สารที่มีฤทธิ์เป็นพิษต่อเซลล์จากเอื้องคำกิ่วและเอื้องแปรงสีฟัน

นายธนาวุฒิ เพชรมีค่า

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CYTOTOXIC CONSTITUENTS FROM *DENDROBIUM CAPILLIPES* AND *DENDROBIUM SECUNDUM*

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Co-advisor	Associate Professor Boonchoo Sritularak, Ph.D.

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ธนาวุฒิ เพชรมีค่า : สารที่มีฤทธิ์เป็นพิษต่อเซลล์จากเอื้องคำกิ่วและเอื้องแปรงสีฟัน. (CYTOTOXIC CONSTITUENTS FROM *DENDROBIUM CAPILLIPES* AND *DENDROBIUM SECUNDUM*) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ศ.ดร. กิตติศักดิ์ ลิขิตวิทยาวุฒิ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร. บุญชู ศรีตุลารักษ์, 175 หน้า.

การศึกษาทางพฤกษเคมีของสารสกัดหยาบด้วยเมทานอลจากต้นเอื้องคำกิ่วและเอื้องแปรงสีฟัน (วงศ์กล้วยไม้) สามารถแยกได้สารใหม่ 2 ชนิดซึ่งเป็นสารกลุ่ม flavonol glycoside คือ quercetin-3-*O*-α-L-rhamnopyranosyl (1⟶2)-β-D-xylopyranoside จากต้นเอื้องคำกิ่วและสารกลุ่ม bibenzyl คือ 5-hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl จากต้นเอื้องแปรงสีฟัน พร้อมกับสารที่เคยมีรายงานมาแล้ว 10 ชนิดโดยแยกได้จากต้นเอื้องคำกิ่ว 7 ชนิด ได้แก่ chrysotobibenzyl, crepidatin, gigantol, chrysotoxine, moscatilin, kaempferol-3-*O*-α-L-rhamnopyranosyl (1⟶2)-β-D-xylopyranoside หรือ lysimachiin และ kaempferol-3-*O*-α-L-rhamnopyranosyl (1⟶2)-β-D-glucopyranoside และจากต้นเอื้องแปรงสีฟัน 3 ชนิด ได้แก่ kaempferol-3,7-*O*-di-α-L-rhamnopyranoside, quercetin-3-*O*-α-L-rhamnopyranoside และ kaempferol-3-*O*-α-L-rhamnopyranoside สารทั้งหมดสามารถพิสูจน์โครงสร้างได้โดยการวิเคราะห์ข้อมูลทางสเปกโตรสโคปี (MS, UV, IR และ NMR) ร่วมกับการเปรียบเทียบข้อมูลที่มีรายงานมาแล้ว จากการศึกษาความเป็นพิษต่อเซลล์ของสารกลุ่ม bibenzyl จากพืชทั้งสองต้น พบว่าสาร moscatilin มีฤทธิ์ดีที่สุดโดยเป็นพิษต่อเซลล์ NCI-H187 (มะเร็งปอด) และ KB (มะเร็งเยื่อบุช่องปาก) แต่ไม่มีฤทธิ์ต่อ MCF-7 (มะเร็งเต้านม) ในขณะที่สาร gigantol และ 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl มีผลต่อเซลล์มะเร็งทั้งสามชนิดแต่มีฤทธิ์อ่อน นอกจากนี้ พบว่าสาร brittonin A, chrysotoxine และ 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl ไม่มีพิษต่อเซลล์ปรกติ

ภาควิชาเภสัชเวทและเภสัชพฤกษศาสตร์ ลายมือชื่อนิสิต .....
สาขาวิชา……เภสัชเวท…… ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก…....
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THANAWUTH PHECHRMEEKHA : CYTOTOXIC CONSTITUENTS FROM *DENDROBIUM CAPILLIPES* AND *DENDROBIUM SECUNDUM*.
ADVISOR : PROF. KITTISAK LIKHITWITAYAWUID, Ph.D.,
CO-ADVISOR : ASSOC. PROF. BOONCHOO SRITULARAK, Ph.D.,

175 pp.

Phytochemical study of the MeOH extracts prepared from *Dendrobium capillipes* Rchb.f. and *Dendrobium secundum* (Blume) Lindl. (Orchidaceae) led to the isolation of two new compounds, including a flavonol glycoside named quercetin-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside from *D. capillipes* and a bibenzyl named 5-hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl from *D. secundum*, along with ten known compounds, including seven compounds from *D. capillipes*: chrysotobibenzyl, crepidatin, gigantol, chrysotoxine, moscatilin, kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside or lysimachiin and kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside; and three compounds from *D. secundum*: kaempferol-3,7-*O*-di-α-L-rhamnopyranoside, quercetin-3-*O*-α-L-rhamnopyranoside and kaempferol-3-*O*-α-L-rhamnopyranoside. Their structures were determined by analysis of their spectroscopic (MS, UV, IR and NMR) data and comparison with previously published values. In the cytoxicity study of the bibenzyls, moscatilin was found to be the most potent compound, inhibiting KB (oral human epidermal carcinoma) and NCI-H187 (human lung cancer) cells, but it had no cytotoxicity against MCF-7 (breast cancer) cells. Gigantol and 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl showed cytotoxicity against all cancer cell lines, but with weak activity. In addition, brittonin A, chrysotoxine and 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl showed no cytotoxicity against normal cells (Vero cells).

