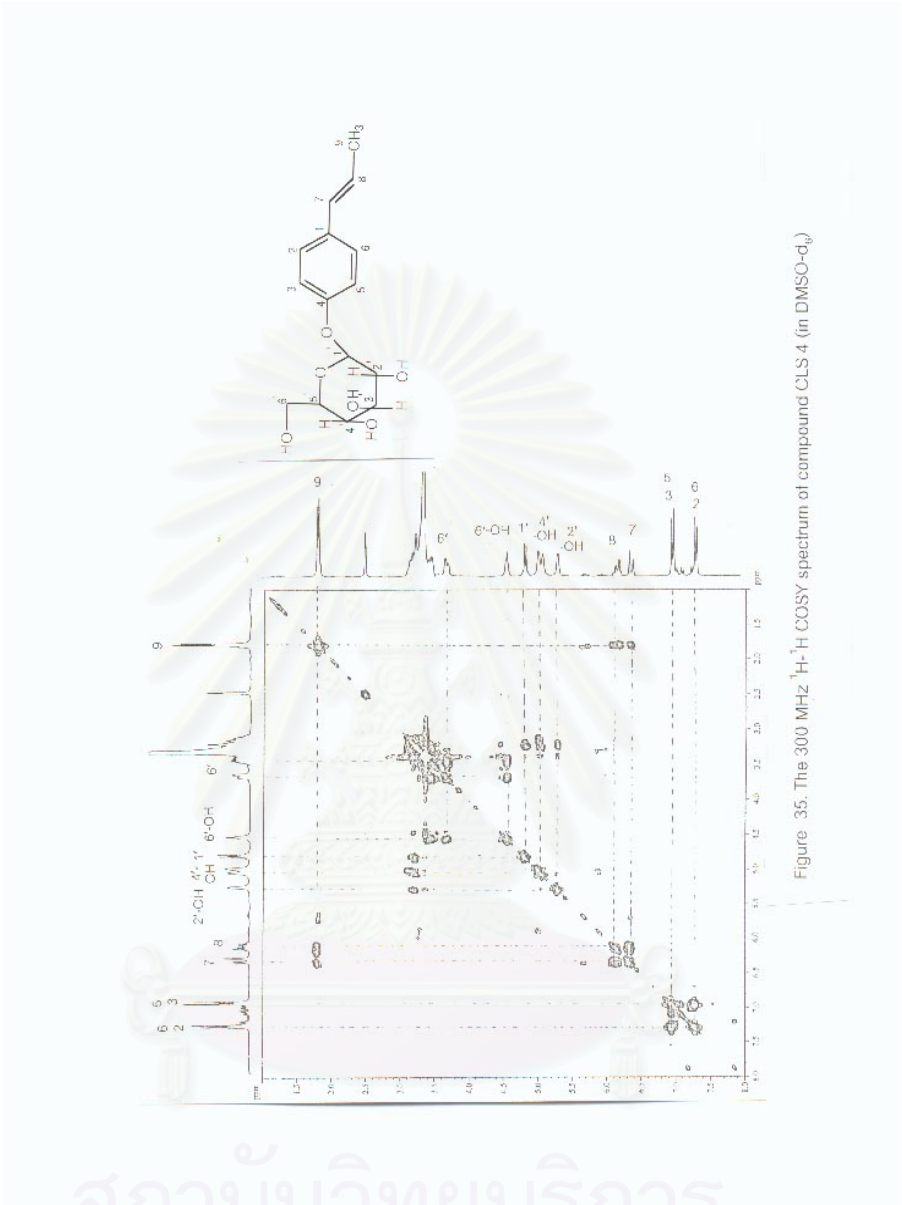


Figure 35 The 300 MHz ^{1}H-^{1}H COSY spectrum of compound CLS 4 (in DMSO-d_6)

