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FREE RADICAL SCAVENGERS FROM *DENDROBIUM DRACONIS*

Miss Mutita Anuwat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Pharmacy Program in Pharmacognosy
Department of Pharmacognosy and Pharmaceutical Botany
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Thesis Title	FREE RADICAL SCAVENGERS FROM *DENDROBIUM DRACONIS*
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มุทิตา อนุวัฒน์ : สารต้านอนุมูลอิสระจากเอื้องเงิน. (FREE RADICAL SCAVENGERS FROM *DENDROBIUM DRACONIS*) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร. บุญชู ศรีตุลารักษ์,อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ศ.ดร. กิตติ ศักดิ์ ลิขิตวิทยาวุฒิ, 126 หน้า.

การศึกษาทางพฤกษเคมีของเอื้องเงิน สามารถแยกสารใหม่ในกลุ่ม Phenanthrene-quinone ได้ 1 ชนิดคือ 5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrene-quinone และสารที่เคยมีรายงานแล้ว 5 ชนิด ได้แก่ hircinol, gigantol, batatasin III, 4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol และ tristin การพิสูจน์โครงสร้างทางเคมีของสารที่แยกได้นี้อาศัยการวิเคราะห์สเปกตรัมของ MS, IR, UV และ NMR ร่วมกับการเปรียบเทียบข้อมูลของสารที่มีรายงานมาแล้ว และได้ทดสอบฤทธิ์ในการจับอนุมูลอิสระของสารที่แยกได้ พบว่า 4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol มีฤทธิ์ในการจับสารอนุมูลอิสระ DPPH ใกล้เคียงกับ Trolox® แต่ไม่มีสารชนิดใดที่มีฤทธิ์ดีในการจับสารอนุมูลอิสระ superoxide

ภาควิชา.เภสัชเวทและเภสัชพฤกษศาสตร์.. ลายมือชื่อนิสิต.....มุทิตา.....อนุวัฒน์.....

สาขาวิชา.....เภสัชเวท..... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....

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Phytochemical study of *Dendrobium draconis* Rchb.f. led to the isolation of a new phenanthrenequinone, namely 5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone, as well as five known compounds including hircinol, gigantol, batatasin III, 4-methoxy-9,10-dihydrophenanthrene -2,5,7-triol and tristin. The identification and structure determination of the isolated compounds were achieved by analysis of their spectroscopic data (MS, IR, UV, NMR) in comparison with previously reported data. Most of the isolated compounds showed appreciable activity against DPPH radical but weak activity against superoxide radical. 4-Methoxy-9,10-dihydrophenanthrene-2,5,7-triol, however, showed DPPH radical scavenging activity comparable to that of Trolox®

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LIST OF SCHEMES

ABBREVIATIONS

α	=	Alpha
Acetone-d_6	=	Deuterated acetone
β	=	Beta
br	=	Broad (for NMR spectra)
C	=	Concentration
ºC	=	Degree Celsius
$CDCl_3$	=	Deuterated chloroform
CH_2Cl_2	=	Dichloromethane
^{13}C NMR	=	Carbon-13 Nuclear Magnetic Resonance
cm	=	Centimeter
1-D	=	One dimensional (for NMR spectra)
2-D	=	Two dimensional (for NMR spectra)
d	=	Doublet (for NMR spectra)
dd	=	Doublet of doublets (for NMR spectra)
DEPT	=	Distortionless Enhancement by Polarization Transfer
δ	=	Chemical shift
ESIMS	=	Electrospray Ionization Mass Spectrrmetry
EtOAc	=	Ethyl acetate
FCC	=	Flash Column Chromatography
g	=	Gram
GF	=	Gel Filtration Chromatography
^1H-NMR	=	Proton Nuclear Magnetic Resonance
HMBC	=	^1H-detected Heteronuclear Multiple Bond Correlation
HSQC	=	^1H-detected Heteronuclear Multiple Quantum Coherence
Hz	=	Hertz
IR	=	Infrared
IC_{50}	=	Concentration showing 50% inhibition
J	=	Coupling constant
Kg	=	Kilogram
L	=	Liter
μl	=	microliter

λ_{max}	=	Wavelength at maximal absorption
ε	=	Molar absorptivity
M^+	=	Molecular ion
m	=	Multiplet (for NMR spectra)
MeOH	=	Methanol
mg	=	Milligram
μg	=	Microgram
MHz	=	Mega Hertz
ml	=	Milliliter
mm	=	Millimeter
m/z	=	Mass to charge ratio
MS	=	Mass spectrum
MW	=	Molecular weight
nm	=	Nanometer
NBT	=	Nitroblue tetrazolium
NMR	=	Nuclear Magnetic Resonance
ppm	=	Part per million
s	=	Singlet (for NMR spectra)
spp.	=	Species
t	=	Triplet (for NMR spectra)
TLC	=	Thin Layer Chromatography
UV-VIS	=	Ultraviolet and Visible spectrophotometry
VLC	=	Vacuum Liquid Column Chromatography
υ_{max}	=	Wave number at maximal absorption

CHAPTER I

INTRODUCTION

Plants of genus *Dendrobium* are members of Orchidaceae family. Their botanical characters have been described by Holttum as follows (Holttum, 1957).

Plants nearly all epiphytic, of sympodium growth, each branch of the sympodium bearing one or more leaves, its stem thin, or fleshy throughout, or fleshy in part only; leaves of various shape, jointed at the base; influorescences usually lateral, of one or many flowers, which sometimes appear singly in succession from a small group of bracts; lateral sepals more or less triangular in shape, their bases jointed to the column-foot, forming a mentum; petals either smaller or larger than the sepals, usually thinner; lip more or less 3-lobed (often only slightly), the base often long and narrow, jointed to the end of the column-foot (Thus forming a closed spur), often with the longitudinal keels but rarely with calli; column with the distinct foot which is often long, the column itself short, with two small lateral horns or arms which in rare cases develop into additional anthers; anther usually attached at its apex by a filament; pollinia 4 in two pairs, or 8 in two groups of four, without or with short caudicles; rostellum small.

The species of *Dendrobium* in Thailand according to Smitinand (2001) are as follows.

Dendrobium acerosum Lindl.	กล้วยไม้มือนาง Kluai mai mue nang (Chumphon); เขาแพะ Khao phae (Chanthaburi).
D. acinaciforme Roxb.	เอื้องตะขาบ Ueng ta khap, เอื้องยอดสร้อย Ueang yot soi (Northern).
D. albosanguineum Lindl.	เอื้องตางัว Ueang ta ngua (Mae Hong Son); เอื้องตึง Ueang tueng (Tak); เอื้องผาเวียง Ueang pha wiang (Bangkok).
D. aloifolium (Blume) Rchb.f.	เอื้องช้าง Ueang chang (Trat); เอื้องมณี Ueang mani (Bangkok).

D. anosmum Lindl.	เอื้องสาย Ueang sai, เอื้องสายหลวง Ueang sai luang (Chiang Mai, Peninsular).
D. aphrodite Rchb.f.	= *D. albosanguineum* Lindl.
D. aphyllum (Roxb.) C.E.C.Fisch.	พอทุกิ Pho-thu-ki (Karen-Mae Hong Son); มอกคำเครือ Mok-kham-khruea (Shan-Mae Hong Son); เอื้องไข่เน่า Ueang khai nao, เอื้องสายไม้ Ueang sai mai (Lampang); เอื้องงวงช้าง Ueang nguang chang (Mae Hong Son); เอื้องย้อยไม้ Ueang yoi mai (Northern); เอื้องล่องแล่ง (Chiang Mai).
D. bambusifolium Parish & Rchb.f.	= *D. salaccense* (Blume) Lindl.
D. bellatulum Rolfe	เอื้องแซะภู Ueang sae phu, เอื้องแซะดอยปุย Ueang sae doi pui (Chiang Mai).
D. bicameratum Lindl.	เอื้องเข็ม Ueang khem (Northern).
D. bilobulatum Seidenf.	กล้วยไม้ก้างปลา Kluai mai kang pla (General).
D. binoculare Rchb.f.	พอนี้โคะโพ Pho-ni-kho-pho, พอผู่ปรึย Pho-phu-prue-ya (Karen-Mae Hong Son); เอื้องคำสาย Ueang kham sai, เอื้องจำปา Ueang champa (Northern).
D. brymerianum Rchb.f.	เอื้องคำฝอย Ueang kham foi, เอื้องคำฝอย
D. calceolaria Carey ex Hook.	= *D. moschatum* (Buch.-Ham) Sw.
D. capilipes Rchb.f.	เอื้องคำกิ่ว Ueang kham kio (Lampang, Phrae); เอื้องคำป๊อก Ueang kham pok, เอื้องคำเอี่ย Ueang kham hia (Chiang Mai); เอื้องมิ้น Ueang min (Northern).
D. cariniferum Rchb.f.	พอมือคาพะโด่ Pho-mue-kha-pha-do (Karen-Mae Hong Son);

	เอื้องกาจก Ueang kachok, เอื้องแซะเหลือง Ueang sae lueang Chiang Mai); เอื้องแซะดง Ueang sae dong (Chiang Mai, Mae Hong Son); เอื้องตึง Ueang tueng (Lampang).
D. christyanum Rchb.f.	เอื้องแซะภูกระดึง Ueang sae phu kradueng (Loei).
D. chrysanthum Lindl.	เอื้องสายมรกต Ueang sai morakot (Bangkok).
D. chrysotoxum Lindl.	พอนี้โคะ Pho-ni-kho (Karen-Mae Hong Son); เอื้องคำ Ueang kham (Northern); เอื้องคำตา Ueang kham ta (Chiang Mai).
D. ciliatum Parish ex Hook.f.	= *D. venustum* Teijsm & Binn.
D. ciliferum Bakh.f	= *D. venustum* Teijsm & Binn.
D. coelogyne Rchb.f. Summerh.	= *Epigeneium amplum* (Lindl.)
D. compactum Rolfe ex W. Hackett	เอื้องข้าวตอก Ueang khao tok (Northern).
D. concinnum Miq.	หางเปีย Hang pia (Narathiwat).
D. crassinode Benson & Rchb.f.	= *D. pendulum* Roxb.
D. crepidatum Lindl. & Paxton	เอื้องสายน้ำขียว Ueang sai nam khiao (Genaral).
D. crocatum Hook.f.	เอื้องนางนวล Ueang nang nuan (Peninsular).
D. cruentum Rchb.f.	ปากนกแก้ว Pak nok kaeo, เอื้องนกแก้ว Ueang mok kaeo (Bangkok).
D. crumenatum Sw.	นกกะยาง Nok kayang (Chon Buri); บวบกลางหาว Buap klang hao (Chiang Mai); แส้พระอินทร์ Sae phra in (Chanthaburi,

	Trat); หวายตะมอย Wai tamoi; เอื้องมาลี Ueang mali (Central, Peninsular); Pi geon orchid.
D. crystallinum Rchb.f.	เอื้องนางฟ่อน Ueang nang fon, เอื้องนิ้วมือพระนารายณ์ Ueang nio phra narai (Chiang Mai); เอื้องสายสามสี Ueang sai sam si (Bangkok).
D. cumulatum Lindl.	เทียนทอง Thian thong, เทียนพญาอินทร์ Thian phaya in, เอื้องสายสี่ดอก Ueang sai si dok (Northern, Southeastern).
D. dalhousieanum Wall.	= *D. pulchellum* Roxb. Ex Lindl.
D. dantaniense Guillaumin	เอื้องเข็ม Ueang khem (Chiang Mai).
D. delacourii Guillaumin	= *D. venustum* Teijsm & Binn.
D. densiflorum Lindl.	เอื้องมอนไข่ Ueang monkKhai; เอื้องมอนไข่เหลี่ยม Ueang mon khai liam; เอื้องมอนไข่เหลือง Ueang mon khai lueang (Northern); เอื้องมอนคำ Ueang monk ham (Chiang Mai).
D. devonianum Paxton	เอื้องเมี่ยง Ueang miang, เอื้องสายผ้าก้ัง Ueang sai pha kang, เอื้องสายพระอินทร์ Ueang sai phra in (Chiang Mai); เอื้องโรจน์เรืองแสง Ueang rot rueng saeng (Bangkok).
D. dickasonii L.O.Williams	เอื้องเคี๊ยะ Ueang khia (Chiang Mai).
D. discolor Lindl.	หวายกลัก Wai klak (Bangkok).
D. dixanthum Rchb.f.	เอื้องคำปอน Ueang kham pon; เอื้องคำป่า Ueang kham pa, เอื้องคำปิว Ueang kham pio, เอื้องเทียน Ueang thian, เอื้องใบไผ่ Ueang bai phai, เอื้องไผ่

	Ueang phai (Northern).
D. draconis Rchb.f.	พอเจ Pho-che (Karen-Mae Hong Son เอื้องเงิน Ueang ngoen (Northern); เอื้องตึง Ueang tueng (Mae Hong Son).
D. ellipsophyllum Tang & Wang	เอื้องทอง Ueang thong (General).
D. exile Schltr.	เอื้องเสี้ยน Ueang sian, แส้พระอินทร์ Sae phra in (General).
D. falconeri Hook.	พอทุด่าง Pho-tu-dang (Karen-Mae Hong Son); เอื้องโรจน์เรืองแสง Ueang rot rueng saeng; เอื้องสายวิสูตร Ueang sai wisut (Bangkok); เอื้องหญ้าแพด Ueang ya phaet (Chiang Mai).
D. farmer Paxton	เอื้องมัจฉาณุ Ueang mat chanu (Bangkok).
D. fimbriatum Hook.	เอื้องคำตาดำ Ueang kham ta dam (Mae Hong Son); เอื้องคำน้อย Ueang kham noi (Chiang Mai); เอื้องแววมยุรา Ueang waeo mayura (Central, Nakhon Ratchasima).
D. fimbriatum Lindl. var. *oculatum* Hook.f.	= *D. fimbriatum* Hook
D. findlayanum Parish & Rchb.f.	พวงหยก Phuang yok, หวายปม Wai pom (Bangkok); เอื้องข้อ Ueang kho (Chiang Mai).
D. formosum Roxb. ex Lindl.	เอื้องขี้ผึ้ง Ueang khi phueng (Peninsular); เอื้องเงินหลวง Ueang ngoen luang, เอื้องตาเหิน Ueang ta hoen (Chiang Mai).
D. friedericksianum Rchb.f.	เหลืองจันทบูร Lueang chantabun, เอื้องนกขมิ้น Ueang nok khamin (Chantaburi); เอื้องเหลืองจันทบูร Ueang lueang chantabun (Bangkok).

D. friedericksianum Rchb.f. var. *oculatum* Seidenf. & Smitinand	= *D. friedericksianum* Rchb.f.
D. fuerstenbergianum Schltr.	เอื้องแซะภูกระดึง Ueang sae phu kradueng (Loei).
D. gibsonii Lindl.	พอนี้โคะโพ Pho-ni-ko-pho, พอผู่ปรึย Pho-phu-prue-ya (Karen-Mae Hong Son); เอื้องคำตา Ueang kham ta, เอื้องคำสาย Ueang kham sai (Northern); เอื้องจำปา Ueang champa (Central).
D. grande Hook.f.	เอื้องแผงใบใหญ่ Ueang phaeng bai yai (Peninsular).
D. gratiotissimum Rchb.f.	เอื้องกิ่งดำ Ueang king dam (Bangkok).
D. gregulus Seidenf.	เอื้องมะต่อม Ueang matom (Chiang Mai).
D. griffithianum Lindl.	เอื้องมัจฉาณุ Ueang matchanu, เอื้องมัจฉาเหลือง Ueang Matcha Lueang (Bangkok).
D. harveyanum Rchb.f.	เอื้องคำฝอย Ueang kham foi, เอื้องคำฝอยอินเดีย Ueang kham foi india (Chiang Mai).
D. hendersonii Hawkes & Heller	หวายตะมอยน้อย Wai tamoi noi (Peninsular).
D. hercoglossum Rchb.f.	เอื้องดอกมะเขือ Ueang dok ma khuea (Bangkok).
D. heterocarpum Lindl.	เอื้องแซะดง Ueang sae dong, เอื้องสีจุน Ueang si chun, เอื้องสีตาล Ueang si tan (Chiang Mai)
D. hildebrandii Rolfe	= *D. signatum* Rchb.f.
D.indivisum (Blume) Miq. var. *indivisum*	ตานเสี้ยนไม้ Tan sian mai (Chumporn).

D. indivisum var. *lampangense* Rolfe	= *D. porphyrophyllum* Guillaumin
D. indivisum var. *pallidum* Seidenf.	ก้างปลา Kang pla (General).
D. infundibulum Lindl.	เอื้องเงินหลวง Ueang ngoen luang (Mae Hong Son); เอื้องตาเหิน Ueang ta hoen (Genaral).
D. intricatum Gagnep.	เอื้องชมพู Ueang chom phu (Chanthaburi).
D. jenkensii Wall. ex Lindl.	เอื้องผึ้งน้อย Ueang phueng noi (Chiang Mai).
D. kanburiense Seidenf.	หวายเมืองกาญจน์ Wai muang kan (Kanchanaburi).
D. leonis (Lindl.) Rchb.f.	เอื้องตะขาบใหญ่ Ueang ta khap yai (General).
D. lindleyi Steud.	โพดอนแหล่ Pho-don-lae (Karen-Mae Hong Son); เอื้องผึ้ง Ueang phueng (Northern).
D. lituiforum Lindl.	เอื้องครั่ง Ueang khrang (Loei); เอื้องสายม่วง Ueang sai muang (Bangkok, Northern).
D. lobbii Teijsm. & Binn.	= *D. villosulum* Lindl.
D. longicornu Lindl.	= *D. wattii* (Hook.f.) Rchb.f.
D. margaitaceum Finet	=*D. christyanum* Rchb.f.
D. moschatum (Buch.-Ham.) Sw.	เอื้องจำปา Ueang champa (Northern).
D. moulmeinense Parish ex Hook.f.	= *D. dixanthum* Rchb.f.
D. nathanielis Rchb.f.	เกล็ดนิ่ม Klet nim (Chanthaburi).
D. nobile Lindl.	เอื้องเค้ากิ่ว Ueang khao kio (Northern).
D. ochreatum Lindl.	เอื้องคำข้อ Ueang kham kho, เอื้องคำผัก

	ปราบ Ueang kham phak prap, เอื้องง่อย Ueang ngoi, เอื้องตะขาบ Ueang ta khap (Chiang Mai).
D. oligophyllum Gagnep.	ข้าวตอกปราจีน Khao tok prachin (General).
D. pachyglossum C.S.P.Parish & Rchb.f.	เอื้องขนหมู Ueang khon mu (Mae Hong Son)
D. pachyphyllum (Kuntze) Bakh.f.	เอื้องน้อย Ueang noi, เอื้องสองใบ Ueang song bai (General).
D. palpebrae Lindl.	เอื้องมัจฉา Ueang mat cha, เอื้องมัจฉาณุ Ueang matchanu (Bangkok).
D. parcum Rchb.f.	เอื้องก้านกิ่ว Ueang kan kio, เอื้องไม้กวาด Ueang mai kwat (Bangkok).
D. parishii Rchb.f.	เอื้องครั่ง Ueang khrang (Northern); เอื้องน้ำครั่ง Ueang nam khrang (Bangkok); เอื้องอัตตากริต Ueang attakrit, เอื้องอินทกริต Ueang inthakrit (Phetchabun).
D. pendulum Roxb.	เอื้องไม้เท้าฤาษี Ueang mai thao ruesi (Bangkok, Chiangmai).
D. pensile Ridl.	หวาย Wai, หวายย้อย Wai Yoi (Narathiwat).
D. porphyrophyllum Guillaumin.	เอื้องลิ้น Ueang lin (Lampang).
D. primulinum Lindl.	เอื้องสายน้ำเขียว Ueang sai nam khiao (Chiang Mai); เอื้องสายน้ำผึ้ง Ueang sai nam phueng, เอื้องสายประสาท Ueang sai prasat, เอื้องสายเหลือง Ueang sai lueang
D. pulchellum Roxb. ex Lindl.	ปะแหน่มีเพ้ย Pa-nae-mi-phoei, พอมียอเอ้ะ Pho-mi-yo-e (Karen-Mae Hong Son); มอกคำตาควาย Mok-kham-ta-khwai

	(Shan-Mae Hong Son); สบเป็ด Soppet (Loei); เอื้องคำตาควาย Ueang kham ta khwai, เอื้องตาควาย Ueang ta khwai (Mae Hong Son); เอื้องช้างน้าว Ueang chang nao (Northern).
D. pychnostachyum Lindl.	เศวตสอดสี Sawet sot si (Chiang Mai); เอื้องเศวตสอดสี Ueang sawet sot si (Bangkok).
D. salaccense (Blume) Lindl.	เอื้องใบไผ่ Ueang bai phai (Chiang Mai).
D. scabrilingue Lindl.	พอดอญ่า Pho-do-ya, พอมือคา Pho-mue-kha, พอหมืนคา Pho-muen-kha, พอแหม่และ Pho-mae-lae (Karen-Mae Hong Son); เอื้องแซะ Ueang sae (Mae Hong Son); เอื้องแซะหอมUeang sae hom (Chiang Mai).
D. secundum (Blume) Lindl.	กับแกะ Kap kae (Loei); คองูเห่า Kho ngu hao (Central); เอื้องแปรงสีฟัน Ueang praeng si fan, เอื้องหงอนไก่ Ueang ngon kai (Northern).
D. seidenfadenii Rchb.f.	เอื้องเกี๊ยะ Ueang kia (Chiang Mai).
D. senile Parish & Rchb.f.	มือชะนี Mue chain, เอื้องขนค่าง Ueang khon khang (Chiang Mai); เอื้องชะนี Ueang chani, เอื้องนางนี Ueang nang ni (Bangkok); เอื้องมือค่าง Ueang mue khang (Mae Hong Son); เอื้องอีฮุย Ueang I hui (Northern).
D. signatum Rchb.f.	เอื้องเค้ากิ่ว Ueang khao kio, เอื้องตีนเป็ด Ueang tin pet (Northern), สะเมิงอาง Sa moeng-ang (Shan-Mae Hong Son),

	เอื้องตีนนก Ueang tin nok (Chiang Mai).
D. stuposum Lindl.	เอื้องสาย Ueang sai (Chiang Mai).
D. sulcatum Lindl.	เอื้องจำปาน่าน Ueang champa nan (Bangkok).
D. superbiens Rchb.f.	หวายคิง Wai khing (Bangkok).
D. superbum Rchb.f.	= *D. anosmum* Lindl.
D. sutepense Rolfe ex downie	เอื้องแซะ Ueang sae, เอื้องแซะมะลิ Ueang sae mali, เอื้องมะลิ Ueang mali (Chiang Mai).
D. terminale Parish & Rchb.f.	เอื้องแผงโสภา Ueang phaeng sopha (Peninsular).
D. thyrsiflorum Rchb.f.	กับแกะ Kap kae (Loei); พอซางดี Pho-sang-di (Karen-Mae Hong Son); ม่อนไข่ใบมน Ueang khai bai mon, เอื้องมอนไข่ใบมน Ueang mon khai bai mon (Northern).
D. tortile Lindl.	ตีนนก Tin nok (Chiang Mai); เอื้องไม้ตึง Ueang mai tueng (Mae Hong Son); เอื้องเค้ากิ่ว Ueang kao kio, เอื้องเค้ากิ่วแม่สะเรียง Ueang kao kio mae sarieng (Northern).
D. trigonopus Rchb.f.	เอื้องคำปากไก่ Ueang kham pak kai, เอื้องคำภู Ueang kham phu (Loei); เอื้องคำเหลี่ยม Ueang kham liam (Chiang Mai).
D. trinervium Ridl.	เทียนลิง Thian ling (Chumporn).
D. unicum Seidenf.	เอื้องครั่งแสด Ueang krang saet, เอื้องสายสีแสด Ueang sai si saet, เอื้องกำลังเอก Ueang kam lang ek (General).
D. venustum Teijsm. & Binn.	ข้าวเหนียวลิง Khao niao ling, เอื้องข้าว

	เหนียวลิง Ueang khao niao ling (General), เอื้องดอกขาม Ueang dok kham, เอื้องดอกมะขาม Ueang dok ma kham, เอื้องมะขาม Ueang ma kham (Phrae).
D. villosum Lindl.	กล้วยหญ้านา Klui ya na (Bangkok).
D. virgineum Rchb.f.	เอื้องนางชี Ueang nang chi, เอื้องชีปะขาว Ueang chi pa khao, เอื้องเงินวิลาศ Ueang ngoen wilat (Northeastern).
D. wardianum Warner	พอเด่นญา Pho-den-ya (Karen-Chiang Mai); เอื้องมณีไตรรงค์ Ueang mani trai rong (Northern).
D. wattii (Hook.f) Rchb.f.	เอื้องแซะ Ueang sae (Northern).
D. ypsilon Seidenf.	เอื้องแบนปากตัด Ueang baen pak tat (General).

Dendrobium draconis Rchb. f. has a local name as Ueang Ngoen. It is found from India, Myanmar, Laos, Cambodia, Vietnam and Thailand. Its hairy stem is about a foot tall. Flowers are short clusters, pure white sepals and petals, lip white with orange-red lines toward the base. The number of flowers are 2-5, with 6.5 cm sized. Their flowering period is on March to April (Curtis, 1950; Seidenfaden, 1985; Vaddhanaphuti, 2005).

Dendrobium draconis Rchb. f. has no previous record of chemical examination. A preliminary study on the methanol extract of this plant showed 75.78 % DPPH reduction at the concentration of 100 µg/ml.

The main objectives in this study are as follows.

1. Isolation and purification of constituents of *D. draconis*.
2. Determination of the chemical structure of each isolated compound.
3. Evaluation of each isolated compound for its free radical scavenging activity.

Figure 1 *Dendrobium draconis* Rchb.f

CHAPTER II

HISTORICAL

1. Chemical constituents of *Dendrobium* spp.

A number of chemical constituents isolated from the genus *Dendrobium* can be classified as bibenzyls of various types. In addition, other classes of natural compounds such as phenanthrenes, sesquiterpenes, fluorenones and miscellaneous substances have been found (Table 1).

Table 1 Distribution of chemical constituents in the genus *Dendrobium*.

Plant and compound	Category	Plant part	Reference
Dendrobium aduncum			
Aduncin [**1**]	Sesquiterpene	Whole plant	Gawell and Leander, 1976
Dendrobium amoenum			
Amoenin [**2**]	Sesquiterpene	Whole plant	Dahmen and Leander, 1978; Majumder *et al*., 1999
Amoenumin [**3**]	Phenanthrene	Whole plant	Veerraju *et al*., 1989
Amoenylin [**4**]	Bibenzyl	Whole plant	Majumder *et al*., 1999
Amotin [**5**]	Sesquiterpene	Whole plant	Dahmen and Leander, 1978; Majumder *et al*., 1999
3,4′-Dihydroxy-5-methoxybibenzyl [**6**]	Bibenzyl	Whole plant	Majumder *et al*., 1999
Flaccidin (Amoenumin) [**3**]	Phenanthrene	Whole plant	Majumder *et al*., 1999
Isoamoenylin [**7**]	Bibenzyl	Whole plant	Majumder *et al*., 1999

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Moscatilin [**8**]	Bibenzyl	Whole plant	Majumder *et al*., 1999
Dendrobium aphyllum			
Batatasin III [**9**]	Bibenzyl	Whole plant	Chen *et al*., 2008
Coelonin [**10**]	Phenanthrene	Whole plant	Chen *et al*., 2008
Dibutyl phthalate [**11**]	Benzoic acid ester	Whole plant	Chen *et al*., 2008
Diisobutyl phthalate [**12**]	Benzoic acid ester	Whole plant	Chen *et al*., 2008
Flavanthrin [**13**]	Biphenanthrene	Whole plant	Chen *et al*., 2008
Gigantol [**14**]	Bibenzyl	Whole plant	Chen *et al*., 2008
p-Hydroxyphenylpropionic methyl ester [**15**]	Phenolic compound	Whole plant	Chen *et al*., 2008
Lusianthridin [**16**]	Phenanthrene	Whole plant	Chen *et al*., 2008
Moscatin [**17**]	Phenanthrene	Whole plant	Chen *et al*., 2008
Dendrobium aurantiacum			
Chrysotobibenzyl [**18**]	Bibenzyl	Stem	Yang *et al*., 2006
Chrysotoxin [**19**]	Bibenzyl	Stem	Yang *et al*., 2006
Coumarin [**20**]	Coumarin	Stem	Yang *et al*., 2006
Defuscin [**21**]	Phenolic compound	Stem	Yang *et al*., 2006

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendroflorin [**22**]	Fluorenone	Stem	Yang *et al*., 2006
Gigantol [**14**]	Bibenzyl	Stem	Yang *et al*., 2006
Kaempferol [**23**]	Flavonol	Stem	Yang *et al*., 2006
Moscatilin [**8**]	Bibenzyl	Stem	Yang *et al*., 2006
Naringenin [**24**]	Flavanone	Stem	Yang *et al*., 2006
n-Octacosyl ferulate [**25**]	Phenylpropanoid	Stem	Yang *et al*., 2006
Taraxerol [**26**]	Triterpene	Stem	Yang *et al*., 2006
Denrobium candidum			
Dendrocandin A [**27**]	Bibenzyl	Stem	Li *et al*., 2008
Dendrocandin B [**28**]	Bibenzyl	Stem	Li *et al*., 2008
Dendrocandin C [**29**]	Bibenzyl	Stem	Li *et al*., 2009a
Dendrocandin D [**30**]	Bibenzyl	Stem	Li *et al*., 2009a
Dendrocandin E [**31**]	Bibenzyl	Stem	Li *et al*., 2009a
Dendrocandin F [**32**]	Bisbibenzyl	Stem	Li *et al*., 2009b
Dendrocandin G [**33**]	Bisbibenzyl	Stem	Li *et al*., 2009b
Dendrocandin H [**34**]	Bibenzyl	Stem	Li *et al*., 2009b
Dendrocandin I [**35**]	Bibenzyl	Stem	Li *et al*., 2009b
Dendrophenol [**36**]	Bibenzyl	Stem	Li *et al*., 2008
4,4′-Dihydroxy-3,5-dimethoxybibenzyl [**37**]	Bibenzyl	Stem	Li *et al*., 2008

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
3,4-Dihydroxy-5,4′-dimethoxybibenzyl [**38**]	Bibenzyl	Stem	Li *et al*., 2008
Gigantol [**14**]	Bibenzyl	Stem	Li *et al*., 2008
3-*O*-Methylgigantol [**39**]	Bibenzyl	Stem	Li *et al*., 2008
Dendrobium cariniferum			
Batatasin III [**9**]	Bibenzyl	Whole plant	Chen *et al*., 2008
Dendrononе [**40**]	Phenanthrene-quinone	Whole plant	Chen *et al*., 2008
Gigantol [**14**]	Bibenzyl	Whole plant	Chen *et al*., 2008
Dendrobium chrysanthum			
Chrysotobibenzyl [**18**]	Bibenzyl	Whole plant	Yang *et al*., 2006
Chrysotoxin [**19**]	Bibenzyl	Whole plant	Yang *et al*., 2006
Crepidatin [**41**]	Bibenzyl	Whole plant	Yang *et al*., 2006
Dendrochrysanene [**42**]	Phenanthrene	Whole plant	Yang *et al*., 2006
Dengibsin [**43**]	Fluorenone	Whole plant	Yang *et al*., 2006
4,4′-Dihydroxy-3,3′,5-trimethoxybibenzyl [**44**]	Bibenzyl	Whole plant	Min *et al*., 1987
Gigantol [**14**]	Bibenzyl	Whole plant	Yang *et al*., 2006
Moscatilin [**8**]	Bibenzyl	Whole plant	Yang *et al*., 2006
Moscatin [**17**]	Phenanthrene	Whole plant	Yang *et al*., 2006

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium chrysotoxum			
Denchrysan A [**45**]	Fluorenone	Whole plant	Chen *et al*., 2008
Dendroflorin [**22**]	Fluorenone	whole plant	Chen *et al*., 2008
2,7-Dihydroxy-8-methoxyphenanthro [4,5,*bcd*]pyran-5-(5*H*)-one [**46**]	Phenanthrene-lactone	Whole plant	Yang *et al*., 2004
(9*R*)-4-Methoxy-9*H*-fluorene-2,5,9-triol [**47**]	Fluorenol	Whole plant	Yang *et al*., 2004
1,4,5-Trihydroxy-7-methoxy-9*H*-fluoren-9-one [**48**]	Fluorenone	Whole plant	Chen *et al*., 2008
Dendrobium crepidatm			
Crepidatin [**41**]	Bibenzyl	Whole plant	Majumder and Chatterjee, 1986
Dendrobium crystallinum			
Apigenin [**49**]	Flavone	Stem	Wang *et al*., 2009
Crystallinin [**50**]	Sesquiterpene	Stem	Wang *et al*., 2009
Crystalltone [**51**]	Phenanthrene-lactone	Stem	Wang *et al*., 2009
Dencryol A [**52**]	Bisbibenzyl	Stem	Wang *et al*., 2009
Dencryol B [**53**]	Bisbibenzyl	Stem	Wang *et al*., 2009
Dendronobilin B [**54**]	Sesquiterpene	Stem	Wang *et al*., 2009

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
6‴-Glucosyl-vitexin [**55**]	Flavone glycoside	Stem	Wang *et al*., 2009
3-Hydroxy-2-methoxy-5,6-dimethylbenzoic acid [**56**]	Hydroxybenzoic acid	Stem	Wang *et al*., 2009
Isoviolanthin [**57**]	Flavone glycoside	Stem	Wang *et al*., 2009
Palmarumycin JC2 [**58**]	Dioxane	Stem	Wang *et al*., 2009
Syringic acid [**59**]	Hydroxybenzoic acid	Stem	Wang *et al*., 2009
Dendrobium cumulatum			
Cumulatin [**60**]	Bibenzyl	Whole plant	Majumder and Pal, 1993
Dendrobium densiflorum			
Ayapin [**61**]	Coumarin	Stem	Fan *et al*., 2001
Cypripedin [**62**]	Phenanthrene-quinone	Stem	Fan *et al*., 2001
Dengibsin [**43**]	Fluorenone	Stem	Fan *et al*., 2001
Densiflorol A [**63**]	Bibenzyl	Stem	Fan *et al*., 2001
Densiflorol B [**64**]	Phenanthrene-quinone	Stem	Fan *et al*., 2001
2,6-Dihydroxy-1,5,7-trimethoxyphenanthrene [**65**]	Phenanthrene	Stem	Fan *et al*., 2001
4,7-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene [**66**]	Phenanthrene	Stem	Fan *et al*., 2001
Gigantol [**14**]	Bibenzyl	Stem	Fan *et al*., 2001
Homoeriodictyol [**67**]	Flavone	Stem	Fan *et al*., 2001

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Moscatilin [**8**]	Bibenzyl	Stem	Fan *et al*., 2001
Moscatin [**17**]	Phenanthrene	Stem	Fan *et al*., 2001
Naringenin [**24**]	Flavanone	Stem	Fan *et al*., 2001
Scoparone [**68**]	Coumarin	Stem	Fan *et al*., 2001
Scopoletin [**69**]	Coumarin	Stem	Fan *et al*., 2001
1,4,7-Trihydroxy-5-methoxy-9*H*-fluoren-9-one [**70**]	Fluorenone	Stem	Fan *et al*., 2001
Tristin [**71**]	Bibenzyl	Stem	Fan *et al*., 2001
Dendrobium falconeri			
Dendrofalconerol A (Dendrocandin F) [**32**]	Bisbibenzyl	Aerial part	Sritularak and Likhitwitaya-wuid, 2009
Dendrofalconerol B [**72**]	Bisbibenzyl	Aerial part	Sritularak and Likhitwitaya-wuid, 2009
Docosanoyl (*E*)-ferulate [**73**]	Cinnamic acid ester	Aerial part	Sritularak and Likhitwitaya Wuid, 2009
p-Hydroxybenzaldehyde [**74**]	Benzaldehyde	Aerial part	Sritularak and Likhitwitaya-wuid, 2009
p-Hydroxybenzoic acid [**75**]	Hydroxybenzoic acid	Aerial part	Sritularak and Likhitwitaya-wuid, 2009
2-(*p*-Hydroxyphenyl) ethyl-*p*-coumarate [**76**]	Phenylpropanoid	Aerial part	Sritularak and Likhitwitaya-wuid, 2009
Tetracosyl (*E*)-*p*-coumarate [**77**]	Phenylpropanoid	Aerialpart	Sritularak and Likhitwitaya-wuid, 2009

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Tetracosyl (*Z*)-*p*-coumarate [**78**]	Phenylpropanoid	Aerial part	Sritularak and Likhitwitaya-wuid, 2009
Dendrobium fimbriatum			
Defuscin [**21**]	Phenylpropanoid	Whole plant	Talapatra *et al*., 1992
Denfigenin [**79**]	Steroid	Whole plant	Talapatra *et al*., 1992
Diosgenin [**80**]	Steroid	Whole plant	Talapatra *et al*., 1992
Dendrobium fuscescens			
Defuscin [**21**]	Phenylpropanoid	Whole plant	Talapatra *et al*., 1992
(-)-Shikimic acid [**81**]	Aliphatic acid	Whole plant	Talapatra *et al*., 1992
Dendrobium gratiosissimun			
Batatasin III [**9**]	Bibenzyl	Stem	Zhang *et al*., 2008a
Dengraol A [**82**]	Bisbibenzyl	Stem	Zhang *et al*., 2008a
Dengraol B [**83**]	Bisbibenzyl	Stem	Zhang *et al*., 2008a
3,4-Dihydroxy-5,4′-dimethoxybibenzyl [**38**]	Bibenzyl	Stem	Zhang *et al*., 2008a
3,4′-Dihydroxy-5-methoxybibenzyl [**6**]	Bibenzyl	Stem	Zhang *et al*., 2008a
Gigantol [**14**]	Bibenzyl	Stem	Zhang *et al*., 2008a
Moscatilin [**8**]	Bibenzyl	Stem	Zhang *et al*., 2008a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
3,5,4′-Trihydroxybibenzyl [**84**]	Bibenzyl	Stem	Zhang *et al*., 2008a
Tristin [**71**]	Bibenzyl	Stem	Zhang *et al*., 2008a
Dendrobium huoshanense			
6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-*β*-galactopyranosyl]apigenin [**85**]	Flavone glycoside	Aerial part	Chang *et al*., 2010
6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin [**86**]	Flavone glycoside	Aerial part	Chang *et al*., 2010
Dimethyl malate [**87**]	Aliphatic acid ester	Aerial part	Chang *et al*., 2010
Isopentyl butyrate [**88**]	Aliphatic acid ester	Aerial part	Chang *et al*., 2010
Isoschaftoside [**89**]	Flavonoid glycoside	Aerial part	Chang *et al*., 2010
Malic acid [**90**]	Aliphatic acid	Aerial part	Chang *et al*., 2010
Phenylacetamide [**91**]	Benzene acetamide	Aerial part	Chang *et al*., 2010
6-*C*-[(2-O-α-Rhamnopyranosyl)-β-glucopyranosyl]-8-*C*-(α-arabinopyranosyl)apigenin [**92**]	Flavone glycoside	Aerial part	Chang *et al*., 2010
Salicylic acid [**93**]	Hydroxybenzoic acid	Aerial part	Chang *et al*., 2010
6-*C*-(β-Xylopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin [**94**]	Flavone glycoside	Aerial part	Chang *et al*., 2010