Department :…Pharmacognosy and.. Pharmaceutical Botany……..	Student's Signature……..
Field of Study :…Pharmacognosy….	Advisor's Signature…….....…....
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ABBREVIATIONS

$[\alpha]^{20}_{D}$	= Specific rotation at Sodium D line (598 nm)
br	= Broad (for NMR spectra)
C	= Concentration
^{o}C	= Degree Celsius
CC	= Column Chromatography
$CDCl_3$	= Deuterated chloroform
CD_3OD	= Deuterated methanol
CH_2Cl_2	= Dichloromethane
cm	= Centimeter
^{13}C NMR	= Carbon-13 Nuclear Magnetic Resonance
1-D	= One dimensional
2-D	= Two dimensional
d	= Doublet (for NMR spectra)
δ	= Chemical shift
dd	= Doublet of doublets (for NMR spectra)
DEPT	= Distortionless Enhancement by Polarization Transfer
DMSO-d_6	= Deuterated dimethyl sulfoxide
ε	= Molar absorptivity
ESI-MS	= Electrospray Ionization Mass Spectroscopy
EtOAc	= Ethyl acetate
FCC	= Flash column chromatography
g	= Gram
GF	= Gel Filtration
Glc	= Glucose
HMBC	= ^{1}H-detected Heteronuclear Multiple Bond Correlation
^{1}H-NMR	= Proton Nuclear Magnetic Resonance
HR	= High resolution (for Mass spectrum)
HSQC	= ^{1}H-detected Heteronuclear Single Quantum Coherence

Hz	= Hertz
IC_{50}	= Concentration exhibiting 50% inhibition
IEC	= Ion exchange chromatography
IR	= Infrared
J	= Coupling constant
Kg	= Kilogram
L	= Liter
λ_{max}	= Wavelength at maximal absorption
M^+	= Molecular ion
m	= Multiplet (for NMR spectra)
MeOH	= Methanol
mg	= Milligram
µg	= Microgram
µL	= microliter
MS	= Mass spectrum
MW	= Molecular weight
m/z	= Mass to charge ratio
nm	= Nanometer
υ_{max}	= Wave number at maximal absorption
NMR	= Nuclear Magnetic Resonace
pet. ether	= Petroleum ether
ppm	= Part per million
Rha	= Rhamnose
s	= Singlet (for NMR spectra)
t	= Triplet (for NMR spectra)
TLC	= Thin Layer Chromatography
UV-VIS	= Ultraviolet and Visible spectrophotometry
VLC	= Vacuum Liquid Chromatography
Xyl	= Xylose

CHAPTER I

INTRODUCTION

Cancer is an illness caused by cell proliferation with uncontrollable rate. According to the data collected between 2005-2009 on the number of deaths and death rates per 100,000 populations, malignant neoplasm or cancer in all forms is the first-ranked cause of death in Thailand (Bureau of Policy and Strategy, Ministry of Public Health, 2009). There are many approaches in the treatment of cancer including surgery, radiation and chemotherapy or combinations these of in order to increase the efficiency of the therapy. Some drugs that are used to treat cancer are originated from natural sources, for example vincristine and paclitaxel. However, discovery of new drugs with higher efficacy and safety for cancer treatment is still needed since most patients treated with chemotherapy can not tolerate side effects of currently used drugs.

Cytotoxicity is the ability of substances to inhibit the growth of cells and the cytotoxicity test is based on the research of anticancer drugs. There are various classes of recently discovered compounds that possess potent cytotoxicity, including acetogenins, alkaloids, terpenoids, flavonoids, lignans and the others (Kim and Park, 2002) but the cytotoxicity of bibenzyls is rarely reported. Interestingly, previous studies have shown that moscatilin, a bibenzyl compound isolated from several *Dendrobium* species (Orchidaceae), displayed strong cytotoxicity (Ho and Chen, 2003), and is now in preclinical trials (Chen *et al*., 2008c). Moreover, several studies on this plant genus reported the presence of chemical constituents with potent cytotoxicity against cancer cells (Zhang *et al*., 2005).

Dendrobium is the biggest genus of Orchidaceae family, represented by more than 1,100 species. The plants of this genus are either epiphytic, or occasionally lithophytic. These plants adapted to widely different habitats and are distributed throughout Asia, Europe and Australia (Seidenfaden, 1985; Guanghua *et al*., 2009).

Plants of the genus *Dendrobium* found in Thailand (Royal Forest Department, The Forest Herbarium, 2001) are more than 90 species as follows.

Dendrobium acerosum Lindl.	**กล้วยไม้มือนาง** Kluai mai mue nang (Chumphon)
D. acinaciforme Roxb.	**เอื้องยอดสร้อย** Ueang yot soi (Northern)
D. albosanguineum Lindl.	**เอื้องตางัว** Ueang ta ngua (Mae Hong Son)
D. aloifolium (Blume) Rchb.f.	**เอื้องมณี** Ueang mani (Bangkok)
D. anosmum Lindl.	**เอื้องสาย** Ueang sai (Chiang Mai, Peninsular)
D. aphyllum (Roxb.) C.E.C.Fisch.	**เอื้องงวงช้าง** Ueang nguang chang (Mae Hong Son)
D. bellatulum Rolfe	**เอื้องแซะภู** Ueng sae phu (Chiang Mai)
D. bicameratum Lindl.	**เอื้องเข็ม** Ueang khem (Northern)
D. bilobulatum Seidenf.	**กล้วยไม้ก้างปลา** Kluai mai kang pla (General)
D. binoculare Rchb.f.	**เอื้องคำสาย** Ueang kham sai (Northern)
D. brymerianum Rchb.f.	**เอื้องคำฝอย** Ueang kham foi (Northern)
D. capillipes Rchb.f.	**เอื้องคำกิ่ว** Ueang kham kio (Lampang, Phrae)
D. cariniferum Rchb.f.	**เอื้องกาจก** Ueang kachok (Chiang Mai)
D. christyanum Rchb.f.	**เอื้องแซะภูกระดึง** Ueang sae phu kradueng (Loei)
D. chrysanthum Lindl.	**เอื้องสายมรกต** Ueang sai morakot (Bangkok)
D. chrysotoxum Lindl.	**เอื้องคำ** Ueang kham (Northern)
D. compactum Rolfe ex Hackett	**เอื้องข้าวตอก** Ueang khao tok (Northern)
D. concinnum Miq.	**หางเปีย** Hang pia (Narathiwat)
D. crepidatum Lindl. & Paxton	**เอื้องสายน้ำเขียว** Ueang sai nam khiao (General)