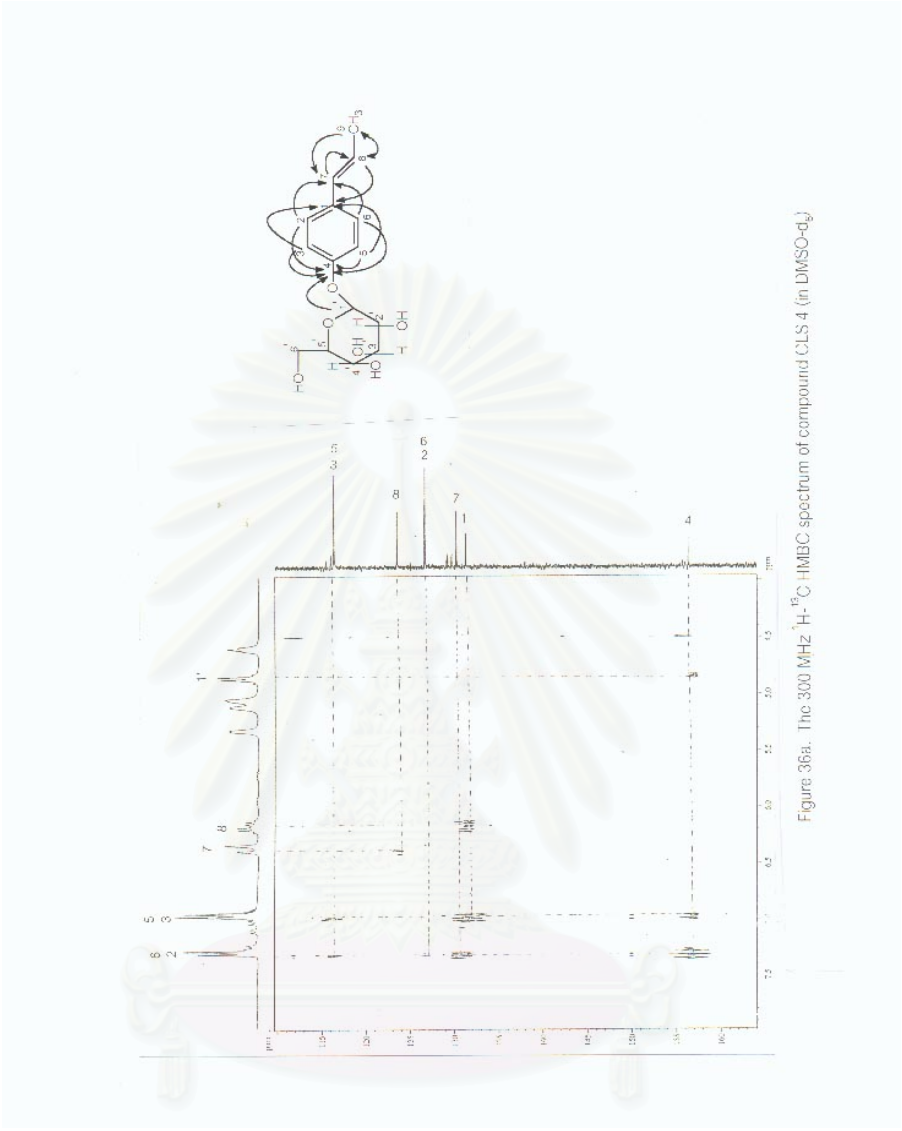


Figure 36a. The 300 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 4 (in DMSO-d_6)

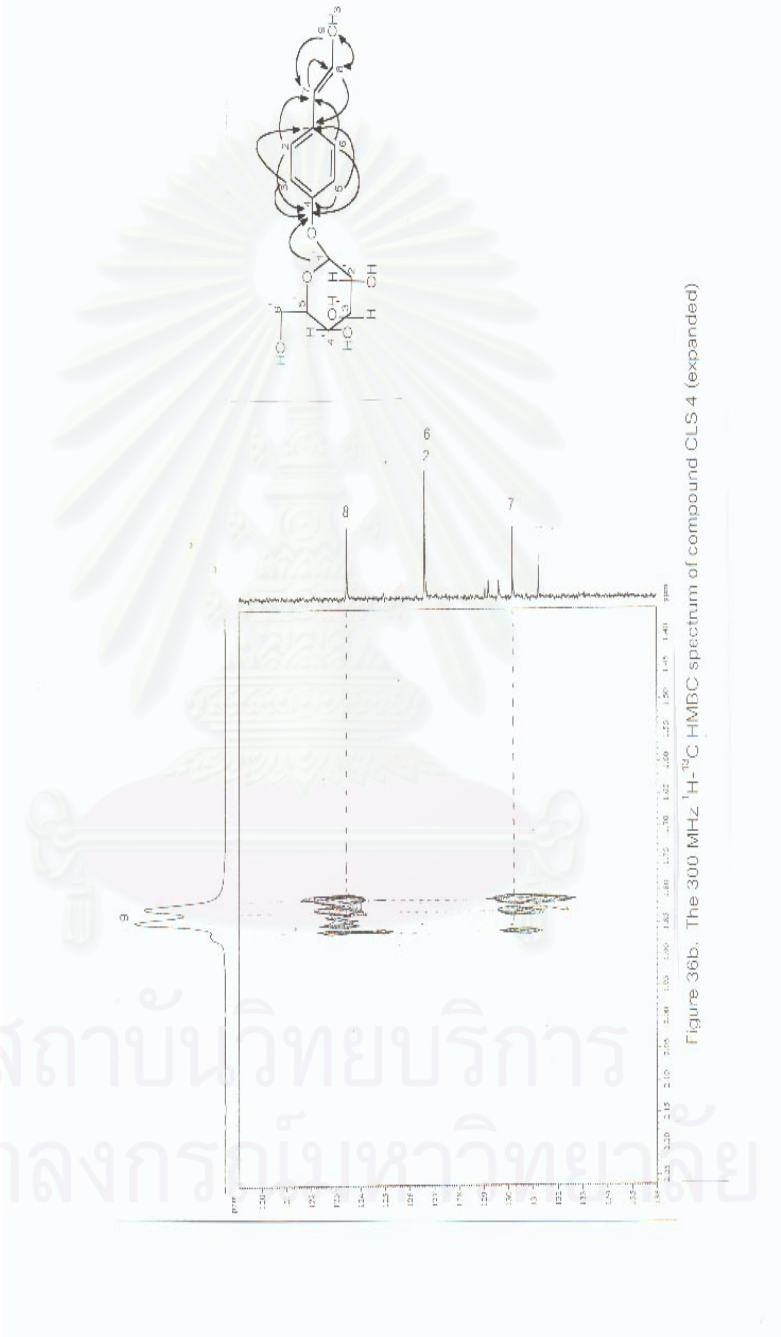


Figure 36b. The 300 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 4 (expanded)

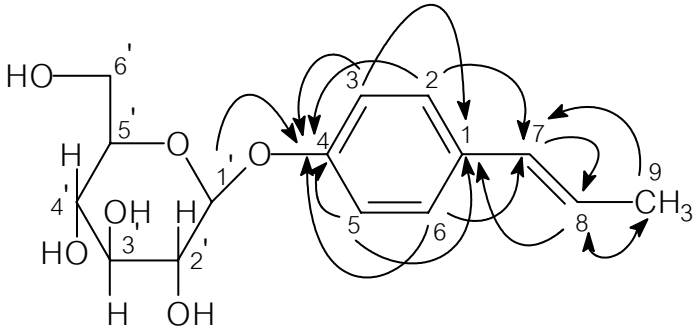
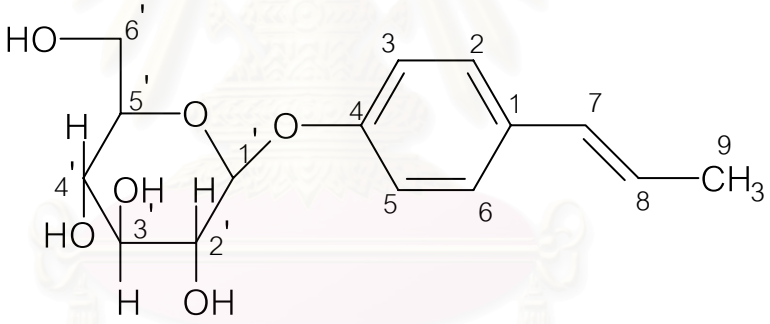