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium loddigesii			
Batatasin III [**9**]	Bibenzyl	Stem	Ito *et al*., 2010
Gigantol [**14**]	Bibenzyl	Stem	Ito *et al*., 2010
Hircinol [**96**]	Phenanthrene	Stem	Ito *et al*., 2010
5-Hydroxy-2,4-dimethoxyphenanthrene [**97**]	Phenanthrene	Stem	Ito *et al*., 2010
Loddigesiinol A [**98**]	Phenanthrene	Stem	Ito *et al*., 2010
Loddigesiinol B [**99**]	Phenanthrene	Stem	Ito *et al*., 2010
Loddigesiinol C [**100**]	Bibenzyl	Stem	Ito *et al*., 2010
Loddigesiinol D [**101**]	Bibenzyl	Stem	Ito *et al*., 2010
Lusianthridin [**16**]	Phenanthrene	Stem	Ito *et al*., 2010
(-)-Medioresinol [**102**]	Lignan	Stem	Ito *et al*., 2010
Moscatilin [**8**]	Bibenzyl	Stem	Chen, Ko and Teng, 1994; Ito *et al*., 2010
Moscatin [**17**]	Phenanthrene	Stem	Chen, *et al*., 1994; Ito *et al*., 2010
(-)-Pinoresinol [**103**]	Lignan	Stem	Ito *et al*., 2010
Rotundatin [**104**]	Phenanthrene	Stem	Ito *et al*., 2010
Sitostenone [**105**]	Steroid	Stem	Ito *et al*., 2010
β-Sitosterol[**106**]	Steroid	Stem	Ito *et al*., 2010
Stigmasterol [**107**]	Steroid	Stem	Ito *et al*., 2010
Dendrobium longicornu			
Aloifol I [**108**]	Bibenzyl	Stem	Hu *et al*., 2008a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Batatasin [**109**]	Bibenzyl	Stem	Hu *et al*., 2008a
Episyringaresinol [**110**]	Lignan	Stem	Hu *et al*., 2008a
Episyringaresinol 4′′-*O*-β-D-glucopyranoside [**111**]	Lignan glycoside	Stem	Hu *et al*., 2008a
Erythro-1-(4-*O*-β-D-glucopyranosyl-3-methoxyphenyl)-2-[4-(3-hydroxypropyl)2,6-dimethoxyphenoxy]-1,3-propanediol [**112**]	Lignan glycoside	Stem	Hu *et al*., 2008a
Eugenyl-*O*-β-D-glucopyranoside [**113**]	Glycoside	Stem	Hu *et al*., 2008a
Gigantol [**14**]	Bibenzyl	Stem	Hu *et al*., 2008
5-Hydroxy-7-methoxy-9,10-dihydrophenanthrene-1,4-dione [**114**]	Phenanthrene-quinone	Stem	Hu *et al*., 2008a
4-[2-(3-Hydroxyphenol)-1-methoxyethyl]-2,6-dimethoxyphenol [**115**]	Bibenzyl	Stem	Hu *et al*., 2008a
Longicornuol A [**116**]	Bibenzyl	Stem	Hu *et al*., 2008a
3-(3-Methoxy,4-hydroxyphenyl)-1-propanol [**117**]	Phenylpropanoid	Stem	Hu *et al*., 2008a
4-Methoxy-9,10-dihydrophenanthrene-2,5,7-triol [**118**]	Phenanthrene	Stem	Hu *et al*., 2008a
Methyl β-orsellinate [**119**]	Phenolic compound	Stem	Hu *et al*., 2008a
Moscatilin [**8**]	Bibenzyl	Stem	Hu *et al*., 2008a
Naringenin [**24**]	Flavanone	Stem	Hu *et al*., 2008a
9-β-D-Ribofuranosyl-9*H*-purin-6-amine [**120**]	Purine nucleotide	Stem	Hu *et al*., 2008a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
(3*S*,4*S*,5*R*)-3,4,5-Trihydroxy-1-cyclohexene carboxylic acid (Shikimic acid) [**81**]	Aliphatic acid	Stem	Hu *et al*., 2008a
3,3′,4-Trihydroxybibenzyl [**121**]	Bibenzyl	Stem	Hu *et al*., 2008a
Tristin [**71**]	Bibenzyl	Stem	Hu *et al*., 2008
Dendrobium moniliforme			
Acanthoside B [**122**]	Lignan glycoside	Stem	Zhao *et al*., 2003
Denbinobin [**123**]	Phenanthraquinone	Stem	Lin *et al*., 2001
Dendromoniliside A [**124**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2003
Dendromoniliside B [**125**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2003
Dendromoniliside C [**126**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2003
Dendromoniliside D [**127**]	Sesquiterpene glycoside	Stem	Lin *et al*., 2001
Dendromoniliside E [**128**]	Bibenzyl glycoside	Stem	Zhao *et al*., 2003
Dendroside A [**129**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2003
Dendroside C [**130**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2003
Dendroside F [**131**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2003
Moniliformin [**132**]	Phenanthraquinone	Stem	Lin *et al*., 2001
Vanilloloside [**133**]	Phenolic glycoside	Stem	Zhao *et al*., 2003

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium moscatum			
Moscatilin [**8**]	Bibenzyl	Whole plant	Majumder and Sen, 1987
Dendrobium nobile			
Bulbophyllanthrin [**134**]	Phenanthrene	Stem	Yang, Sung and Kim, 2007
Chrysotobibenzyl [**18**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Chrysotoxin [**19**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Coelonin [**10**]	Phenanthrene	Stem	Yang *et al*., 2007; Hwang *et al*., 2010
Confusarin [**135**]	Phenanthrene	Stem	Zhang *et al*., 2008b
Crepidatin [**41**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Denbinobin [**123**]	Phenanthrene-quinone	Stem	Yang *et al*., 2007
Dendrobane A [**136**]	Sesquiterpene	Stem	Ye and Zhao, 2002
Dendrobin A [**137**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Dendrobine [**138**]	Sesquiterpene alkaloid	Stem	Wang, Zhao, and Che, 1985; Ye and Zhao, 2002
Dendroflorin [**22**]	Fluorenone	Stem	Zhang *et al*., 2007a
Dendronobilin A [**139**]	Sesquiterpene	Stem	Zhang *et al*., 2007b

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendronobilin B [**54**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin C [**140**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin D [**141**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin E [**142**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin F [**143**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin G [**144**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin H [**145**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin I [**146**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin J [**147**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin K [**148**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobilin L [**149**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobilin M [**150**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobilin N [**151**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobiloside A [**152**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2001; Ye and Zhao, 2002

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendronobiloside B [**153**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2001; Ye and Zhao, 2002
Dendronobiloside C [**154**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendronobiloside D [**155**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendronobiloside E [**156**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendroside A [**129**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2001; Ye and Zhao, 2002
Dendroside B [**157**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendroside C [**130**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendroside D [**158**]	Sesquiterpene glycoside	Stem	Ye *et al*., 2002
Dendroside E [**159**]	Sesquiterpene glycoside	Stem	Ye *et al*., 2002
Dendroside F [**131**]	Sesquiterpene glycoside	Stem	Ye *et al*., 2002
Dendroside G [**160**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
3,7-Dihydroxy-2,4-dimethoxyphenanthrene [**161**]	Phenanthrene	Stem	Zhang *et al*., 2008b
4,5-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene [**162**]	Phenanthrene	Stem	Yang *et al*., 2007
2,2′-Dihydroxy-3,3′,4,4′,7,7′-hexamethoxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene [**163**]	Biphenanthrene	Stem	Yang *et al*., 2007

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
4,5-Dihydroxy-3,3′-dimethoxybibenzyl [**164**]	Bibenzyl	Stem	Ye and Zhao, 2002
2,8-Dihydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene [**165**]	Phenanthrene	Stem	Yang *et al*., 2007
2,8-Dihydroxy-3,4,7-trimethoxyphenanthrene [**166**]	Phenanthrene	Stem	Yang *et al*., 2007
2,5-Dihydroxy-3,4-dimethoxyphenanthrene [**167**]	Phenanthrene	Stem	Yang *et al*., 2007
4,5-Dihydroxy-3,7-dimethoxydihydrophenan-threne [**168**]	Phenanthrene	Stem	Ye and Zhao, 2002
2,5-Dihydroxy-4,9-dimethoxyphenanthrene [**169**]	Phenanthrene	Stem	Zhang *et al*., 2008b
3,4′-Dihydroxy-5,5′-dimethoxydihydrostilbene [**170**]	Bibenzyl	Stem	Hwang *et al*., 2010
7,12-Dihydroxy-5-hydroxymethyl-11-isopropyl-6-methyl-9-oxatricyclo[6.2.1.$0^{2,6}$]undecan-10-one-15-*O*-β-D-glucopyranoside [**171**]	Sesquiterpene glycoside	Stem	Shu *et al*., 2004
5,7-Dimethoxyphenanthrene-2,6-diol [**172**]	Phenanthrene	Stem	Hwang *et al*., 2010
Ephemeranthol A [**173**]	Phenanthrene	Stem	Yang et al., 2007; Hwang *et al*., 2010
Ephemeranthol C [**174**]	Phenanthrene	Stem	Hwang *et al*., 2010
Erianthridin [**175**]	Phenanthrene	Stem	Yang *et al*., 2007; Hwang *et al*., 2010

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Fimbriatone [**176**]	Phenanthrene	Stem	Zhang *et al*., 2008b
Fimbriol B [**177**]	Phenanthrene	Stem	Yang *et al*., 2007; Hwang *et al*., 2010
Flavanthridin [**178**]	Phenanthrene	Stem	Hwang *et al*., 2010
Flavanthrinin [**179**]	Phenanthrene	Stem	Zhang *et al*., 2008b
Gigantol [**14**]	Bibenzyl	Stem	Zhang *et al*., 2007
Hircinol [**96**]	Phenanthrene	Stem	Hwang *et al*., 2010
3-Hydroxy-2,4,7-trimethoxy-9,10-dihydrophenanthrene [**180**]	Phenanthrene	Stem	Yang *et al*., 2007
3-Hydroxy-2,4,7-trimethoxyphenanthrene [**181**]	Phenanthrene	Stem	Yang *et al*., 2007
3-Hydroxy-2-oxodendrobine [**182**]	Sesquiterpene alkaloid	Stem	Wang, Zhao, and Che, 1985
4-Hydroxy-3,3′,5-trimethoxybibenzyl [**183**]	Bibenzyl	Stem	Ye and Zhao, 2002
2-Hydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene [**184**]	Phenanthrene	Stem	Yang *et al*., 2007
2-Hydroxy-4,7-dimethoxy-9,10-dihydrophenanthrene [**185**]	Phenanthrene	Stem	Yang *et al*., 2007
Lirioresinol A [**186**]	Lignan	Stem	Zhang *et al*., 2008b
Lusianthridin [**16**]	Phenanthrene	Stem	Yang *et al*., 2007; Hwang *et al*., 2010

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Medioresinol [**187**]	Lignan	Stem	Zhang *et al*., 2008(b)
Moscatilin [**8**]	Bibenzyl	Stem	Yang et al., 2007; Hwang *et al*., 2010
Nobilin A [**188**]	Bibenzyl	Stem	Zhang *et al*., 2006
Nobilin B [**189**]	Bibenzyl	Stem	Zhang *et al*., 2006
Nobilin C [**190**]	Bibenzyl	Stem	Zhang *et al*., 2006
Nobilin D [**191**]	Bibenzyl	Stem	Zhang *et al*., 2007
Nobilin E [**192**]	Bisbibenzyl	Stem	Zhang *et al*., 2007
Nobilone [**193**]	Fluorenone	Stem	Zhang *et al*., 2007
Nudol [**194**]	Phenanthrene	Stem	Yang *et al*., 2007
Pinoresinol [**195**]	Lignan	Stem	Zhang *et al*., 2008(b)
Plicatol A [**196**]	Phenanthrene	Stem	Yang *et al*., 2007
Protocatechuic acid [**197**]	Benzoic acid derivatives	Stem	Ye and Zhao, 2002
2,3,5-Trihydroxy-4,9-dimethoxyphenanthrene [**198**]	Phenanthrene	Stem	Yang *et al*., 2007
10β,12,14-Trihydroxyalloaromadendrane [**199**]	Sesquiterpene	Stem	Ye and Zhao, 2002
3,4,8-Trimethoxyphenanthrene-2,5-diol [**200**]	Phenanthrene	Stem	Hwang *et al*., 2010

Table 1 (continued)

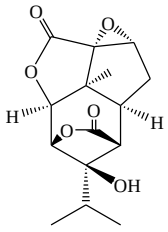
Plant and compound	Category	Plant part	Reference
Syringaresinol [**201**]	Lignan	Stem	Zhang *et al*., 2008(b)
Dendrobium ochreatum			
Dendrosteroside [**202**]	Steroid glycoside	Whole plant	Behr and Leander, 1976
Epi-ochreasteroside [**203**]	Steroid glycoside	Whole plant	Behr and Leander, 1976
Ochreasteroside [**204**]	Steroid glycoside	Whole plant	Behr and Leander, 1976
Dendrobium plicatile			
Batatasin [**109**]	Bibenzyl	Stem	Yamaki and Honda, 1996
2,2′-Dimethoxy-4,4′-7,7′-tetrahydroxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene [**205**]	Biphenanthrene	Stem	Yamaki and Honda, 1996
Ephemeranthoquinone [**206**]	Phenanthrene-quinone	Stem	Yamaki and Honda, 1996
Epheranthol B [**207**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Erianthridin [**175**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Lusianthridin [**16**]	Phenanthrene	Stem	Yamaki and Honda, 1996
3-*O*-Methylgigantol [**39**]	Bibenzyl	Stem	Yamaki and Honda, 1996
Plicatol A [**196**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Plicatol B [**208**]	Phenanthrene	Stem	Yamaki and Honda, 1996

Table 1 (continued)

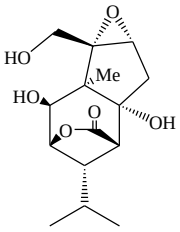
Plant and compound	Category	Plant part	Reference
Plicatol C [**209**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Dendrobium rotundatum			
Batatasin III [**9**]	Bibenzyl	Whole plant	Majumder and Pal, 1992
2,7-Dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene [**210**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
2,7-Dihydroxy-3,4,6-trimethoxyphenanthrene [**211**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Moscatin [**17**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Nudol [**194**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Rotundatin [**103**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Dendrobium thyrsiflorum			
Chrysophanol [**212**]	Anthraquinone	Stem	Zhang *et al*., 2005
Daucosterol [**213**]	Steroid glycoside	Stem	Zhang *et al*., 2005
Denthyrsin [**214**]	Bicoumarin	Stem	Zhang *et al*., 2005
Denthyrsinin [**215**]	Phenanthrene	Stem	Zhang *et al*., 2005
Denthyrsinol [**216**]	Biphenanthrene	Stem	Zhang *et al*., 2005
Physcion [**219**]	Anthraquinone	Stem	Zhang *et al*., 2005
Scoparone [**67**]	Coumarin	Stem	Zhang *et al*., 2005
β-Sitosterol [**106**]	Steroid	Stem	Zhang *et al*., 2005

Table 1 (continued)

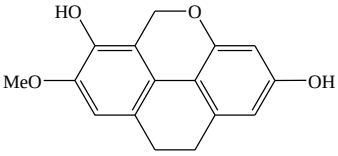
Plant and compound	Category	Plant part	Reference
Dendrobium trigonopus			
Gigantol [**14**]	Bibenzyl	Stem	Hu *et al*., 2008b
Hircinol [**96**]	Phenanthrene	Stem	Hu *et al*., 2008b
3-(4-Hydroxy-3-methoxyphenyl)-2-propen-1-ol [**220**]	Phenylpropanoid	Stem	Hu *et al*., 2008b
Moscatin [**17**]	Phenanthrene	Stem	Hu *et al*., 2008b
Naringenin [**24**]	Flavanone	Stem	Hu *et al*., 2008b
(-)-Syringaresinol [**221**]	Lignan	Stem	Hu *et al*., 2008b
Trigonopol A [**222**]	Bibenzyl	Stem	Hu *et al*., 2008b
Trigonopol B [**223**]	Bibenzyl	Stem	Hu *et al*., 2008b
Tristin [**71**]	Bibenzyl	Stem	Hu *et al*., 2008b



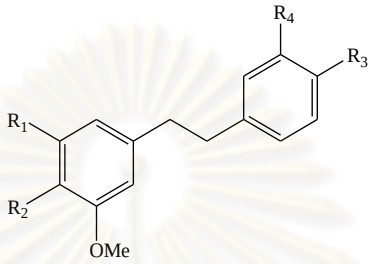
[**1**] Aduncin



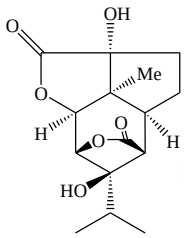
[**2**] Amoenin



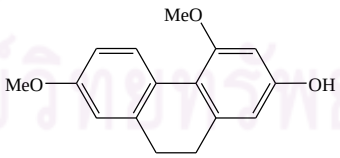
[**3**] Amoenumin



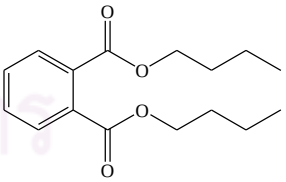
	R_1	R_2	R_3	R_4
[**4**] Amoenylin	OMe	OH	OMe	H
[**6**] 3,4′-Dihydroxy-5-methoxybibenzyl	OH	H	OH	H
[**7**] Isoamoenylin	OMe	OMe	H	OH
[**8**] Moscatilin	OMe	OH	OH	OMe
[**9**] Batatasin III	OH	H	H	OH
[**14**] Gigantol	OH	H	OH	OMe



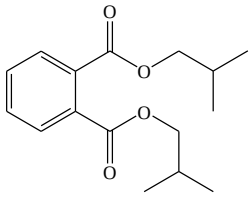
[**5**] Amotin



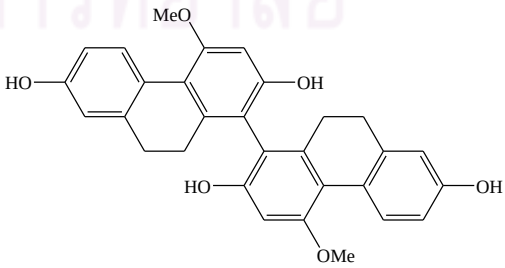
[**10**] Coelonin



[**11**] Dibutyl phthalate

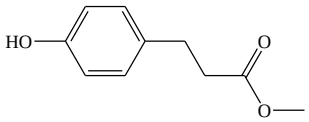


[**12**] Diisobutyl phthalate

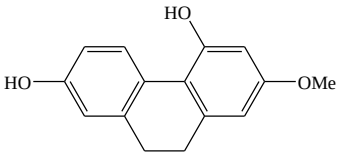


[**13**] Flavanthrin

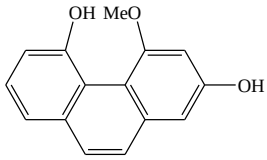
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp.



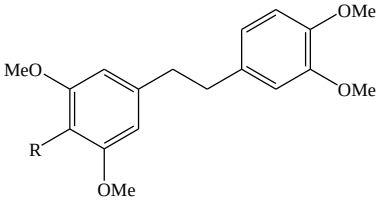
[**15**] *p*-Hydroxyphenylpropionic methyl ester



[**16**] Lusianthridin

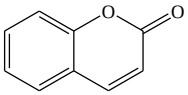


[**17**] Moscatin

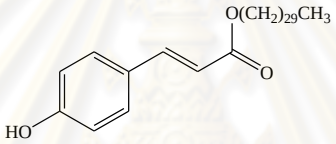


[**18**] Chrysotobibenzyl R = OMe

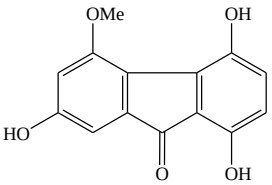
[**19**] Chrysotoxin R = OH



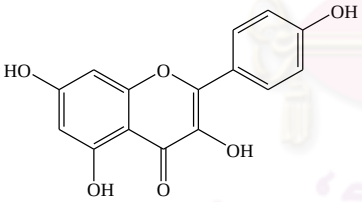
[**20**] Coumarin



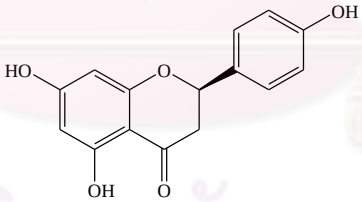
[**21**] Defuscin



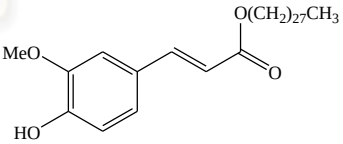
[**22**] Dendroflorin



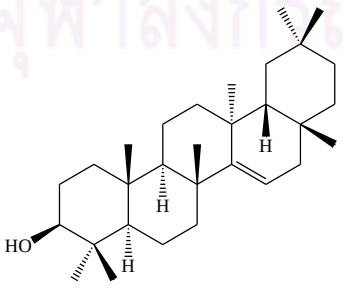
[**23**] Kaempferol



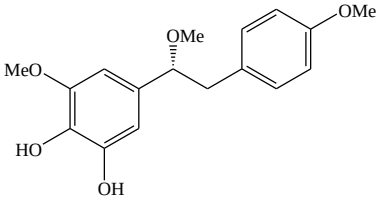
[**24**] Naringenin



[**25**] *n*-Octacosyl ferulate

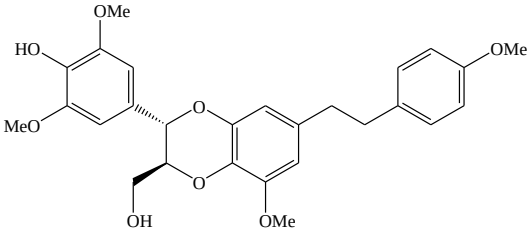


[**26**] Taraxerol

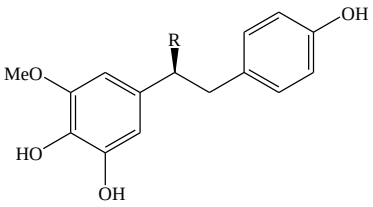


[**27**] Dendrocandin A

Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**

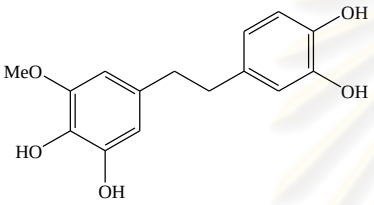


[**28**] Dendrocandin B

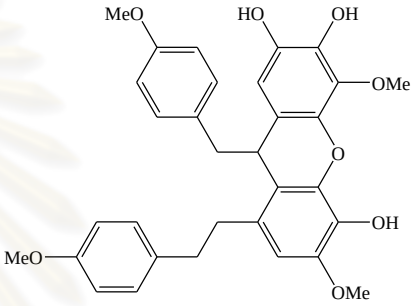


[**29**] Dendrocandin C R = OMe

[**30**] Dendrocandin D R = OEt

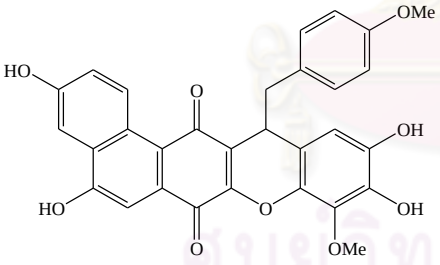


[**31**] Dendrocandin E

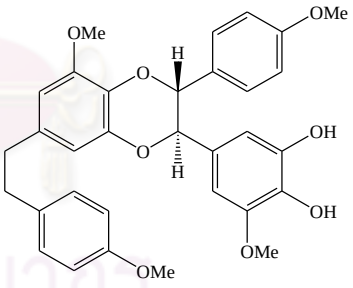


[**32**] Dendrocandin F R = OMe

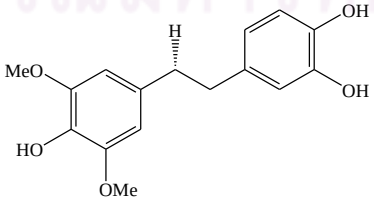
[**33**] Dendrocandin G R = OH



[**34**] Dendrocandin H

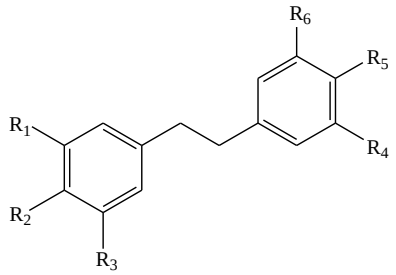


[**35**] Dendrocandin I

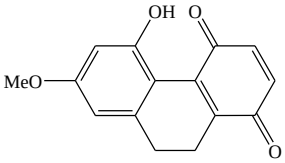


[**36**] Dendrophenol

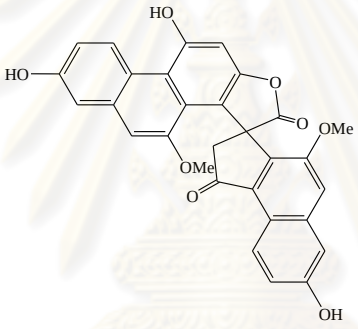
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



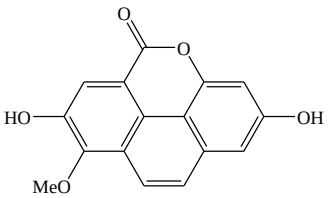
	R_1	R_2	R_3	R_4	R_5	R_6
[**37**] 4,4′-Dihydroxy-3,5-dimethoxybibenzyl	OMe	OH	OMe	H	OH	H
[**38**] 3,4-Dihydroxy-5,4′-dimethoxybibenzyl	OH	OH	OMe	H	OMe	H
[**39**] 3-*O*-Methylgigantol	OMe	OMe	H	OH	H	OMe
[**41**] Crepidatin	OMe	OMe	OMe	OMe	OH	H
[**44**] 4,4′-Dihydroxy-3,3′,5-trimethoxybibenzyl	OMe	OH	OMe	H	OH	OMe



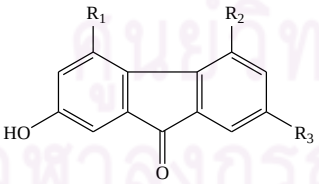
[**40**] Dendronone



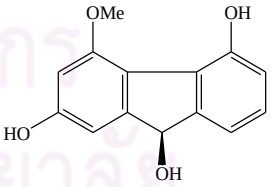
[**42**] Dendrochrysanene



[**46**] 2,7-Dihydroxy-8-methoxyphenanthro [4,5,*bcd*]pyran-5-(5*H*)-one

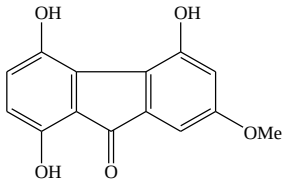


	R_1	R_2	R_3
[**43**] Dengibsin	OMe	OH	H
[**45**] Denchrysan A	OH	OMe	OH

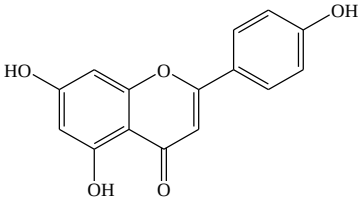


[**47**] (9*R*)-4-Methoxy-9*H*-fluorene-2,5,9-triol

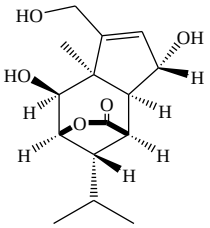
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



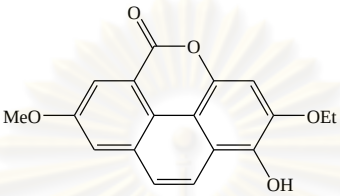
[**48**] 1,4,5-Trihydroxy-7-methoxy-9*H*-fluoren-9-one



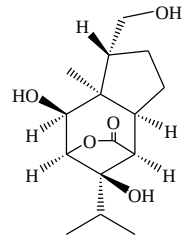
[**49**] Apigenin



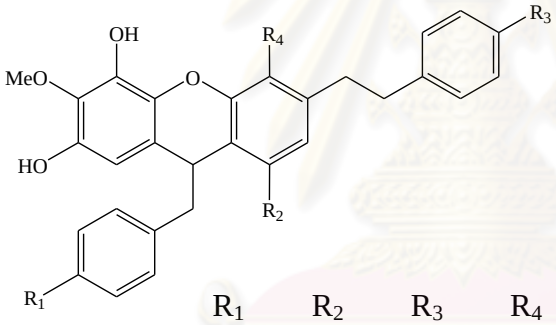
[**50**] Crystallinin



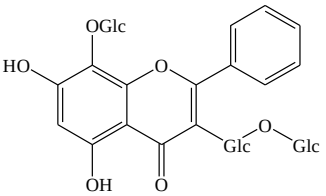
[**51**] Crystalltone



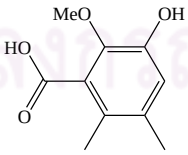
[**54**] Dendronobilin B



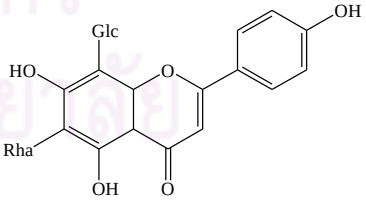
	R_1	R_2	R_3	R_4
[**52**] Dencryol A	OMe	OH	OH	H
[**53**] Dencryol B	OH	OMe	OMe	OH



[**55**] 6′′′-Glucosyl-vitexin

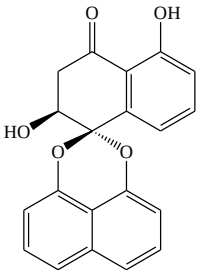


[**56**] 3-Hydroxy-2-methoxy-5,6-dimethylbenzoic acid

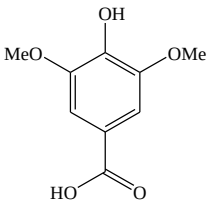


[**57**] Isoviolanthin

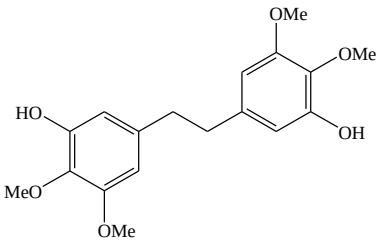
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



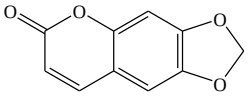
[**58**] Palmarumycin JC2



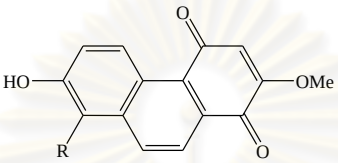
[**59**] Syringic acid



[**60**] Cumulatin

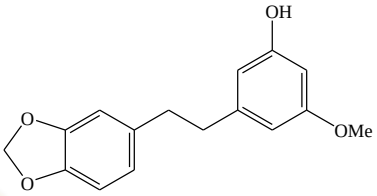


[**61**] Ayapin

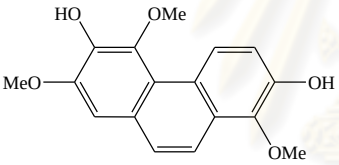


[**62**] Cypripedin R = OMe

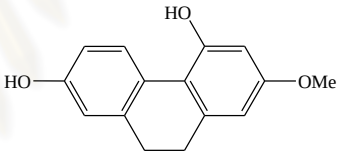
[**64**] Densiflorol B R = H



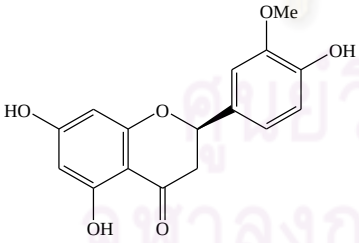
[**63**] Densiflorol A



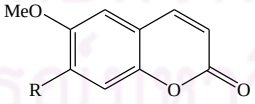
[**65**] 2,6-Dihydroxy-1,5,7 -trimethoxyphenanthrene



[**66**] 4,7-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene

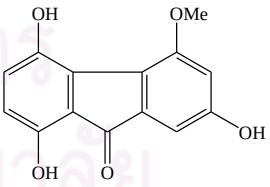


[**67**] Homoeriodictyol



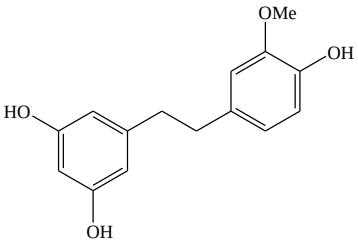
[**68**] Scoparone R = OMe

[**69**] Scopoletin R = OH

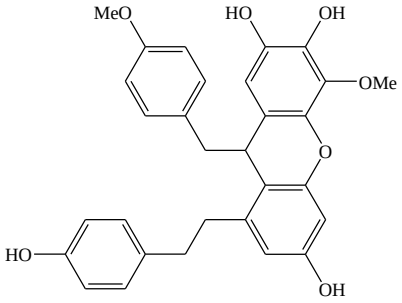


[**70**] 1,4,7-Trihydroxy-5-methoxy-9*H*-fluoren-9-one

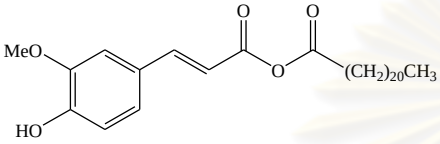
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



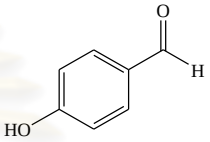
[**71**] Tristin



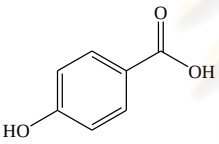
[**72**] Dendrofalconerol B



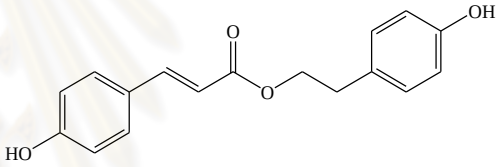
[**73**] Docosanoyl (*E*)-ferulate



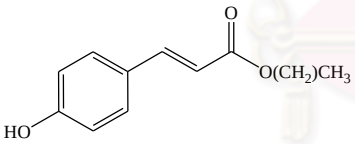
[**74**] *p*-Hydroxybenzaldehyde



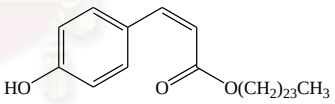
[**75**] *p*-Hydroxybenzoic acid



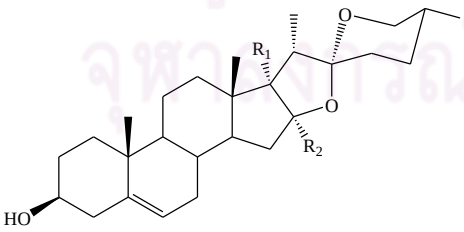
[**76**] 2-(*p*-Hydroxyphenyl) ethyl-*p*-coumarate



[**77**] Tetracosyl (*E*)-*p*-coumarate

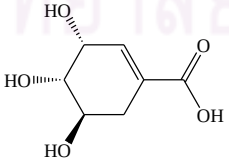


[**78**] Tetracosyl (*Z*)-*p*-coumarate



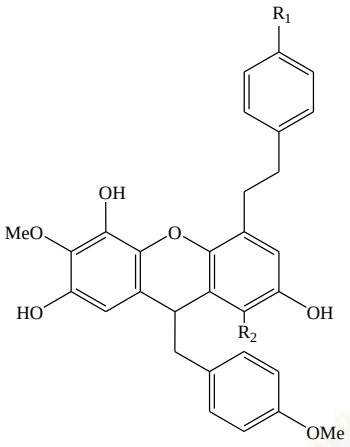
[**79**] Denfigenin $R_1 = R_2 = OH$

[**80**] Diosgenin $R_1 = R_2 = H$



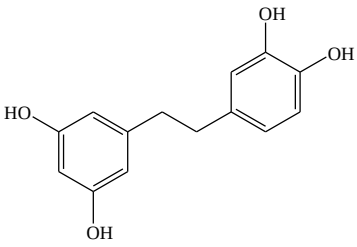
[**81**] (-)-Shikimic acid

Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**

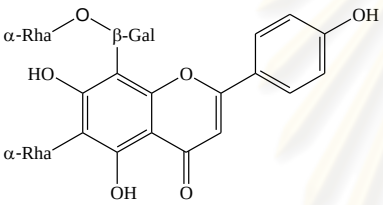


[**82**] Dengraol A R_1 = OH R_2 = H

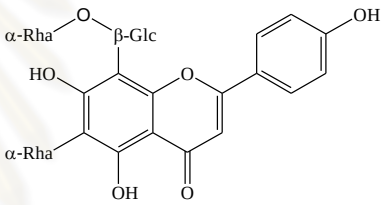
[**83**] Dengraol B R_1 = OMe R_2 = OMe



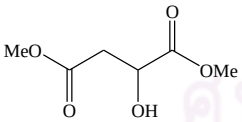
[**84**] 3,5,4′-Trihydroxybibenzyl



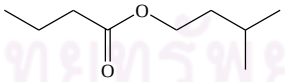
[**85**] 6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-galactopyranosyl]apigenin



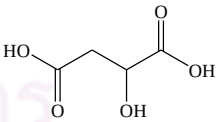
[**86**] 6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin



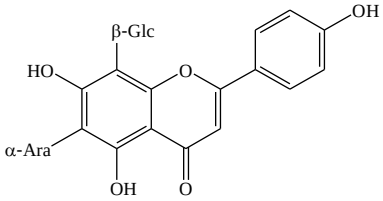
[**87**] Dimethyl malate



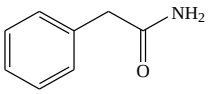
[**88**] Isopentyl butyrate



[**90**] Malic acid

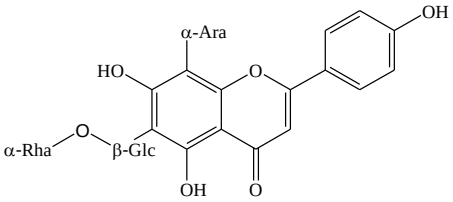


[**89**] Isoschaftoside

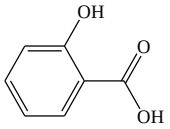


[**91**] Phenylacetamide

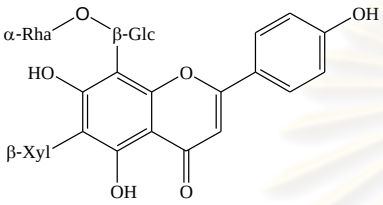
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



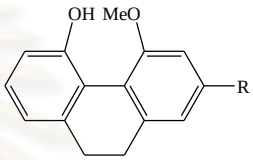
[**92**] 6-*C*-[(2-O-α-Rhamnopyranosyl)-β-glucopyranosyl]-8-*C*-(α-arabinopyranosyl)apigenin



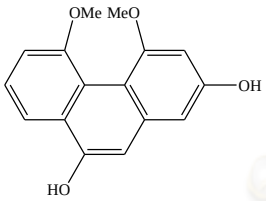
[**93**] Salicylic acid



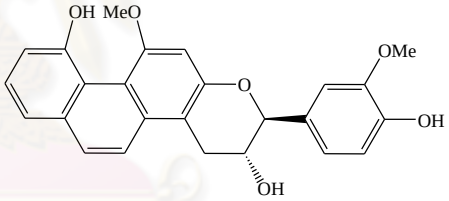
[**94**] 6-*C*-(β-Xylopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin



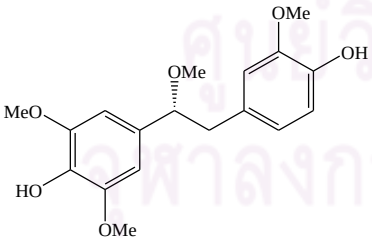
[**96**] Hircinol R = OH
[**97**] 5-Hydroxy-2,4-dimethoxyphenanthrene R = OMe



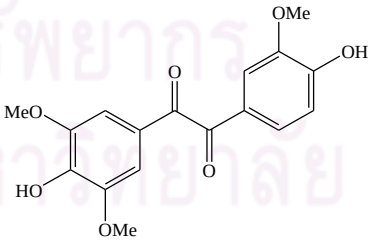
[**98**] Loddigesiinol A



[**99**] Loddigesiinol B

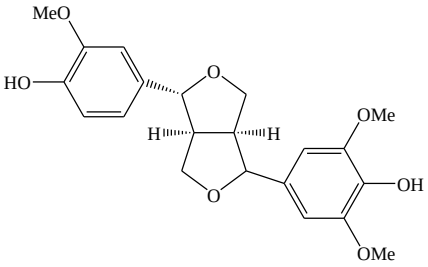


[**100**] Loddigesiinol C

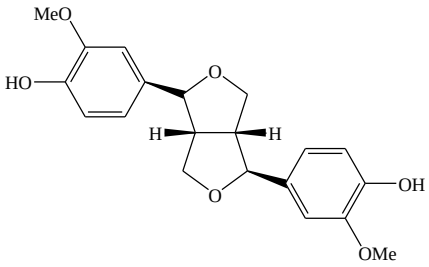


[**101**] Loddigesiinol D

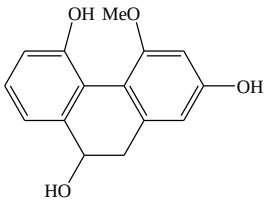
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



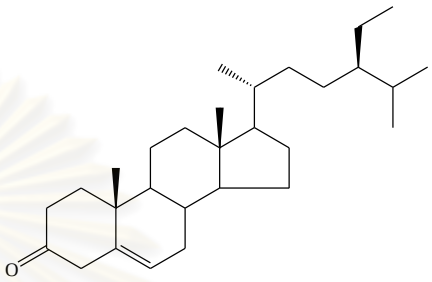
[**102**] (-)-Medioresinol



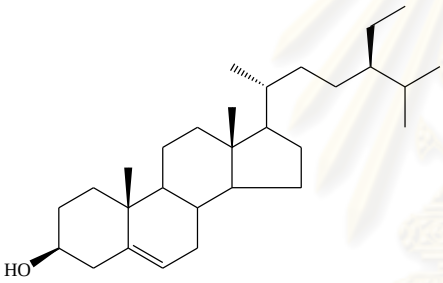
[**103**] (-)-Pinoresinol



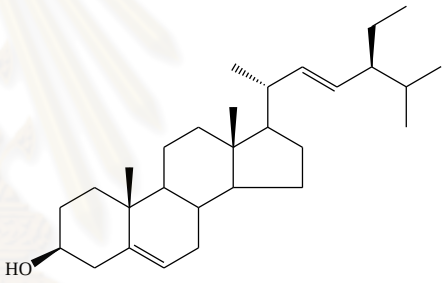
[**104**] Rotundatin



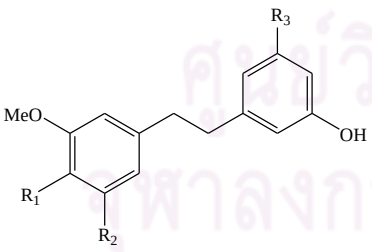
[**105**] Sitostenone



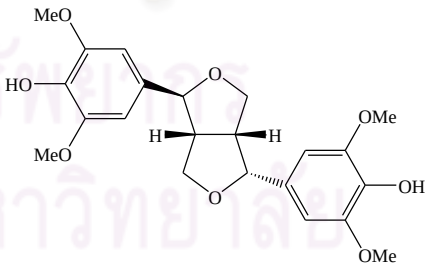
[**106**] β-Sitosterol



[**107**] Stigmasterol

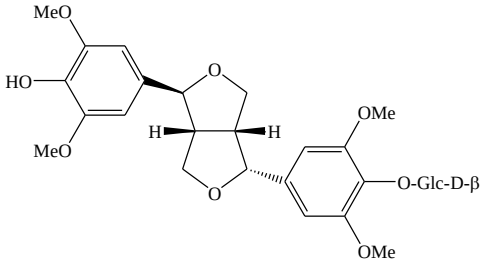


	R_1	R_2	R_3
[**108**] Aloifol I	OH	OMe	H
[**109**] Batatasin	H	H	OH

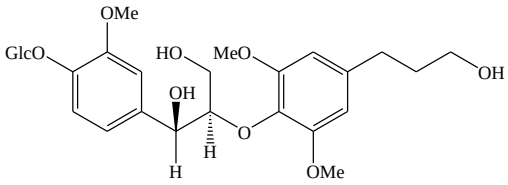


[**110**] Episyringaresinol

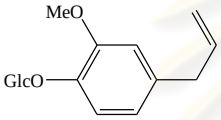
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