D. crocatum Hook.f.	**เอื้องนางนวล** Ueang nang nuan (Peninsular)
D. cruentum Rchb.f.	**เอื้องนกแก้ว** Ueang nok kaeo (Bangkok)
D. crumenatum Sw.	**หวายตะมอย** Wai tamoi (Central, Peninsular)
D. crystallinum Rchb.f.	**เอื้องนางฟ้อน** Ueang nang fon (Chiang Mai)
D. cumulatum Lindl.	**เอื้องสายสี่ดอก** Ueang sai si dok (Northern, Southeastern)
D. dantaniense Guillaumin	**เอื้องเข็ม** Ueang khem (Chiang Mai)
D. densiflorum Lindl.	**เอื้องมอนไข่** Ueang mon khai (Northern)
D. devonianum Paxton	**เอื้องเมี่ยง** Ueang miang (Chiang Mai)
D. dickasonii L.O. Williams	**เอื้องเคี้ยะ** Ueang khia (Chiang Mai)
D. discolor Lindl.	**หวายกลัก** Wai klak (Bangkok)
D. dixanthum Rchb.f.	**เอื้องเทียน** Ueang thian (Northern)
D. draconis Rchb.f.	**เอื้องเงิน** Ueang ngoen (Northern)
D. ellipsophyllum Tang & Wang	**เอื้องทอง** Ueang thong (General)
D. exile Schltr.	**เอื้องเสี้ยน** Ueang sian (General)
D. falconeri Hook.	**เอื้องสายวิสูตร** Ueang sai wisut (Bangkok)
D. farmeri Paxton	**เอื้องมัจฉาณุ** Ueang mat chanu (Bangkok)
D. fimbriatum Hook.	**เอื้องคำน้อย** Ueang kham noi (Chiang Mai)
D. findlayanum Parish & Rchb.f.	**พวงหยก** Phuang yok (Bangkok)
D. formosum Roxb. ex Lindl.	**เอื้องเงินหลวง** Ueang ngoen luang (Chiang Mai)

D. friedericksianum Rchb.f.	**เอื้องเหลืองจันทบูร** Ueang Lueang chantabun (Bangkok)
D. fuerstenbergianum Schltr.	**เอื้องแซะภูกระดึง** Ueang sae phukradueng (Loei)
D. gibsonii Lindl.	**เอื้องคำสาย** Ueang kham sai (Northern)
D. grande Hook.f	**เอื้องแผงใบใหญ่** Ueang pheang 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 (Bangkok)
D. harveyanum Rchb.f.	**เอื้องคำฝอย** Ueang kham foi (Chiang Mai)
D. hendersonii Hawkes & Heller	**หวายตะมอยน้อย** Wai tamoi noi (Peninsular)
D. hercoglossum Rchb.f.	**เอื้องดอกมะเขือ** Ueang dok ma kuea (Bangkok)
D. heterocarpum Lindl.	**เอื้องสีตาล** Ueang si tan (Chiang Mai)
D. indivisum (Blume) Miq. var. *indivisum*	**ตานเสี้ยนไม้** Tan sian mai (Chumphon)
D. indivisum (Blume) Miq. var. *pallidum* Seidenf.	**ก้างปลา** Kang pla (General)
D. infundibulum Lindl.	**เอื้องตาเหิน** Ueang ta hoen (General)
D. intricatum Gagnep.	**เอื้องชมพู** Ueang chom phu (Chanthaburi)
D. jenkinsii 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.	**เอื้องผึ้ง** Ueang phueng (Northern)
D. lituiflorum Lindl.	**เอื้องสายม่วง** Ueang sai muang (Bangkok, Northern)
D. moschatum (Buch.-Ham.) Sw.	**เอื้องจำปา** Ueang champa (Northern)
D. nathanielis Rchb.f.	**เกล็ดนิ่ม** Klet nim (Chantaburi)
D. nobile Lindl.	**เอื้องเค้ากิ่ว** Ueang khao kio (Northern)
D. ochreatum Lindl.	**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 (General)
D. palpebrae Lindl.	**เอื้องมัจฉา** Ueang mat cha, **เอื้องมัจฉาณุ** Ueang mat chanu (Bangkok)
D. parcum Rchb.f.	**เอื้องก้านกิ่ว** Ueang kan kio (Bangkok)
D. parishii Rchb.f.	**เอื้องครั่ง** Ueang khrang (Northern)
D. pendulum Roxb.	**เอื้องไม้เท้าฤาษี** Ueang mai thao ruesi (Bangkok, Chiang Mai)
D. pensile Ridl.	**หวาย** Wai (Narathiwat)
D. porphyrophyllum Guillaumin	**เอื้องลิ้น** Ueang lin (Lampang)
D. primulinum Lindl.	**เอื้องสายประสาท** Ueang sai prasat (Bangkok)

D. pulchellum Roxb. ex Lindl.	**เอื้องคำตาควาย** Ueang kham ta khwai (Mae Hong Son)
D. pychnostachyum Lindl.	**เศวตสอดสี** Sawet sot si (Chiang Mai)
D. salaccense (Blume) Lindl.	**เอื้องใบไผ่** Ueang bai phai (Chiang Mai)
D. scabrilingue Lindl.	**เอื้องแซะ** Ueang sae (Mae Hong Son)
D. secundum (Blume) Lindl.	**เอื้องแปรงสีฟัน** Ueang preang si fan (Bangkok)
D. seidenfadenii Rchb.f.	**เอื้องเกี๊ยะ** Ueang kia (Chiang Mai)
D. senile Parish & Rchb.f.	**เอื้องชะนี** Ueang chain (Bangkok)
D. signatum Rchb.f.	**เอื้องเค้ากิ่ว** Ueang khao kio (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. sutepense Rolfe ex Downie	**เอื้องมะลิ** Ueang mali (Chiang Mai)
D. terminale Parish & Rchb.f	**เอื้องแผงโสภา** Ueang phaeng sopha (Peninsular)
D. thyrsiflorum Rchb.f	**เอื้องมอนไข่ใบมน** Ueang mon khai bai mon (Northern)
D. tortile Lindl.	**เอื้องไม้ตึง** Ueang mai tueng (Mae Hong Son)
D. trigonopus Rchb.f.	**เอื้องคำเหลี่ยม** Ueang kham liam (Chiang Mai)
D. trinervium Ridl.	**เทียนลิง** Thian ling (Chumphon)
D. unicum Seidenf.	**เอื้องครั่งแสด** Ueang krang saet (General)
D. uniflorum Griff.	**เอื้องทอง** Ueang thong (Pattani)