Figure 37. Major HMBC correlations of CLS 4

Therefore, compound CLS 4 was the phenylpropanoid glucoside 4-(1-propenyl)-phenol β -*D*-glucopyranoside (*p*-propenylphenol β-*D*-glucopyranoside). The compound was initially reported as a constituent of the petals of *Lilium cordatum* Thinb. of the family Liliaceae (Nakano *et al*., 1989).



p-Propenylphenol β -*D*-glucopyranoside

Table 19. Comparison of ^{13}C NMR data of *p*-propenylphenol β-*D*-glucopyranoside (in C_5D_5N) (Nakano *et al*., 1989) and compound CLS 4 (in DMSO-d_6)

Carbon	Chemical shift (δ) ppm	
	Literature value	CLS 4
1	132.4	131.2
2	127.3	126.6
3	117.1	116.3
4	157.6	156.3
5	117.1	116.3
6	127.3	126.6
7	130.9	130.2
8	123.7	123.5
9	18.3	18.4
1′	102.2	100.5
2′	74.9	73.4
3′	78.5	76.7
4′	71.4	69.9
5′	78.8	77.1
6′	62.4	60.9

Table 20. ^{1}H and ^{13}C NMR data of *p*-propenylphenol β-*D*-glucopyranoside (compound CLS 4)

Position	δ_C	δ_H	HMBC correlations
1	131.2	-	
2	126.6	7.28, *d*, *J* = 8.5 Hz	C-4, C-7
3	116.3	6.94, *d*, *J* = 8.5 Hz	C-1, C-4
4	156.3	-	-
5	116.3	6.94, *d*, *J* = 8.5 Hz	C-1, C-4
6	126.6	7.28, *d*, *J* = 8.5 Hz	C-4, C-7
7	130.2	6.34, *d*, *J* = 15.9 Hz	C-8
8	123.5	6.13, *dq*, *J* = 15.9, 6.3 Hz	C-1, C-9
9	18.4	1.81, *d*, *J* = 6.3 Hz	C-7, C-8
1′	100.5	4.81, *d*, *J* = 7.2 Hz	C-4
2′	73.4	3.15-3.30, *m*	
3′	76.7	3.15-3.30, *m*	
4′	69.9	3.15-3.30, *m*	
5′	77.1	3.15-3.30, *m*	
6′	60.9	3.69, *dd*, *J* = 11.6, 3.9 Hz	
		3.44, *dd*, *J* = 11.6, 5.7 Hz	

5. Identification of diosmetin-7-*O*-β-*D*-glucopyranoside (compound CLS 5)

Compound CLS 5 was crystallized as yellow powder from chloroform. EI mass spectrum (Figure 38) gave molecular ion peak at *m/z* 462, corresponding to the molecular formula $C_{22}H_{22}O_{11}$, and fragment ion peak at *m/z* 431, 429, 283 and 267 resulted from the losses of one methoxyl, two hydroxyls, one sugar and one sugar plus one hydroxyl, respectively.

The IR spectrum (Figure 39) revealed prominent absorption bands at 3413 and 1638 cm^{-1}, suggesting the presence of hydroxyl group(s) and chelated carbonyl, respectively, whereas the UV absorption maxima at 252 and 342 nm suggested a flavone structure (Figure 40).

The ^{1}H NMR spectrum of CLS 5 (Figure 41) displayed a characteristic one proton singlet at δ 6.83 ppm for H-3 of a flavone nucleus and a typical meta-coupled pattern for the A-ring (H-6, δ 6.44 ppm, *br s* and H-8, δ 6.81 ppm, *br s*). The downfield ^{1}H signal at δ 12.94 ppm suggested a carbonyl-chelated hydroxyl group at C-5. The B-ring showed a sharp singlet integrated for three protons at δ 3.70 ppm of methoxyl group substituted at C-4′. A doublet at δ 7.10 ppm (H-5′) ortho-coupled (*J* = 8.4 Hz) to another broad doublet at δ 7.57 ppm (H-6′), together with a broad singlet at δ 7.45 ppm (H-2′), demonstrated the substitution pattern of this aromatic ring as 3′-4′-disubstituted, with a hydroxy group at position 3′. The anomeric proton appeared at δ 5.07 ppm (*d*, *J* = 6.7 Hz), suggesting a β - glucosidic linkage, while the more upfield proton from δ 3.17 to 3.45 ppm were those of the sugar protons.

The ^{13}C NMR (Figure 42) DEPT (Figure 43) and HMQC spectra (Figure 44) showed 22 signals belonging to one methyl, one methylene, 11 methine, and 9 quaternary carbons. Most carbon chemical shifts of CLS 5 are similar to those of compound CLS 3 except for the B-ring part. The carbon NMR data for its flavonoid aglycone are also in accordance with the flavone diosmetin (Agrawal, 1989). Slight differences in the vicinity of position 7 proved that a glucosyl moiety was attached to that position.