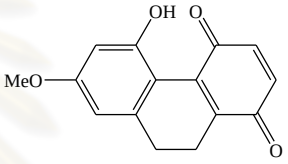
[**111**] Episyringaresinol 4′′ -*O*-β-D-glucopyranoside



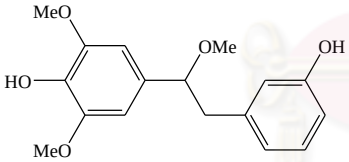
[**112**] Erythro-1-(4-*O*-β-D-glucopyranosyl-3-methoxyphenyl) -2-[4-(3-hydroxypropyl)2,6-dimethoxyphenoxy]-1,3-propanediol



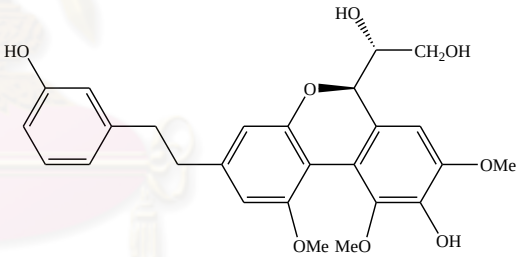
[**113**] Eugenyl-*O*-β-D-glucopyranoside



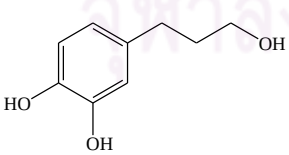
[**114**] 5-Hydroxy-7-methoxy-9,10-dihydrophenanthrene-1,4-dione



[**115**] 4-[2-(3-Hydroxyphenol)-1-methoxyethyl]-2,6-dimethoxyphenol

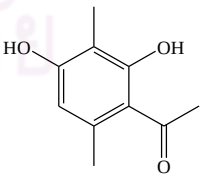


[**116**] Longicornuol A



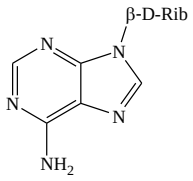
[**117**] 3-(3-Methoxy,4-hydroxyphenyl)-1-propanol

[**118**] 4-Methoxy-9,10-dihydrophenanthrene-2,5,7-triol

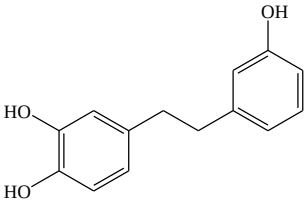


[**119**] Methyl β-orsellinate

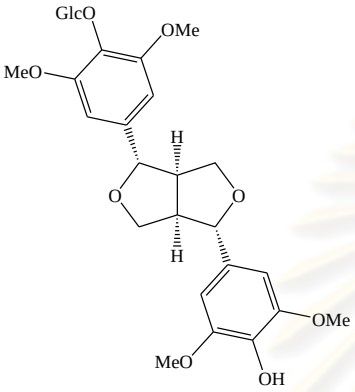
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



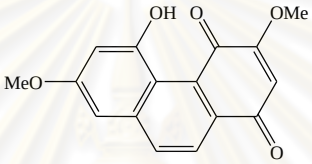
[**120**] 9-β-D-Ribofuranosyl-9*H*-purin-6-amine



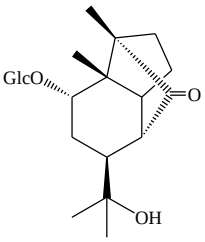
[**121**] 3,3′,4-Trihydroxybibenzyl



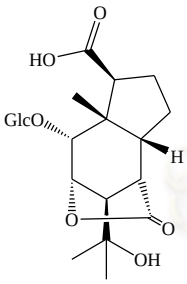
[**122**] Acanthoside B



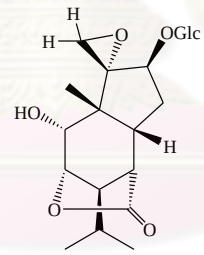
[**123**] Denbinobin



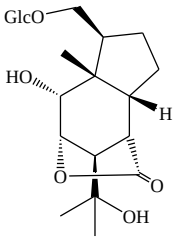
[**124**] Dendromoniliside A



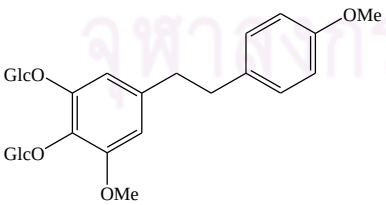
[**125**] Dendromoniliside B



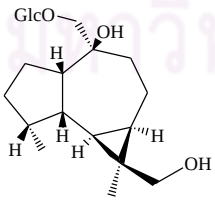
[**126**] Dendromoniliside C



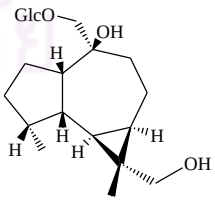
[**127**] Dendromoniliside D



[**128**] Dendromoniliside E

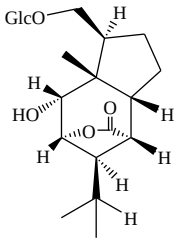


[**129**] Dendroside A

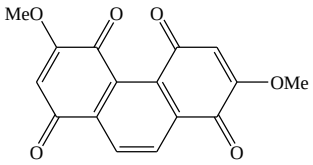


[**130**] Dendroside C

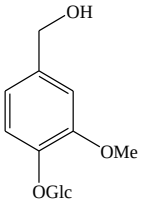
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



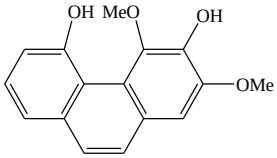
[**131**] Dendroside F



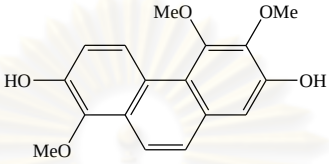
[**132**] Moniliformin



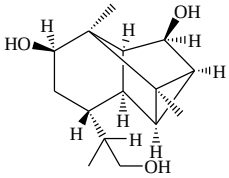
[**133**] Vanilloloside



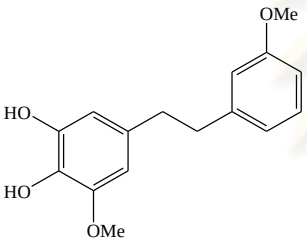
[**134**] Bulbophyllanthrin



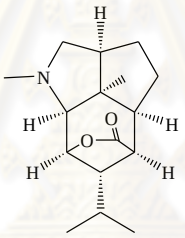
[**135**] Confusarin



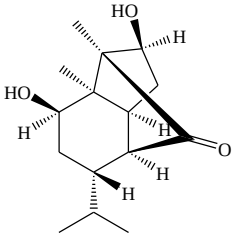
[**136**] Dendrobane A



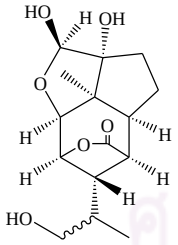
[**137**] Dendrobin A



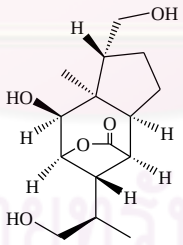
[**138**] Dendrobine



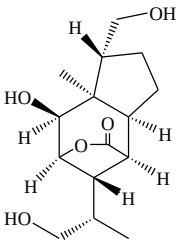
[**139**] Dendronobilin A



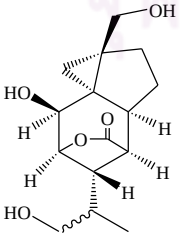
[**140**] Dendronobilin C



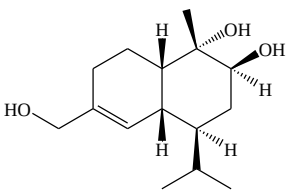
[**141**] Dendronobilin D



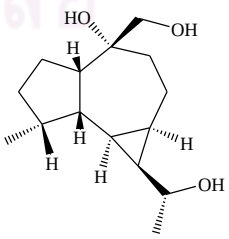
[**142**] Dendronobilin E



[**143**] Dendronobilin F

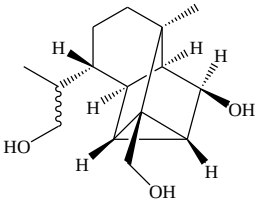


[**144**] Dendronobilin G

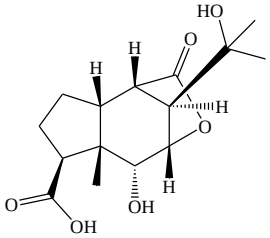


[**145**] Dendronobilin H

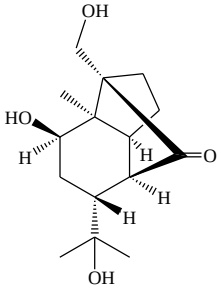
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



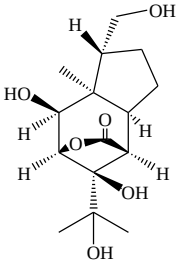
[**146**] Dendronobilin I



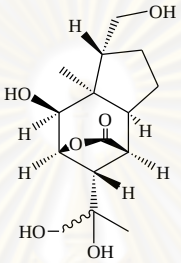
[**147**] Dendronobilin J



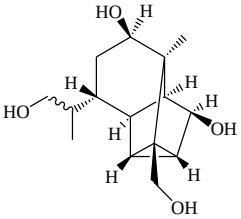
[**148**] Dendronobilin K



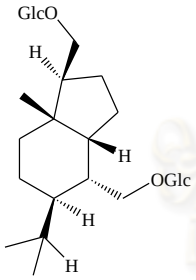
[**149**] Dendronobilin L



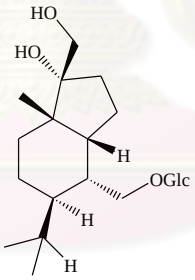
[**150**] Dendronobilin M



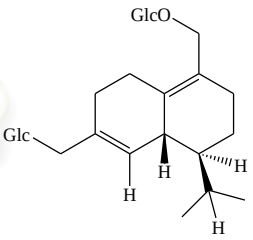
[**151**] Dendronobilin N



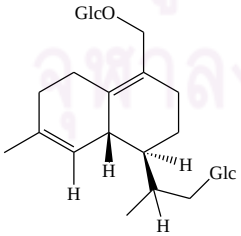
[**152**] Dendronobiloside A



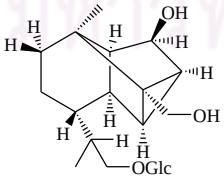
[**153**] Dendronobiloside B



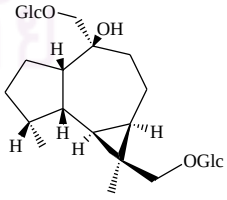
[**154**] Dendronobiloside C



[**155**] Dendronobiloside D

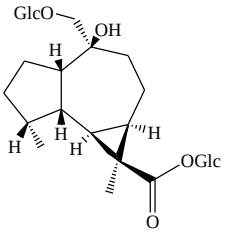


[**156**] Dendronobiloside E

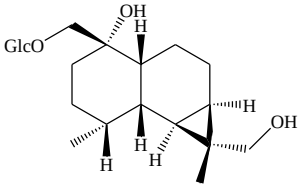


[**157**] Dendroside B

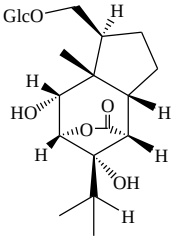
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



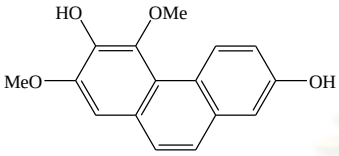
[**158**] Dendroside D



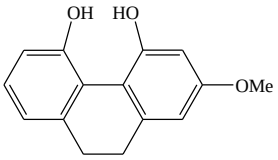
[**159**] Dendroside E



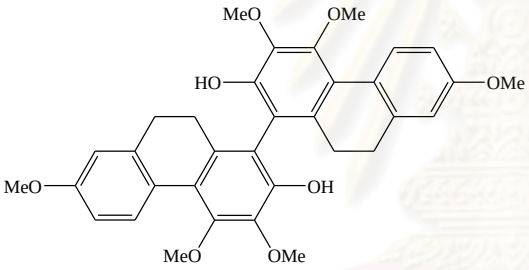
[**160**] Dendroside G



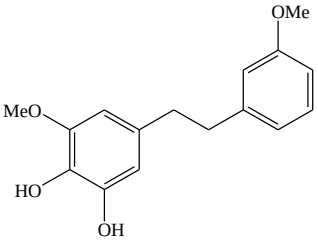
[**161**] 3,7-Dihydroxy-2,4-dimethoxyphenanthrene



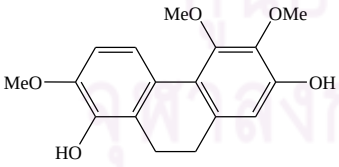
[**162**] 4,5-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene



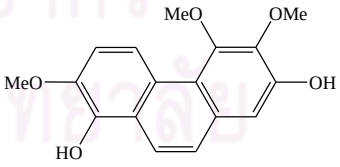
[**163**] 2,2′-Dihydroxy-3,3′,4,4′,7,7′-hexamethoxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene



[**164**] 4,5-Dihydroxy-3,3′-dimethoxybibenzyl

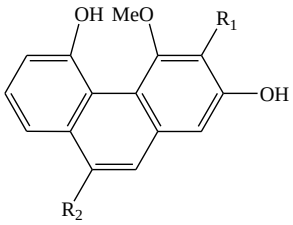


[**165**] 2,8-Dihydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene



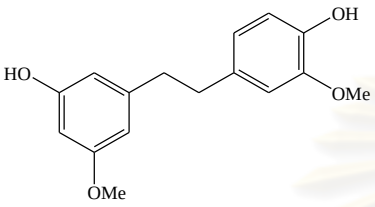
[**166**] 2,8-Dihydroxy-3,4,7-trimethoxyphenanthrene

Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**

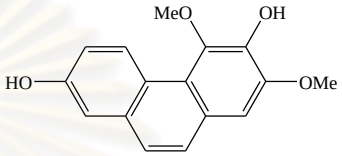


[**167**] 2,5-Dihydroxy-3,4-dimethoxyphenanthrene R_1 = OMe R_2 = H

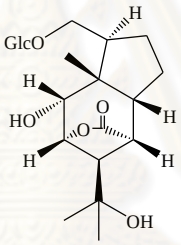
[**169**] 2,5-Dihydroxy-4,9-dimethoxyphenanthrene R_1 = H R_2 = OMe



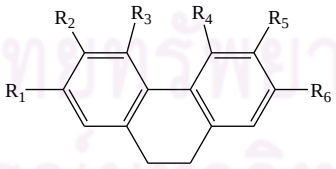
[**170**] 3,4′-Dihydroxy-5,5′-dimethoxydihydrostilbene



[**172**] 5,7- Dimethoxyphenanthrene-2,6-diol

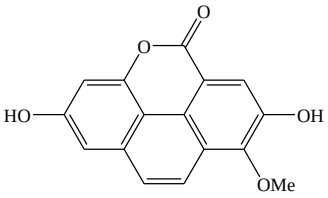


[**171**] 7,12-Dihydroxy-5-hydroxymethyl-11-isopropyl-6-methyl-9-oxatricyclo [6.2.1.$0^{2,6}$]undecan-10-one-15-*O*-β-D-glucopyranoside

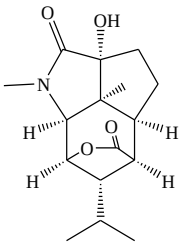


	R_1	R_2	R_3	R_4	R_5	R_6
[**168**] 4,5-Dihydroxy-3,7-dimethoxydihydrophenanthrene	OMe	H	OH	OH	OMe	H
[**173**] Ephemeranthol A	OMe	OMe	OH	H	H	OH
[**174**] Ephemeranthol C	H	H	OH	OMe	OH	OH
[**175**] Erianthridin	OH	H	H	OMe	OMe	OH

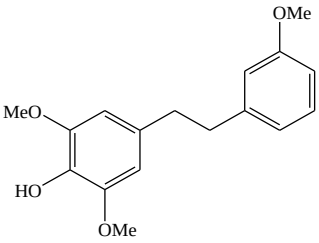
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



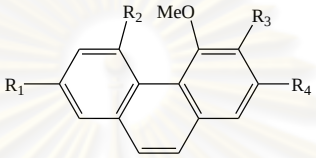
[**176**] Fimbriatone



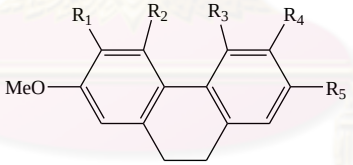
[**182**] 3-Hydroxy-2-oxodendrobine



[**183**] 4-Hydroxy-3,3′,5-trimethoxybibenzyl

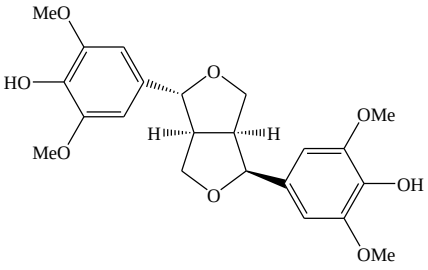


	R_1	R_2	R_3	R_4
[**177**] Fimbriol B	H	OH	OH	OH
[**179**] Flavanthrinin	OH	H	H	OH
[**181**] 3-Hydroxy-2,4,7-trimethoxyphenanthrene	OMe	H	OH	OMe

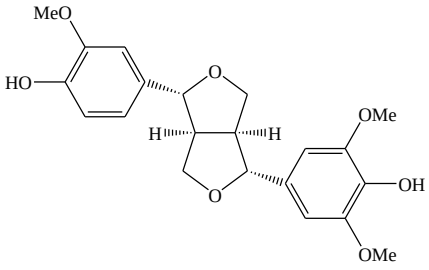


	R_1	R_2	R_3	R_4	R_5
[**178**] Flavanthridin	OH	OMe	H	H	OH
[**180**] 3-Hydroxy-2,4,7-trimethoxy-9,10-dihydrophenanthrene	H	H	OMe	OH	OMe
[**184**] 2-Hydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene	H	H	OMe	H	OH
[**185**] 2-Hydroxy-4,7-dimethoxy-9,10-dihydrophenanthrene	H	H	OMe	OH	OMe

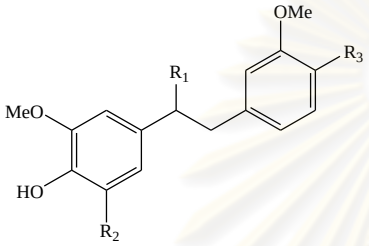
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



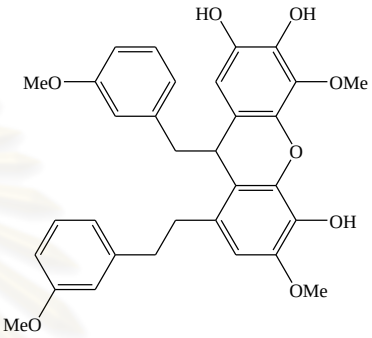
[**186**] Lirioresinol A



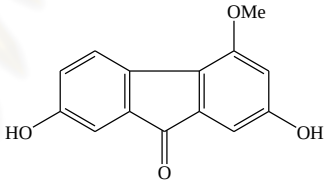
[**187**] Medioresinol



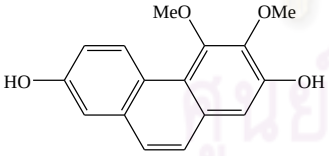
	R_1	R_2	R_3
[**188**] Nobilin A	OMe	OH	H
[**189**] Nobilin B	OMe	OMe	OH
[**190**] Nobilin C	OMe	OMe	OMe
[**191**] Nobilin D	OH	OMe	OH



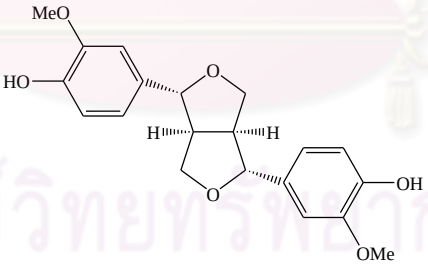
[**192**] Nobilin E



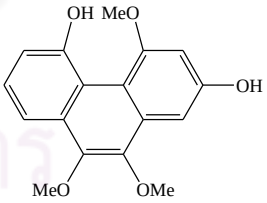
[**193**] Nobilone



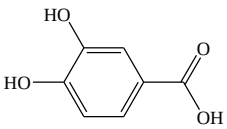
[**194**] Nudol



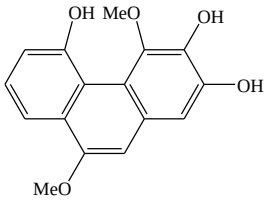
[**195**] Pinoresinol



[**196**] Plicatol A

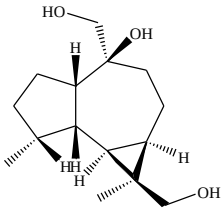


[**197**] Protocatechuic acid

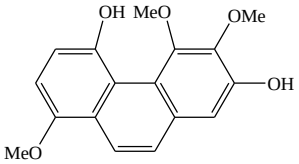


[**198**] 2,3,5-Trihydroxy-4,9- dimethoxyphenanthrene

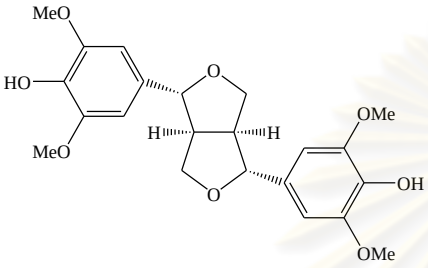
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



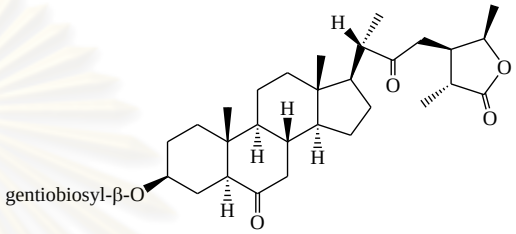
[**199**] 10β,12,14-Trihydroxy-Alloaromadendrane



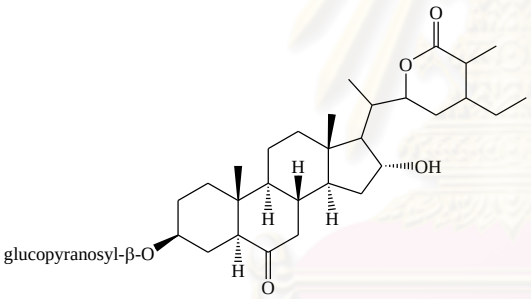
[**200**] 3,4,8-Trimethoxyphenanthrene-2,5-diol



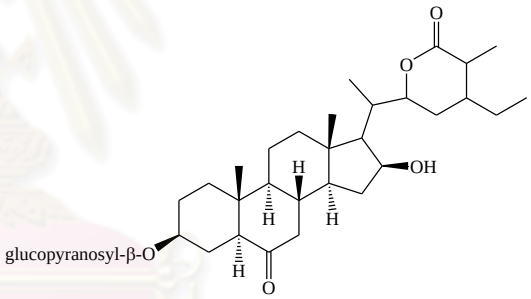
[**201**] Syringaresinol



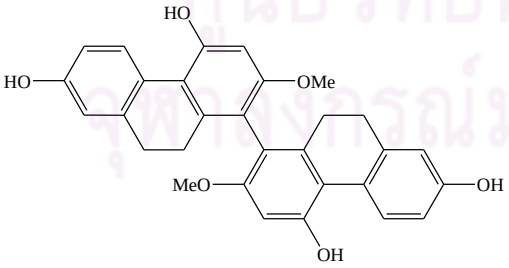
[**202**] Dendrosteroside



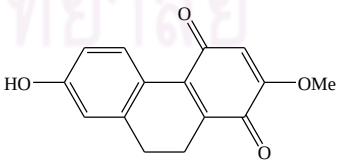
[**203**] Epi-ochreasteroside



[**204**] Ochreasteroside

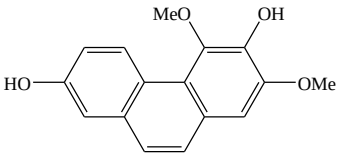


[**205**] 2,2′-Dimethoxy-4,4′-7,7′-tetrahydroxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene

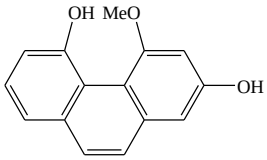


[**206**] Ephemeranthoquinone

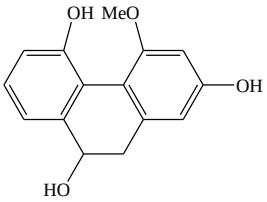
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



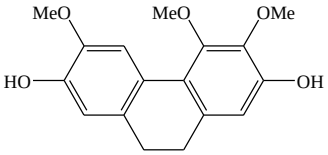
[**207**] Epheranthol B



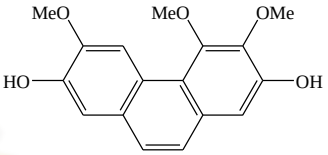
[**208**] Plicatol B



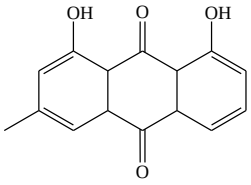
[**209**] Plicatol C



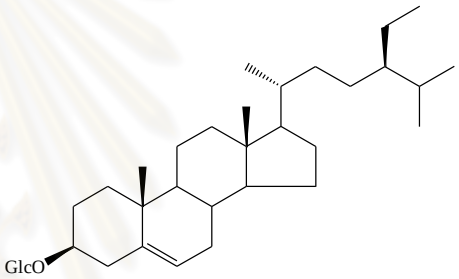
[**210**] 2,7-Dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene



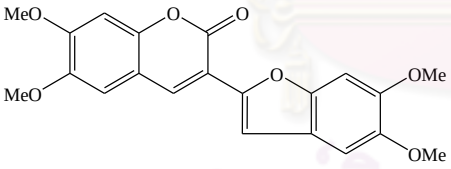
[**211**] 2,7-Dihydroxy-3,4,6-trimethoxyphenanthrene



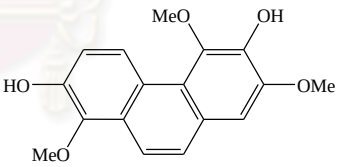
[**212**] Chrysophanol



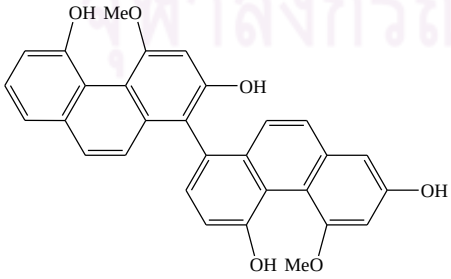
[**213**] Daucosterol



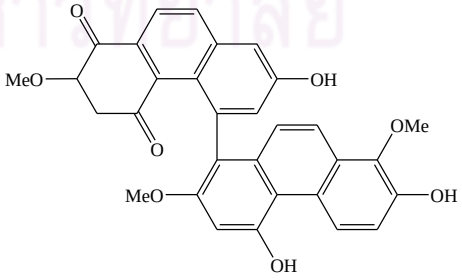
[**214**] Denthyrsin



[**215**] Denthyrsinin

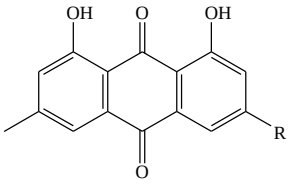


[**216**] Denthyrsinol

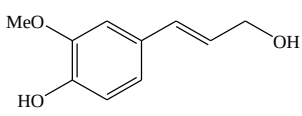


[**217**] Denthyrsinone

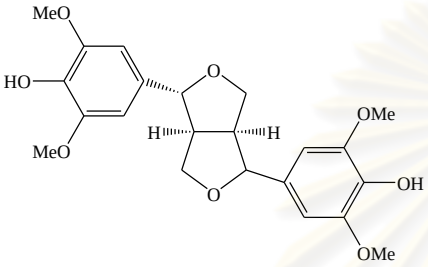
Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**



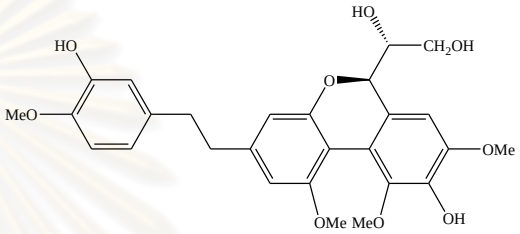
[**218**] Emodin R = OH
[**219**] Physcion R = OMe



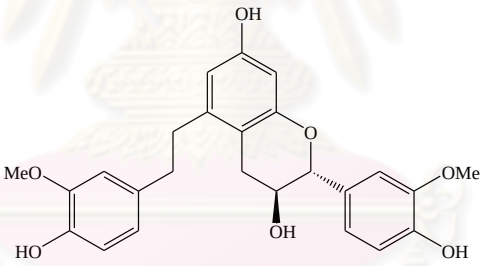
[**220**] 3-(4-Hydroxy-3- methoxyphenyl)-2- propen-1-ol



[**221**] (-)-Syringaresinol



[**222**] Trigonopol A



[**223**] Trigonopol B

Figure 2 Structure of compounds previously isolated from *Dendrobium* spp. **(continued)**

2. Traditional uses and biological activities of *Dendrobium* constituents

Plants of the genus *Dendrobium* were used in traditional medicine in many countries. In China, the stems of *Dendrobium* spp. were used as tea, for treating fever, sunstroke, thirst and weakness, due to their cooling effect. *Dendrobium nobile* was prescribed for stomach pain and fever. In Korea, China and Japan, *D. moniliforme* was used in the treatment of peptic ulcer, impotence, joints pain and used as nutrient for patients. In Indo-China, *D. crumenatum* was used for ulcers and pain, the pounded leaves were covered burn wounds and pimples, the warm juice of pseudobulbs were used as ear drop to relieve ear pain. In Malay Peninsula, *D. blumei* and *D. subulatum* were used as poultice for skin eruptions and headache, respectively. In the treatment of abcites, *D. pumilum* or *D. quadrangulare* were used. (Perry and Metzger, 1980).

In Thailand, an infusion or tea from the aerial parts of *D. draconis* is remedial for fever, and as a blood enhancer (Chuakul *et al*., 1995).

Regarding the biological activities of compounds from *Dendrobium* plants, moscatilin, crepidatin, gigantol, chrysotoxin, nobilin E and dendroflorin showed free radical scavenging activity (Zhang *et al*., 2007). Antiplatelet aggregration activity was observed for moscatilin, gigantol, scoparone and scopoletin (Fan *et al*., 2001). Dendroflorin, 1,4,5-trihydroxy-7-methoxy-9*H*-fluoren-9-one and denchrysan A had cytotoxic activity against hepatoma cells (Chen *et al*., 2008). Denbinobin was found to be an anti-inflammatory agent (Lin *et al*., 2001). Dendrobine and dendromine demonstrated neuroprotective effect (Wang *et al*., 2010).

CHAPTER III

EXPERIMENTAL

1. Source of plant materials

Dendrobium draconis samples were purchased from Jatujak market, Bangkok, in September 2009. Authentication was performed by comparison with a herbarium specimen (BKF No. 122029) at the National Park, Wildlife and Plant Conservation Department, Ministry of Natural Resources and Environment. A voucher specimen (BS-092552) has been deposited at Department of Pharmacognosy and Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand.

2. General techniques

2.1 Analytical thin-layer chromatography (TLC)

Technique	:	One dimension, ascending
Absorbent	:	Silica gel 60 F_{254} (E. Merck) precoated plate
Layer thickness	:	0.2 mm
Distance	:	6.5 cm
Temperature	:	Laboratory temperature (30-35ºC)
Detection	:	1. Ultraviolet light at wavelengths of 254 and 365 nm. 2. Anisaldehyde and heating at 105°C for 10 min.

2.2 Column chromatography

2.2.1 Vacuum liquid column chromatography

Adsorbent	:	Silica gel 60 (No.7734) particle size 0.063-0.200 mm (E. Merck)
Packing method	:	Dry packing
Sample loading	:	The sample was dissolved in a small amount of organic solvent, mixed with a small quantity of adsorbent, triturated, dried and then placed gently on top of the column.
Detection	:	Fractions were examined by TLC under UV light at the wavelengths of 254 and 365 nm.

2.2.2 Flash column chromatography

Adsorbent	:	Silica gel 60 (No.9385) particle size 0.040-0.063 mm (E. Merck)
Packing method	:	Wet packing
Sample loading	:	The sample was dissolved in a small amount eluent and then applied gently on top of the column.
Detection	:	Fractions were examined in the same way as described in section 2.2.1

2.2.3 Gel filtration chromatography

Adsorbent	:	Sephadex LH 20 (Pharmacia)
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 amount eluent and then applied gently on top of the column.

2.3 Spectroscopy

2.3.1 Mass spectra

Mass spectra were recorded on a Micromass LCT mass spectrometer (ESI-TOF-MS). (National Center for Genetic Engineering and Biotechnology).

2.3.2 Infrared (IR) spectra

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

2.3.3 Ultraviolet (UV) absorption spectra

UV (in methanol) spectra were obtained on a Shimadzu UV-160A UV/vis spectrophotometer (Pharmaceutical Research Instrument Center, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

2.3.4 Proton and carbon-13 nuclear magnetic resonance (^{1}H and ^{13}C-NMR) spectra

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Bruker Avance DPX-300 FT-NMR spectrometer (Faculty of Pharmaceutical Sciences, Chulalongkorn University).

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained on a JEOL JMN-A 500 NMR spectrometer (Scientific and Technological Research Equipment Center, Chulalongkorn University).

Solvents for NMR spectra were deuterated chloroform (chloroform-*d*) and deuterated acetone (acetone-d_6). Chemical shifts were reported in ppm scale using the chemical shift of the solvent as the reference signal.

2.4 Solvents

All organic solvents employed throughout this work were of commercial grade and were redistilled prior to use.

3. Extraction and isolation

3.1 Extraction

Dried powdered stems of *D. draconis* (1.8 kg) were extracted with MeOH (3 x 10 L) at room temperature to give a viscous mass of dried extract (112.29 g) after evaporation of the solvent.

3.2 Separation of MeOH extract

The MeOH extract (112.29 g) was separated by vacuum liquid column chromatography using a sintered glass filter column of silica gel (No.7734, 250 g). The MeOH extract was dissolved in a small amount of MeOH, triturated with silica gel (No.7734) and dried under vacuum. Elution was performed in a polarity gradient manner with mixtures of *n*-hexane and EtOAc (10:0 to 0:10) and CH_2Cl_2-MeOH (10:0 to 0:10) respectively. The eluates were collected 250 ml per fraction and examined by TLC (silica gel, EtOAc- *n*-hexane 6:4) to yield 30 fractions. Fractions (30 fractions) with similar chromatographic pattern were combined to yield 10 fractions: A (124.6 mg), B (4.55 g), C (3.05 g), D (5.51 g), E (1.44 g), F (2.14 g), G (526.3 mg), H (11.7 g), I (17.23 g), and J (54.17 g).

3.2.1 Isolation of compound DD1 (hircinol)

Fraction F (2.14 g) was fractionated on a silica gel (No. 9385) column. Elution was performed in a polarity gradient manner with mixtures of *n*-hexane-EtOAc (10:0 to 0:10) and CH_2Cl_2-MeOH (10:0 to 0:10) respectively. Fractions (29 fractions) showing similar chromatographic patterns were combined (TLC, silica gel, EtOAc-*n*-hexane 1:1) to yield 7 fractions: F1 (1.17 g), F2 (624.5 mg), F3 (141.3 mg), F4 (61.9 mg), F5 (58.5 mg), F6 (58.1 mg), F7 (23.1 mg).

Fraction F1 (1.17 g) was repeatedly fractionated by column chromatography (silica gel, gradient mixtures of *n*-hexane-EtOAc 10:0 to 0:10) to yield 19 fractions. Fractions with similar chromatographic patterns were combined (TLC, silica gel, EtOAc-*n*-hexane 3:7) to give 6 fractions: F1A (123.1 mg), F1B (305.8 mg), F1C (112.3 mg), F1D (105.8 mg), F1E (113 mg), and F1F (348.7 mg).

Fraction F1E (113 mg) was further purified on a Sephadex LH20 column (acetone) to give compound DD1 as a white powder (2.5 mg, R_f 0.2, silica gel, EtOAc-*n*-hexane 3:7). It was identified as hircinol [**96**].

3.2.2 Isolation of compound DD2 (gigantol)

Fraction F2 (624.5 mg) was further separated on a Sephadex LH20 column (acetone). Eighteen fractions were combined according to their TLC patterns (silica gel, EtOAc-*n*-hexane 1:1) to yield 7 fractions: F2A (15.8 mg), F2B (20.1 mg), F2C (414.1 mg), F2D (18.7 mg), F2E (101.1 mg), F2F (20.1 mg), and F2G (21.1 mg).

Fraction F2C (414.1 mg) was repeatedly fractionated on column chromatography (silica gel, gradient mixtures of *n*-hexane-EtOAc 10:0 to 0:10) to give compound DD2 as a brown amorphous solid (115.2 mg, R_f 0.42, silica gel, EtOAc-*n*-hexane 1:1). It was identified as gigantol [**14**].

3.2.3 Isolation of compound DD3 (batatasin III)

Fraction F2E (101.1 mg) was subjected to column chromatography (silica gel, gradient mixtures of CH_2Cl_2-MeOH 10:0 to 0:10) to give compound DD2 as a colourless amorphous solid (115.2 mg, R_f 0.4, silica gel, EtOAc-*n*-hexane 1:1). It was identified as batatasin III [**9**].

3.2.4 Isolation of compound DD4 (5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone)

Fraction G (526.3 mg) was fractionated on a silica gel (No. 9385) column. Elution was performed in a polarity gradient manner with mixtures of *n*-hexane-EtOAc (10:0 to 0:10). Fractions (18 fractions) showing similar chromatographic patterns were combined (TLC, silica gel, EtOAc-*n*-hexane 1:1) to yield 10 fractions: G1 (14.8 mg), G2 (10.4 mg), G3 (15.2 mg), G4 (29.9 mg), G5 (42.2 mg), G6 (58.1 mg), G7 (157.0 mg), G8 (22.9 mg), G9 (49.3 mg), and G10 (38.6 mg).

Fraction G7 (157.0 mg) was further purified on a Sephadex LH20 column (acetone) to yield, after chromatographic examination (TLC, silica gel, EtOAc-*n*-hexane 4:6), 6 fractions: G7A (5.2 mg), G7B (10.8 mg), G7C (12.5 mg), G7D (14.9 mg), G7E (83 mg), and G7F (16.9 mg).

Fraction G7E (83 mg) was fractionated by column chromatography (silica gel, gradient mixtures of *n*-hexane-EtOAc 10:0 to 0:10) to yield, after chromatographic examination (TLC, silica gel, EtOAc-*n*-hexane 1:1), 6 fractions: G7E1 (1.3 mg), G7E2 (1.3 mg), G7E3 (1.6 mg), G7E4 (4.3 mg), G7E5 (68.5 mg), G7E6 (3.2 mg).

Fraction G7E5 (68.5 mg) was repeatedly fractionated on a flash column (silica gel, gradient mixtures of *n*-hexane-EtOAc 10:0 to 0:10) to give compound DD4 as a reddish powder (3 mg, R_f 0.36, silica gel, EtOAc-*n*-hexane 1:1). It was identified as a new compound named 5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone [**224**].

3.2.5 Isolation of compound DD5 (4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol)

Fraction H (11.7 g) was fractionated by vacuum liquid column chromatography on silica gel (No. 9385). Elution was performed in a polarity gradient manner with mixtures of *n*-hexane-EtOAc (10:0 to 0:10) and CH_2Cl_2-MeOH (10:0 to 0:10), respectively. Fractions (41 fractions) showing similar chromatographic patterns were combined (TLC, silica gel, MeOH-CH_2Cl_2 1:9) to yield 10 fractions: H1 (57.2 mg), H2 (153.3 mg), H3 (86.6 mg), H4 (99.9 mg), H5 (1.23 g), H6 (1.36 g), H7 (2.21 g), H8 (1.65 g), H9 (2.81 g), and H10 (1.98 g).

Fraction H7 (2.21 g) was separated by flash column chromatography (silica gel, gradient mixture of hexane-EtOAc (10:0 to 0:10) and CH_2Cl_2-MeOH (10:0 to 0:10), respectively. Thirty eight fractions with similar chromatographic patterns (TLC, silica gel, EtOAc-*n*-hexane 1:1) were combined to yield 11 fractions: H7A (35.8 mg), H7B (76.3 mg), H7C (80.2 mg), H7D (282.8 mg), H7E (105.0 mg), H7F (414.8 mg), H7G (85.3 mg), H7H (70.1 mg), H7I (168.2 mg), H7J (221.3 mg), and H7K (90.8 mg).

Fraction H7E (105 mg) was repeatedly fractionated on a flash column (silica gel, gradient mixtures of *n*-hexane-EtOAc 10:0 to 0:10) to yield 6 fractions after TLC examination (silica gel, EtOAc-*n*-hexane 1:1): H7E1 (11.2 mg), H7E2 (9.8 mg), H7E3 (7.9 mg), H7E4 (10.3 mg), H7E5 (52.3 mg), and H7E6 (12.8 mg).

Purification of fraction H7E5 (52.3 mg) on a flash column (silica gel, gradient mixtures of CH_2Cl_2-MeOH 10:0 to 0:10) gave compound DD5 as a red amorphous powder (22 mg, R_f 0.30, silica gel, EtOAc-*n*-hexane 1:1). It was identified as 4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol [**118**].