D. venustum Teijsm. & Binn	**ข้าวเหนียวลิง** Khao niao ling (Central)
D. villosulum Lindl.	**กล้วยหญ้านา** Kluai ya na (Bangkok)
D. virgineum Rchb.f.	**เอื้องเงินวิลาศ** Ueang ngoen wilat (Northern)
D. wardianum Warner	**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 capillipes Rchb.f. is known in Thai as Ueang kham kio or Ueang kham pok. Its fleshy stems are unbranched and nearly compressed fusiform, 8-15 cm, with many obtuse longitudinal ridges and few internodes. It has 2-4 narrowly oblong leaves near the apex of the stem in the size of 10-12 × 1-1.5 cm. The bright yellow flowers are on 2-3 cm pseudobulb, with the lip being much longer than their sepals and petals. The number of flowers are 3-5 with 3 cm sized. Flowering period is between February to April (Vaddhanaphuti, 2005). The plant is widely found in Thailand, and also in northeastern India, Burma, China and Vietnam. In China, *Dendrobium capillipes* stem has been used traditionally as decoction to treat indigestion (Lee, Xiao and Pei, 2008).

Dendrobium secundum (Blume) Lindl. has a local name as Ueang preang si fan. It is found from China, Burma, Indonesia and Thailand. Its fleshy stems are cylindrical, to 100 cm long (usually less); leaves to 10 by 4 cm; inflorescences from the upper nodes only, to about 12 cm long, with many closely placed small flowers all pointing to one side, bright mauve-pink (or rarely white) with orange lip; flowers to 1.8 cm long and 0.6 cm wide; upper sepal to 7 by 4 mm; mentum curved; petals very narrow; lip forming a long spur at the base with the column-foot (Holttum, 1957). Flowering period is between February to April (Vaddhanaphuti, 2005).

In this study we attempted to investigate the chemical constituents of *Dendrobium capillipes*, of which the methanol extract showed cytotoxicity against KB (Oral cavity cancer) cells with an IC_{50} value of 16.67 μg/mL. The chemical

constituents of this plant had not been studied previously. In addition, we re-examined the chemical components of *Dendrobium secundum*, a plant partially studied in an earlier investigation (Sritularak, Duangrak and Likhitwitawuid, 2011). The cytotoxic principles were isolated and identified from both plants. The results from this study should be useful for chemotaxomic study of plants in the genus *Dendrobium*, as well as the development of new anticancer drugs.

The main objectives of this research were:

1. Separation and isolation of chemical constituents from *Dendrobium capillipes* and *Dendrobium secundum.*
2. Identification of the structures of isolated compounds.
3. Study of isolated compounds for cytotoxicity.

Figure 1 *Dendrobium capillipes* Rchb.f.

Figure 2 *Dendrobium secundum* (Blume) Lindl.

CHAPTER II

HISTORICAL

1. Chemical constituents of *Dendrobium* species

The phytochemical studies of plants in the genus *Dendrobium* focused mainly on the principles of the stem, which was part used in the Shi-Hu formulation, as well as the whole plant. These studies reported the isolation of various classes of secondary metabolites such as bibenzyls (dihydrostilbenes), phenanthrenes, fluorenones (biphenyls) and sesquiterpenes (Hossain, 2011). Particularly, bibenzyls and phenanthrenes were the most compounds commonly found in plants of this genus (Chen *et al.*, 2008a). The naturally occurring bibenzyls have been reported not only in Orchidaceae, but also in liverworts, a member of bryophyte (non vascular plant) and in species of certain families such as Cannabaceae and Dioscoreaceae. For phenanthrenes, usually occur in family Orchidaceae, Juncaceae, Stemonaceae, Euphorbiaceae, Dioscoreaceae, Ulmaceae and are also found in liverworts (Xiao *et al.*, 2008).

The chemical constituents found in plants of the genus *Dendrobium* are shown in 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	Majumder, Guha and Sen, 1999
Amoenumin [**3**]	Phenanthrene	Whole plant	Veerraju *et al.*, 1989
Amoenylin [**4**]	Bibenzyl	Whole plant	Majumder *et al.*, 1999

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Amotin [**5**]	Sesquiterpene	Whole plant	Majumder *et al.*, 1999
3,4′-Dihydroxy-5-methoxybibenzyl [**6**]	Bibenzyl	Whole plant	Majumder *et al.*, 1999
Flaccidin (Amoenumin) [**3**]	Phenanthrene	Whole plant	Veerraju *et al*., 1989
Isoamoenylin [**7**]	Bibenzyl	Whole plant	Majumder *et al.*, 1999
Moscatilin [**8**]	Bibenzyl	Whole plant	Majumder *et al.*, 1999
Dendrobium aphyllum			
Batatasin III [**9**]	Bibenzyl	Whole plant	Chen *et al.*, 2008a
Coelonin [**10**]	Phenanthrene	Whole plant	Chen *et al.*, 2008a
Dibutyl phthalate [**11**]	Benzoic acid ester	Whole plant	Chen *et al.*, 2008a
Diisobutyl phthalate [**12**]	Benzoic acid ester	Whole plant	Chen *et al.*, 2008a
Flavanthrin [**13**]	Biphenanthrene	Whole plant	Chen *et al.*, 2008a
Gigantol [**14**]	Bibenzyl	Whole plant	Chen *et al.*, 2008a
p-Hydroxyphenyl propanoic methyl ester [**15**]	Phenolic compound	Whole plant	Chen *et al.*, 2008a
Lusianthridin [**16**]	Phenanthrene	Whole plant	Chen *et al.*, 2008a
Moscatin [**17**]	Phenanthrene	Whole plant	Chen *et al.*, 2008a
Dendrobium aurantiacum **var. *denneanum***			
Chrysotobibenzyl [**18**]	Bibenzyl	Stem	Yang, Wang and Xu, 2006a
Chrysotoxine [**19**]	Bibenzyl	Stem	Yang *et al*., 2006a
Coumarin [**20**]	Coumarin	Stem	Yang *et al*., 2006a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Crepidatin [**21**]	Bibenzyl	Whole plant	Liu *et al*., 2009b
Defuscin [**22**]	Phenolic compound	Stem	Yang *et al*., 2006a
Dendroflorin [**23**]	Fluorenone	Stem	Yang *et al*., 2006a
Dengibsin [**24**]	Fluorenone	Stem	Yang *et al*., 2006a
Gigantol [**14**]	Bibenzyl	Whole plant	Liu *et al*., 2009b
Kaempferol [**25**]	Flavonol	Stem	Yang *et al*., 2006a
Luteolin [**26**]	Flavone	Whole plant	Liu *et al*., 2009b
Moscatilin [**8**]	Bibenzyl	Stem	Yang *et al*., 2006a
Moscatin [**17**]	Phenanthrene	Whole plant	Liu *et al*., 2009b
Naringenin [**27**]	Flavanone	Stem	Yang *et al*., 2006a
n-Octacosyl ferulate [**28**]	Phenolic compound	Stem	Yang *et al*., 2006a
Stigmasterol [**29**]	Steroid	Whole plant	Liu *et al*., 2009b
Taraxerol [**30**]	Triterpene	Stem	Yang *et al*., 2006a
Dendrobium candidum			
Dendrocandin A [**31**]	Bibenzyl	Stem	Li *et al.*, 2008
Dendrocandin B [**32**]	Bibenzyl	Stem	Li *et al.*, 2008
Dendrophenol [**33**]	Bibenzyl	Stem	Li *et al.*, 2008
3,4-Dihydroxy-5,4′-dimethoxybibenzyl [**34**]	Bibenzyl	Stem	Li *et al.*, 2008
4,4′-Dihydroxy-3,5-dimethoxybibenzyl [**35**]	Bibenzyl	Stem	Li *et al.*, 2008
Gigantol [**14**]	Bibenzyl	Stem	Li *et al.*, 2008
3-*O*-Methylgigantol [**36**]	Bibenzyl	Stem	Li *et al.*, 2008