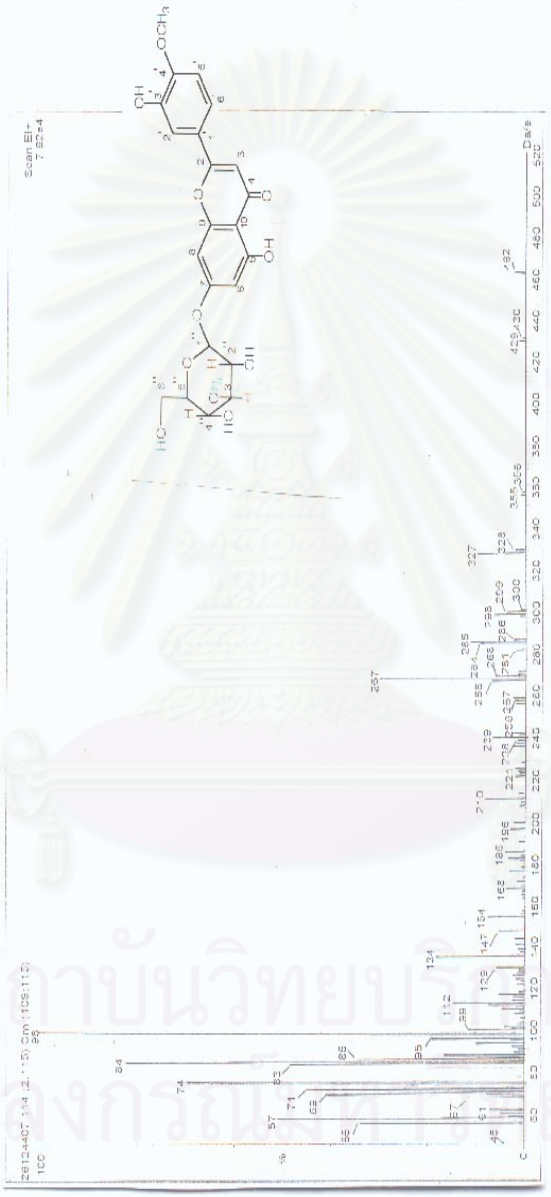


Figure 38. EIMS of compound CLS 5

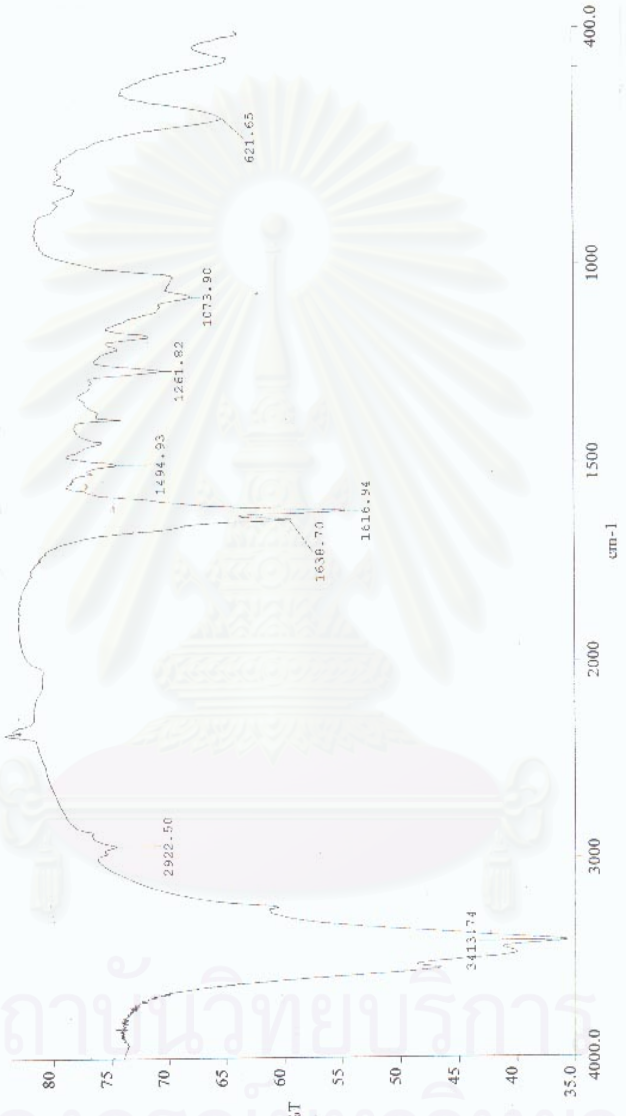


Figure 39. IR spectrum of compound CLS-5