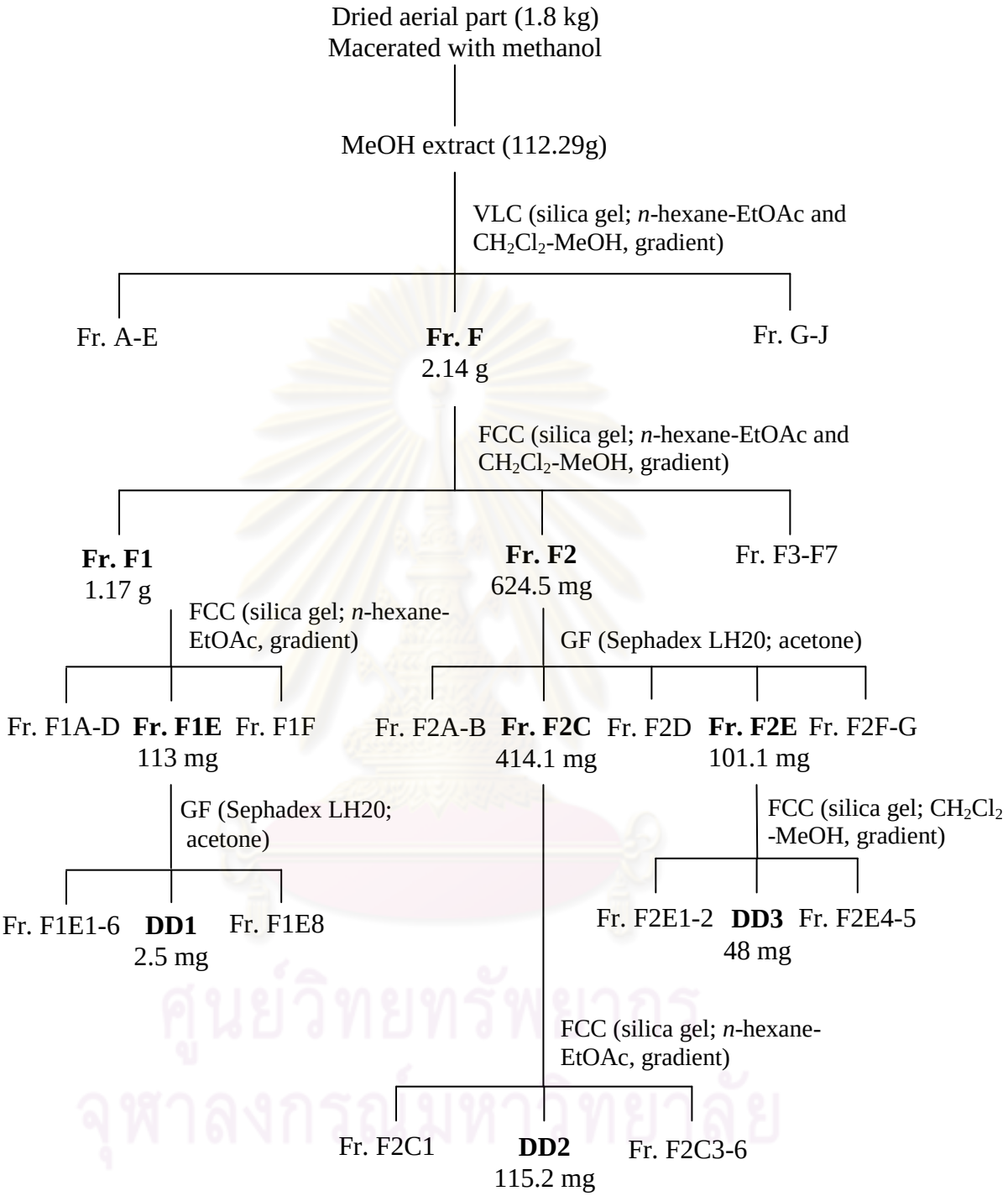
3.2.6 Isolation of compound DD6 (tristin)

Fraction H8 (1.65 g) was fractionated on a silica gel (No. 9385) column. Elution was performed in a polarity gradient manner with mixtures of CH_2Cl_2-MeOH (10:0 to 0:10). Fractions (19 fractions) showing similar chromatographic patterns were combined (TLC, silica gel, MeOH-CH_2Cl_2 0.5:9.5) to yield 6 fractions: H8A (46.8 mg), H8B (131.5 mg), H8C (125.5 mg), H8D (507.2 mg), H8E (152.9 mg), and H8F (291.8 mg).

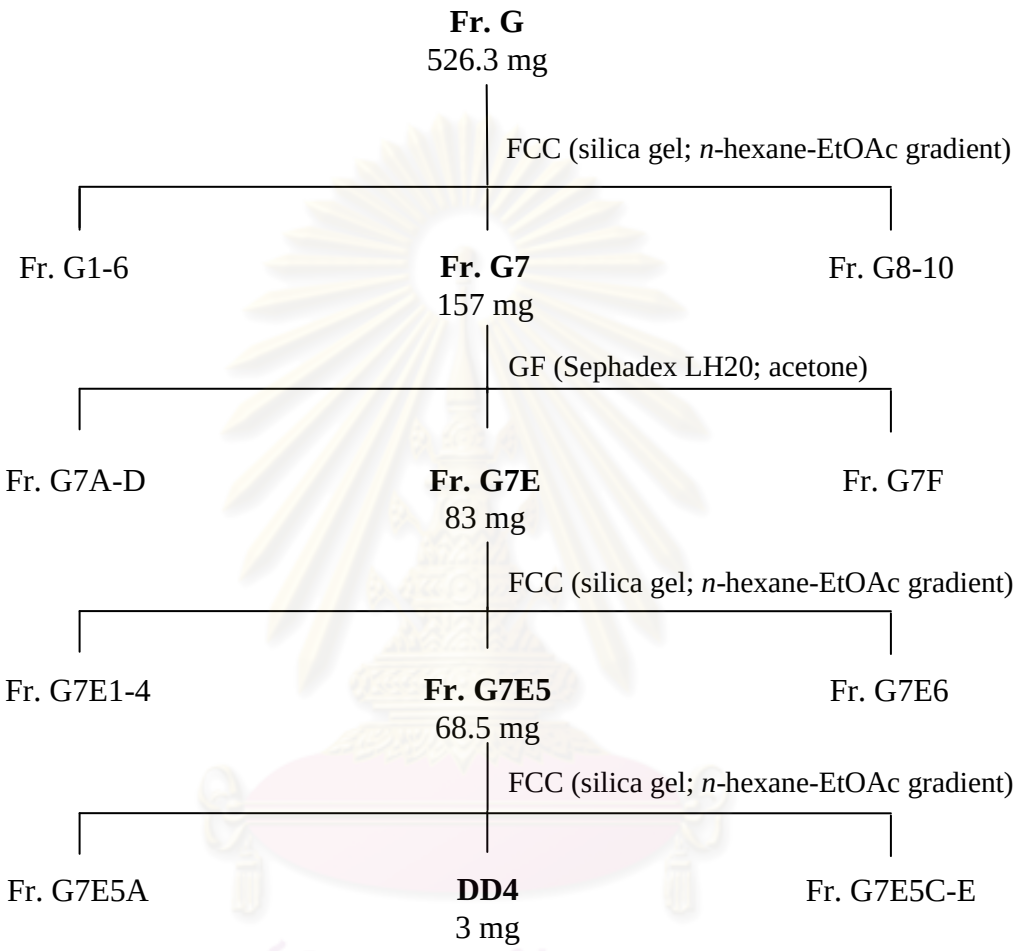
Fraction H8A (46.8 mg) was repeatedly fractionated on a flash column (silica gel, gradient mixtures of CH_2Cl_2-MeOH 10:0 to 0:10) to yield 6 fractions after TLC examination (silica gel, MeOH-CH_2Cl_2 0.5:9.5): H8A1 (1.2 mg), H8A2 (1.7 mg), H8A3 (2.5 mg), H8A4 (2.1 mg), H8A5 (30.0 mg), H8A6 (6.8 mg).

Fraction H8A5 (30 mg) was further purified on a Sephadex LH20 column (acetone) to yield 10 fractions. Fraction showing similar chromatographic patterns were combined (TLC, silica gel, MeOH-CH_2Cl_2 1:9) to give 8 fractions: H8A5A (1.8 mg), H8A5B (1.2 mg), H8A5C (1.7 mg), H8A5D (1.8 mg), H8A5E (13.8 mg), H8A5F (4.2 mg), H8A5G (2.0 mg), and H8A5H (2.5 mg).

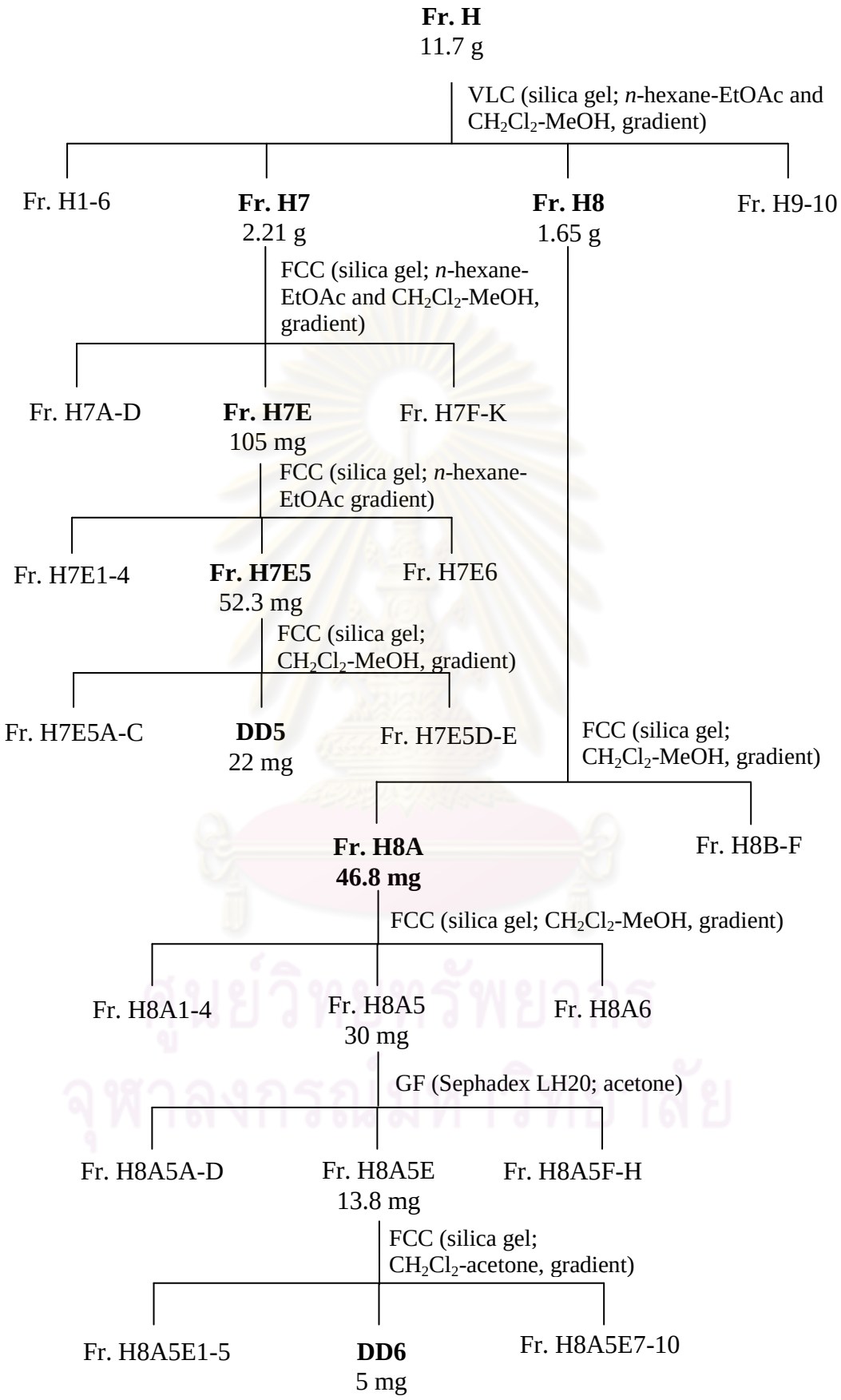
Fraction H8A5E (13.8 mg) was further fractionated on a flash column (silica gel, gradient mixtures of CH_2Cl_2-Acetone 10:0 to 0:10) to give compound DD6 as a brown gum (5 mg, R_f 0.28, silica gel, Acetone -CH_2Cl_2 1:9). It was identified as tristin [**71**].



Scheme 1 Separation of fraction F of MeOH extract



Scheme 2 Separation of fraction G of MeOH extract



Scheme 3 Separation of fraction H of MeOH extract

4. Physical and spectral data of isolated compounds

4.1 Compound DD1 (hircinol)

Compound DD1 was obtained as a white powder, soluble in acetone (2.0 mg, 1.22 x 10^{-3} % based on dried weight of stem).

ESIMS : $[M+H]^+$ at *m/z* 243.10; **Figure 3**

IR : 3164 cm^{-1}, 1618 cm^{-1}, 1459 cm^{-1}; **Figure 4**

UV : λ_{max} nm (log ε), in methanol; **Figure 5**

222 (4.56), 273 (4.22), 302 (4.05)

^{1}H NMR : δ ppm, 500 MHz, in acetone-d_6; see **Table 2, Figure 8**

^{13}C NMR : δ ppm, 75 MHz, in acetone-d_6; see **Table 2, Figure 6**

4.2 Compound DD2 (gigantol)

Compound DD2 was obtained as a brown amorphous solid, soluble in CH_2Cl_2 (115.2 mg, 0.64 % based on dried weight of stem).

ESIMS : $[M+H]^+$ at *m/z* 275.13; **Figure 11**

IR : 3391 cm^{-1}, 1614 cm^{-1}, 1589 cm^{-1}, 1271 cm^{-1}; **Figure 12**

UV : λ_{max} nm (log ε), in methanol; **Figure 13**

225 (4.14), 281 (3.68)

^{1}H NMR : δ ppm, 300 MHz, in $CDCl_3$; see **Table 3, Figure 14**

^{13}C NMR : δ ppm, 75 MHz, in $CDCl_3$; see **Table 3, Figure 15**

4.3 Compound DD3 (batatasin III)

Compound DD3 was obtained as a colourless amorphous solid, soluble in CH_2Cl_2 (48 mg, 2.67 x 10^{-2} % based on dried weight of stem).

ESIMS : $[M+H]^+$ at *m/z* 245.12; **Figure 19**

IR : 3318 cm^{-1}, 1614 cm^{-1}, 1594 cm^{-1}, 1455 $cm^{-}1$, 1196 cm^{-1}; **Figure 20**

UV : λ_{max} nm (log ε), in methanol; **Figure 21**

223 (4.08), 275 (3.52)

^{1}H NMR : δ ppm, 300 MHz, in $CDCl_3$; see **Table 4, Figure 22**

^{13}C NMR : δ ppm, 75 MHz, in $CDCl_3$; see **Table 4, Figure 23**

4.4 Compound DD4 (5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone**)**

Compound DD4 was obtained as a reddish powder, soluble in CH_2Cl_2 (3 mg, 1.67 x 10^{-3} % based on dried weight of stem).

HRESIMS **:** $[M+H]^+$ at *m/z* 257.0817; **Figure 27**

IR **:** 3363 cm^{-1}, 1733 cm^{-1} , 1603 cm^{-1}, 1464 cm^{-1}; **Figure 28**

UV **:** λ_{max} nm (log ε), in methanol; **Figure 29**

223 (4.32), 250 (4.08), 485 (3.50)

^{1}H NMR **:** δ ppm, 500 MHz, in $CDCl_3$; see **Table 5, Figure 33**

^{13}C NMR **:** δ ppm, 125 MHz, in $CDCl_3$; see **Table 5, Figure 30**

4.5 Compound DD5 (4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol)

Compound DD5 was obtained as a red amorphous powder, soluble in CH_2Cl_2 (22 mg, 1.22 x 10^{-2}% based on dried weight of stem).

ESIMS **:** $[M+Na]^+$ at *m/z* 281.08; **Figure 39**

IR **:** 3306 cm^{-1}, 1620 cm^{-1} , 1586 cm^{-1}, 1454 cm^{-1}; **Figure 40**

UV **:** λ_{max} nm (log ε), in methanol; **Figure 41**

222 (4.51), 275 (4.30)

^{1}H NMR **:** δ ppm, 500 MHz, in $CDCl_3$; see **Table 6, Figure 42**

^{13}C NMR **:** δ ppm, 125 MHz, in $CDCl_3$; see **Table 6, Figure 45**

4.6 Compound DD6 (tristin)

Compound DD6 was obtained as a brown amorphous solid, soluble in acetone (5.0 mg, 2.78 x 10^{-3} % based on dried weight of stem).

ESIMS **:** $[M+H]^+$ at *m/z* 261.11; **Figure 52**

IR **:** 3749 cm^{-1}, 3353 cm^{-1}, 1602 cm^{-1}, 1515 cm^{-1}, 1463 cm^{-1}; **Figure 53**

UV **:** λ_{max} nm (log ε), in methanol; **Figure 54**

226 (5.08), 281 (4.59)

^{1}H NMR **:** δ ppm, 300 MHz, in acetone-d_6; see **Table 7, Figure 56**

^{13}C NMR **:** δ ppm, 75 MHz, in acetone-d_6; see **Table 7, Figure 55**

5. Determination of free radical scavenging activity

5.1 DPPH radical scavenging activity assay

5.1.1 Preparation of test sample

The assay was performed according to a previous reported method (Braca *et al*., 2002).

The test compound (1 mg) was dissolved in 1 ml methanol (or suitable solvent) and diluted with methanol until a suitable range of concentration (μg/ml) was obtained. The concentration was expressed as μM in final concentration. For example, DD1 (MW 242) at 1 mg/ml was equal to 4132 μM [1 mg/(1ml x 242)]. For each well, 20 μl of test solution was added to the reaction mixture to furnish the total volume of 200 μl. The final concentration was calculated using the formula below.

$$N_1V_1 = N_2V_2$$

N_1 = Beginning concentration (μM)

V_1 = Beginning volume (μl)

N_2 = Final concentration (μM)

V_2 = Final volume (μl)

Thus, the final concentration of DD1 solution = 4132 μM x 20 μl / 200 μl

= 413.2 μM

5.1.2 Preparation of DPPH solution (100 μM)

DPPH (2 mg) was dissolved in 100 ml of methanol, and the solution was stirred for 30 min.

5.1.3 Measurement of activity

The test sample (20 μl) was added to 180 μl DPPH solution (100 μM) in 96-well plate. The solution mixture was incubated at 37ºC for 30 min and then the absorbance of each well was measured at 510 nm. The DPPH solution (180 μl) mixed with methanol (20 μl) was used as a negative control while quercetin and Trolox® were used as positive controls.

5.1.4 Calculation of percent inhibition of DPPH free radical scavenging activity

The percentage of DPPH reduction was calculated as follows.

$$\% \text{ DPPH reduction} = [(A-B) \times 100] / A$$

A = The absorbance of DPPH solution after incubation at 510 nm

B = The absorbance of the reaction mixture after incubation at 510 nm

For IC_{50} evaluation of pure compounds, a graph showing concentration versus % DPPH reduction was plotted. The IC_{50} was calculated from the graph.

5.2 Assay of superoxide radical ($O_2^{\bullet -}$) scavenging activity

5.2.1 Preparation of test sample

The assay was conducted according to a previous reported method (Dasgupta and De, 2004)

The test compound (2.5 mg) was dissolved in 1 ml methanol (or suitable solvent) and diluted with 30 % methanol in 50 mM sodium phosphate buffer (pH 7.8) until a suitable range of concentration (µg/ml) was obtained. For each well, 80 µl of test solution was added to the reaction mixture to furnish the total volume of 200 µl. The final concentration was calculated using the formula below.

$$N_1V_1 = N_2V_2$$

N_1 = Beginning concentration (µg)

V_1 = Beginning volume (µl)

N_2 = Final concentration (µg)

V_2 = Final volume (µl)

5.2.2 Preparation of reaction mixture

Each 200 µl reaction mixture contained 50 mM sodium phosphate buffer (pH 7.8), 130 mM methionine, 20 µM riboflavin, 1 mM EDTA, NBT (750 µM) and 80 µl sample solution.

5.2.3 Measurement of activity

The test sample (80 µl) was added to the mixture of 130 mM methionine (20 µl), 20 µM riboflavin (20 µl), 1 mM EDTA (20 µl), and 50 mM sodium phosphate buffer (40 µl) in a 96-well plate. Then 750 µM NBT (20 µl) was added. The solution mixture was illuminated by a fluorescent lamp for 10 min, and then the absorbance of each well was measured at 570 nm. The entire reaction assembly was enclosed in a box lined with aluminium foil. Identical plates with reaction mixture were kept in the dark and served as blanks. The reaction solution (120 µl) mixed with 30 % methanol in buffer (80 µl) was used as a negative control while Trolox® was used as a positive control.

5.2.4 Calculation of percent inhibition of superoxide radical ($O_2^{\bullet -}$) scavenging activity

The percentage of NBT reduction was calculated as follows.

$$\% \text{ NBT reduction} = [(A_L - A_D) - (B_L - B_D)] \times 100 / (A_L - A_D)$$

A_L = The absorbance of NBT solution after illumination at 570 nm

A_D = The absorbance of NBT solution that were kept in the dark at 570 nm

B_L = The absorbance of the reaction mixture after illumination at 570 nm

B_D = The absorbance of the reaction mixture that were kept in the dark at 570 nm

CHAPTER IV

RESULTS AND DISCUSSION

The dried powdered of *Dendrobium draconis* (1.8 kg) was macerated with methanol. The methanol extract (112.29 g) was separated using several chromatographic techniques to afford six pure compounds (DD1-DD6). The structure determinations of all isolates were carried out by interpretation of their UV, IR, MS and NMR data, and further comfirmed by comparison with literature values.

1. Structure determination of isolated compounds

1.1 Structure determination of compound DD1

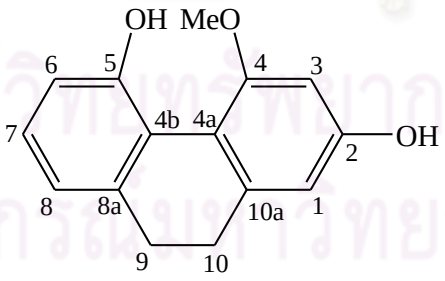
Compound DD1 was obtained as a white powder. The ESI mass spectrum (Figure 3) showed a molecular ion $[M+H]^+$ at *m/z* 243.10, suggesting the molecular formula $C_{15}H_{14}O_3$. In the IR spectrum (Figure 4), absorption peaks at 3164, 1618, and 1459 cm^{-1} indicated the presence of hydroxy groups and aromatic rings. Its UV spectrum (Figure 5) showed absorption bands at 222, 273, and 302 nm, typical of 9,10-dihydrophenanthrene.

The ^{13}C NMR, DEPT 90 and DEPT 135 spectra (Figures 6-7 and Table 2) revealed 15 carbon atoms, including 5 methine carbons, 7 quaternary carbons, a methoxyl carbon and two methylene carbons. The two methylene carbons [δ 32.0 (C-9) and 32.1 (C-10)] were consistent with four protons at δ 2.65 (4H, br s, H_2-9 and H_2-10). The ^1H NMR spectrum (Figure8 and Table 2) revealed *meta*-coupled signals at δ 6.47 (1H, d, *J* = 2.5 Hz, H-3) and 6.50 (1H, d, *J* = 2.5 Hz, H-1), indicating the presence of tetrasubstituted phenyl group. A spin system at δ 6.79 (1H, dd, *J* = 7.5, 1.5 Hz, H-8), 7.07 (1H, t, *J* = 7.5 Hz, H-7) and 6.85 (1H, dd, *J* = 7.5, 1.5 Hz, H-6) indicates the presence of 1,2,3-trisubstituted phenyl group. The existence of these two aromatic rings and two methylenes indicated a 9,10-dihydrophenanthrene skeleton. A methoxyl group at δ 2.65 (3H, s, MeO-4) should be located at C-4 since the methoxyl protons exhibited NOESY interaction with H-3, but not with H-1 (Figures 9-10).

Based on the above spectral evidence and through the comparison of its previous reported data (Fisch, Flick and Arditti, 1973; Coxon, Ogundana, and Dennis, 1982), it was identified as hircinol [**96**].

Table 2 NMR Spectral data of compound DD1 and hircinol (acetone-d_6)

Position	DD1		Hircinol	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	6.50 (d, 2.5)	107.3	6.51 (s)	109.9
2	-	160.7	-	158.4
3	6.47 (d, 2.5)	102.4	6.51 (s)	100.0
4	-	153.0	-	154.6
4a	-	122.0	-	128.7
4b	-	114.8	-	114.7
5	-	155.3	-	156.3
6	6.85 (dd, 7.5, 1.5)	117.0		118.2
7	7.07 (t, 7.5)	128.0	6.77-7.32 (m)	128.1
8	6.79 (dd, 7.5, 1.5)	120.7		120.0
8a	-	141.8	-	141.3
9	2.65 (br s)	32.0	2.64 (br s)	31.6
10	2.65 (br s)	32.1	2.64 (br s)	31.8
10a	-	143.4	-	144.1
OMe	3.78 (s)	55.4	3.89 (s)	57.3



Hircinol [**96**]

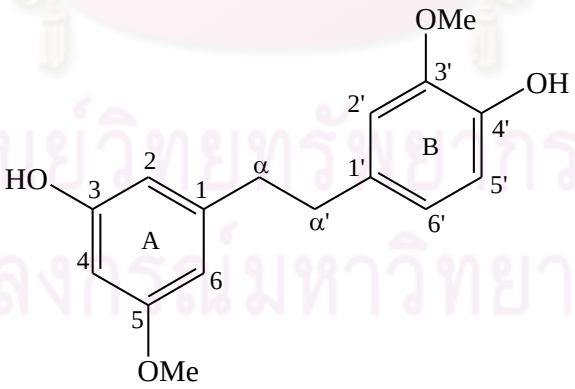
1.2 Structure determination of compound DD2

Compound DD2 was isolated as a brown amorphous solid. The ESI mass spectrum (Figure 11) showed a molecular ion $[M+H]^+$ at *m/z* 275.13, suggesting the molecular formula $C_{16}H_{18}O_4$. The IR spectrum (Figure 12) showed characteristic bands at 3391, 1614, 1589, and 1271 cm^{-1} indicating the presence of hydroxy groups and aromatic rings. The UV spectrum (Figure 13) showed absorption bands at 225 and 281 nm, indicative of a bibenzyl derivatives. This was supported by the presence of methylene protons at δ 2.82 (4H, br s) in the ^{1}H NMR spectrum (Figure 14 and Table 3), and the appearance of two methylene carbon signals at δ 37.1 (C- α) and δ 38.1 (C- α′) in the ^{13}C NMR spectrum (Figure 15 and Table 3). The ^{13}C NMR, DEPT 90 and DEPT 135 spectra (Figures 15-16 and Table 3) displayed 16 carbon signals, corresponding to two methoxyls, two methylenes, six methines, two quaternaries and four oxygenated carbons. The ^{1}H NMR spectrum (Figure 13 and Table 3) of compound DD2 also showed signals for two methoxyls at δ 3.76 (3H, s) and δ 3.84 (3H, s). On ring A, two oxygenated substituents were placed on *m*-positions in relation to C-1, as supported by the presence of three *meta*-coupled aromatic protons at δ 6.31 (1H, br s, H-4) and 6.35 (2H, br s, H-6). The first methoxyl (δ 3.76, 3H, s, MeO-5) was located at C-5 of ring A, as shown by its NOESY interaction with H-4 and H-6 (Figures 17-18). On ring B, the ^{1}H NMR exhibited an ABM splitting system at δ 6.67 (1H, br s, H-2′), δ 6.70 (1H, br d, J = 8.1 Hz, H-6′) and δ 6.87 (1H, br d, J = 8.1 Hz, H-5′). The second methoxyl (δ 3.84, 3H, s, MeO-3′) should be situated at C-3′ according to its NOESY correlation with H-2′.

From the above observations and through comparison of its previous reported data (Juneja, Sharma, and Tandon, 1985; Juneja, Sharma, and Tandon, 1987), DD2 was identified as gigantol [**14**].

Table 3 NMR Spectral data of compound DD2 and gigantol ($CDCl_3$)

Position	DD2		Gigantol	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	-	144.4	-	144.4
2	6.35 (br s)	108.2	6.29 (br s)	108.1
3	-	156.6	-	156.7
4	6.31 (br s)	99.1	6.29 (br s)	99.2
5	-	160.6	-	160.9
6	6.35 (br s)	106.6	6.29 (br s)	106.9
α	2.82 (br s)	37.1	2.83 (br s)	37.1
α′	2.82 (br s)	38.1	2.83 (br s)	38.1
1′	-	133.8	-	133.7
2′	6.67 (br s)	114.2	6.65 (d, 2.0)	114.3
3′	-	146.3	-	146.3
4′	-	143.6	-	143.8
5′	6.87 (br d, 8.1)	111.3	6.81 (d, 9.0)	111.4
6′	6.70 (br d, 8.1)	121.0	6.77 (dd, 2.0, 9.0)	121.0
3′-OMe	3.84 (s)	55.8	3.85 (s)	55.9
5-OMe	3.76 (s)	55.2	3.77 (s)	55.2



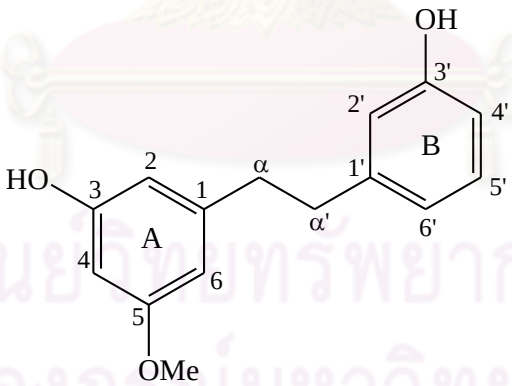
1.3 Structure determination of compound DD3

Compound DD3 was isolated as a colourless amorphous solid. The ESI mass spectrum (Figure 19) showed a molecular ion $[M+H]^+$ at *m/z* 245.12, corresponding to $C_{15}H_{17}O_3$, suggesting the molecular formula $C_{15}H_{16}O_3$. The IR spectrum (Figure 20) showed absorption bands at 3318, 1614, 1594, 1455, and 1196 cm^{-1}, indicating the presence of hydroxy groups and aromatic rings. The UV spectrum (Figure 21) showed absorption bands at 223 and 275 nm, indicative of a bibenzyl derivative. This was supported by the presence of methylene protons at δ 2.79 (4H, br s, H_2-α and H_2-α′) in the ^{1}H NMR spectrum (Figure 22 and Table 4) and two methylene carbons at δ 37.2 (C- α) and δ 37.5 (C- α′) in the ^{13}C NMR spectrum (Figures 23 and Table 4). The ^{13}C NMR, DEPT 90 and DEPT 135 spectra (Figures 23-24 and Table 4) of compound DD3 displayed 15 carbon signals, corresponding to a methoxyl, two methylenes, seven methines, two quaternaries and three oxygenated carbons. The ^{1}H NMR spectrum (Figure 22) of compound DD3 also showed a methoxyl signal at δ 3.73 (3H, s, MeO-5) . On ring A, a 3-H multiplet at δ 6.29 indicated the presence of three *meta*-coupled protons similar to those presented in ring A of compound DD2. A methoxyl was located at C-5 of ring A. This was confirmed by its NOESY interaction with H-4 and H-6 (Figures 25-26). On ring B, the ^{1}H NMR also displayed four protons signals at δ 7.14 (1H, t, *J* = 7.8 Hz, H-5′), 6.75 (1H, br d, *J* = 7.5 Hz, H-6′), 6.68 (1H, dd, *J* = 7.5, 1.8 Hz, H-4′), and 6.64 (1H, br s, H-2′) indicating a 1,3-disubstituted aromatic ring.

Based on the above spectral evidence and through comparison of its previously reported data (Hashimoto *et al*., 1974; Sachdev and Kulshreshtha, 1986; Majumder, Roychowdhury, and Chakraborty, 1997), DD3 was identified as batatasin III [**9**].

Table 4 NMR Spectral data of compound DD3 and batatasin III ($CDCl_3$)

Position	DD3		Batatasin III	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	-	144.5	-	145.0
2	6.29 (br d, 2.1)	106.9	6.25 (d)	106.3
3	-	156.5	-	159.2
4	6.33 (br s)	99.2	6.34 (d)	99.9
5	-	160.7	-	161.9
6	6.27 (br s)	108.2	6.25 (d)	108.8
α	2.79 (br s)	37.2	2.83 (s)	36.7
α′	2.79 (br s)	37.5	2.83 (s)	36.9
1′	-	143.5	-	144.3
2′	6.64 (br s)	115.5	6.70 (m)	116.2
3′	-	155.4	-	158.2
4′	6.68 (dd, 7.5, 1.8)	113.0	6.70 (m)	113.6
5′	7.14 (t, 7.5)	129.5	7.15 (t, 8.0)	130.0
6′	6.75 (br d, 7.5)	121.0	6.70 (m)	120.4
5-OMe	3.73 (s)	55.3	3.76 (s)	55.6



Batatasin III [**9**]

1.4 Structure determination of Compound DD4

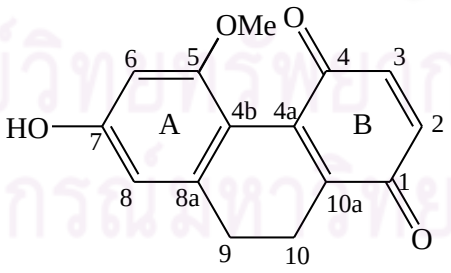
Compound DD4 was isolated as a reddish powder. The positive HRESIMS (Figure 27) exhibited an $[M+H]^+$ at *m/z* 257.0817 (calcd. for 257.0813; $C_{15}H_{13}O_4$), suggesting the molecular formula $C_{15}H_{12}O_4$. The IR spectrum (Figure 28) showed absorption bands for hydroxyl (3363 cm^{-1}), ketone (1733 cm^{-1}) and aromatic (1603, 1464 cm^{-1}) groups. The UV absorptions at 485 and 250 nm (Figure 29) and the ^{13}C NMR (Figure 30 and Table 5) signals at δ 185.4 (C-1) and δ 185.7 (C-4) were indicative of a phenanthrenequinone structure (Bhaskar *et al*., 1991). The olefinic protons at δ 6.68 (1H, d, *J* = 10.0 Hz, H-2) and δ 6.78 (1H, d, *J* = 10.0 Hz, H-3) exhibited HMBC correlations with C-1 and C-4, respectively (Figures 31-32 and Table 5), confirming the quinone structure (ring B). Compound DD4 should have a 9,10-dihydro partial structure, as suggested from the presence of the ^1H NMR signals for two pairs of methylene protons at δ 2.55 (H_2-10) and δ 2.60 (H_2-9) (Figure 33), which correlated to the carbons at δ 20.1 (C-10) and δ 28.5 (C-9) in the HSQC spectrum (Figures 34-35). The ^1H NMR spectrum of DD4 (Figure 33) also showed signals for a methoxyl group (δ 3.73, s, 3H) and two *meta*-coupled aromatic protons at δ 6.31 (1H, d, *J* = 2.0 Hz) and δ 6.33 (1H, d, *J* = 2.0 Hz) assignable to H-8 and H-6, respectively. These assignments were confirmed by the HMBC correlation from H-8 to C-9 (Figure 36), and the NOESY cross-peak between H-8 and H_2-9 (Figures 37-38). From the above observations, it appears that DD4 should have a structure similar to dendronone (5-hydroxy-7-methoxy-9,10-dihydrophenanthrene-1,4-dione), a phenanthrenequinone earlier reported from from *Dendrobium cariniferum* and *D. longicornu* (Chen *et al*., 2008; Hu *et al*., 2008a). However, in structure DD4 the methoxyl group should be located at C-5 since the methoxyl protons exhibited NOESY interaction with H-6, but not with H-8 (Figures 37-38). This was further confirmed by the ^2J HMBC correlation from H-8 to C-7, which was a hydroxylated carbon (Figures 31-32).

Based on the above spectral evidence, compound DD4 was characterized as 5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone. Prior to this study, the structure of DD4 was hitherto unknown.

Table 5 NMR Spectral data of compound DD4 ($CDCl_3$)

Position	DD4		
	δ_H (mult., *J* in Hz)	**δ_C**	**HMBC (correlation with ^{1}H)**
1	-	185.4	-
2	6.68 (d, 10.0)	135.1	1*
3	6.78 (d, 10.0)	137.2	4*, 4a
4	-	185.7	-
4a	-	140.9	-
4b	-	112.3	-
5	-	158.9	-
6	6.33 (d, 2.0)	98.6	4b, 5*, 7*, 8
7	-	158.8	-
8	6.31 (d, 2.0)	107.4	4b, 6, 7*, 9
8a	-	143.1	-
9	2.60 (m)	28.5	4b, 8, 8a*, 10*, 10a
10	2.55 (m)	20.1	9*
10a	-	139.8	-
5-OMe	3.73 (s)	55.8	5

*Two-bond coupling



5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone [**224**]

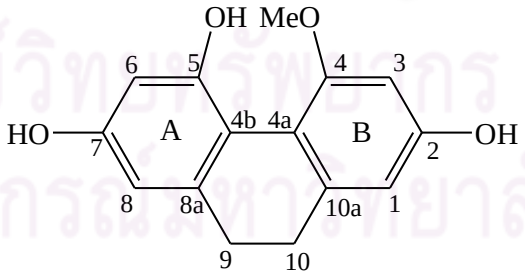
1.5 Structure determination of compound DD5

Compound DD5 was obtained as a red amorphous powder. The ESI mass spectrum (Figure 39) showed a molecular ion $[M+Na]^+$ at *m/z* 281.08, corresponding to the molecular formula $C_{15}H_{14}O_4$. The IR spectrum (Figure 40) showed hydroxyl groups (3306 cm^{-1}) and aromatic rings (1620, 1586 and 1454 cm^{-1}). The UV spectrum (Figure 41) showed absorption bands at 222 and 275 nm, were suggestive a of 9,10-dihydrophenanthrene. This was supported by the presence of the ^1H NMR spectrum (Figure 42) showed signals of two pairs of methylene protons at δ 2.62 (H_2-9 and H_2-10), which correlated to the carbons at δ 31.0 (C-9) and δ 31.1 (C-10) in the HSQC spectrum (Figures 43-44). The ^{13}C NMR spectrum (Figure 45 and Table 6) displayed 15 carbon atoms, including 12 aromatic carbons, a methoxy, and two secondary carbons. The ^1H NMR spectrum of DD5 (Figure 42) also showed signals for a methoxyl group at δ 3.92 (3H, s). On ring A, the ^1H NMR spectrum showed signals for two *meta*-coupled aromatic protons at δ 6.40 (1H, d, *J* = 2.5 Hz, H-6) and 6.37 (1H, d, *J* = 2.5 Hz, H-8), these assignment were supported by HMBC correlation from H-8 to C-9 (Figures 46-47), and NOESY cross-peak between H-8 and H_2-9 (Figures 48-49). On ring B, the presence of two *meta*-coupled aromatic protons at δ 6.47 (1H, d, *J* = 2.5 Hz) and 6.48 (1H, d, *J* = 2.5 Hz) assignable to H-1 and H-3, respectively. This was confirmed by the correlation of H-1 to C-10 in the HMBC spectrum (Figure 47), and the NOESY cross-peak between H-1 and H_2-10 (Figures 48-49). A methoxyl group was linked to C-4, observed from the HMBC correlation (Figure 50) from OMe-4 to C-4 and its NOESY interaction with H-3. The NOESY cross-peak between H-1 and H_2-10 was also observed (Figure 48-49). The whole structure was proved further by the HMBC correlations (H-9/C-8, H-9/C-4b, H-10/C-1, H-10/C-4a) (Figure 51).

Based on the above spectral evidence and comparison to the earlier reported data (Hu *et al*., 2008a), this compound was identified as 4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol **[118]**.

Table 6 NMR Spectral data of compound DD5 ($CDCl_3$) and 4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol (acetone-d_6)

Position	**DD5** ($CDCl_3$)		**4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol** (acetone-d_6)	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	6.47 (d, 2.5)	109.3	6.35 (d,2.5)	109.9
2	-	154.9	-	157.6
3	6.48 (d, 2.5)	99.3	6.31 (d, 2.5)	100.0
4	-	154.5	-	155.5
4a	-	115.6	-	115.1
4b	-	113.7	-	113.6
5	-	154.8	-	155.9
6	6.40 (d, 2.5)	104.2	6.52 (d, 2.3)	104.6
7	-	155.3	-	157.9
8	6.37 (d, 2.5)	107.6	6.57 (d, 2.3)	108.1
8a	-	142.1	-	142.4
9	2.62 (br s)	31.1	2.56 (m)	31.9
10	2.62 (br s)	31.0	2.56 (m)	32.0
10a	-	143.1	-	143.3
7-OMe	3.92 (s)	57.2	3.94 (s)	57.3



4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol **[118]**

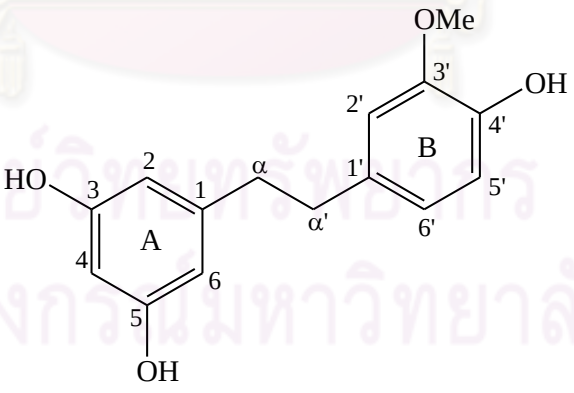
1.6 Structure determination of compound DD6

Compound DD6 was obtained as a brown gum. The ESI mass spectrum (Figure 52) showed a molecular ion $[M+H]^+$ at *m/z z* 261.11, suggesting the molecular formula $C_{15}H_{16}O_4$. The IR spectrum (Figure 53) showed absorption bands at 3353, 1602, 1515, and 1463 cm^{-1}, indicating the presence of hydroxy groups and aromatic rings. The UV spectrum (Figure 54) showed absorption bands at 226 and 281 nm, indicative of a bibenzyl derivative. Two methylene carbon signals appeared at δ 38.0 (C- α) and δ 39.0 (C- α′) in the ^{13}C NMR spectrum (Figure 55 and Table 7). The ^{1}H NMR spectrum (Figure 56 and Table 7) of compound DD6 showed signals for an aromatic methoxyl at δ 3.79 (3H, s). On ring A, the presence of a broad singlet at δ 6.20 (2H, br s, H-2 and H-6) and a broad singlet at δ 6.18 (1H, br s, H-4) suggested the substitution of two hydroxyls on m-position in relation to C-1. On ring B, a three-proton ABM spin system [(δ 6.79, br s, H-2′), (δ 6.70, d, *J* = 7.8 Hz, H-5′), (δ 6.66, br s, H-6′)] was observed. Comparison of ^{13}C NMR data of DD6 with those of compound DD2, revealed their structured similarity, particulary in ring B with regard to the substitution of a methoxyl at C-3′ and a hydroxyl at C-4′.