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium cariniferum			
Batatasin III [**9**]	Bibenzyl	Stem	Chen *et al.*, 2008b
Daucosterol [**37**]	Steroid glycoside	Whole plant	Liu *et al.*, 2009a
Dendrononе [**38**]	Phenanthrene	Stem	Chen *et al.*, 2008b
Gigantol [**14**]	Bibenzyl	Stem	Chen *et al.*, 2008b
Stigmasterol [**29**]	Steroid	Whole plant	Liu *et al.*, 2009a
3,3′,5-Trihydroxybibenzyl [**39**]	Bibenzyl	Whole plant	Liu *et al.*, 2009a
Dendrobium chrysanthum			
Chrysotobibenzyl [**18**]	Bibenzyl	Stem	Yang *et al*., 2006b
Chrysotoxine [**19**]	Bibenzyl	Stem	Yang *et al*., 2006b
Crepidatin [**21**]	Bibenzyl	Stem	Yang *et al*., 2006b
Dendrochrysanene [**40**]	Phenanthrene	Stem	Yang *et al*., 2006b
Dengibsin [**24**]	Fluorenone	Stem	Yang *et al*., 2006b
2,5-Dihydroxy-4,9-dimethoxylphenanthrene [**41**]	Phenanthrene	Stem	Yang *et al*., 2006b
Gigantol [**14**]	Bibenzyl	Stem	Yang *et al*., 2006b
Moscatilin [**8**]	Bibenzyl	Stem	Yang *et al*., 2006b
Moscatin [**17**]	Phenanthrene	Stem	Yang *et al*., 2006b
Dendrobium chryseum			
Chrysotobibenzyl [**18**]	Bibenzyl	Stem	Ma *et al*., 1998
Chrysotoxine [**19**]	Bibenzyl	Stem	Ma *et al*., 1998
Confusarin [**42**]	Phenanthrene	Stem	Ma *et al*., 1998
2,6-Dimethoxy benzoquinone [**43**]	Benzoquinone	Stem	Ma *et al*., 1998
β-Sitosterol [**44**]	Steroid	Stem	Ma *et al*., 1998

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium chrysotoxum			
Batatasin III [**9**]	Bibenzyl	Whole plant	Li *et al.*, 2009a
Daucosterol [**37**]	Steroid glycoside	Whole plant	Li *et al.*, 2009a
Denchrysan B [**45**]	Fluorenone	Whole plant	Li *et al.*, 2009a
Dengibsin [**24**]	Fluorenone	Whole plant	Li *et al.*, 2009a
Densiflorol B [**46**]	Phenanthrene	Whole plant	Li *et al.*, 2009a
3,7-Dihydroxy-2,4-di methoxyphenanthrene [**47**]	Phenanthrene	Whole plant	Li *et al.*, 2009a
4,9-Dimethoxy phenanthrene-2,5-diol [**41**]	Phenanthrene	Whole plant	Li *et al.*, 2009a
Gigantol [**14**]	Bibenzyl	Whole plant	Li *et al.*, 2009a
Moscatin [**17**]	Phenanthrene	Whole plant	Li *et al.*, 2009a
Stigmasterol [**29**]	Steroid	Whole plant	Li *et al.*, 2009a
Vanillic acid [**48**]	Benzoic acid derivative	Whole plant	Li *et al.*, 2009a
Dendrobium clavatum* var. *auranteacum			
Aliphatic acids [**49**]	Aliphatic acid	Stem	Chang, Lin and Chen, 2001
Aliphatic alcohols [**50**]	Aliphatic alcohol	Stem	Chang *et al.*, 2001
Alkyl 4′-hydroxy-*trans*-cinnamates [**51**]	Cinnamate	Stem	Chang *et al.*, 2001
Alkyl *trans*-ferulates [**52**]	Cinnamate	Stem	Chang *et al.*, 2001
Campesterol [**53**]	Steroid	Stem	Chang *et al.*, 2001
Coumarin [**20**]	Coumarin	Stem	Chang *et al.*, 2001
β-Sitosterol [**44**]	Steroid	Stem	Chang *et al.*, 2001
Stigmast-4-en-3-one [**54**]	Steroid	Stem	Chang *et al.*, 2001
Stigmasterol [**29**]	Steroid	Stem	Chang *et al.*, 2001