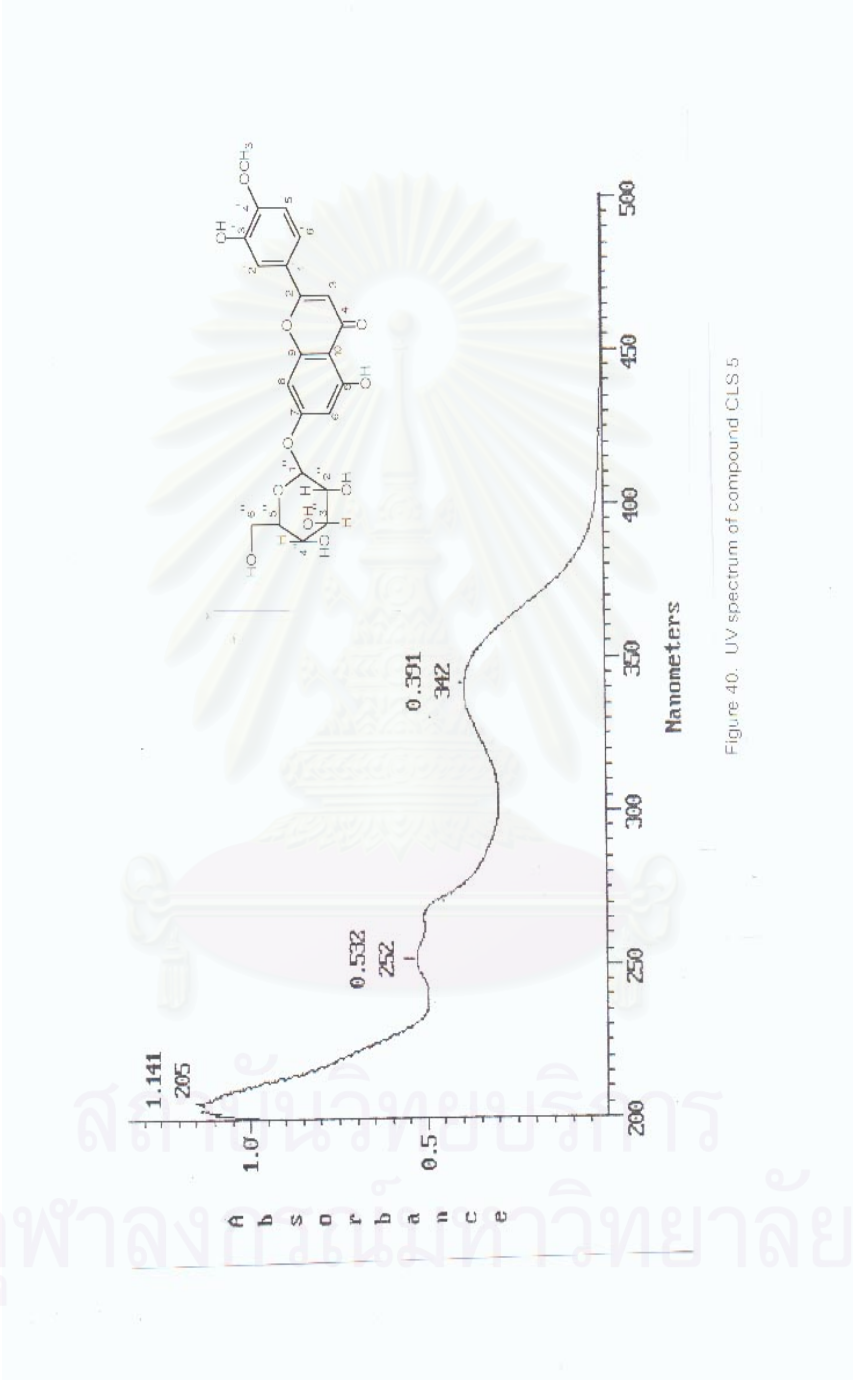


Figure 40. UV spectrum of compound CLS 5

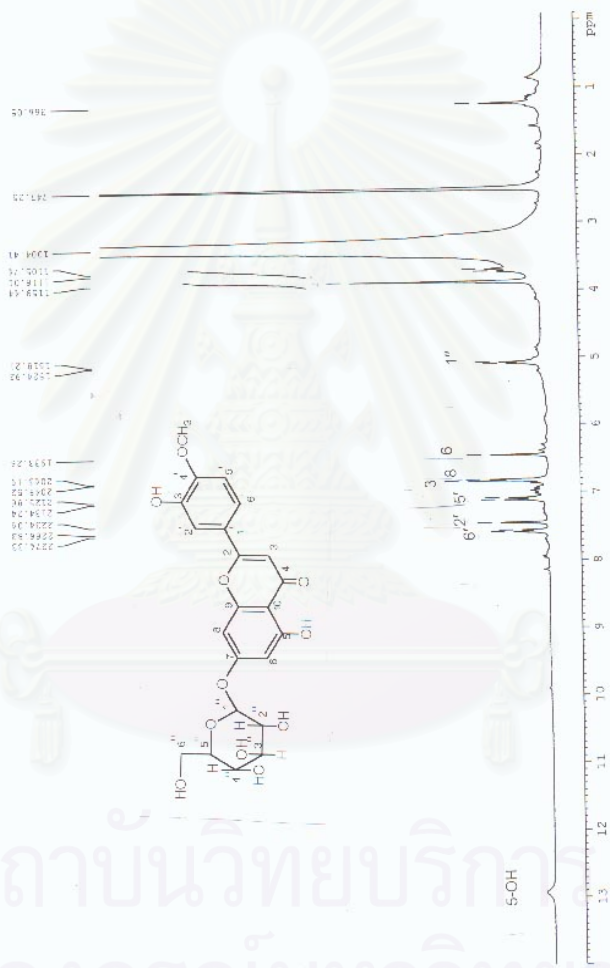


Figure 41. The 300 MHz ^{1}H NMR spectrum of compound CLS 5 (in DMSO-d_6)