Through comparison of these data with reported values, compound DD6 was identified as tristin [**71**] (Majumder and Pal, 1992; Leong, Harrison, and Powell, 1999).

Table 7 NMR Spectral data of compound DD6 and tristin (acetone-d_6)

Position	DD6		Tristin	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	-	145.6	-	145.5
2	6.20 (br s)	107.8	6.22 (m)	107.8
3	-	159.3	-	159.3
4	6.18 (br s)	101.1	6.18 (t, 2.1)	101.1
5	-	159.3	-	159.3
6	6.20 (br s)	107.8	6.22 (m)	107.8
α	2.82 (br s)	38.0	2.74 (m)	37.9
α′	2.82 (br s)	39.0	2.74 (m)	39.0
1′	-	134.2	-	134.2
2′	6.79 (br s)	115.5	6.80 (d, 1.7)	115.5
3′	-	148.1	-	148.1
4′	-	145.2	-	145.1
5′	6.70 (d, 7.8)	113.0	6.72 (d, 8)	112.9
6′	6.66 (br s)	121.6	6.65 (dd, 8.0, 1.7)	121.5
3′-OMe	3.79 (s)	56.2	3.80 (s)	56.2



Tristin [**71**]

2. Free radical scavenging activity

Free radicals can be defined as molecules or molecular chemical species containing unpaired electron(s) in atomic or molecular orbitals. In living system radicals originated from oxygen are the most important class of radical species, including superoxide ($O_2^{\bullet -}$), peroxyl ($ROO^{\bullet}$), alkoxyl ($RO^{\bullet}$), hydroxyl ($HO^{\bullet}$), nitric oxide ($NO^{\bullet}$) and hydrogen peroxide (H_2O_2). Oxygen free radicals or reactive oxygen species (ROS), and reactive nitrogen species (RNS) are produced from normal cellular metabolism, which can be either harmful or beneficial to living systems. Beneficial effects of ROS represent at low or moderate concentration, that act as secondary messengers controlling various normal physiological functions. The overproduction of ROS/RNS, causing harmful effects of free radicals, is termed oxidative stress and nitrosative stress. This may occur in living system when the generation of ROS/RNS exceeds the system's ability to neutralise and eliminate them. The excess ROS/RNS can damage DNA, proteins and lipids, causing human disease and ageing (Pietta, 2000; Valko *et al*., 2007).

Human have antioxidant systems to protect against free radicals. These systems include enzymatic antioxidants, such as superoxide dimustase (SOD), glutathione peroxidase (GPx), and catalase (CAT) and non-enzymatic antioxidants, such as vitamin C, vitamin E, glutathione (GSH), and carotenoids. The mechanisms of antioxidant action can include (1) suppressing ROS formation by inhibition of enzymes or chelating trace elements involved in free radical production; (2) scavenging ROS; and (3) upregulating or protecting antioxidant defences. Besides these defences antioxidants, others defence mechanisms against free radicals involve, preventative mechanisms, repair mechanisms, and physical defences. (Pietta, 2000; Valko *et al*., 2007).

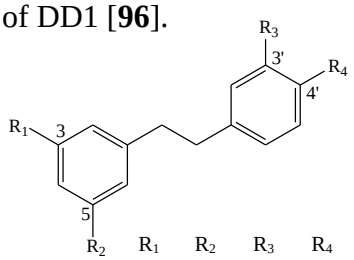
The MeOH extract of *D. draconis* showed free radical scavenging activity. Isolated compounds were first test at 100 μg/ml. Compounds exhibiting more than 50% inhibition were further evaluated for IC_{50} values. Quercetin and Trolox® were employed as positive controls. The results were summarized in Table 8.

Table 8 Percentage of DPPH and NBT reduction by isolated compounds from *D. draconis*

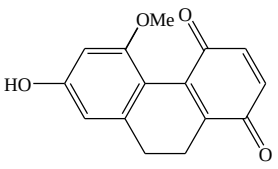
Compound	% DPPH reduction		%NBT reduction at 100 µg/ml
	at 100 µg/ml	IC_{50} (µM) Mean ± SD	
MeOH extract	75.78	-	-
DD1 [**96**]	95.05	22.32± 1.04	51.11
DD2 [**14**]	93.24	17.75± 0.51	66.23
DD3 [**9**]	36.31	-	62.36
DD4 [**224**]	54.16	283.38± 13.7	33.03
DD5 [**118**]	85.65	10.22± 0.14	53.87
DD6 [**71**]	89.77	24.07± 1.60	63.47
Quercetin	95.42	2.46± 0.08	-
Trolox®	96.43	11.67± 0.44	95.57

From Table 8, six pure compounds were tested for free radical scavenging activity. All compounds, except for DD3, showed appreciable DPPH free radical scavenging activity, but with magnitude less than that of quercetin or Trolox®. 4-Methoxy-9,10-dihydrophenanthrene-2,5,7-triol (DD5) [**118**] however, showed antioxidant potency comparable to that of Trolox® (IC_{50} 10.22 and 11.67 µM, respectively). None of the tested compounds showed strong superoxide radical scavenging activity.

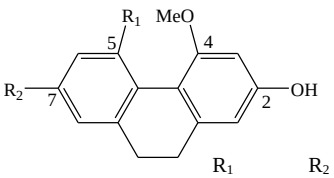
In the case of bibenzyls, the substitution of hydroxy or methoxy group on C-4′ affect the free radical scavenging capacity. Thus DD3 [**9**] is less potent than others tested bibenzyls. For phenanthrene derivatives, the presence of hydroxy group on C-7 is required for the activity. For example, DD5 [**118**] showed stronger activity than that of DD1 [**96**].



	R_1	R_2	R_3	R_4
DD2 [**14**]	OH	OMe	OMe	OH
DD3 [**9**]	OH	OMe	OH	H
DD6 [**71**]	OH	OH	OMe	OH



DD4 [**224**]



	R_1	R_2
DD1 [**96**]	OH	H
DD5 [**118**]	OH	OH

CHAPTER V

CONCLUSION

In this study, a new phenanthrenequinone (5-methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone [**224**]), two known 9,10-dihydrophenanthrene (hircinol [**96**] and 4-methoxy-9,10-dihydrophenanthrene-2,5,7-triol **[118**]), along with three known bibenzyl derivatives (gigantol [**14**], batatasin III [**9**] and tristin [**71**]) were isolated from the MeOH extract of the orchid *Dendrobium draconis* Rchb.f. (Orchidaceae). The isolated compounds were tested for free radical scavenging activity. 4-Methoxy-9,10-dihydrophenanthrene-2,5,7-triol **[118**] showed DPPH scavenging acivity comparable to that of Trolox®, but none of the tested compounds showed superoxide radical scavenging activity. Thus free radical scavengers from *D. draconis* provide possibilities for application in medicine and cosmetic.

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APPENDIX

Low resolution report

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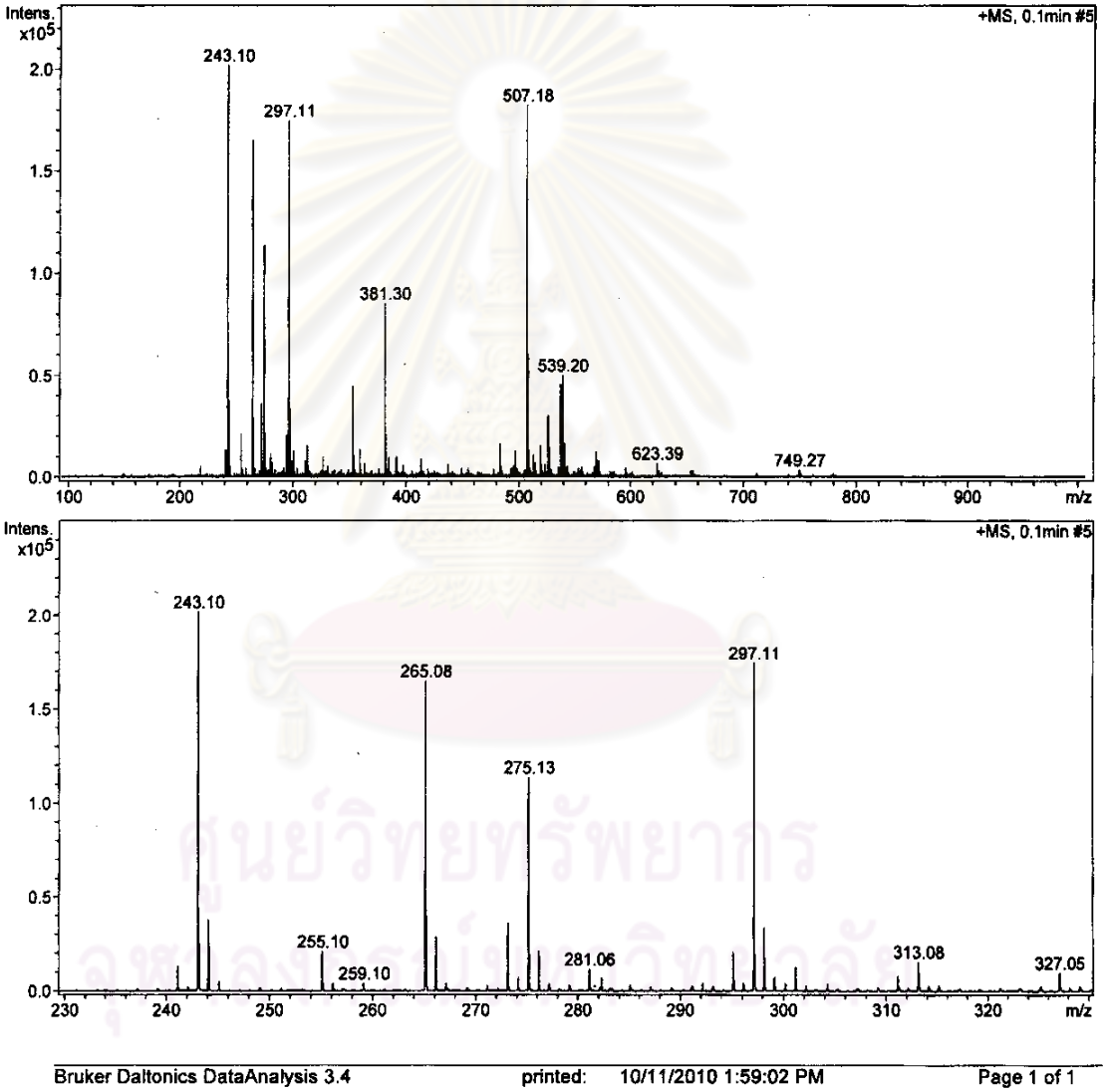

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Figure 3 Mass spectrum of compound DD1

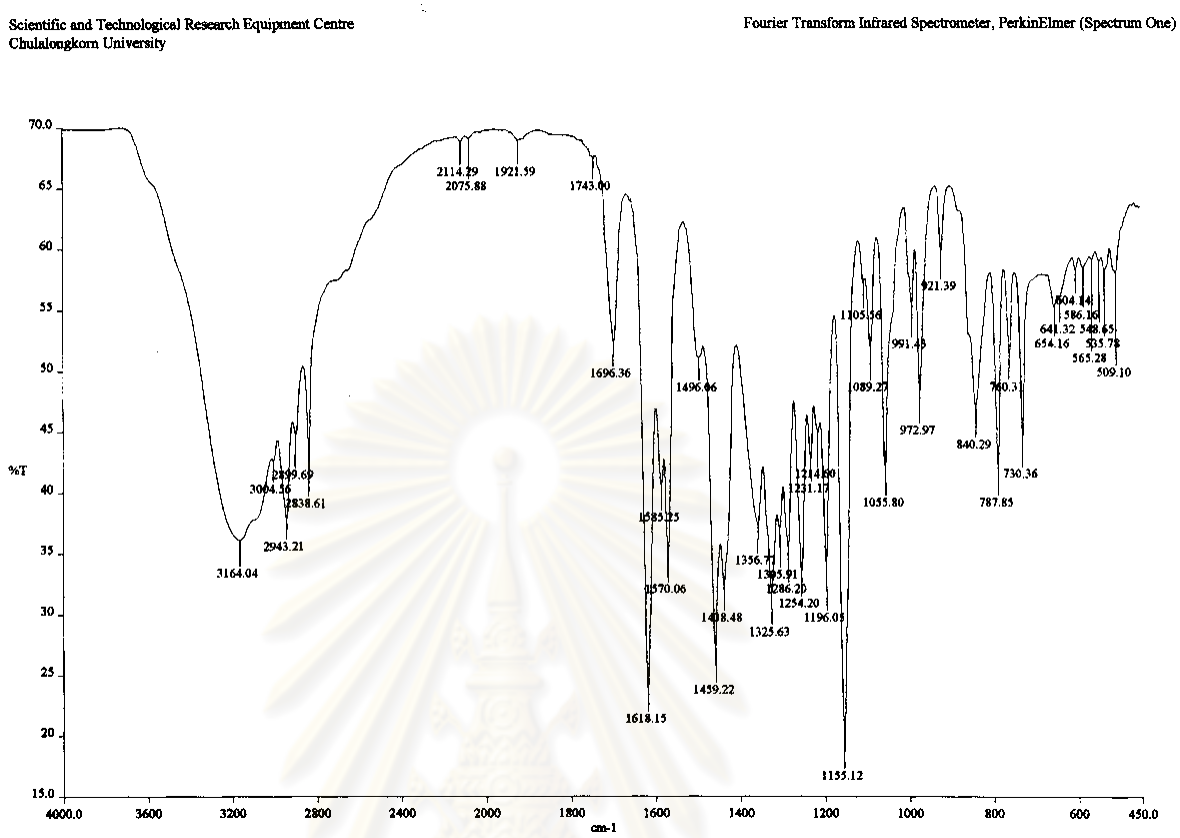

Figure 4 IR spectrum of compound DD1

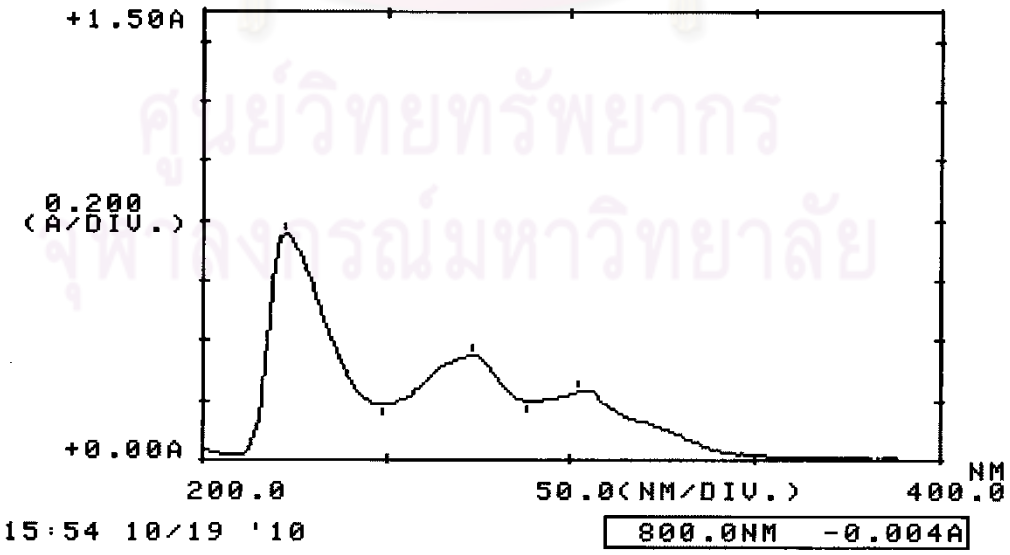

Figure 5 UV spectrum of compound DD1

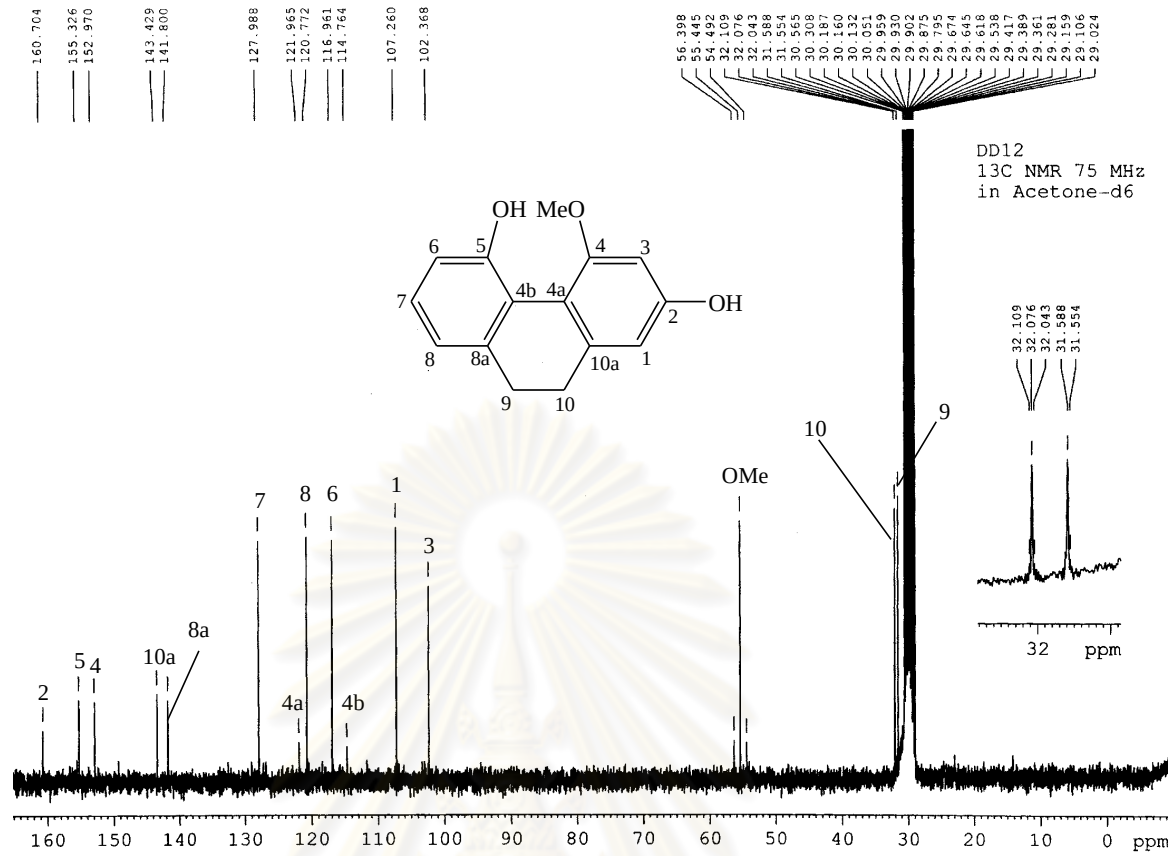

Figure 6 ^{13}C-NMR (75 MHz) Spectrum of compound DD1 (acetone-d_6)

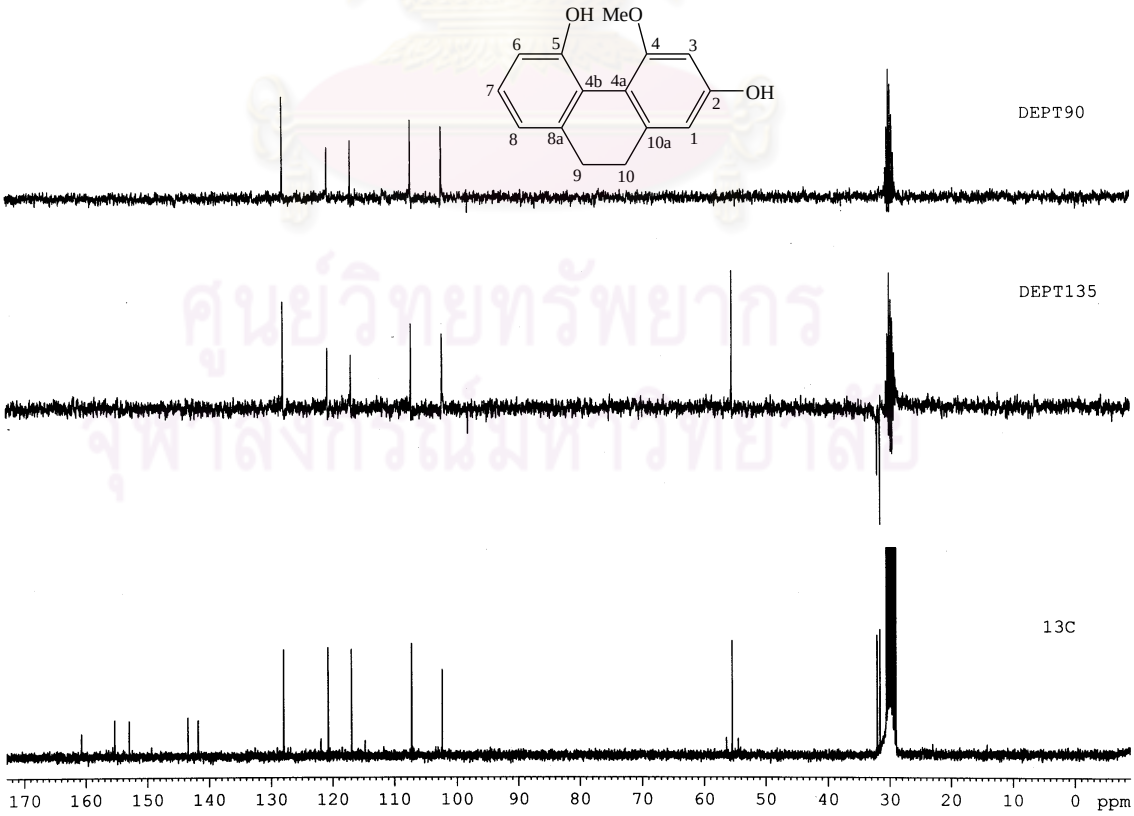

Figure 7 DEPT Spectra of compound DD1 (acetone-d_6)

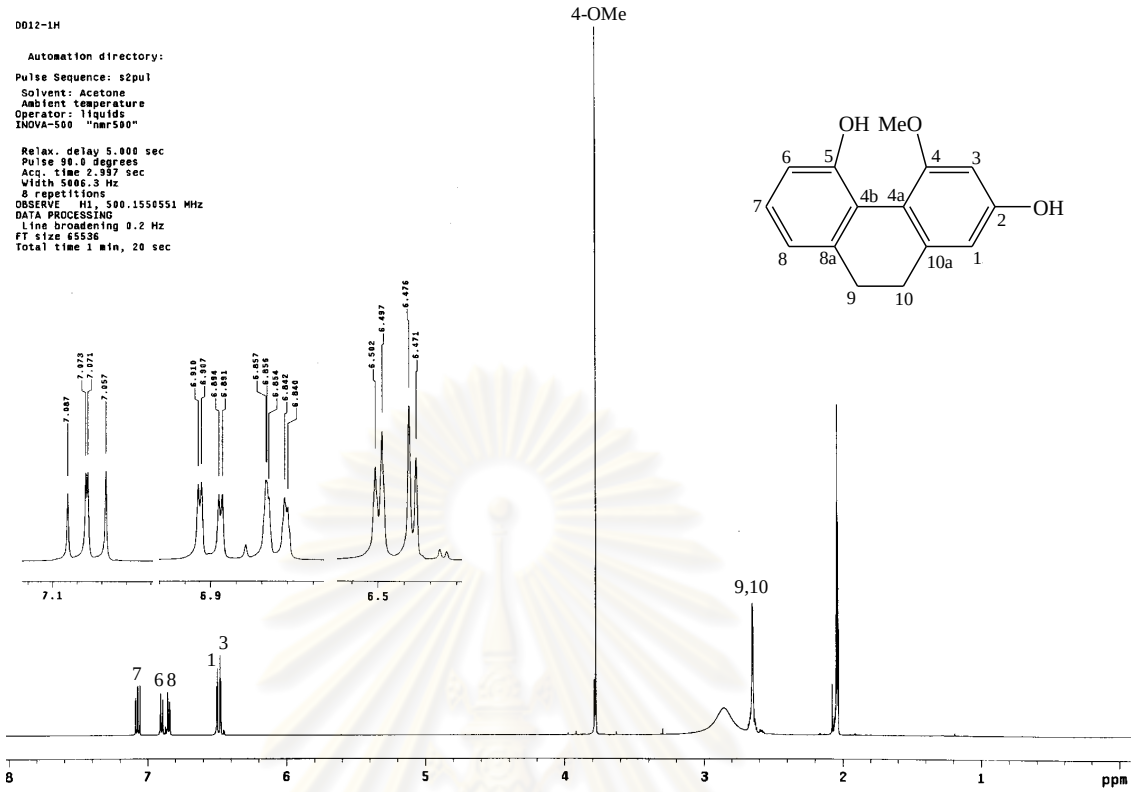

Figure 8 ^{1}H-NMR (500 MHz) Spectrum of compound DD1 (acetone-d_6)

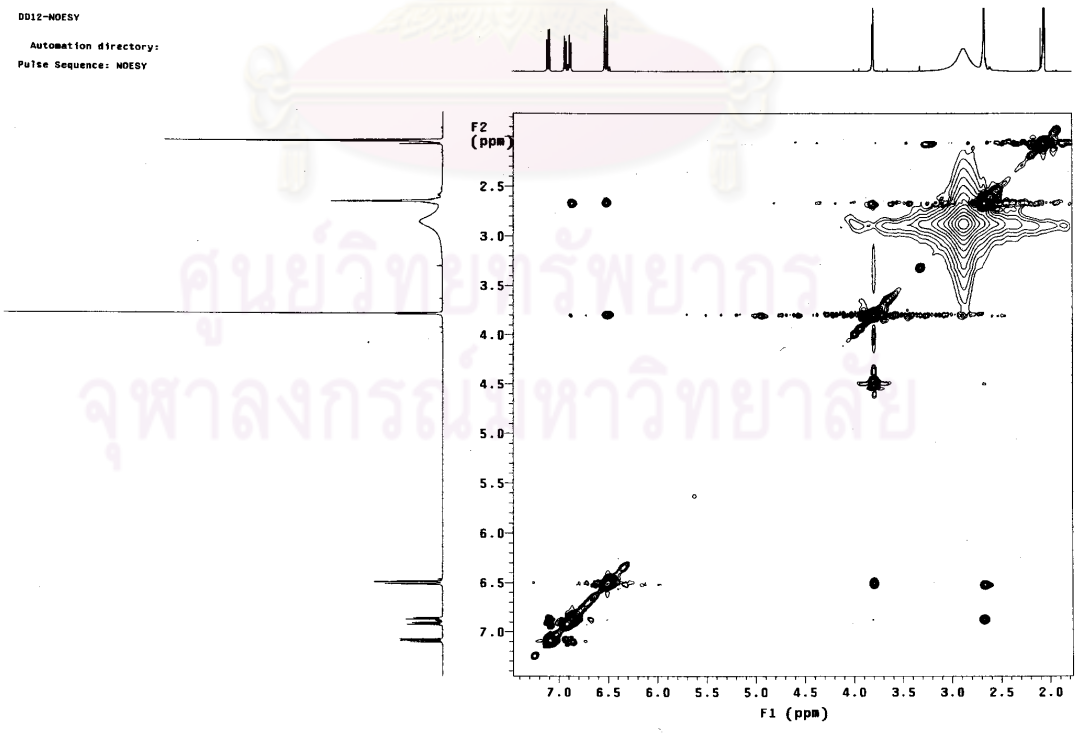

Figure 9 NOESY Spectrum of compound DD1 (acetone-d_6)

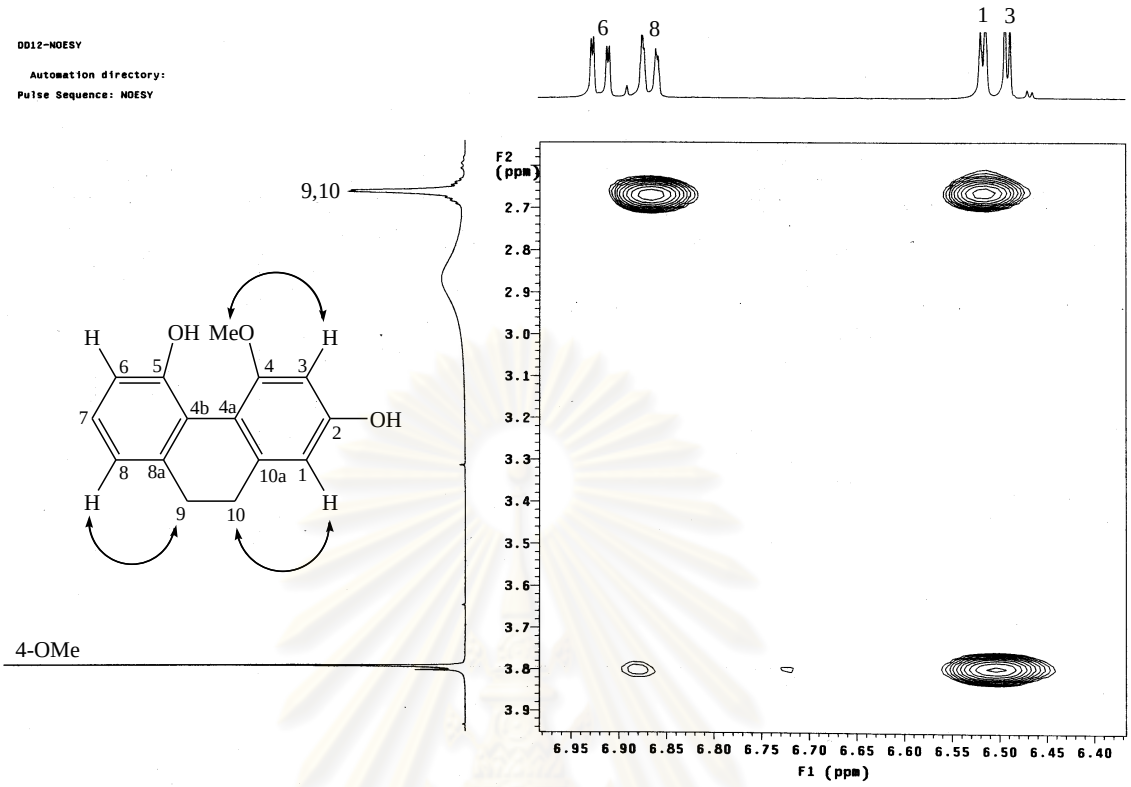

Figure 10 NOESY Spectrum of compound DD1 (acetone-d_6)
(δ_H 2.60-3.90, δ_H 6.95- 6.40)

Low resolution report

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Acquisition Parameter

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Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

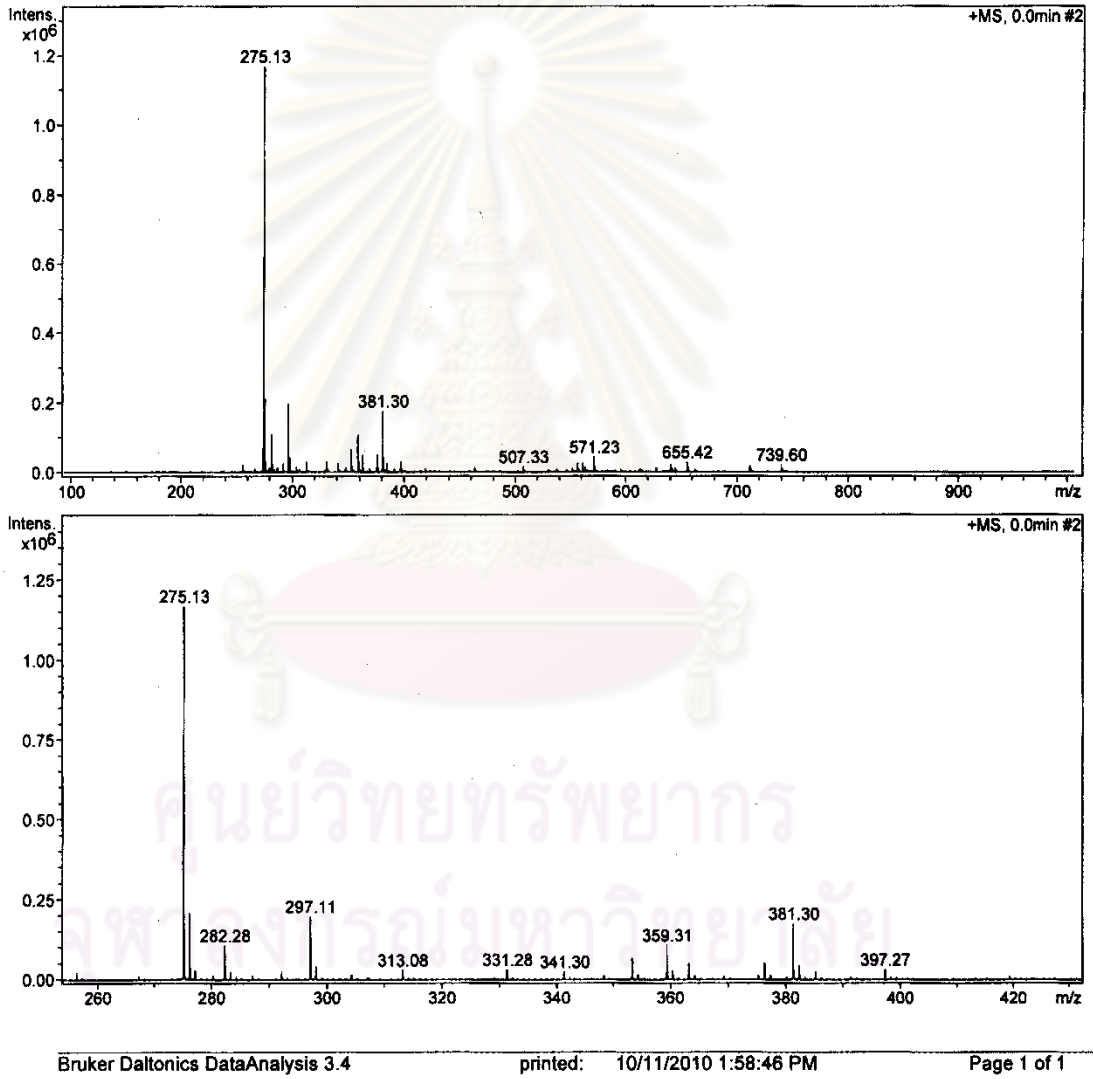

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Figure 11 Mass spectrum of compound DD2

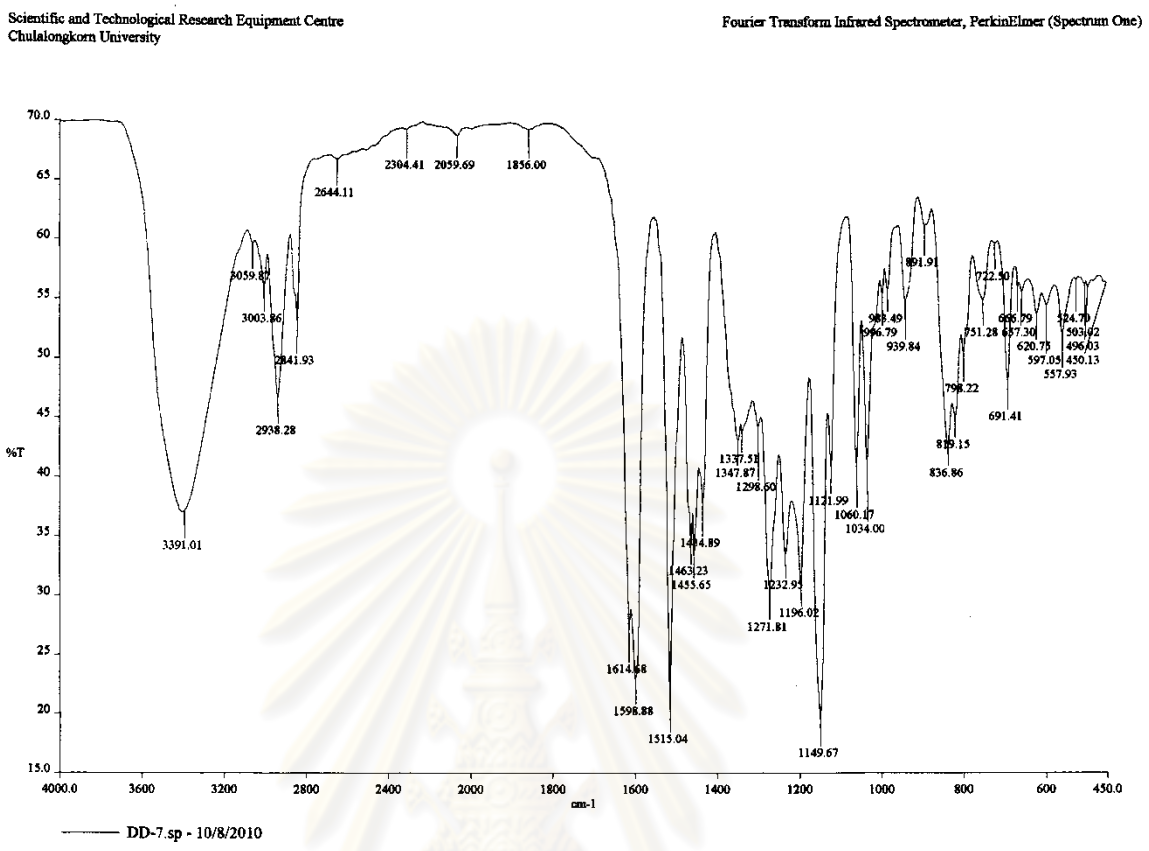


Figure 12 IR spectrum of compound DD2

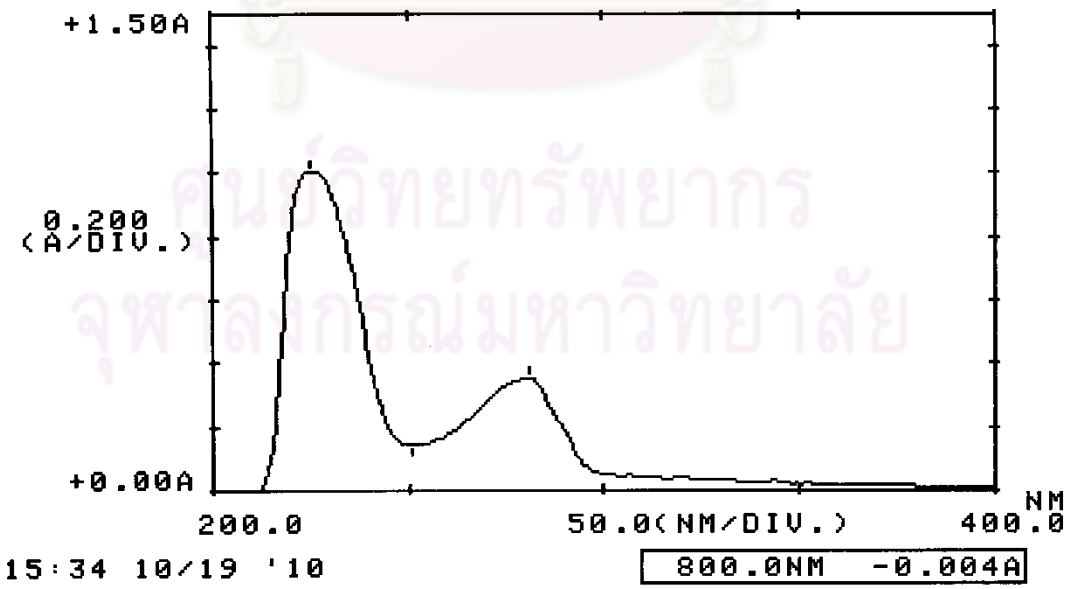


Figure 13 UV spectrum of compound DD2

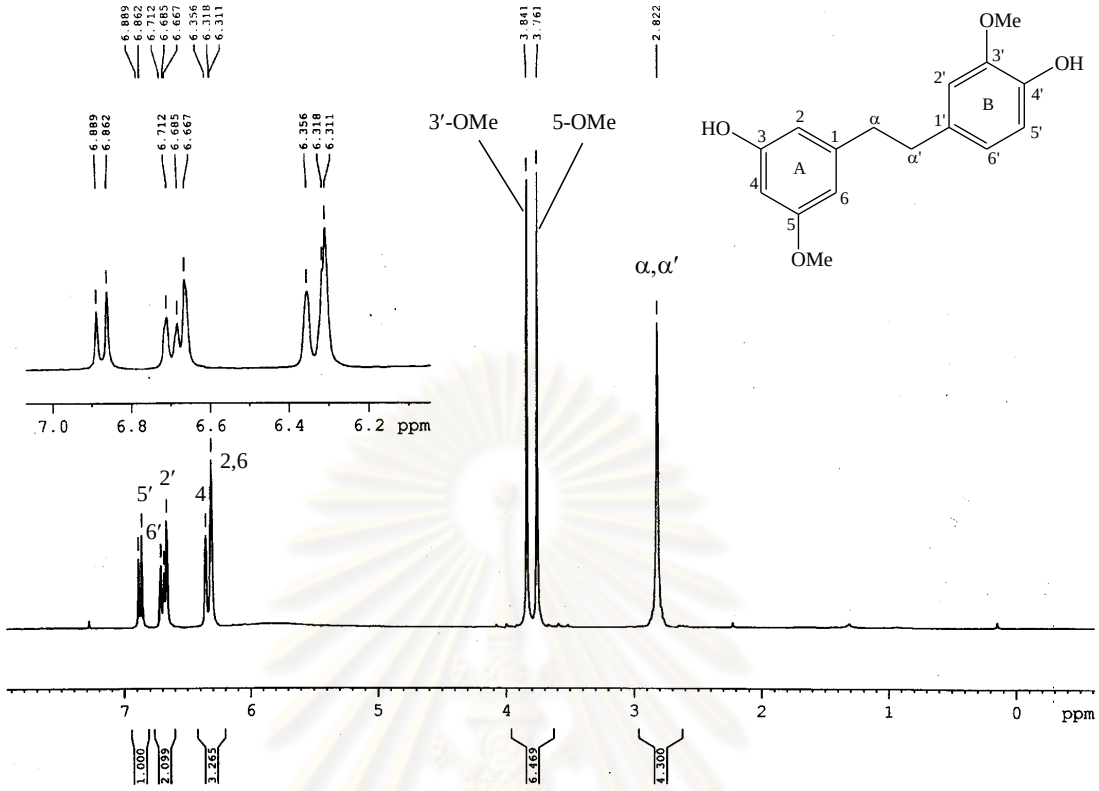


Figure 14 ^{1}H-NMR (300 MHz) Spectrum of compound DD2 ($CDCl_3$)