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium crepidatum			
Crepidatin [**21**]	Bibenzyl	Whole plant	Majumder and Chatterjee, 1989
Dendrobium crystallinum			
Apigenin [**55**]	Flavone	Stem	Wang *et al.*, 2009
Crystallinin [**56**]	Sesquiterpene	Stem	Wang *et al.*, 2009
Crystalltone [**57**]	Phenanthrene	Stem	Wang *et al.*, 2009
Dencryol A [**58**]	Bisbibenzyl	Stem	Wang *et al.*, 2009
Dencryol B [**59**]	Bisbibenzyl	Stem	Wang *et al.*, 2009
Dendronobilin B [**60**]	Sesquiterpene	Stem	Wang *et al.*, 2009
6‴-Glucosyl-vitexin [**61**]	Flavone glycoside	Stem	Wang *et al.*, 2009
3-Hydroxy-2-methoxy-5,6-dimethylbenzoic acid [**62**]	Benzoic acid derivative	Stem	Wang *et al.*, 2009
Isoviolanthin [**63**]	Flavone glycoside	Stem	Wang *et al.*, 2009
Palmarumycin JC2 [**64**]	Naphthalene	Stem	Wang *et al.*, 2009
Syringic acid [**65**]	Benzoic acid derivative	Stem	Wang *et al.*, 2009
Dendrobium cumulatum			
Cumulatin [**66**]	Bibenzyl	Whole plant	Majumder and Pal, 1993
Dendrobium densiflorum			
Ayapin [**67**]	Coumarin	Stem	Fan *et al.*, 2001
Cypripedin [**68**]	Phenanthrene	Stem	Fan *et al.*, 2001
Dengibsin [**24**]	Fluorenone	Stem	Fan *et al.*, 2001
Densiflorol A [**69**]	Bibenzyl	Stem	Fan *et al.*, 2001
Densiflorol B [**46**]	Phenanthrene	Stem	Fan *et al.*, 2001

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
4,7-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene [**70**]	Phenanthrene	Stem	Fan *et al.*, 2001
2,6-Dihydroxy-1,5,7-tri methoxyphenanthrene [**71**]	Phenanthrene	Stem	Fan *et al.*, 2001
Gigantol [**14**]	Bibenzyl	Stem	Fan *et al.*, 2001
Homoeriodictyol [**72**]	Flavanone	Stem	Fan *et al.*, 2001
Moscatilin [**8**]	Bibenzyl	Stem	Fan *et al.*, 2001
Moscatin [**17**]	Phenanthrene	Stem	Fan *et al.*, 2001
Naringenin [**27**]	Flavanone	Stem	Fan *et al.*, 2001
Scoparone [**73**]	Coumarin	Stem	Fan *et al.*, 2001
Scopoletin [**74**]	Coumarin	Stem	Fan *et al.*, 2001
1,4,7-Trihydroxy-5-methoxy-9H-fluoren-9-one [**75**]	Fluorenone	Stem	Fan *et al.*, 2001
Tristin [**76**]	Bibenzyl	Stem	Fan *et al.*, 2001
Dendrobium draconis			
Batatasin III [**9**]	Bibenzyl	Stem	Sritularak, Anuwat and Likhitwitayawuid, 2011a
Gigantol [**14**]	Bibenzyl	Stem	Sritularak *et al.*, 2011a
Hircinol [**77**]	Phenanthrene	Stem	Sritularak *et al.*, 2011a
7-Methoxy-9,10-dihydro phenanthrene-2,4,5-triol [**78**]	Phenanthrene	Stem	Sritularak *et al.*, 2011a
5-Methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone [**79**]	Phenanthrene	Stem	Sritularak *et al.*, 2011a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium falconeri			
Dendrofalconerol A [**80**]	Bisbibenzyl	Stem	Sritularak and Likhitwitayawuid, 2009
Dendrofalconerol B [**81**]	Bisbibenzyl	Stem	Sritularak and Likhitwitayawuid, 2009
Docosanoyl (*E*)-ferulate [**82**]	Phenylpropanoid	Stem	Sritularak and Likhitwitayawuid, 2009
p-Hydroxybenzaldehyde [**83**]	Phenolic compound	Stem	Sritularak and Likhitwitayawuid, 2009
p-Hydroxybenzoic acid [**84**]	Phenolic compound	Stem	Sritularak and Likhitwitayawuid, 2009
2-(*p*-Hydroxyphenyl) ethyl *p*-coumarate [**85**]	Phenylpropanoid	Stem	Sritularak and Likhitwitayawuid, 2009
Tetracosyl (*E*)-*p*-coumarate [**86**]	Phenylpropanoid	Stem	Sritularak and Likhitwitayawuid, 2009
Tetracosyl (*Z*)-*p*-coumarate [**87**]	Phenylpropanoid	Stem	Sritularak and Likhitwitayawuid, 2009

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium fimbriatum			
Defuscin [**22**]	Phenylpropanoid	Whole plant	Talapatra, Bhaumik and Talapatra, 1992
Denfigenin [**88**]	Steroid	Whole plant	Talapatra *et al.*, 1992
Diosgenin [**89**]	Steroid	Whole plant	Talapatra *et al.*, 1992
Dendrobium findlayanum			
Crystallinin [**56**]	Sesquiterpene	Whole plant	Qin *et al.*, 2011
Findlayanin [**90**]	Sesquiterpene	Whole plant	Qin *et al.*, 2011
Dendrobium fuscescens			
Defuscin [**22**]	Phenylpropanoid	Whole plant	Talapatra, Das and Talapatra, 1989
(-)-Shikimic acid [**91**]	Aliphatic acid	Whole plant	Talapatra *et al.*, 1989
Dendrobium gratiosissimum			
Batatasin III [**9**]	Bibenzyl	Stem	Zhang *et al.*, 2008a
Dengraol A [**92**]	Bisbibenzyl	Stem	Zhang *et al.*, 2008a
Dengraol B [**93**]	Bisbibenzyl	Stem	Zhang *et al.*, 2008a
3,4-Dihydroxy-5,4′-dimethoxybibenzyl [**34**]	Bibenzyl	Stem	Zhang *et al.*, 2008a
3,4′-Dihydroxy-5-methoxybibenzyl [**6**]	Bibenzyl	Stem	Zhang *et al.*, 2008a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Gigantol [**14**]	Bibenzyl	Stem	Zhang *et al.*, 2008a
Moscatilin [**8**]	Bibenzyl	Stem	Zhang *et al.*, 2008a
3,5,4′-Trihydroxybibenzyl [**94**]	Bibenzyl	Stem	Zhang *et al.*, 2008a
Tristin [**76**]	Bibenzyl	Stem	Zhang *et al.*, 2008a
Dendrobium huoshanense			
6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-galactopyranosyl]apigenin [**95**]	Flavone glycoside	Aerial part	Chang *et al.*, 2010
6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin [**96**]	Flavone glycoside	Aerial part	Chang *et al.*, 2010
Dimethyl malate [**97**]	Aliphatic acid ester	Aerial part	Chang *et al.*, 2010
Isopentyl butyrate [**98**]	Aliphatic acid ester	Aerial part	Chang *et al.*, 2010
Isoschaftoside [**99**]	Flavone glycoside	Aerial part	Chang *et al.*, 2010
Malic acid [**100**]	Aliphatic acid	Aerial part	Chang *et al.*, 2010
N-Phenylacetamide [**101**]	Aromatic compound	Aerial part	Chang *et al.*, 2010