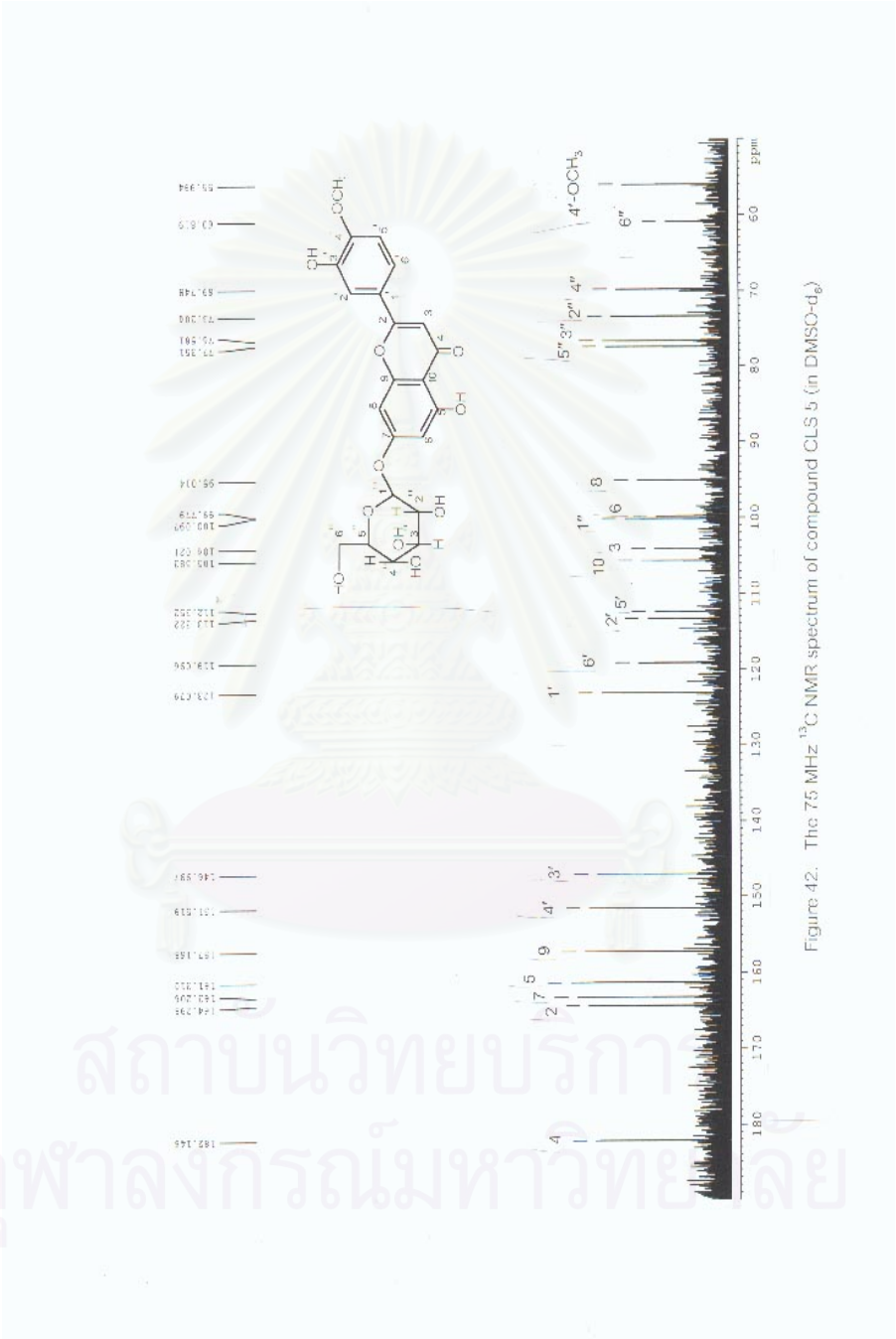


Figure 42. The 75 MHz ^{13}C NMR spectrum of compound CLS 5 (in DMSO-d_6)

Figure 43. The 75 MHz ^{13}C DEPT NMR spectra of compound CLS-5 (in DMSO-d_6)

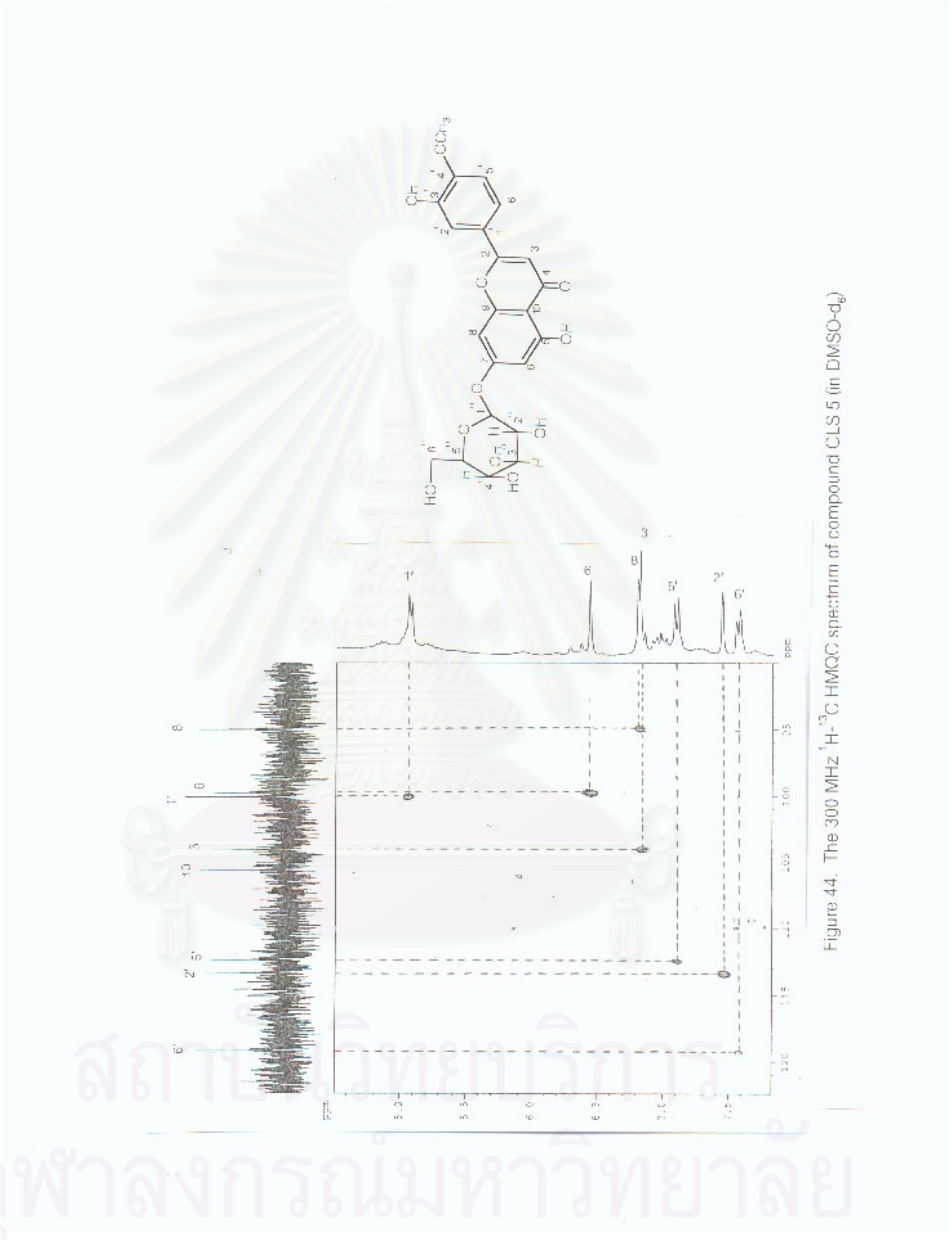
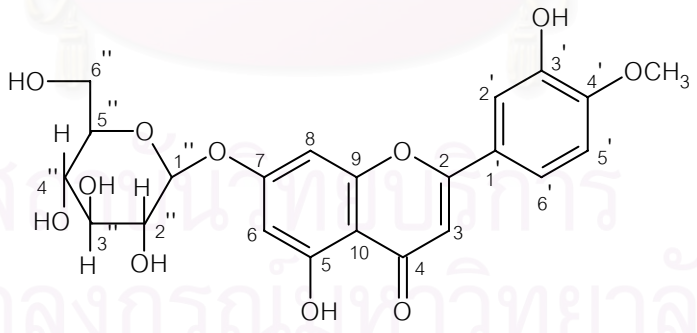