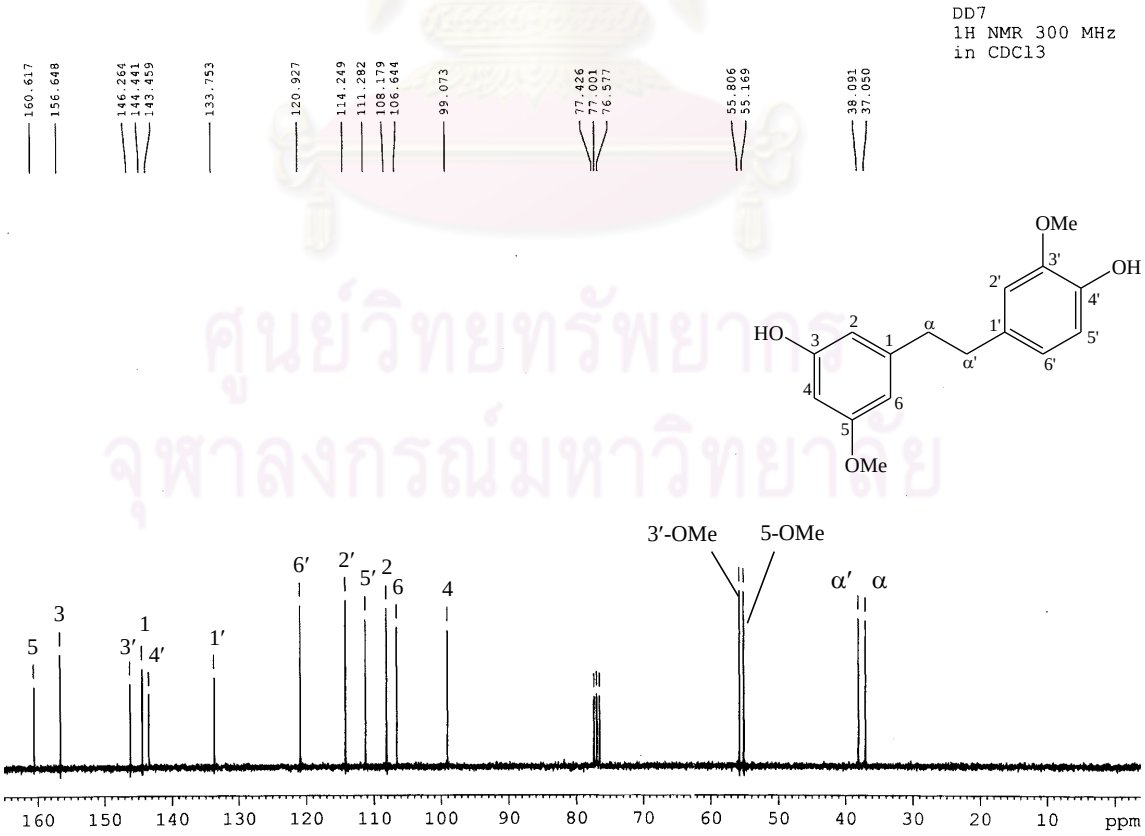


Figure 15 ^{13}C-NMR (75 MHz) Spectrum of compound DD2 ($CDCl_3$)

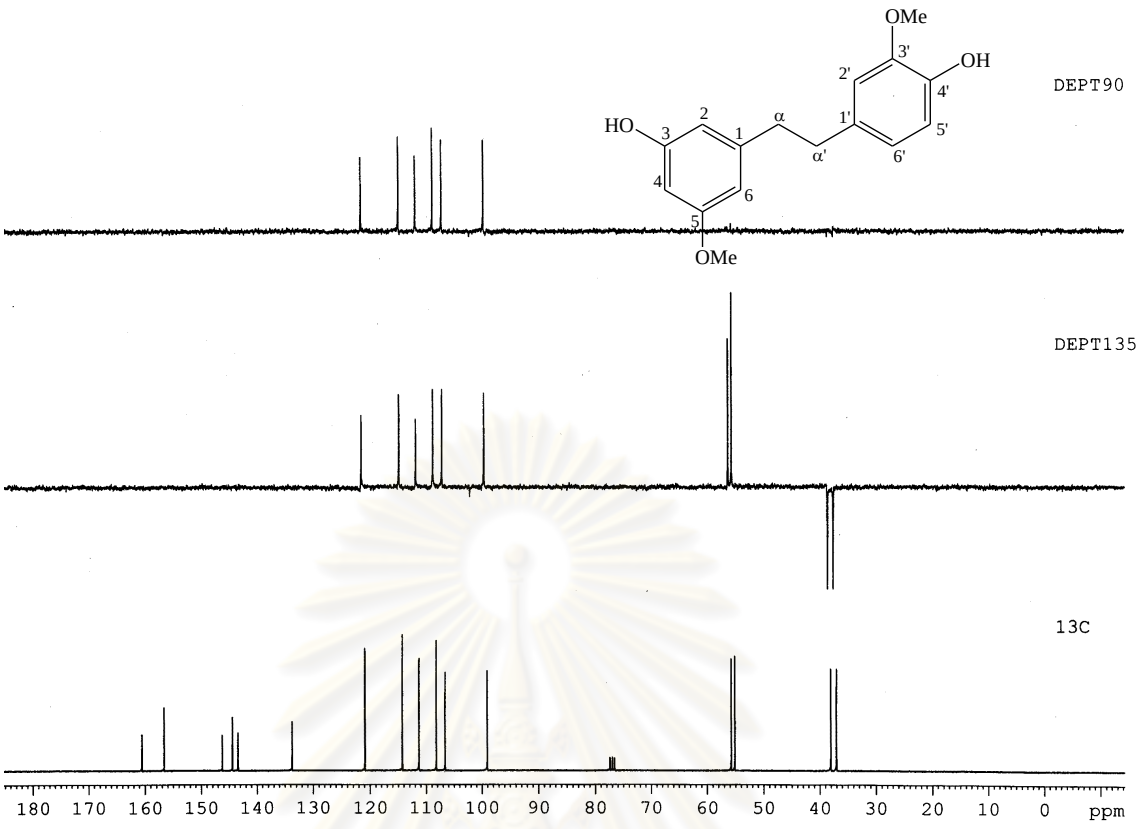


Figure 16 DEPT Spectra of compound DD2 ($CDCl_3$)

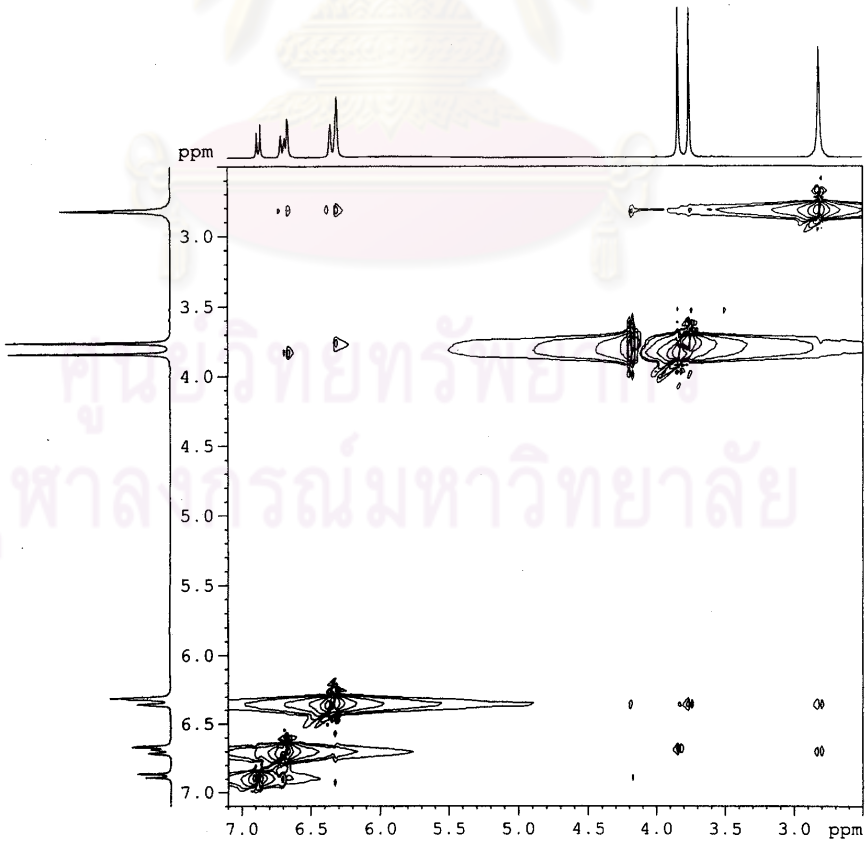


Figure 17 NOESY Spectrum of compound DD2 ($CDCl_3$)

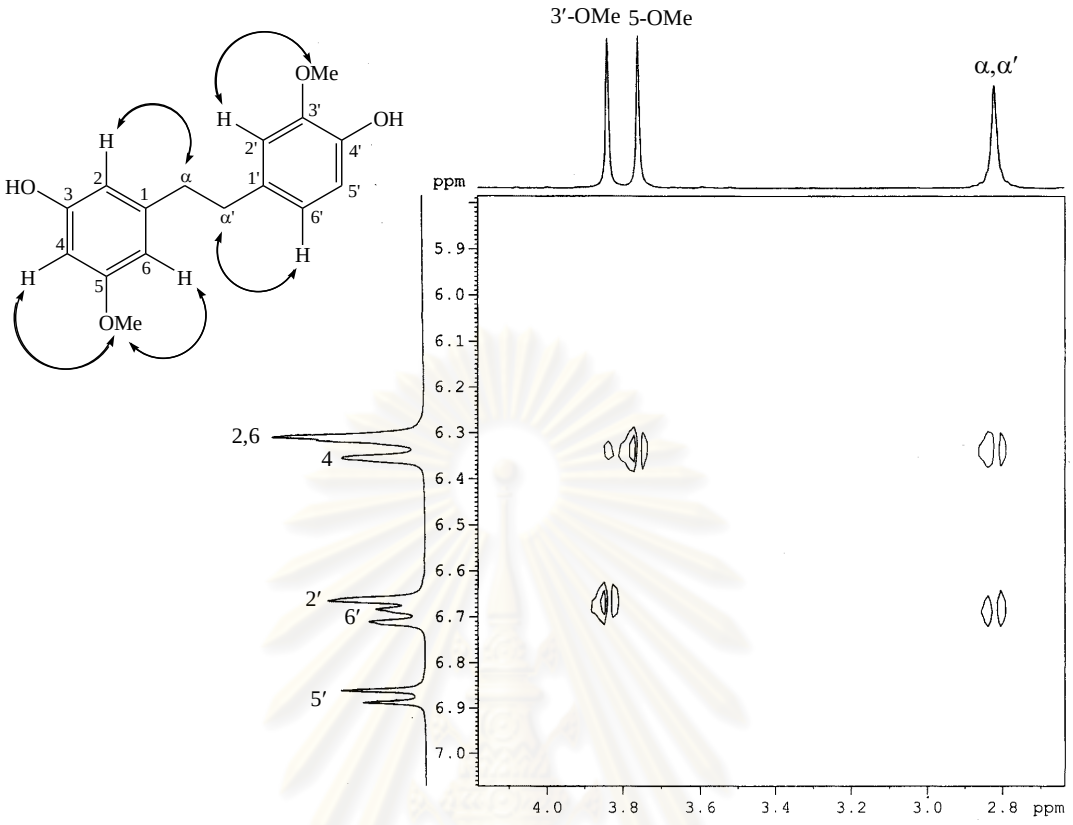


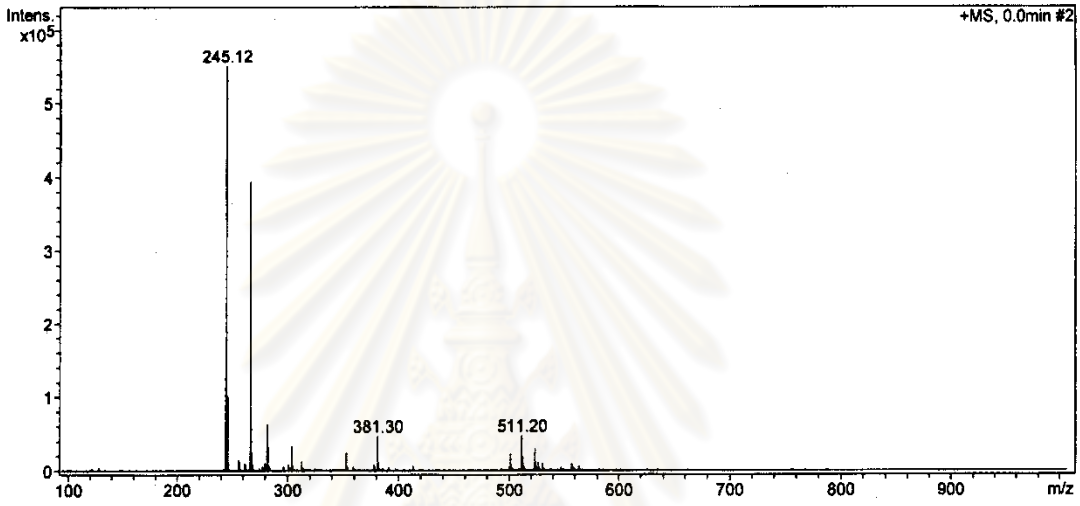
Figure 18 NOESY Spectrum of compound DD2 ($CDCl_3$)
(δ_H 5.80-7.10, δ_H 4.10- 2.70)

Low resolution report

		Acquisition Date	10/11/2010 1:54:32 PM
Analysis Name	D:\Data\customer\D13.d		
Method	NaFormate_pos_infusion.m	Operator	Sutichai Ext: 3560
Sample Name	D13	Instrument	micrOTOF Bruker

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 °C
Scan Begin	100 m/z	Set Capillary	4000 V	Set Dry Gas	6.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



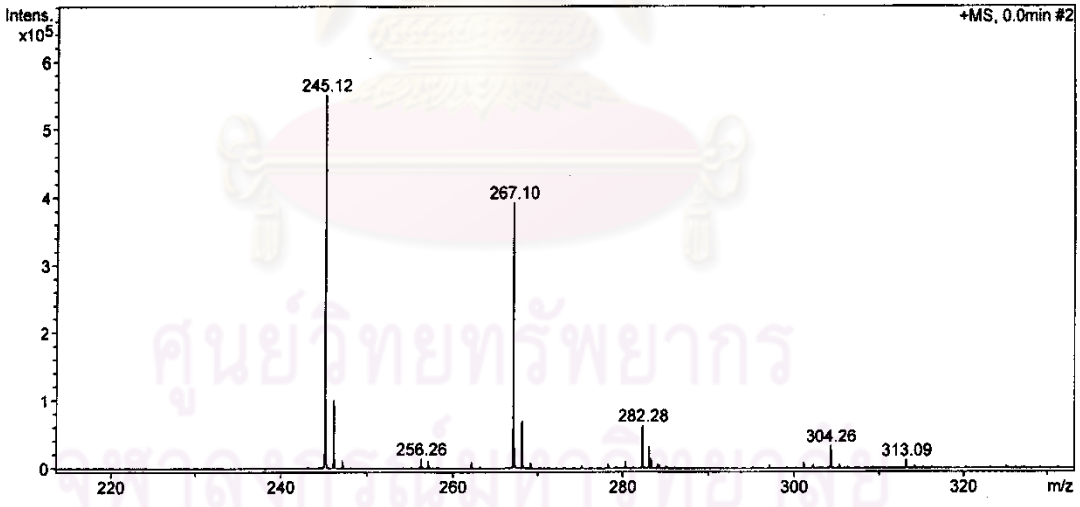


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Figure 19 Mass Spectrum of compound DD3

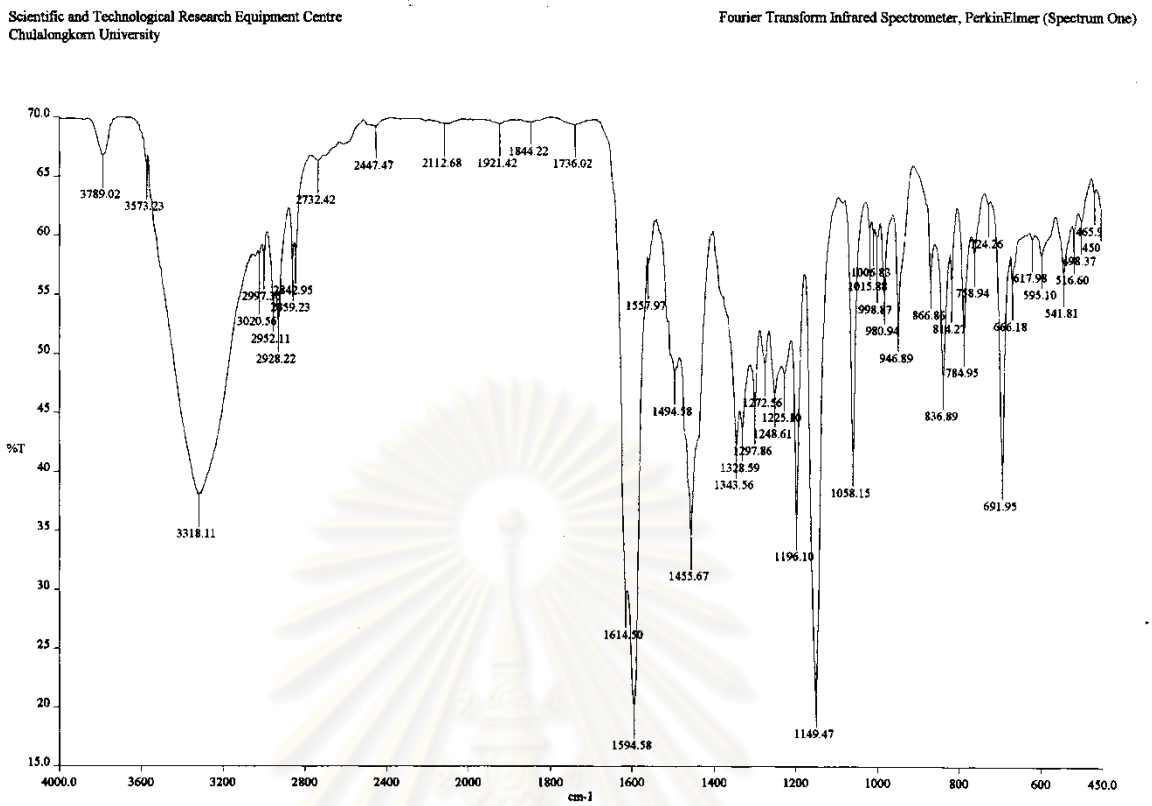

Figure 20 IR Spectrum of compound DD3

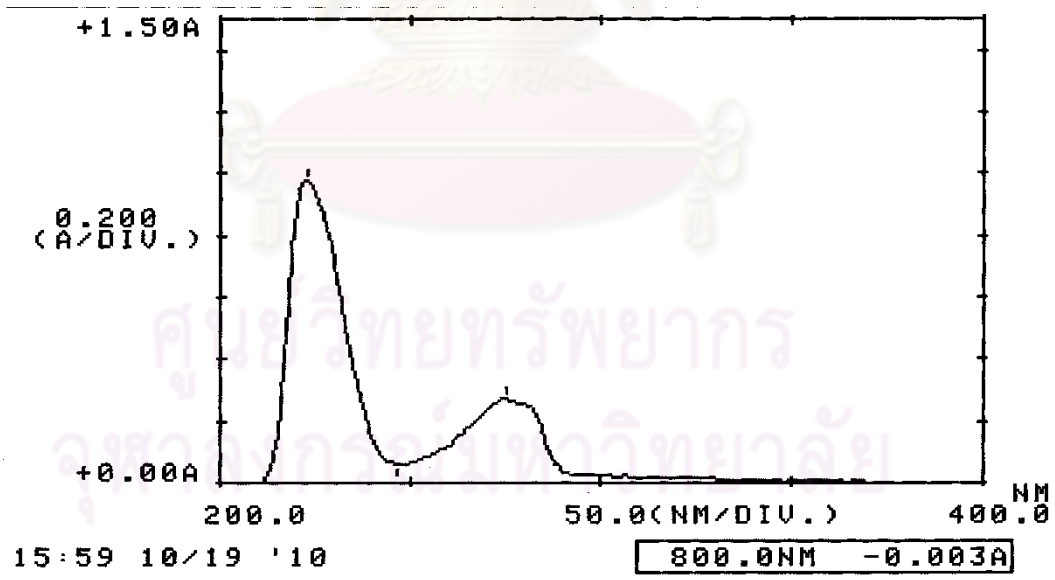

Figure 21 UV Spectrum of compound DD3

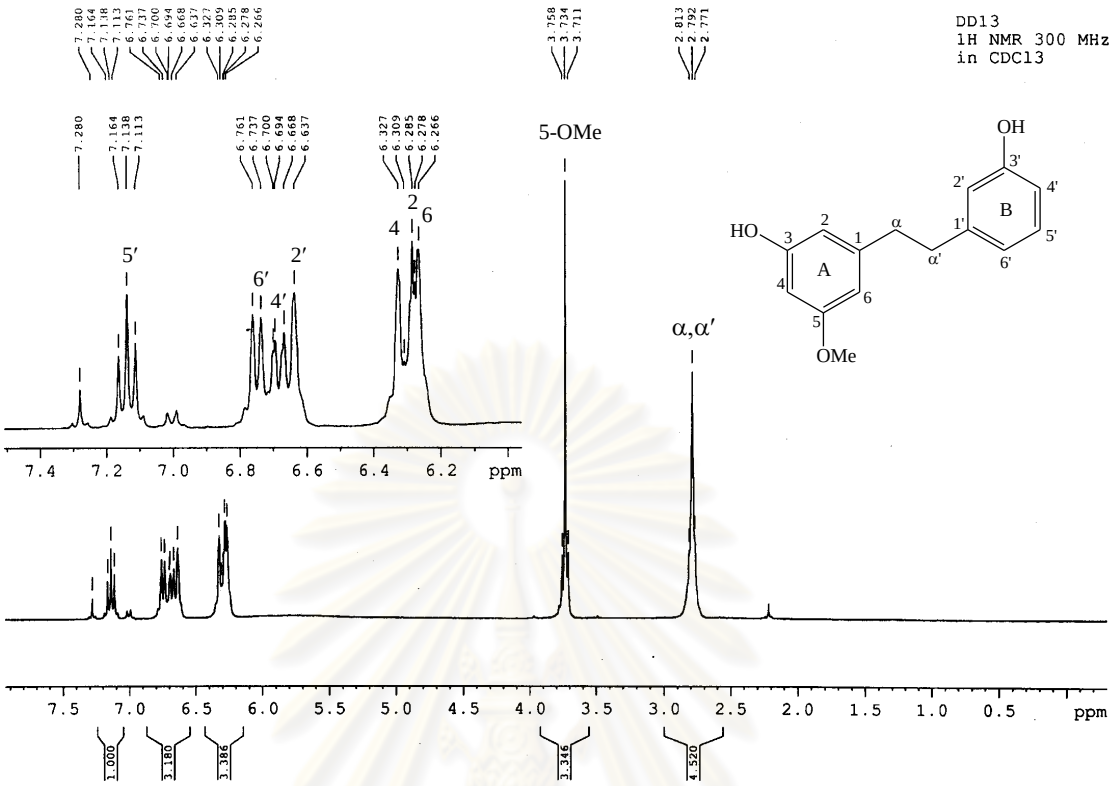

Figure 22 ^{1}H-NMR (300 MHz) Spectrum of compound DD3 ($CDCl_3$)

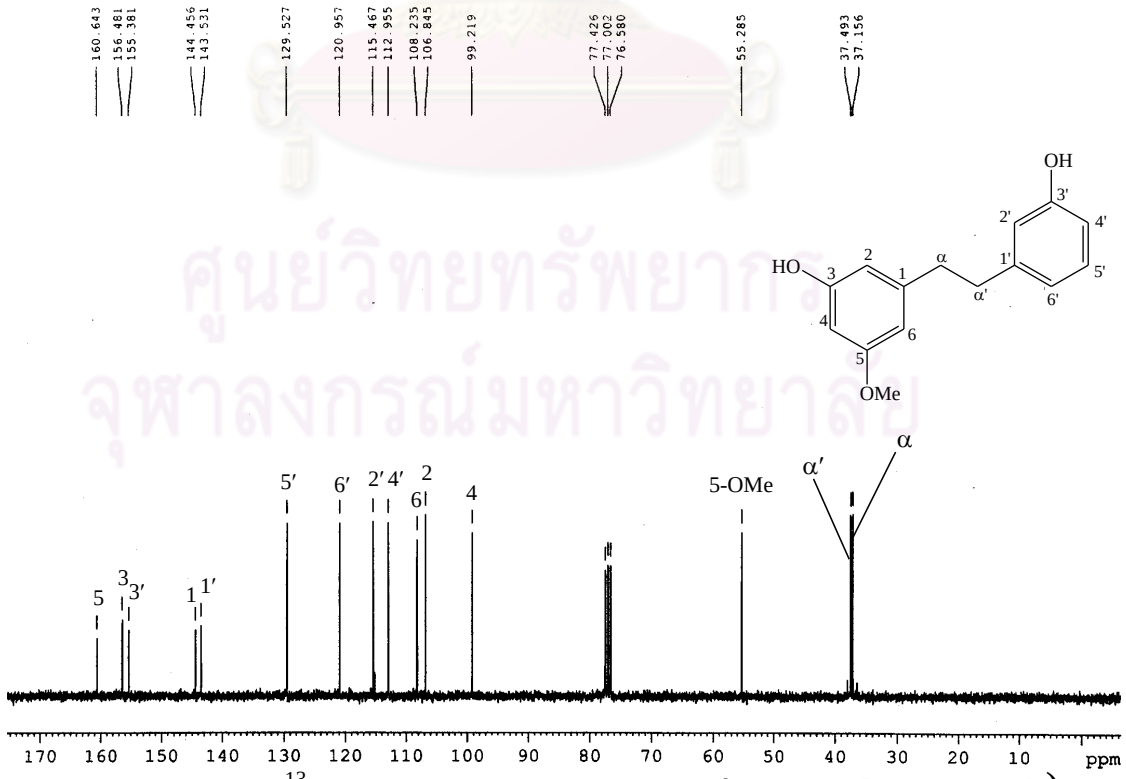

Figure 23 ^{13}C-NMR (300 MHz) Spectrum of compound DD3 ($CDCl_3$)

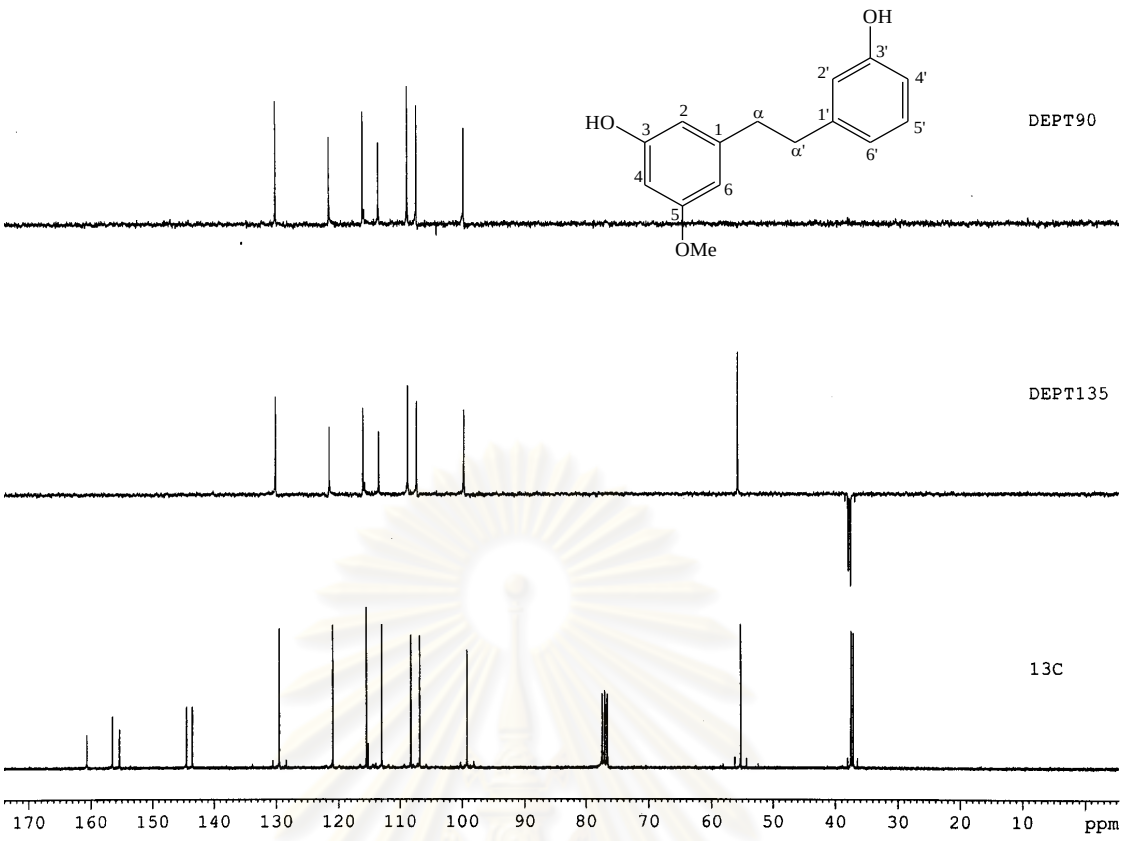

Figure 24 DEPT Spectra of compound DD3 ($CDCl_3$)

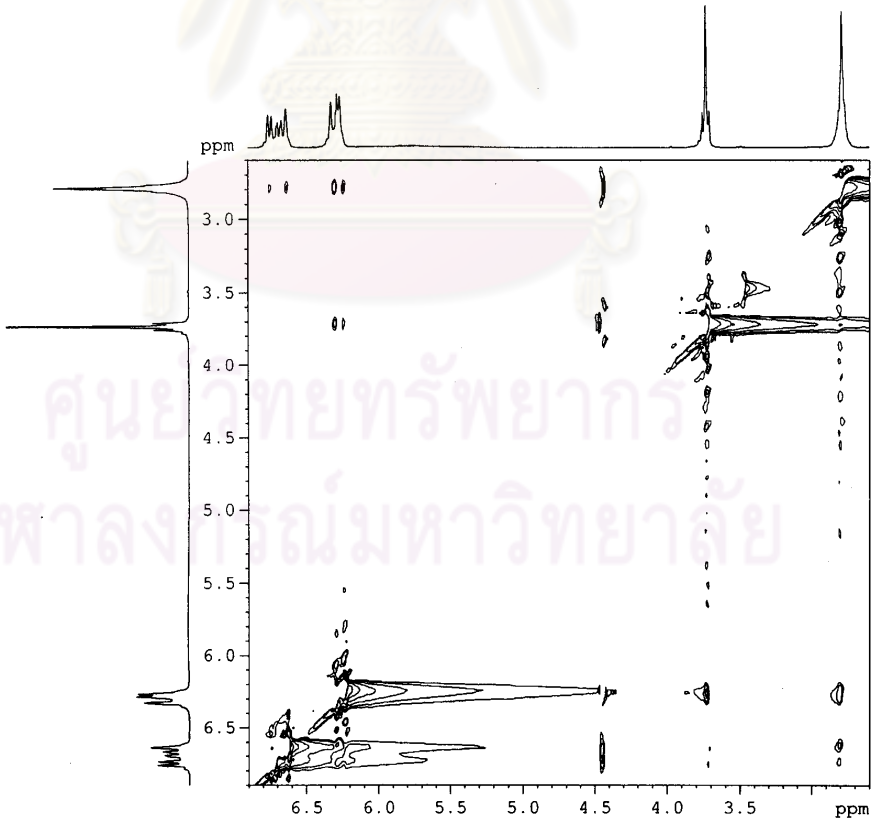

Figure 25 NOESY Spectrum of compound DD3 ($CDCl_3$)

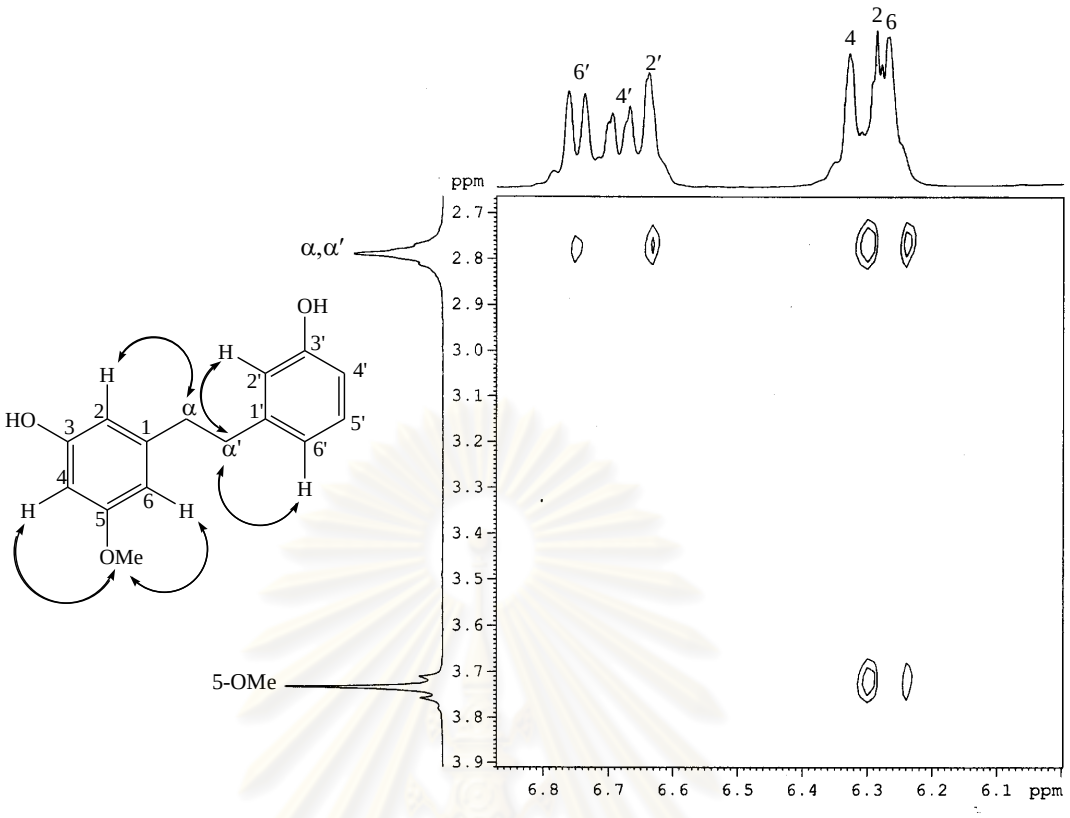

Figure 26 NOESY Spectrum of compound DD3 ($CDCl_3$)
(δ_H 2.70-3.90, δ_H 6.90- 6.00)

High resolution report

		Acquisition Date	5/31/2010 2:24:43 PM
Analysis Name	D:\Data\Dua\DD17.d		
Method	NaFormate_pos_infusion.m	Operator	Sutichai Ext: 3560
Sample Name	DD17	Instrument	micrOTOF Bruker
		Calibrate by	Sodium Formate

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 °C
Scan Begin	100 m/z	Set Capillary	4000 V	Set Dry Gas	6.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

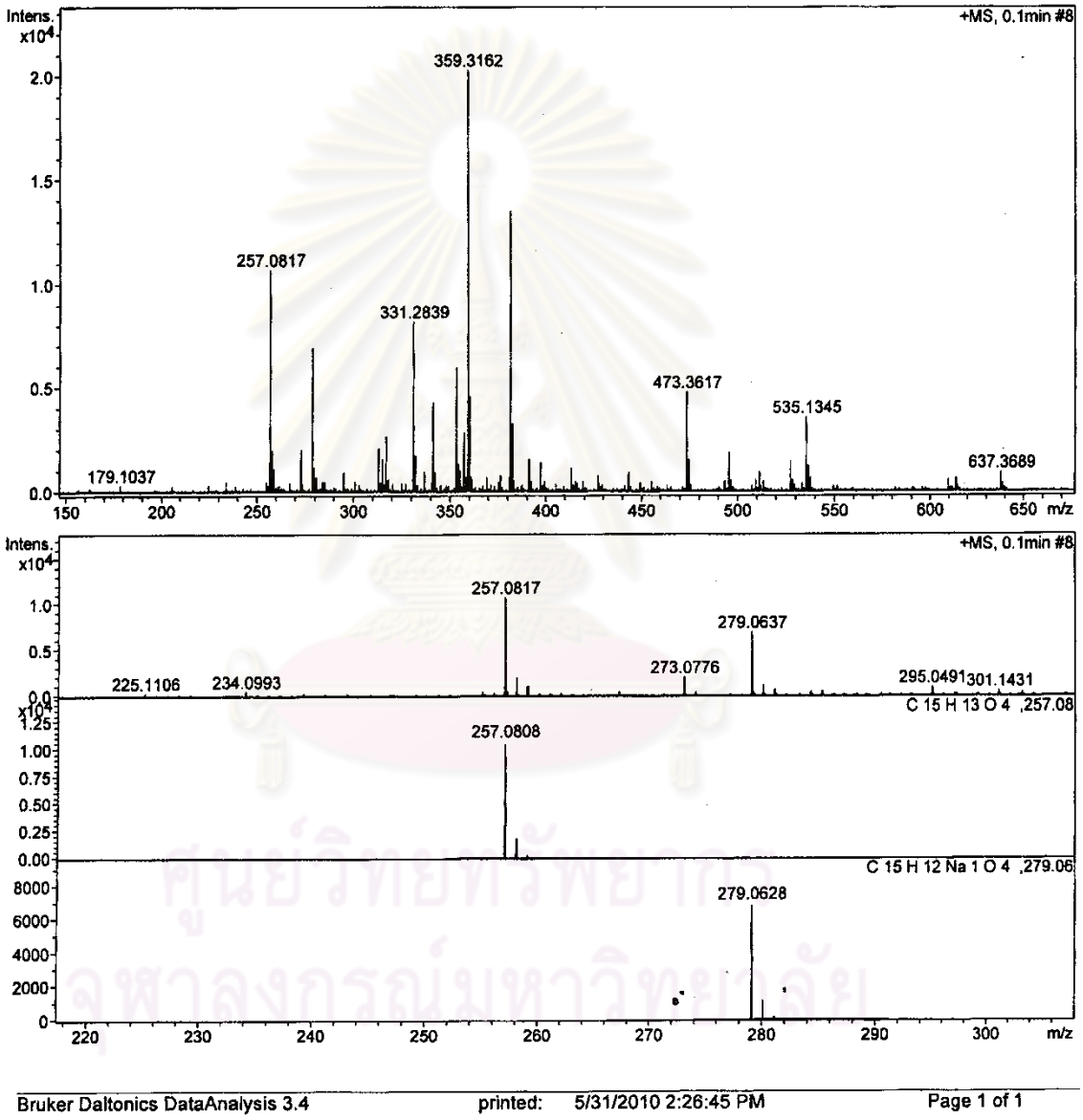

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Figure 27 Mass Spectrum of compound DD4