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
6-*C*-[(2-*O*-α-Rhamnopyranosyl)-β-glucopyranosyl]-8-*C*-(α-arabinopyranosyl) apigenin [**102**]	Flavone glycoside	Aerial part	Chang *et al.*, 2010
Salicylic acid [**103**]	Hydroxybenzoic acid	Aerial part	Chang *et al.*, 2010
Shikimic acid [**91**]	Aliphatic acid	Aerial part	Chang *et al.*, 2010
6-*C*-(β-Xylopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl] apigenin [**104**]	Flavone glycoside	Aerial part	Chang *et al.*, 2010
Dendrobium loddigesii			
Batatasin III [**9**]	Bibenzyl	Whole plant	Ito *et al.*, 2010
Dehydrovomifoliol [**105**]	Terpenoid	Whole plant	Ito *et al.*, 2010
Gigantol [**14**]	Bibenzyl	Whole plant	Ito *et al.*, 2010
Hircinol [**77**]	Phenanthrene	Whole plant	Ito *et al.*, 2010
5-Hydroxy-2,4-dimethoxy phenanthrene [**106**]	Phenanthrene	Whole plant	Ito *et al.*, 2010
Loddigesiinol A [**107**]	Phenanthrene	Whole plant	Ito *et al.*, 2010
Loddigesiinol B [**108**]	Phenanthrene	Whole plant	Ito *et al.*, 2010
Loddigesiinol C [**109**]	Bibenzyl	Whole plant	Ito *et al.*, 2010
Loddigesiinol D [**110**]	Bibenzyl	Whole plant	Ito *et al.*, 2010
Lusianthridin [**16**]	Phenanthrene	Whole plant	Ito *et al.*, 2010
(-)-Medioresinol [**111**]	Lignan	Whole plant	Ito *et al.*, 2010
Moscatilin [**8**]	Bibenzyl	Whole plant	Chen *et al.*, 1994 ; Ito *et al.*, 2010
Moscatin [**17**]	Phenanthrene	Whole plant	Chen *et al.*, 1994 ; Ito *et al.*, 2010
(-)-Pinoresinol [**112**]	Lignan	Whole plant	Ito *et al.*, 2010

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Rotundatin [**113**]	Phenanthrene	Whole plant	Ito *et al.*, 2010
Sitostenone [**114**]	Steroid	Whole plant	Ito *et al.*, 2010
β -Sitosterol [**44**]	Steroid	Whole plant	Ito *et al.*, 2010
Stigmasterol [**29**]	Steroid	Whole plant	Ito *et al.*, 2010
Dendrobium longicornu			
Aloifol I [**115**]	Bibenzyl	Stem	Hu *et al*., 2008a
Batatasin [**116**]	Bibenzyl	Stem	Hu *et al*., 2008a
Bis (2-ethylhexyl) phthalate [**117]**	Benzoic acid ester	Whole plant	Li *et al*., 2009
Dibutyl phthalate [**11**]	Benzoic acid ester	Whole plant	Li *et al*., 2009
n-Docosyl *trans*-ferulate [**118**]	Phenylpropanoid	Whole plant	Li *et al*., 2009
Episyringaresinol [**119**]	Lignan	Stem	Hu *et al*., 2008a
Episyringaresinol 4′′-*O*-β-D-glucopyranoside [**120**]	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 [**121**]	Lignan glycoside	Stem	Hu *et al*., 2008a
Ethylhaematommate [**122**]	Phenolic compound	Whole plant	Li *et al*., 2009
Eugenyl *O*-β-D-glucopyranoside [**123**]	Glycoside	Stem	Hu *et al*., 2008a
Ferulaldehyde [**124**]	Phenylpropanoid	Whole plant	Li *et al*., 2009