Figure 44. The 300 MHz ^{1}H-^{13}C HMQC spectrum of compound CLS 5 (in DMSO-d_6)

The HMBC spectrum (Figure 45a-45b) confirmed the placement of methoxyl group at position 4′ and a glucose unit at position 7. The experiment also showed cross peaks between H-3 (δ 6.83 ppm) and C-2 (δ 163.2 ppm) and C-4 (δ 182.2 ppm), whereas H-6 (δ 6.44 ppm) showed long-range coupling with C-5 (δ 161.3 ppm), C-7 (δ 164.3 ppm), C-8 (δ 95.1 ppm) and C-10 (δ 105.6 ppm). Similarly, H-8 signal (δ 6.81 ppm) displayed correlated peaks with C-6 (δ 99.8 ppm), C-7, C-9 (δ 157.2 ppm) and C-10. For The B-ring, the proton signal of H-2′ (δ 7.45 ppm) showed cross peaks with C-2 (δ 164.3 ppm), C-3′ (δ 147.0 ppm) and C-6′ (δ 119.1 ppm), respectively. The proton signals at δ 7.10 ppm (H-5′) was correlated with both C-3′ and C-4′ (δ 55.8 ppm), whereas H-6′ signal (δ 7.57 ppm) correlated with C-2, C-2′ (δ 113.3 ppm) and C-4′, therefore confirming the substitution pattern of this ring. Major HMBC correlations in the structure of compound CLS 5 can be summarized as shown in Figure 46.

Compound CLS 5 was thus identified as the flavone glycoside diosmetin-7-*O*-β-*D*-glucopyranoside. Anton and Duquenois (1968) have isolated and elucidated the structure of this compound from the leaves of *Cassia marilandica* (Family Leguminosae). However, this is the first report of the occurrence of this compound in the family Euphorbiaceae.



Diosmetin-7-*O*-β-*D*-glucopyranoside

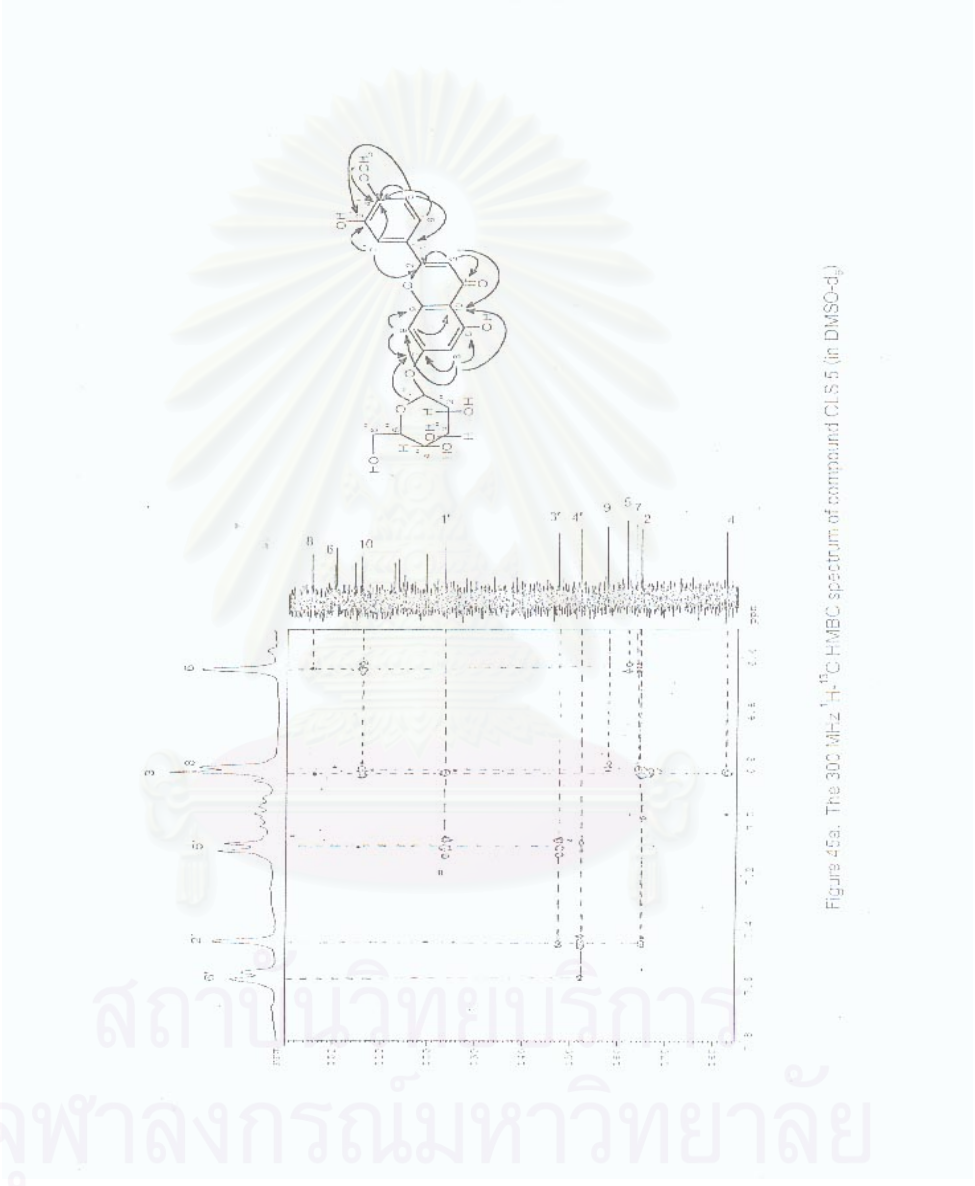


Figure 45a. The 300 MHz ^{1}H-^{13}C HMBC spectrum of compound CLS 5 (in DMSO-d_6)