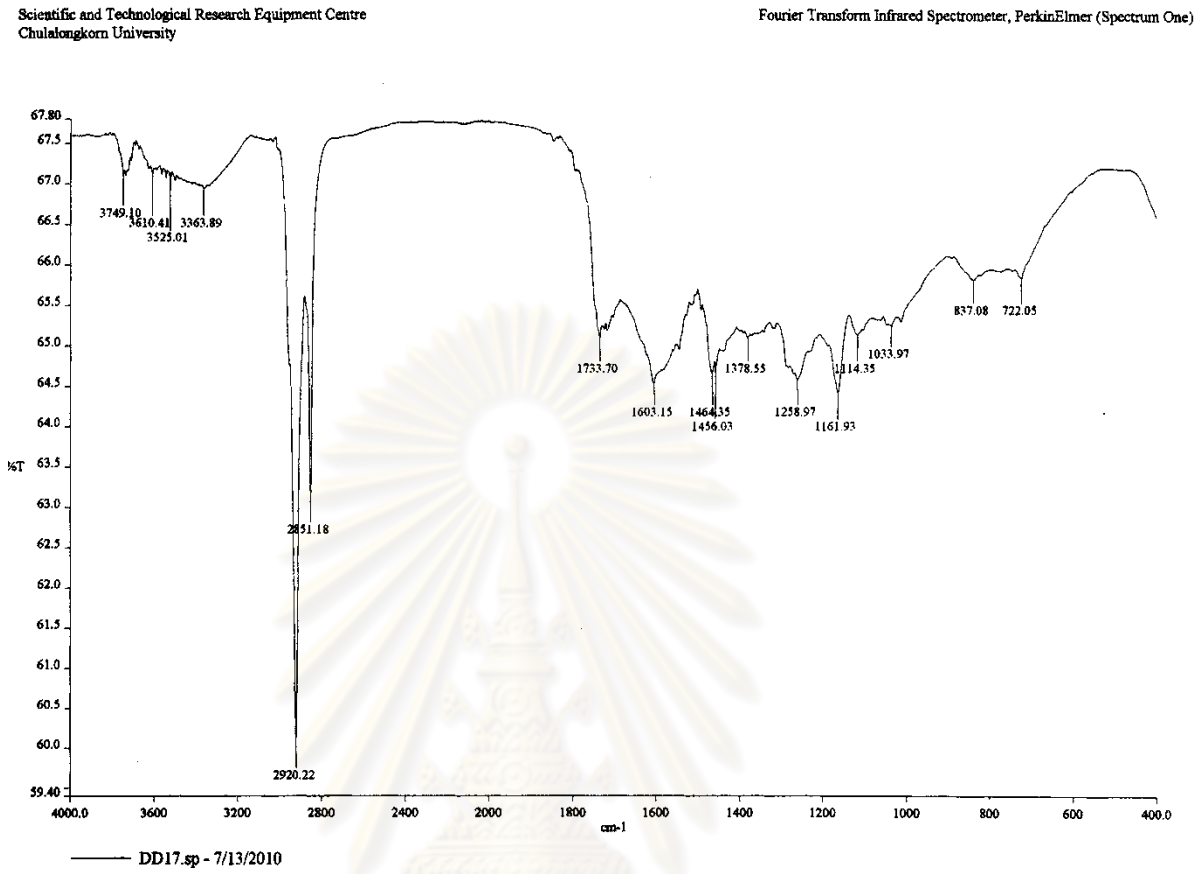


Figure 28 IR Spectrum of compound DD4

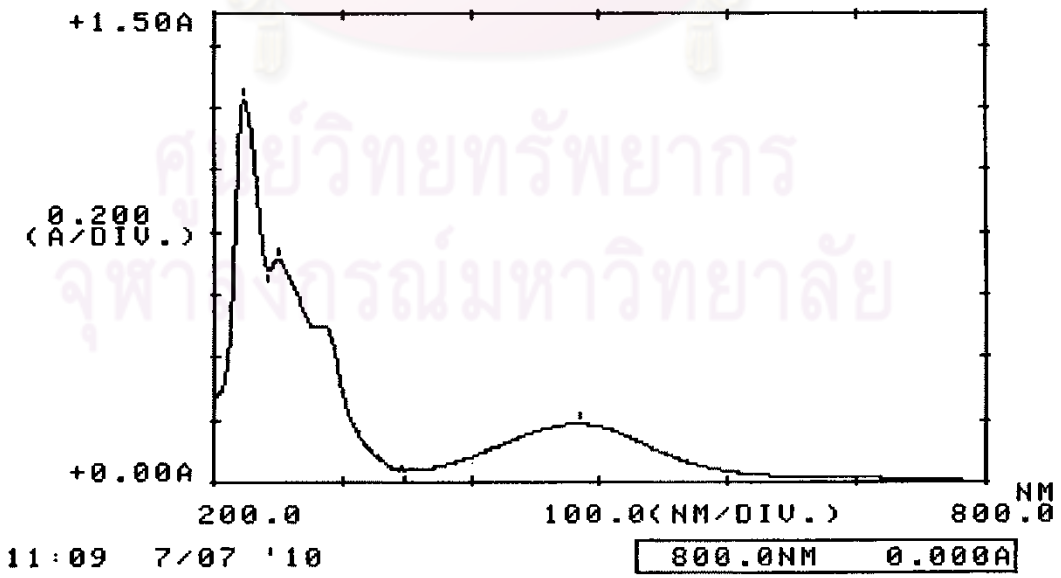


Figure 29 UV Spectrum of compound DD4

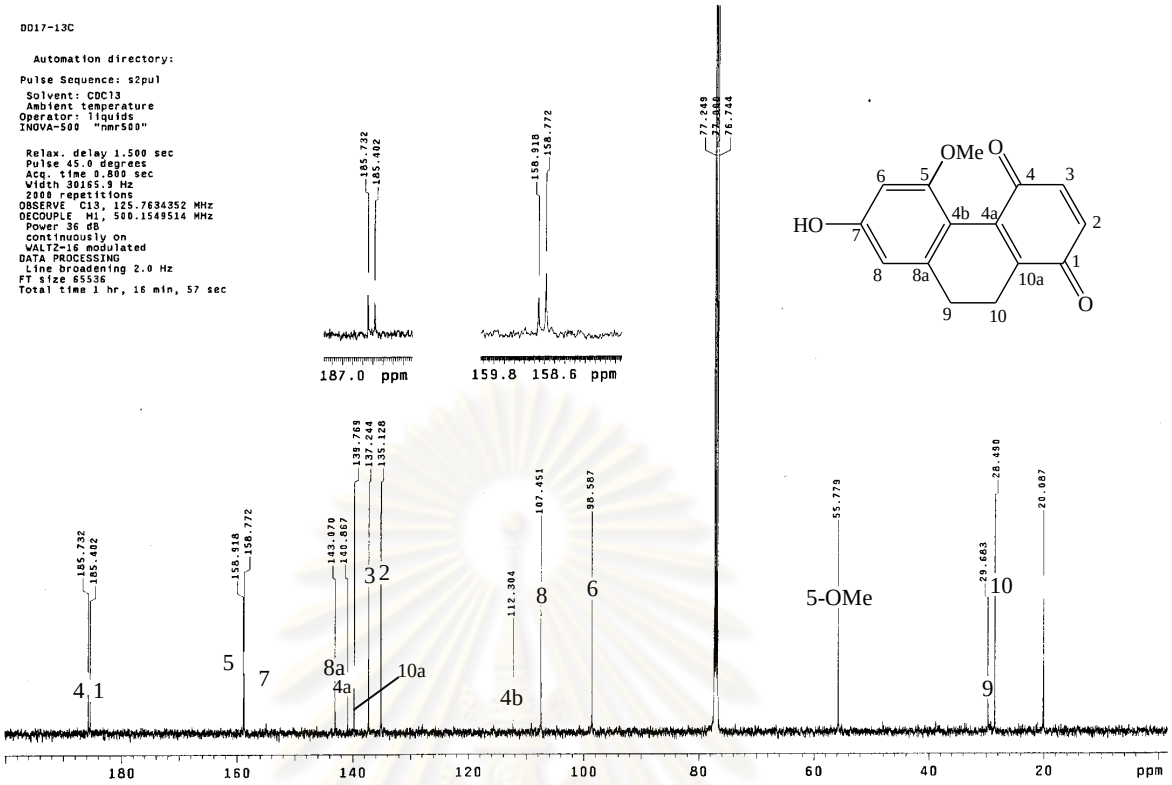


Figure 30 ^{13}C-NMR (125 MHz) Spectrum of compound DD4 ($CDCl_3$)

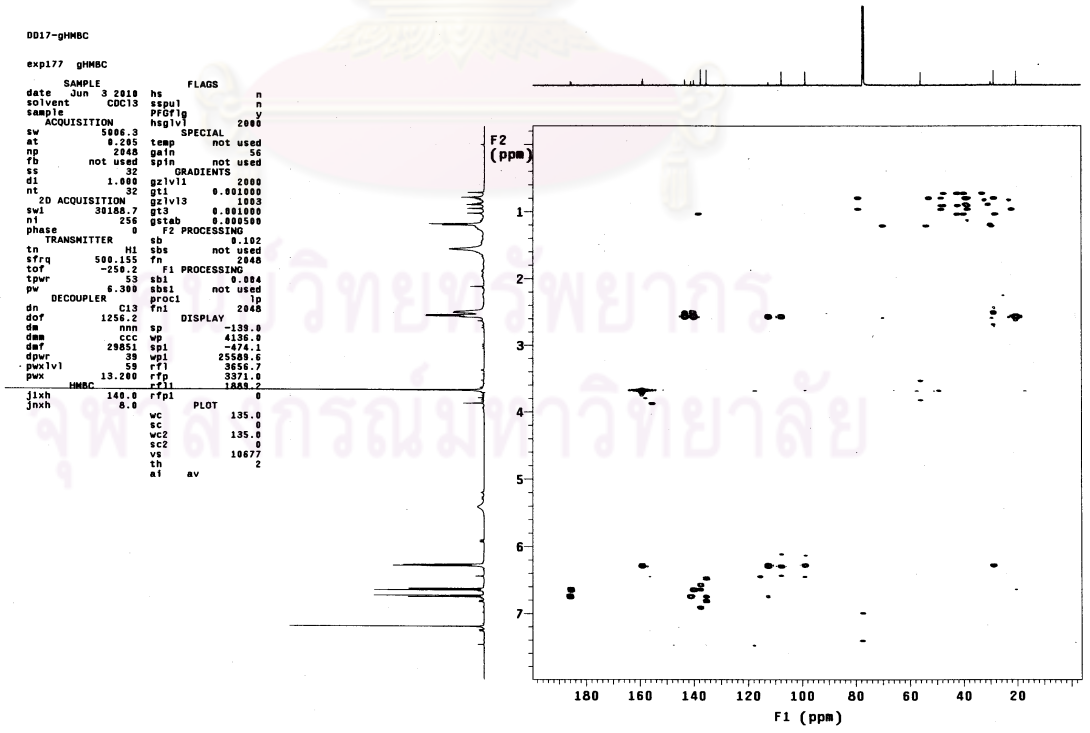


Figure 31 HMBC Spectrum of compound DD4 ($CDCl_3$)

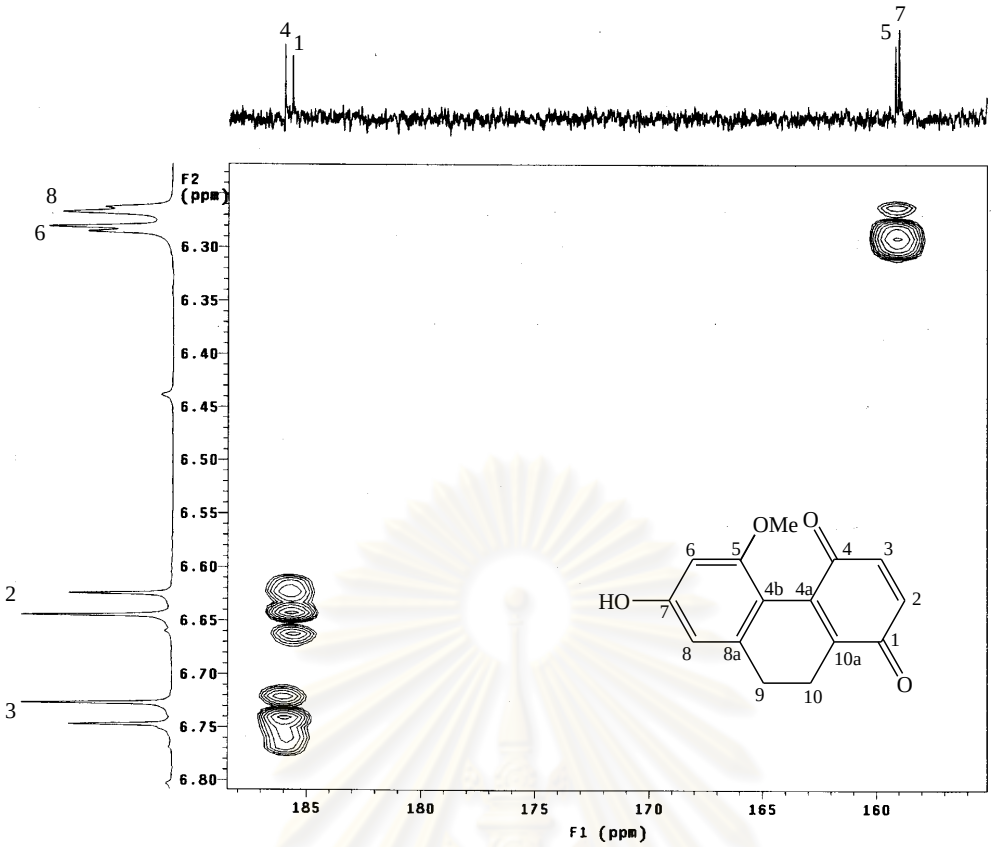


Figure 32 HMBC Spectrum of compound DD4 ($CDCl_3$)
(δ_H 6.25-6.80, δ_C 190.0-155.0)

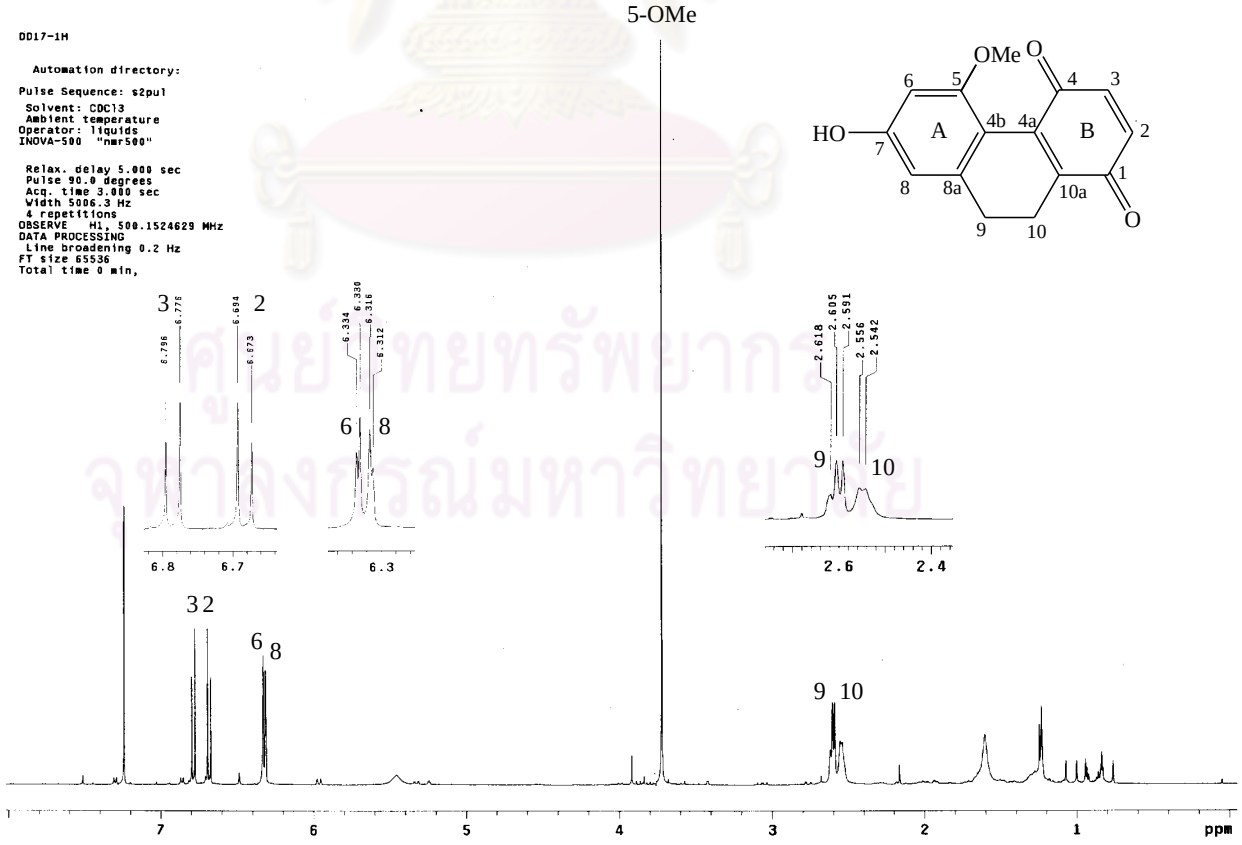


Figure 33 ^{1}H-NMR (500 MHz) Spectrum of compound DD4 ($CDCl_3$)

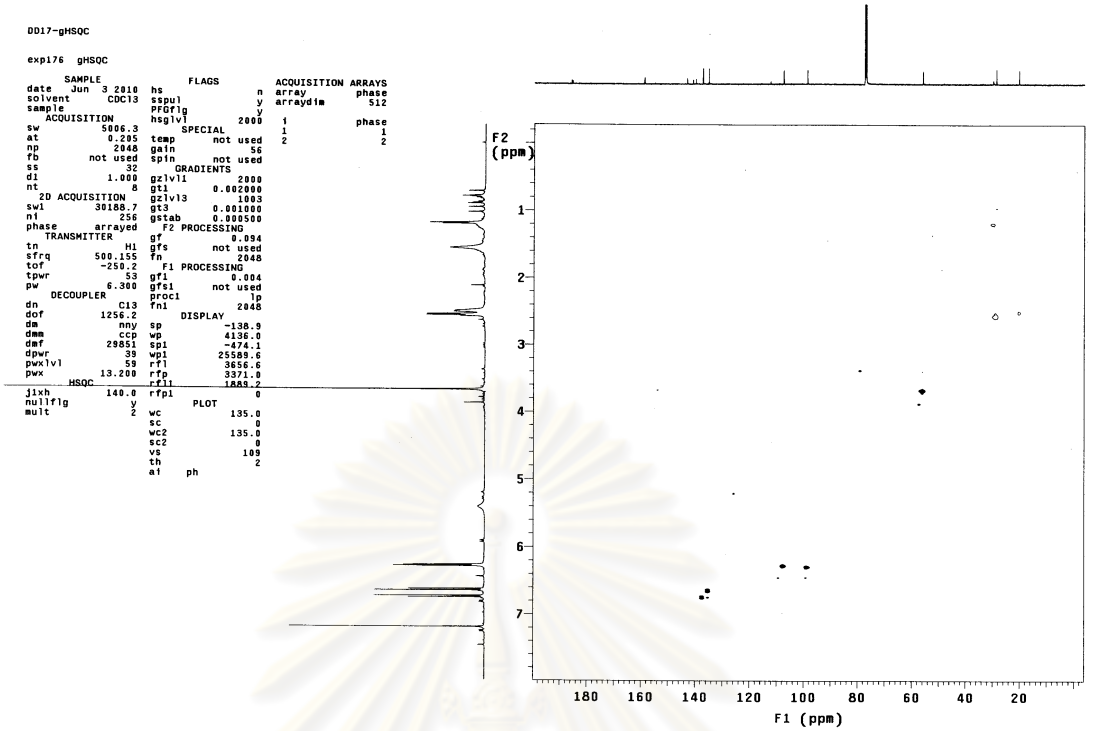


Figure 34 HSQC Spectrum of compound DD4 ($CDCl_3$)

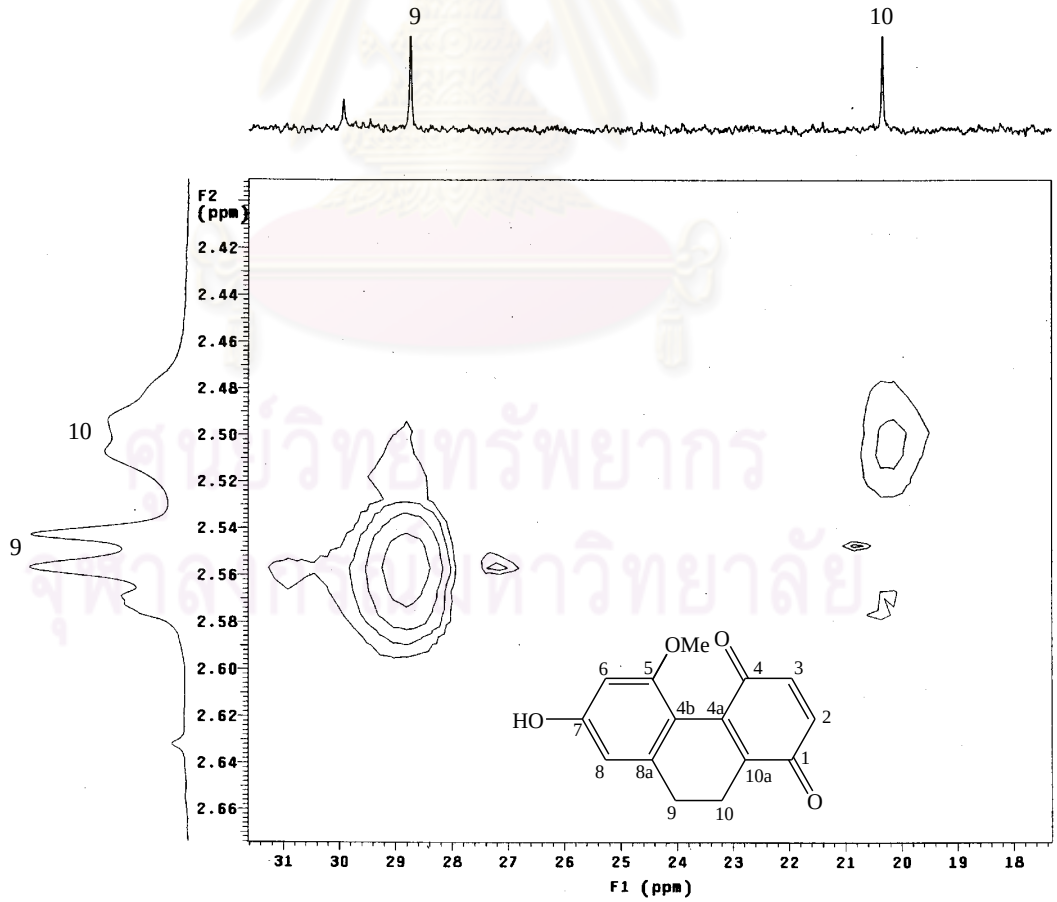


Figure 35 HSQC Spectrum of compound DD4 ($CDCl_3$)
(δ_H 2.40-2.66, δ_C 31.0-18.0)

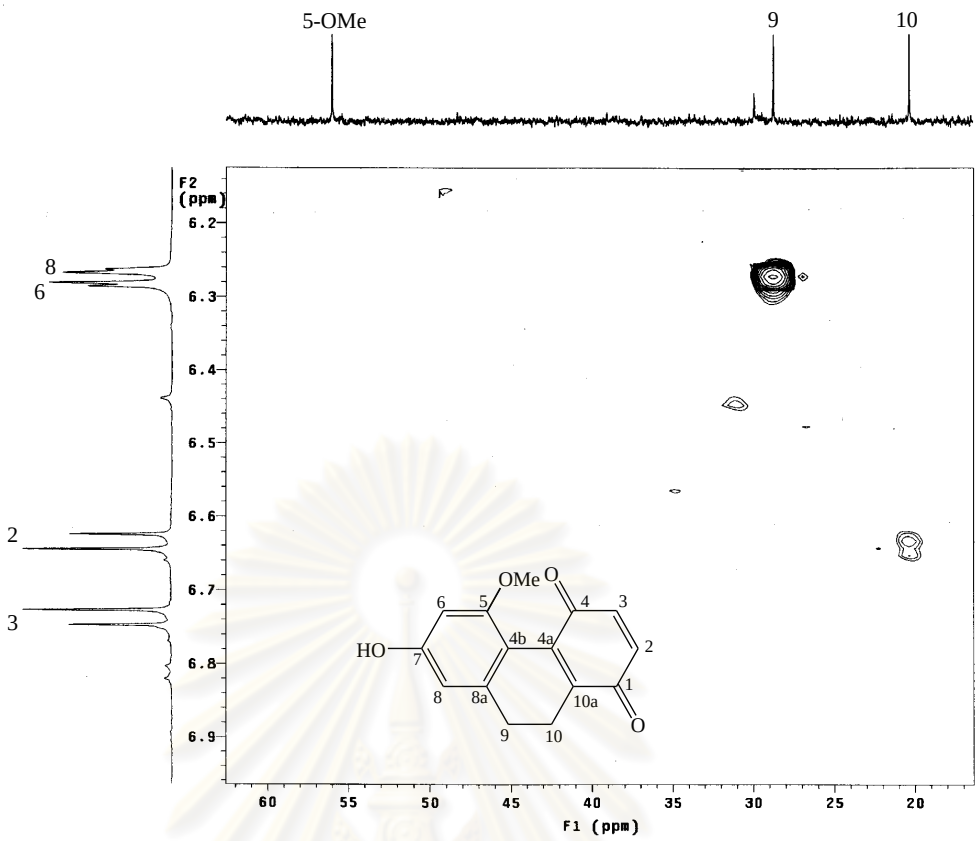


Figure 36 HMBC Spectrum of compound DD4 ($CDCl_3$)
(δ_H 6.20-6.90, δ_C 60.0-17.0)

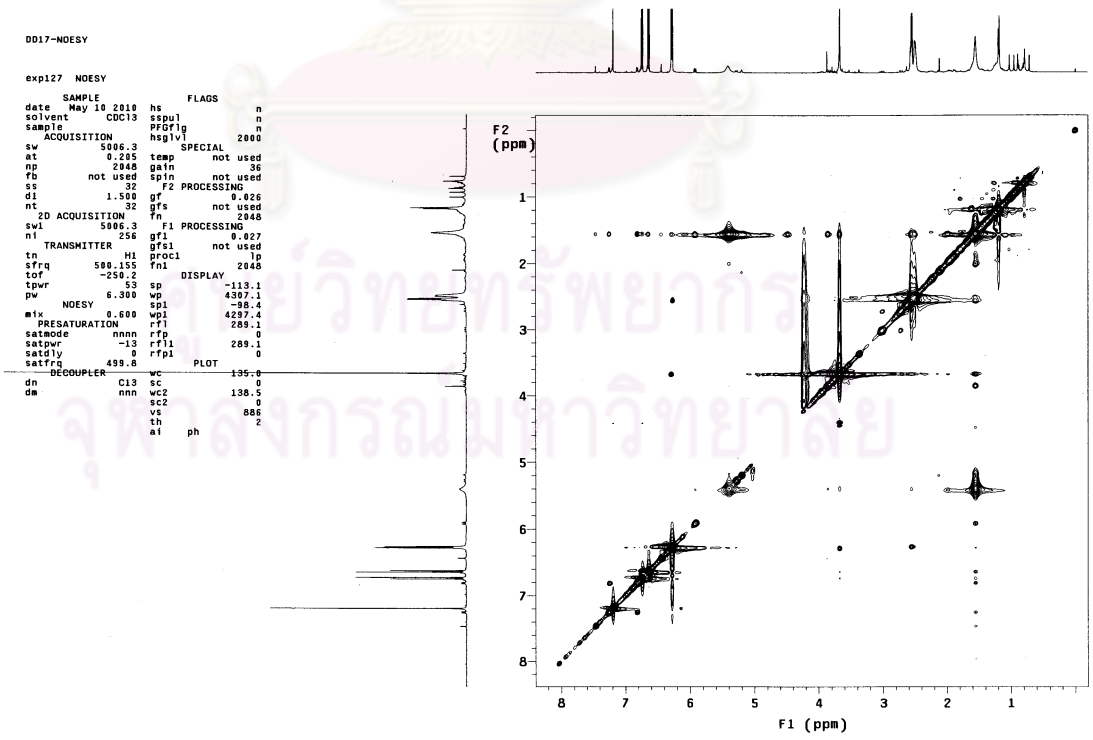


Figure 37 NOESY Spectrum of compound DD4 ($CDCl_3$)

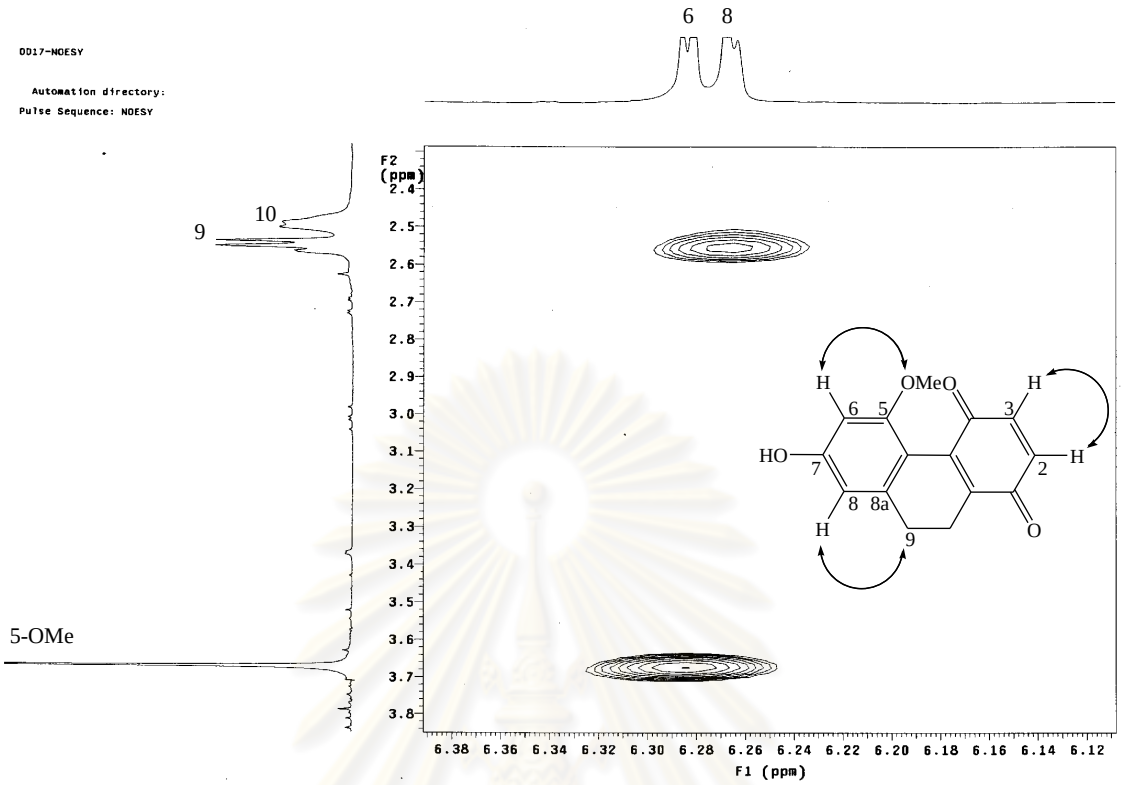


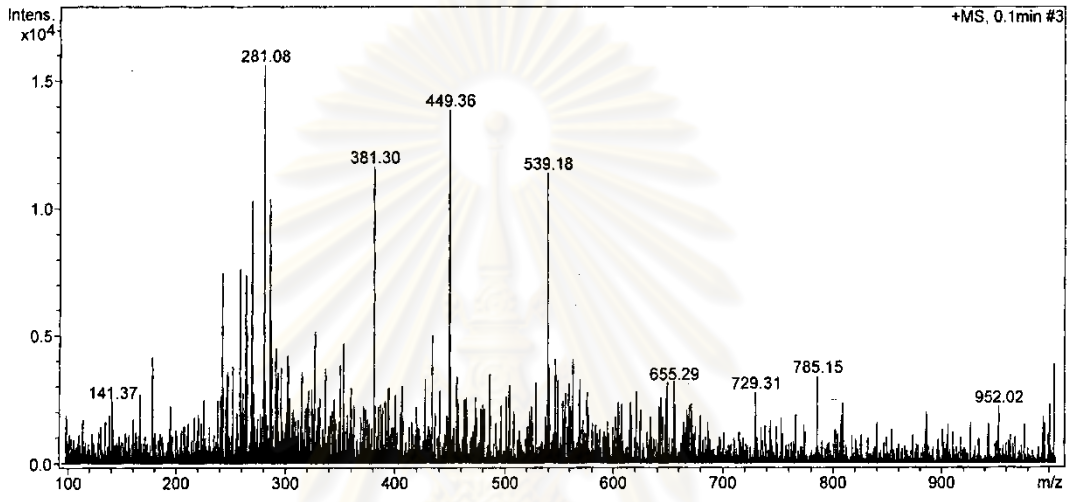
Figure 38 NOESY Spectrum of compound DD4 ($CDCl_3$)
(δ_H 2.30-3.80, δ_H 6.38-6.12)

Low resolution report

		Acquisition Date	6/21/2010 4:44:27 PM
Analysis Name	D:\Data\Dua\DD25.d		
Method	NaFormate_pos_infusion.m	Operator	Sutichai Ext: 3560
Sample Name	DD25	Instrument	micrOTOF Bruker

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 °C
Scan Begin	100 m/z	Set Capillary	4000 V	Set Dry Gas	6.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



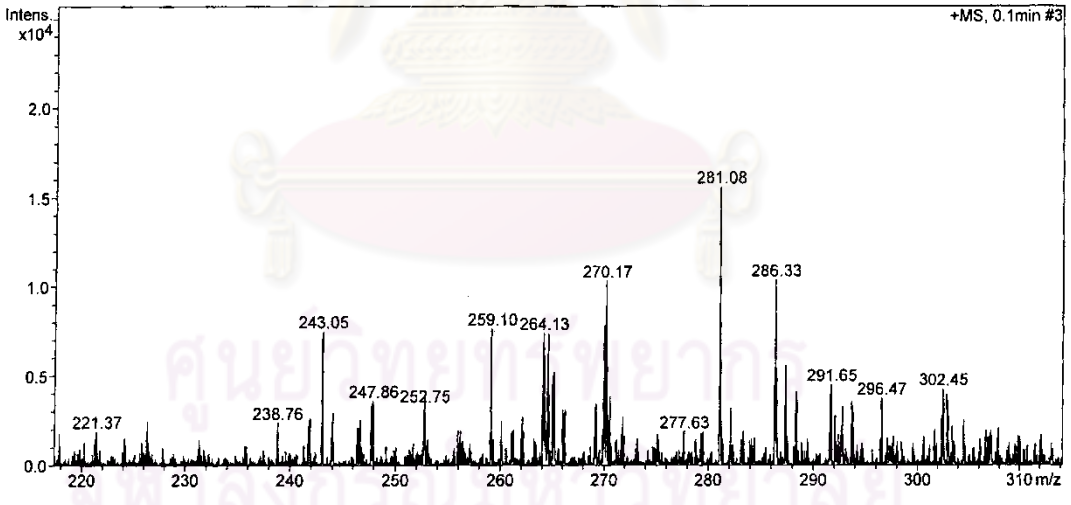


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Figure 39 Mass Spectrum of compound DD5

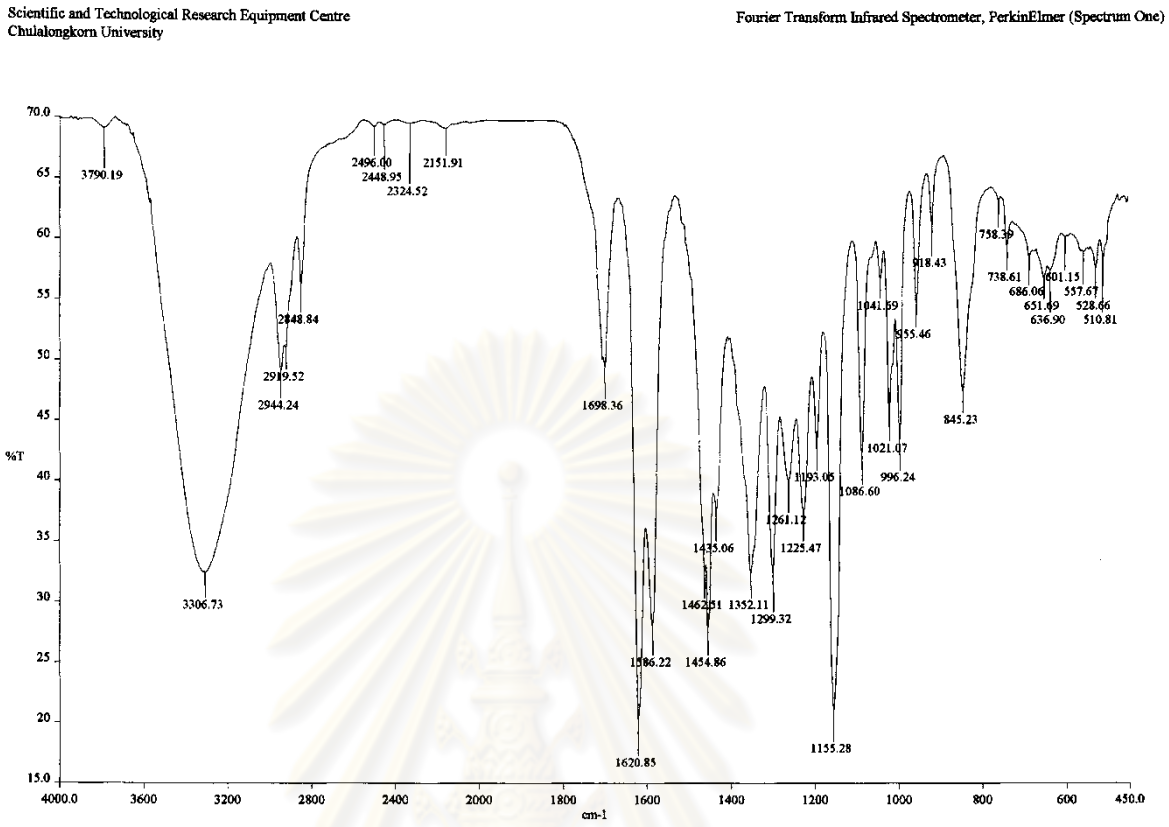


Figure 40 IR Spectrum of compound DD5

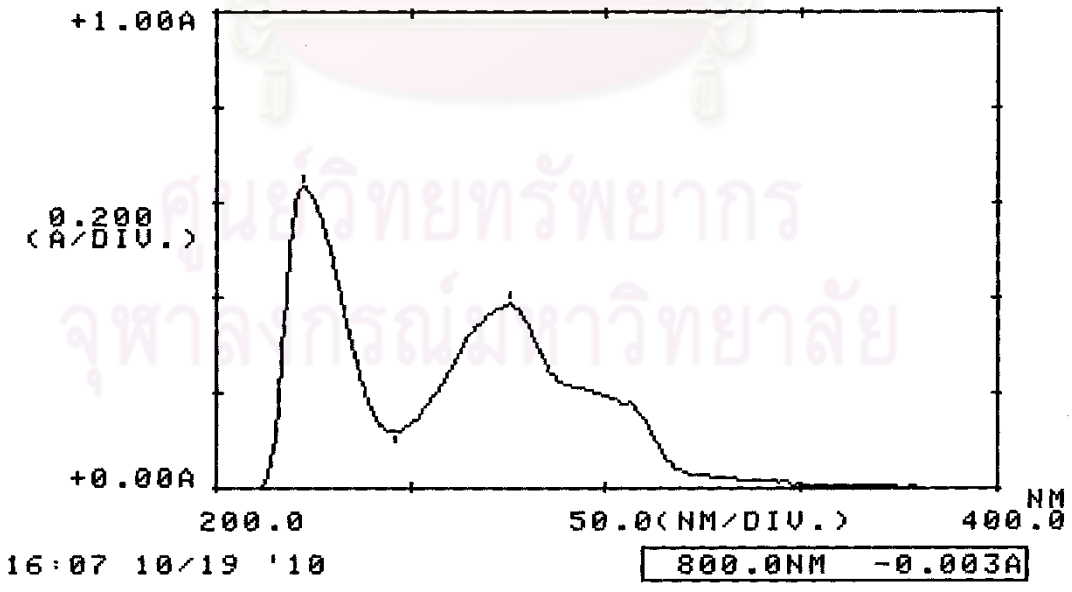


Figure 41 UV Spectrum of compound DD5

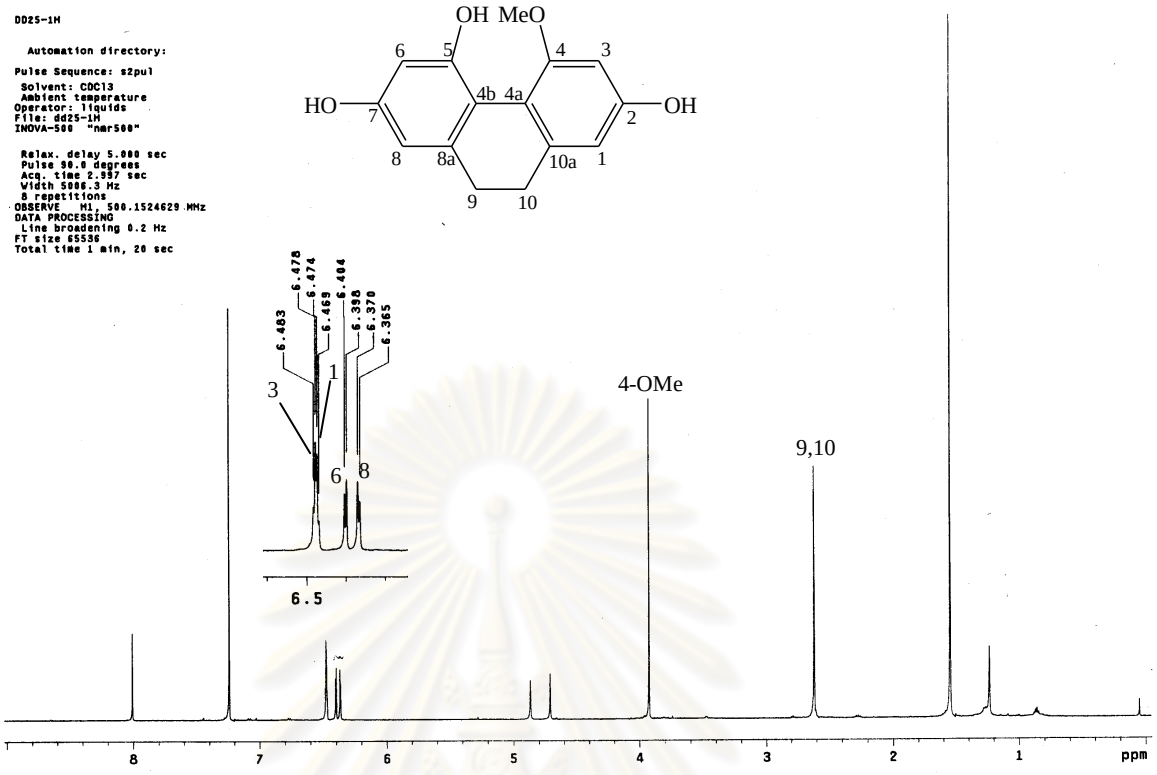


Figure 42 ^{1}H Spectrum (500 MHz) of compound DD5 ($CDCl_3$)