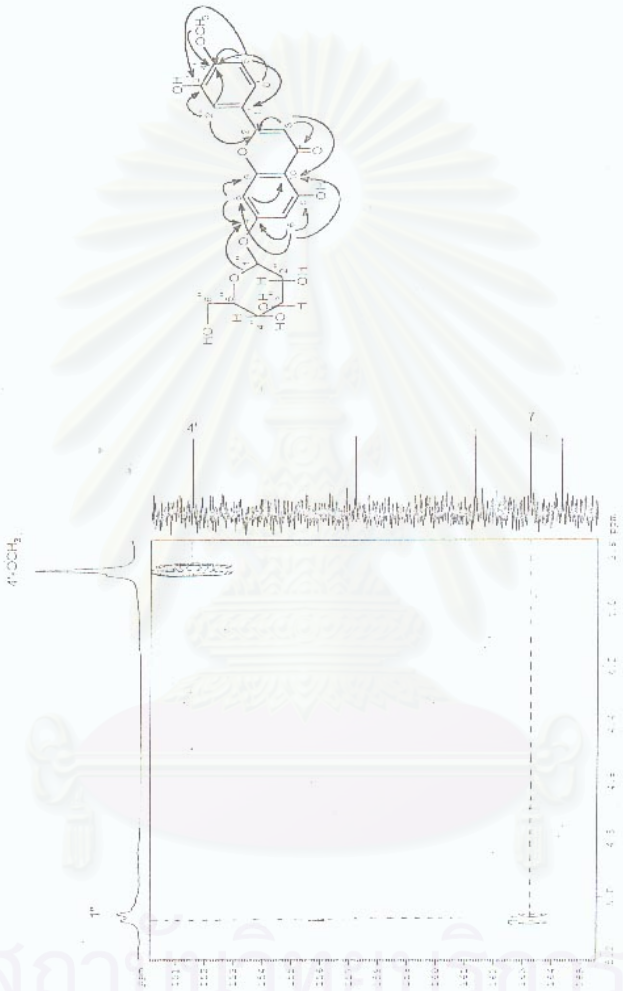


Figure 45a. The 300 MHz ^{1}H- ^{13}C HMBC spectrum of compound CLS 6 (expanded)

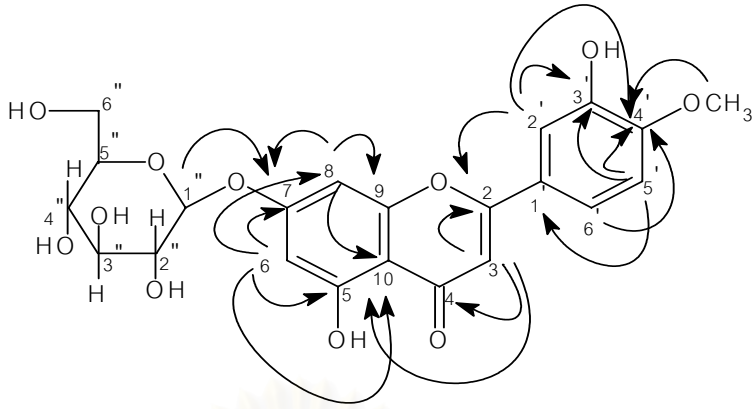


Figure 46. Major HMBC correlations of CLS 5

Table 21. ^{1}H and ^{13}C NMR data of diosmetin-7-*O*-β-*D*-glucopyranoside (compound CLS 5)

Position	δ_C	δ_H	HMBC correlations
2	164.3	-	
3	104.0	6.83, *s*	C-2, C-4, C-10
4	182.2	-	
5	161.3	-	
6	99.8	6.44, *br s*	C-5, C-7, C-8, C-10
7	163.2	-	
8	95.0	6.81, *br s*	C-7, C-9, C-10
9	157.2	-	
10	105.6	-	
1′	123.1	-	
2′	113.3	7.45, *br s*	C-2, C-3′, C-4′
3′	147.0	-	
4′	151.5	-	
5′	112.4	7.10, *d*, *J* = 8.4 Hz	C-1′, C-3′, C-4′
6′	119.1	7.57, *br d*, *J* = 8.4 Hz	C-4′
4′ - OCH_3	56.0	3.87, *s*	C-4′
5-OH		12.94, *br s*	
1″	100.1	5.07, *d*, *J* = 6.7 Hz	C-7
2″	73.3	3.17-3.70, *m*	
3″	76.6	3.17-3.70, *m*	
4″	69.8	3.17-3.70, *m*	
5″	77.4	3.17-3.70, *m*	
6″	60.8	3.17-3.70, *m*	

CHAPTER V

CONCLUSION

Five compounds were isolated from the leaves of *Cleidion spiciflorum* (Burm. f.) Merr. by chromatographic techniques. From the hexane extract, a linear diterpene, *trans*-phytol, was isolated. Two flavone glycosides, acacetin-7-*O*-β-*D*-glucopyranoside (tilianin) and diosmetin-7-*O*-β-*D*-glucopyranoside, and a phenylpropanoid glycoside, *p*-propenylphenol-β-*D*-glucopyranoside were isolated from the chloroform extract. The lanostane triterpene, (24*S*)-24-methyl-5α-lanosta-9(11),25-dien-3β-ol was isolated from both hexane and chloroform extract . This is the first report of chemical constituents of this plant genus.

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