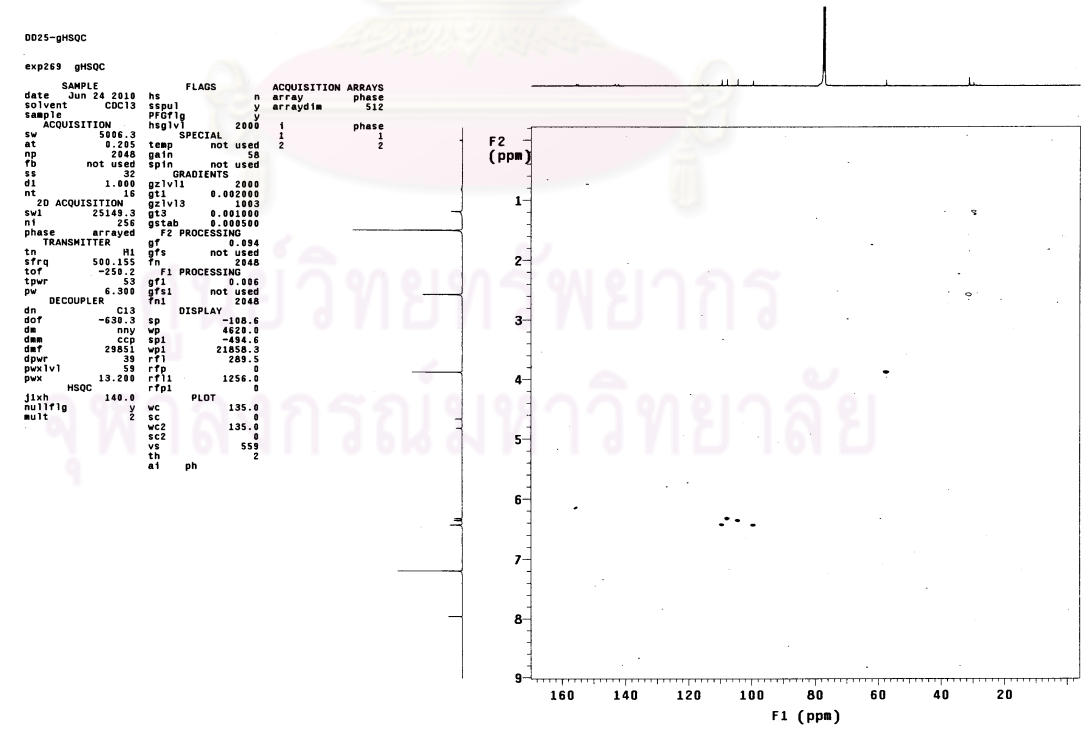


Figure 43 HSQC Spectrum of compound DD5 ($CDCl_3$)

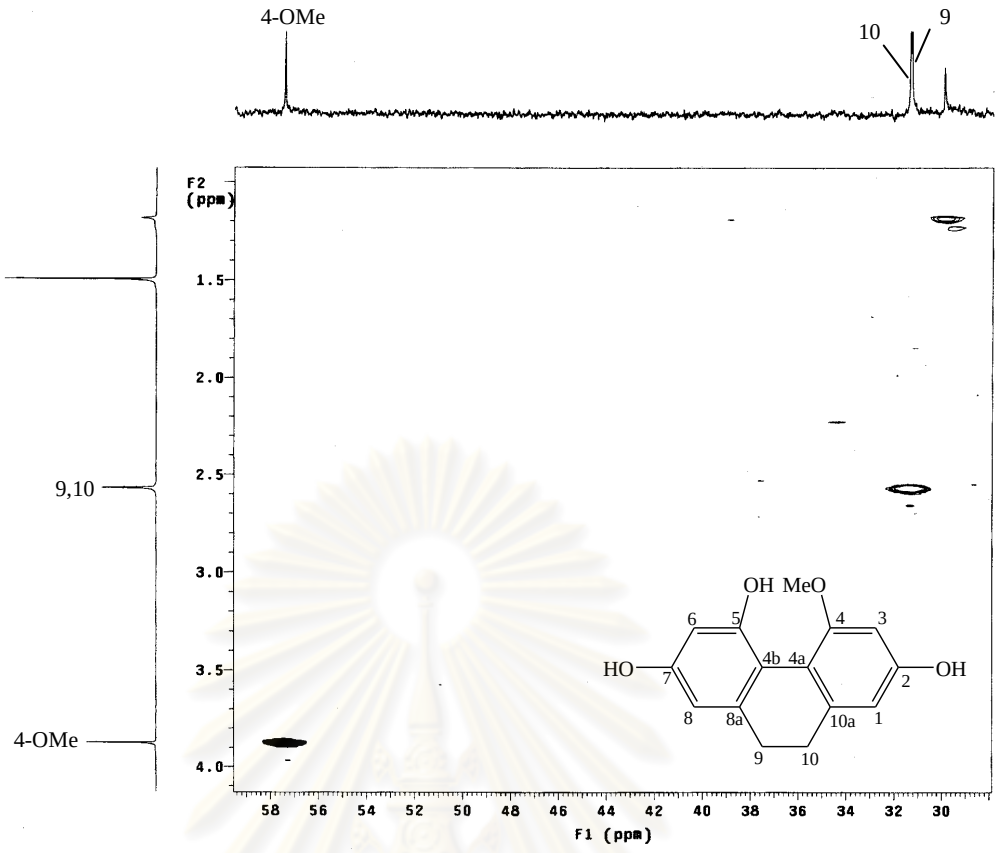


Figure 44 HSQC Spectrum of compound DD5 ($CDCl_3$)
(δ_H 1.00-4.00, δ_C 58.0-30.0)

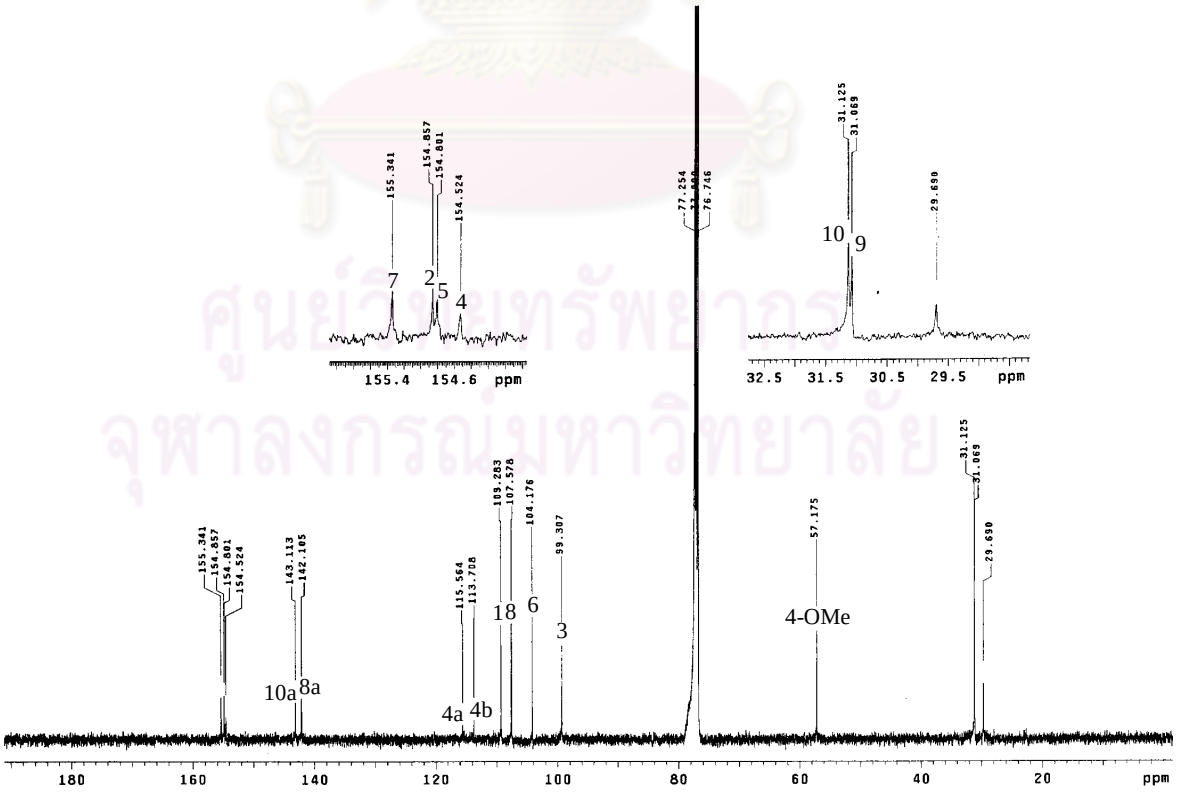


Figure 45 ^{13}C Spectrum (125 MHz) of compound DD5 ($CDCl_3$)

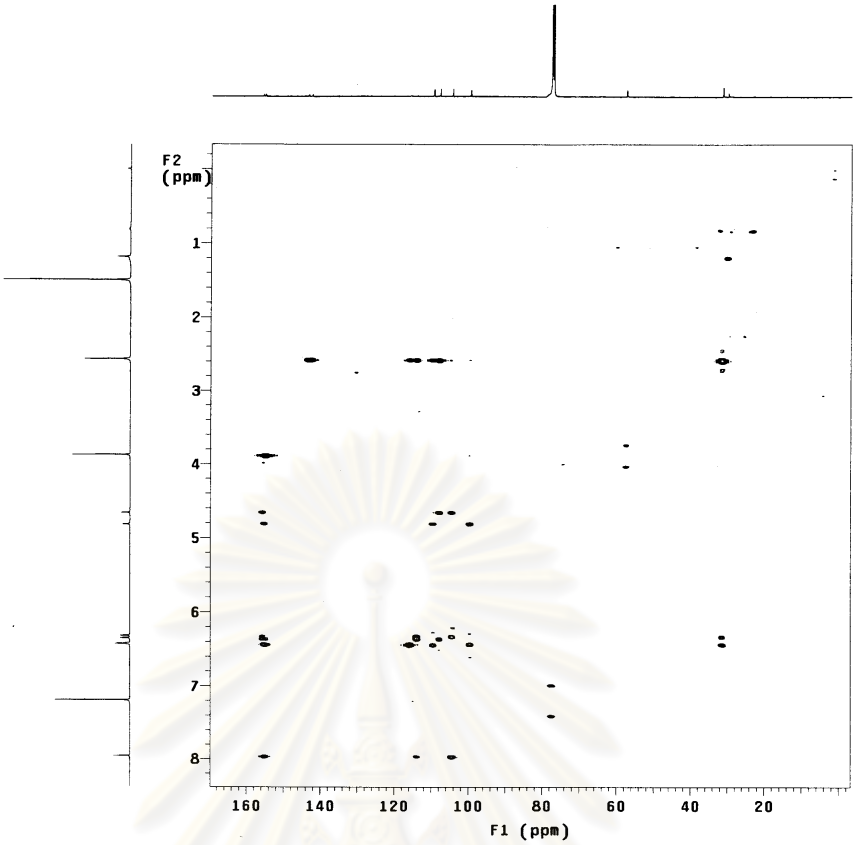


Figure 46 HMBC Spectrum of compound DD5 ($CDCl_3$)

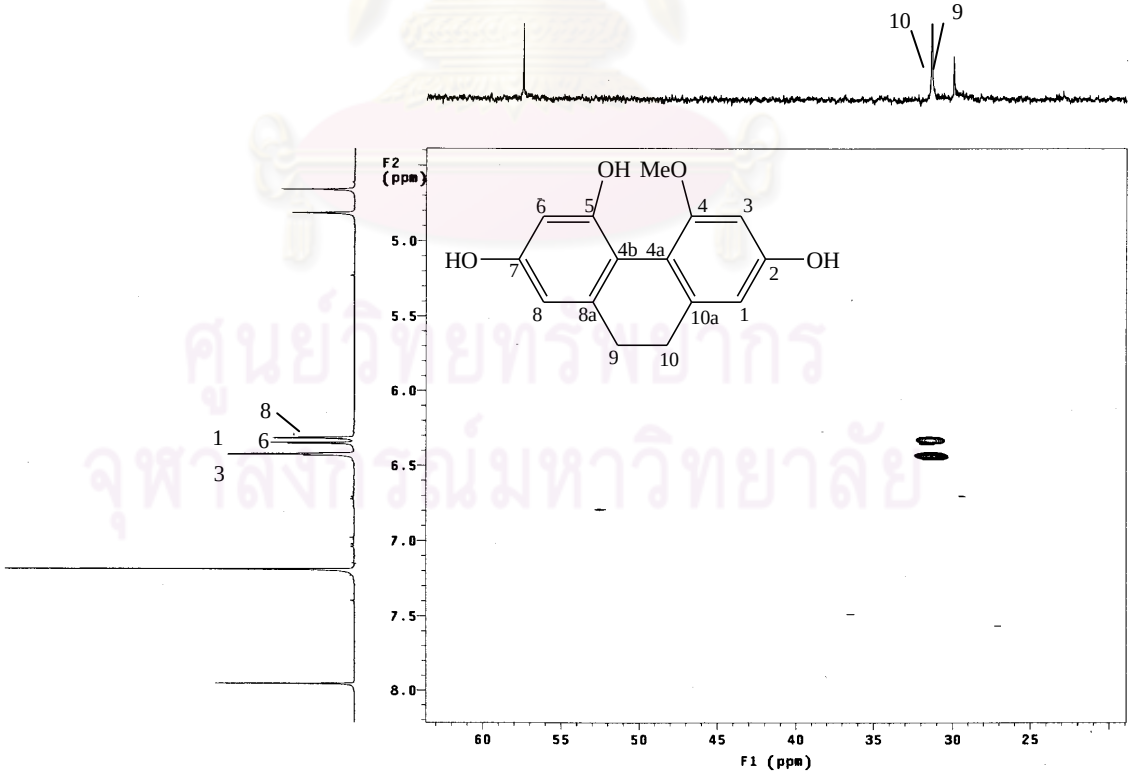


Figure 47 HMBC Spectrum of compound DD5 ($CDCl_3$)
(δ_H 4.50-8.00, δ_C 64.0-20.0)

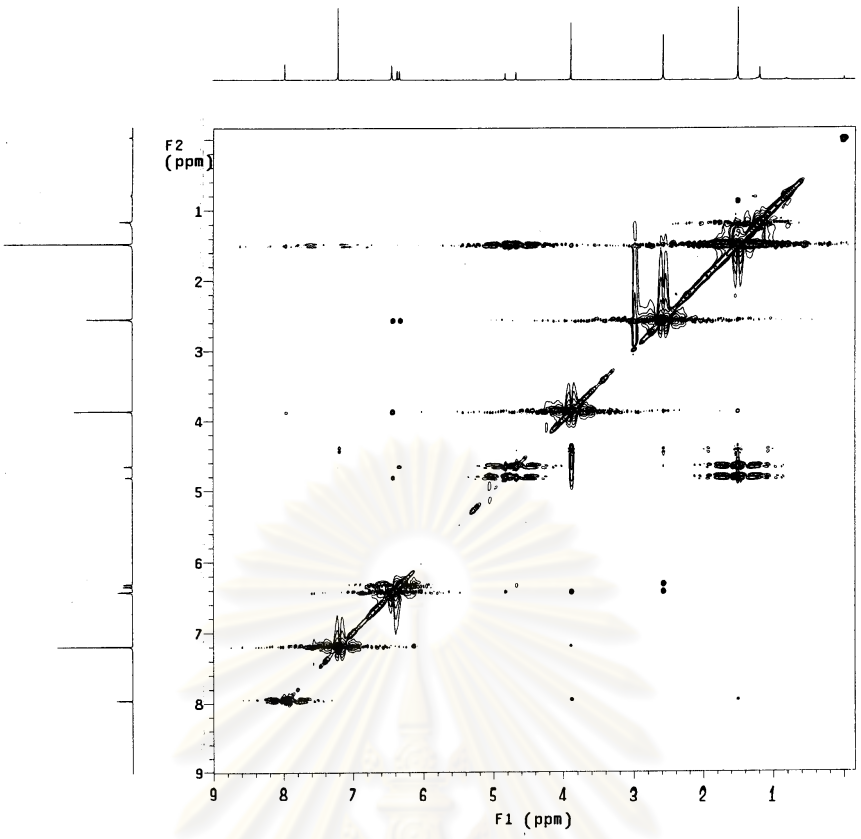


Figure 48 NOESY Spectrum of compound DD5 ($CDCl_3$)

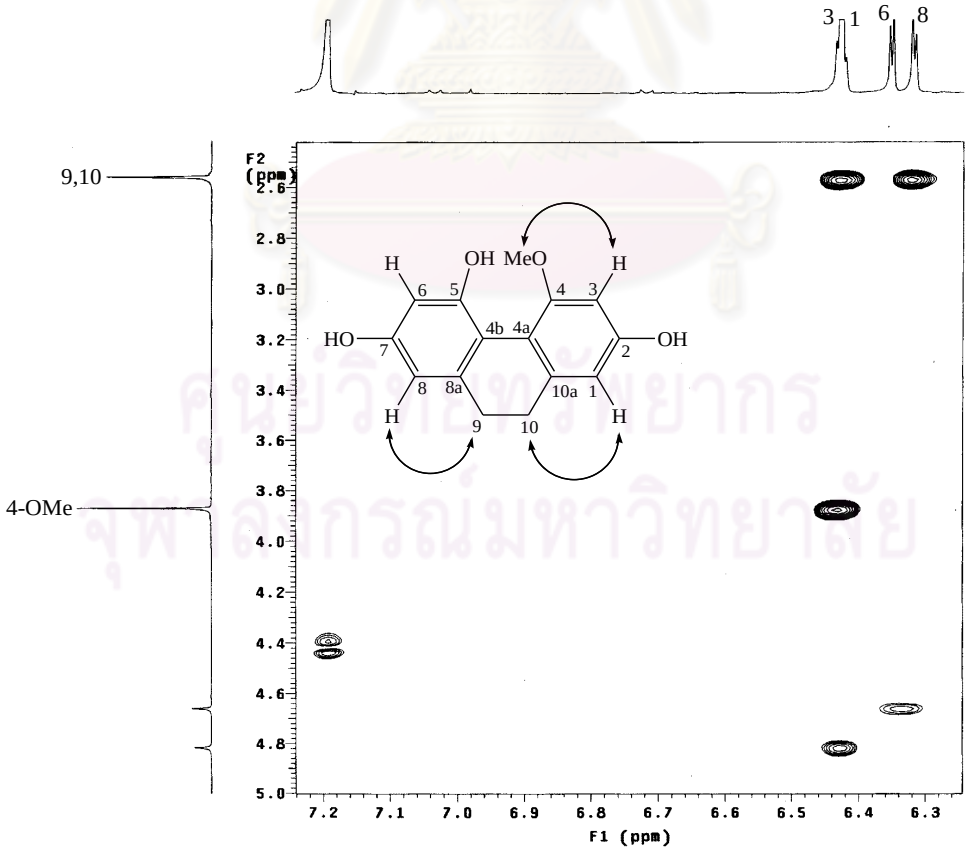


Figure 49 NOESY Spectrum of compound DD5 ($CDCl_3$)
(δ_H 2.50-5.00, δ_H 7.20-6.26)

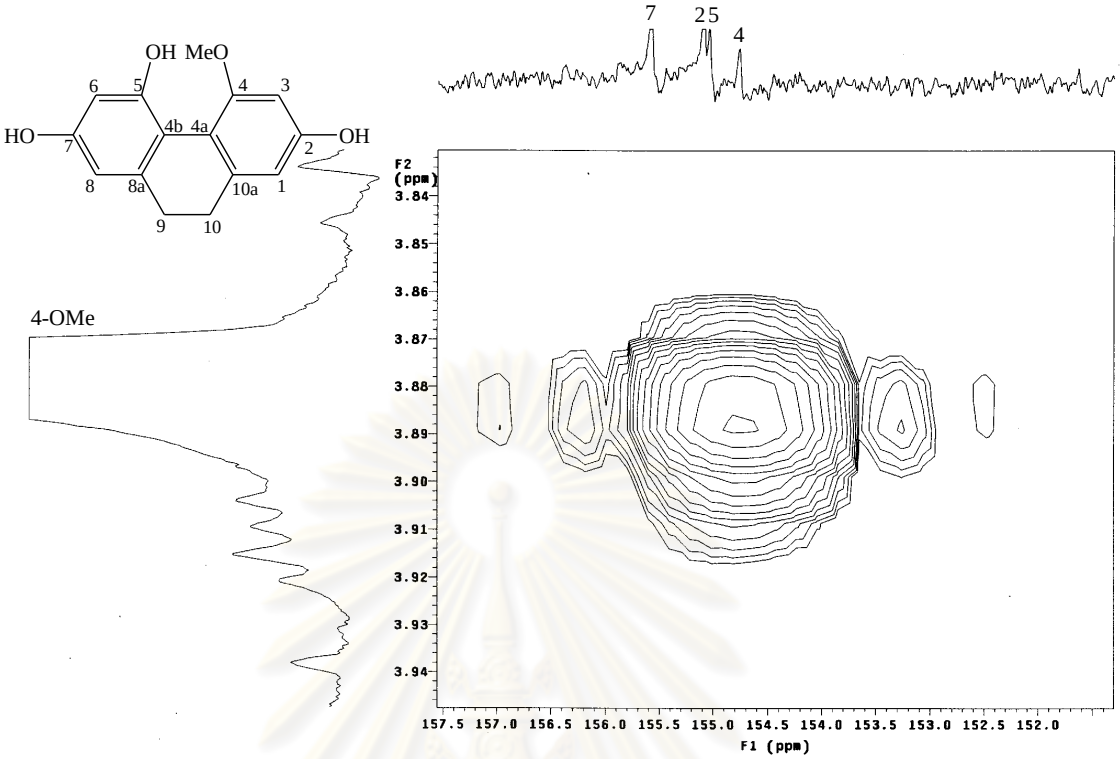


Figure 50 HMBC Spectrum of compound DD5 ($CDCl_3$)
(δ_H 3.84-3.94, δ_C 157.5-152.0)

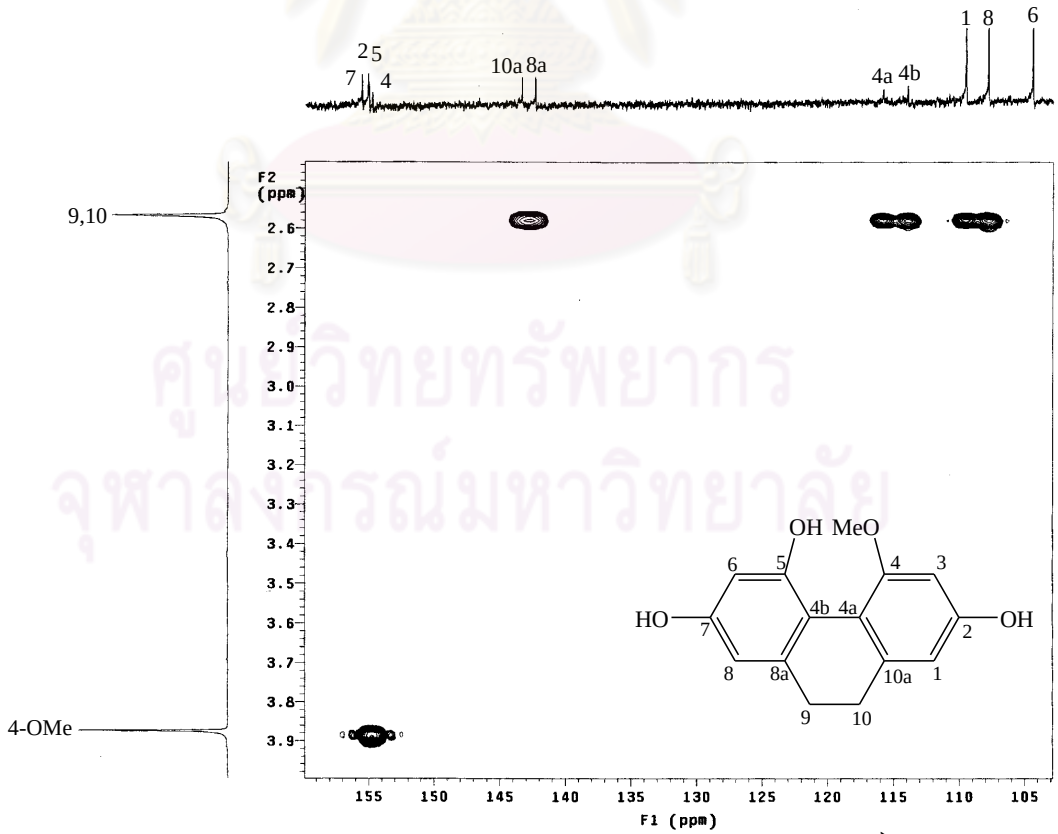


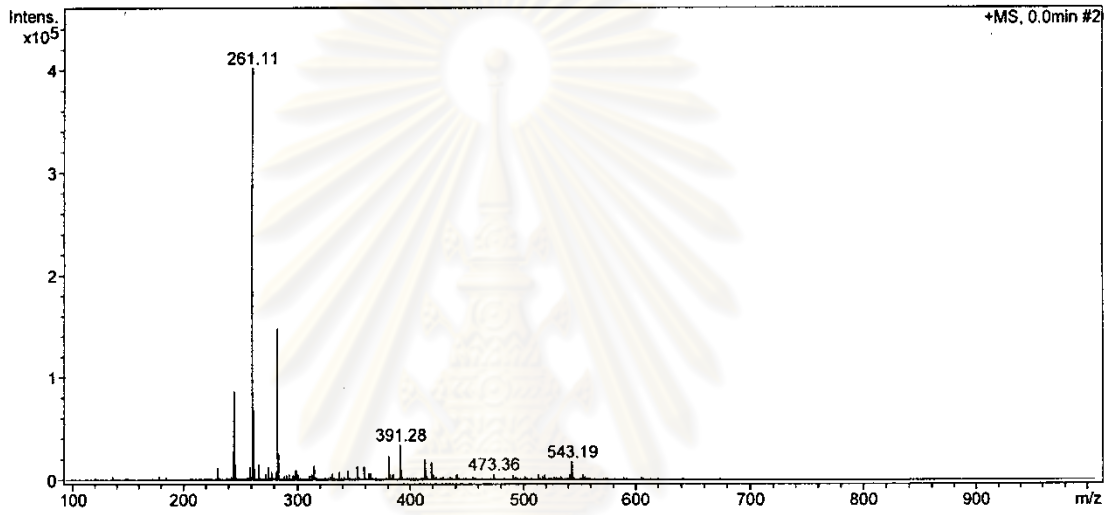
Figure 51 HMBC Spectrum of compound DD5 ($CDCl_3$)
(δ_H 2.50-3.86, δ_C 160.0-107.0)

Low resolution report

		Acquisition Date	10/11/2010 1:55:44 PM
Analysis Name	D:\Data\customer\D26.d		
Method	NaFormate_pos_infusion.m	Operator	Sutichai Ext: 3560
Sample Name	D26	Instrument	micrOTOF Bruker

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 °C
Scan Begin	100 m/z	Set Capillary	4000 V	Set Dry Gas	6.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



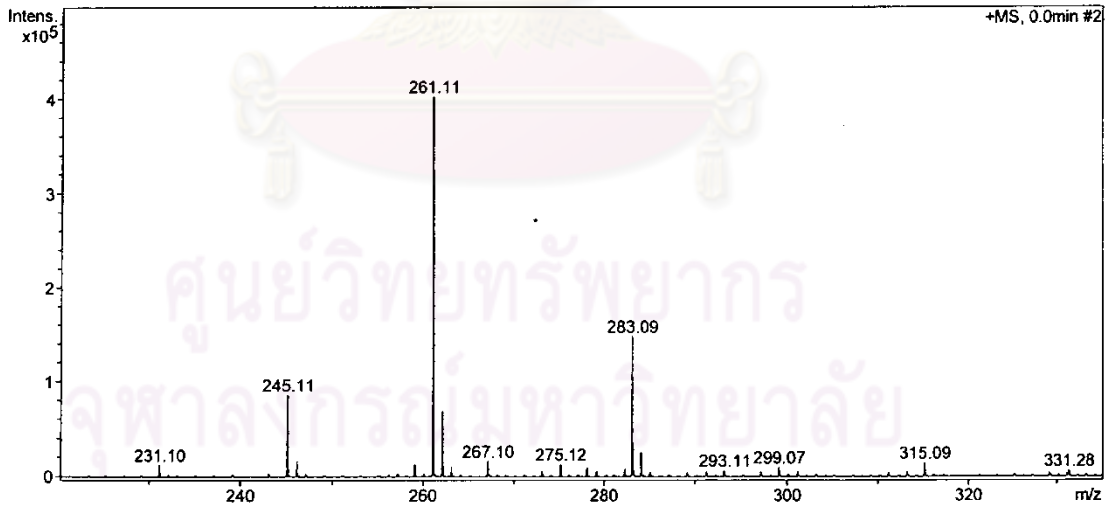


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Figure 52 Mass Spectrum of compound DD6

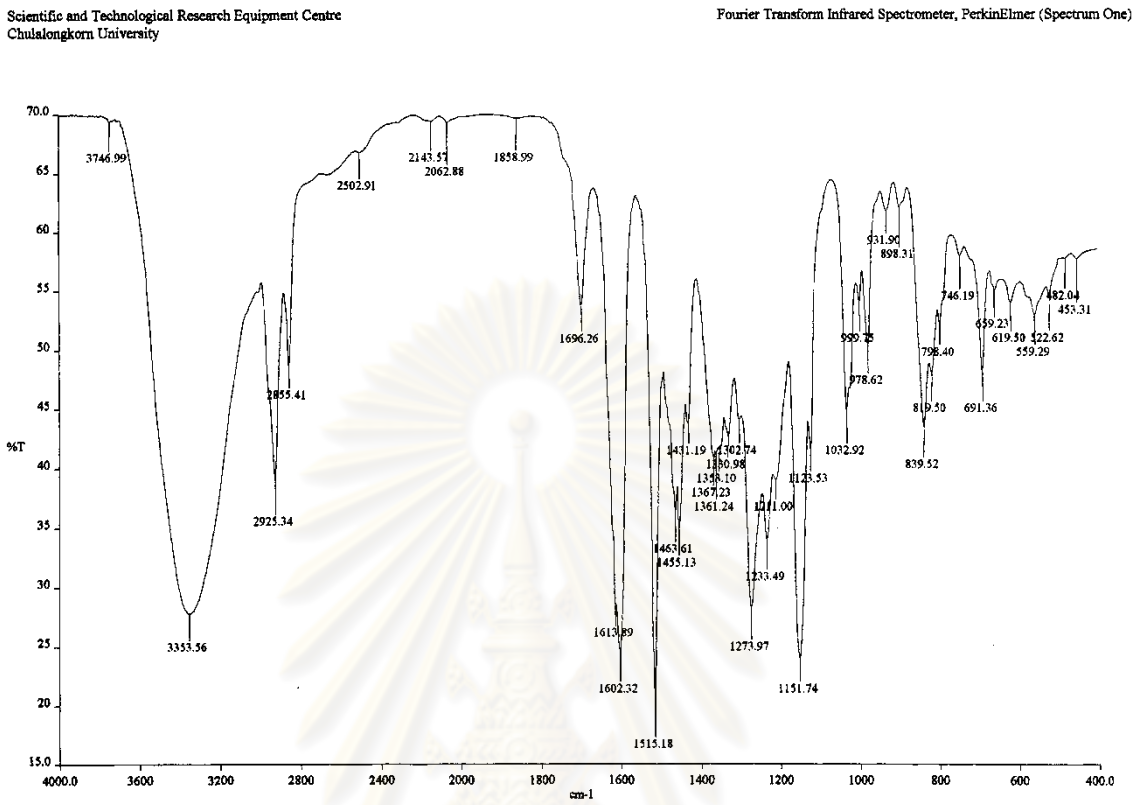

Figure **53** IR Spectrum of compound DD6

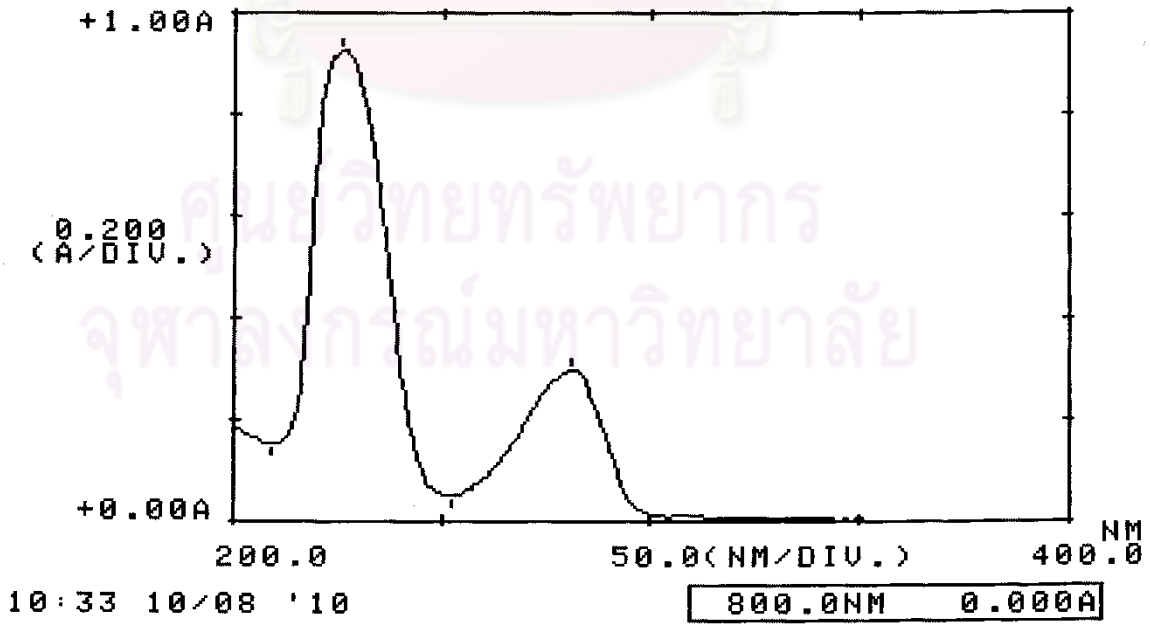

Figure **54** UV Spectrum of compound DD6

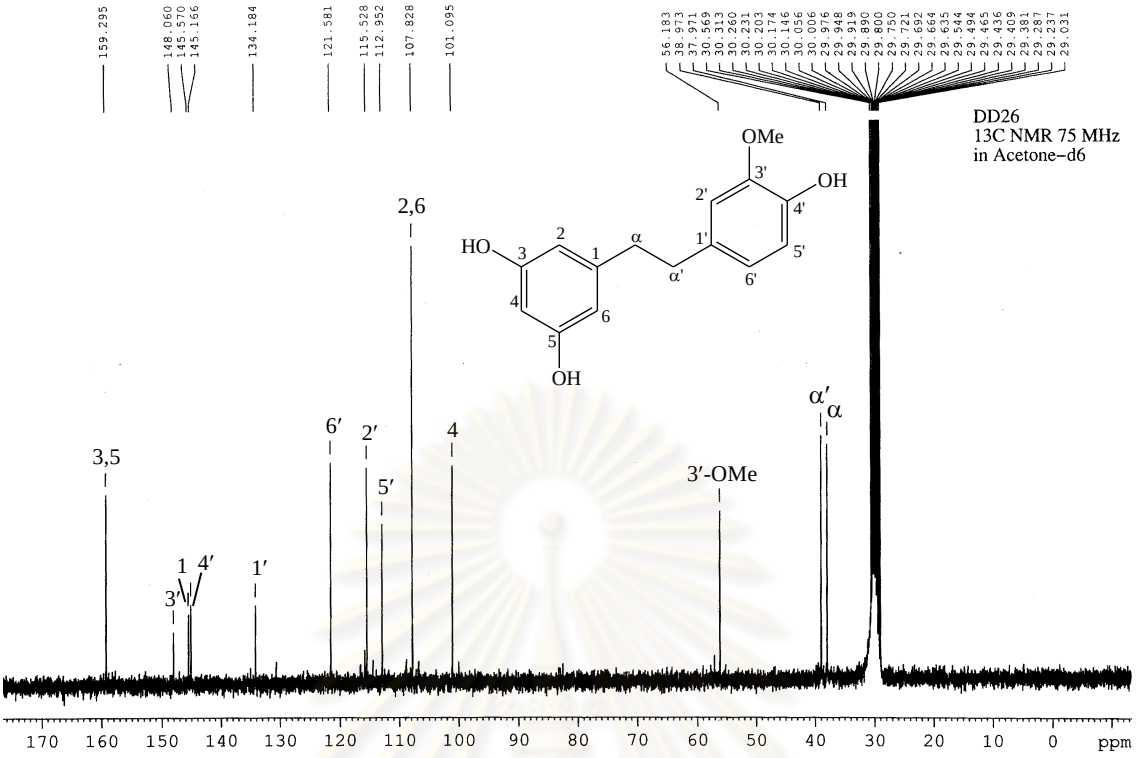

Figure **55** ^{13}C Spectrum (75 MHz) of compound DD6 (acetone-d_6)

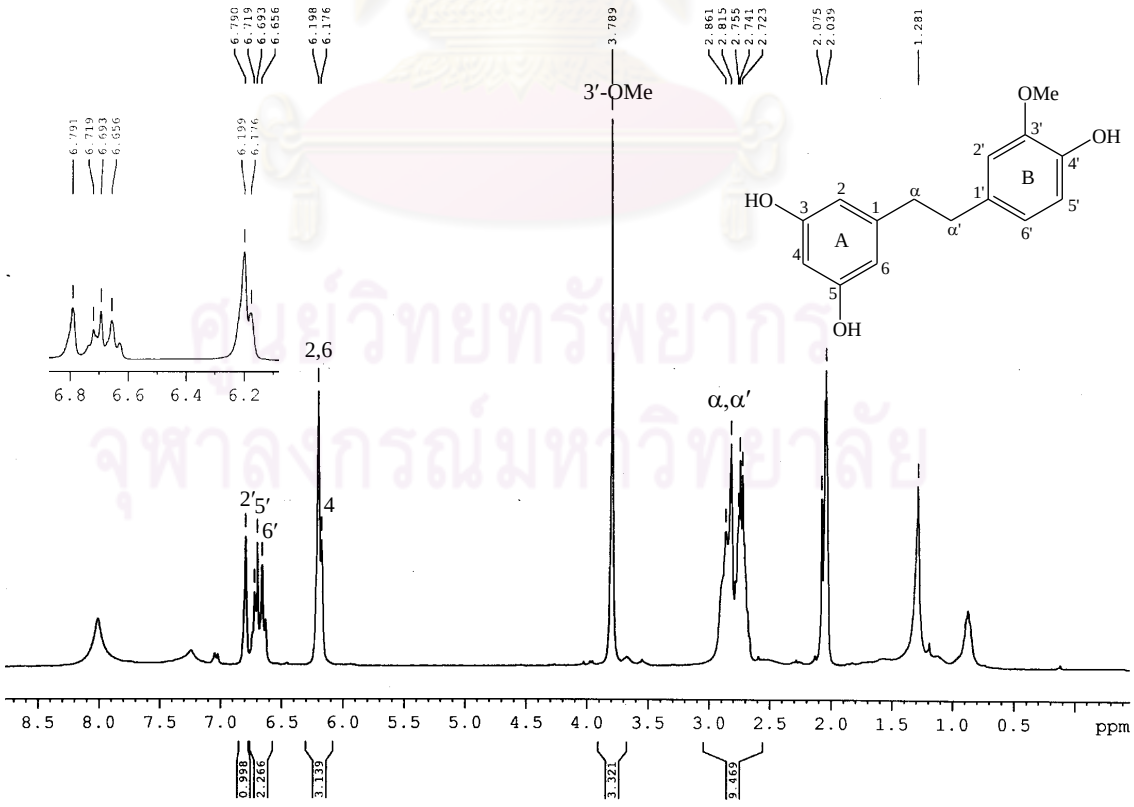

Figure **56** ^{1}H Spectrum (300 MHz) of compound DD6 (acetone-d_6)

VITA

Miss Mutita Anuwat was born on February 1, 1981 in Nakhonsithammarat, Thailand. She received her Bachelor's degree of Science in Pharmacy in 2004 from the Faculty of Pharmaceutical Sciences, Prince of Songkla University, Thailand.

Poster Presentation

Mutita Anuwat, Boonchoo Sritularak and Kittisak Likhitwitayawuid. Chemical constituents of *Dendrobium draconis* and their free radical scavenging activity. Abstract of The 9th NRCT-JSPS Joint Seminar, December 8-9, 2010. Chulalongkorn University, Bangkok, p. 117.

Publication

Boonchoo Sritularak, Mutita Anuwat and Kittisak Likhitwitayawuid. 2011. A new phenanthrenequinone from *Dendrobium draconis*. Journal of Asian Natural Products Research 13 : 251-255.