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Gallic acid [**125**]	Phenolic compound	Whole plant	Li *et al*., 2009
Gigantol [**14**]	Bibenzyl	Stem	Hu *et al*., 2008a
5-Hydroxy-7-methoxy-9,10-dihydrophenanthrene-1,4-dione (Dendrononе) [**38**]	Phenanthrene	Stem	Hu *et al*., 2008a
4-[2-(3-Hydroxyphenol)-1-methoxyethyl]-2,6-dimethoxyphenol [**126**]	Bibenzyl	Stem	Hu *et al*., 2008a
Longicornuol A [**127**]	Bibenzyl	Stem	Hu *et al*., 2008a
4-Methoxy-9,10-dihydrophenanthrene-2,5,7-triol [**128**]	Phenanthrene	Stem	Hu *et al*., 2008a
3-(3-Methoxy,4-hydroxyphenyl)-1-propanol [**129**]	Phenylpropanoid	Stem	Hu *et al*., 2008a
Methyl β-orsellinate [**130**]	Phenolic compound	Stem	Hu *et al*., 2008a
Moscatilin [**8**]	Bibenzyl	Stem	Hu *et al*., 2008a
Naringenin [**27**]	Flavanone	Stem	Hu *et al*., 2008a
9-β-D-Ribofuranosyl-9H-purin-6-amine [**131**]	Purine nucleotide	Stem	Hu *et al*., 2008a
Shikimic acid [**91**]	Aliphatic acid	Stem	Hu *et al*., 2008a
β-Sitosterol [**44**]	Steroid	Stem	Hu *et al*., 2008a
3,3′,4-Trihydroxybibenzyl [**132**]	Bibenzyl	Stem	Hu *et al*., 2008a
Tristin [**76**]	Bibenzyl	Stem	Hu *et al*., 2008a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobium moniliforme			
Acanthoside B [**133**]	Lignan glycoside	Stem	Zhao *et al.*, 2003
Daucosterol [**37**]	Steroid glycoside	Stem	Bi, Wang and Xu, 2004
Denbinobin [**134**]	Phenanthrene	Stem	Lin *et al.*, 2001
Dendromoniliside A [**135**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
Dendromoniliside B [**136**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
Dendromoniliside C [**137**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
Dendromoniliside D [**138**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
Dendromoniliside E **[139**]	Bibenzyl glycoside	Stem	Zhao *et al.*, 2003
Dendroside A [**140**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
Dendroside C [**141**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
Dendroside F [**142**]	Sesquiterpene glycoside	Stem	Zhao *et al.*, 2003
α-Dihydropicrotoxinin [**143**]	Sesquiterpene	Stem	Bi *et al.*, 2004
3,4-Dihydroxy-5,4′-dimethoxybibenzyl [**34**]	Bibenzyl	Stem	Bi *et al.*, 2004
Moniliformin [**144**]	Phenanthrene	Stem	Lin *et al.*, 2001
n-Nonacosane [**145**]	Long chain hydrocarbon	Stem	Bi *et al.*, 2004
n-Octacosyl ferulate [**28**]	Phenolic compound	Stem	Bi *et al.*, 2004

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
β-Sitosterol [**44**]	Steroid	Stem	Bi *et al.*, 2004
n-Triacontyl *p*-hydroxy-cis-cinnamate [**146**]	Phenolic compound	Stem	Bi *et al.*, 2004
Vanilloside [**147**]	Phenolic glycoside	Stem	Zhao *et al.*, 2003
Dendrobium moscatum			
Moscatilin [**8**]	Bibenzyl	Whole plant	Majumder and Sen, 1987
Dendrobium nobile			
Bulbophyllanthrin [**148**]	Phenanthrene	Stem	Yang, Sung and Kim, 2007
Chrysotobibenzyl [**18**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Chrysotoxine [**19**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Coelonin [**10**]	Phenanthrene	Stem	Yang *et al*., 2007 ; Hwang *et al*., 2010
Confusarin [**42**]	Phenanthrene	Stem	Zhang *et al*., 2008b
Crepidatin [**21**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Denbinobin [**134**]	Phenanthrene	Stem	Ye and Zhao, 2002; Yang *et al*., 2007
Dendrobane A [**149**]	Sesquiterpene	Stem	Zhang *et al*., 2007a

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendrobin A **[150]**	Bibenzyl	Stem	Wang, Zhao and Che, 1985; Ye and Zhao, 2002
Dendrobine [**151**]	Sesquiterpene alkaloid	Stem	Zhang *et al*., 2007a
Dendroflorin [**23**]	Fluorenone	Stem	Zhang *et al*., 2007b
Dendronobilin A [**152**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin B [**60**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin C [**153**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin D [**154**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin E [**155**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin F [**156**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin G [**157**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin H [**158**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin I [**159**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin J [**160**]	Sesquiterpene	Stem	Zhang *et al*., 2007b
Dendronobilin K [**161**]	Sesquiterpene	Stem	Zhang *et al*., 2008c

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendronobilin L [**162**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobilin M [**163**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobilin N [**164**]	Sesquiterpene	Stem	Zhang *et al*., 2008c
Dendronobiloside A [**165**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2001; Ye and Zhao, 2002
Dendronobiloside B [**166**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2001; Ye and Zhao, 2002
Dendronobiloside C [**167**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendronobiloside D [**168**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendronobiloside E [**169**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendroside A [**140**]	Sesquiterpene glycoside	Stem	Zhao *et al*., 2001; Ye and Zhao, 2002
Dendroside B [**170**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendroside C [**141**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
Dendroside D [**171**]	Sesquiterpene glycoside	Stem	Ye, Qin and Zhao, 2002
Dendroside E [**172**]	Sesquiterpene glycoside	Stem	Ye *et al.*, 2002
Dendroside F [**142**]	Sesquiterpene glycoside	Stem	Ye *et al.*, 2002

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Dendroside G [**173**]	Sesquiterpene glycoside	Stem	Ye and Zhao, 2002
4,5-Dihydroxy-3,3′-dimethoxybibenzyl (Dendrobin A) [**150**]	Bibenzyl	Stem	Ye and Zhao, 2002
4,5-Dihydroxy-3,7-dimethoxy-9,10-dihydrophenanthrene [**174**]	Phenanthrene	Stem	Ye and Zhao, 2002
3,4′-Dihydroxy-5,5′-di methoxydihydrostilbene [**175**]	Bibenzyl	Stem	Hwang *et al*., 2010
2,5-Dihydroxy-3,4-di methoxyphenanthrene [**176**]	Phenanthrene	Stem	Yang *et al*., 2007
2,5-Dihydroxy-4,9-di methoxyphenanthrene (4,9-Dimethoxylphenanthrene-2,5-diol) [**41**]	Phenanthrene	Stem	Zhang *et al*., 2008b
3,7-Dihydroxy-2,4-di methoxyphenanthrene [**47**]	Phenanthrene	Stem	Zhang *et al*., 2008b
2,2′-Dihydroxy-3,3′,4,4′,7,7′-hexamethoxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene [**177**]	Biphenanthrene	Stem	Yang *et al*., 2007
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 (Dendromoniliside D) [**138**]	Sesquiterpene glycoside	Stem	Shu, Zhang and Guo, 2004

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
4,5-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene [**178**]	Phenanthrene	Stem	Yang *et al*., 2007
2,8-Dihydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene [**179**]	Phenanthrene	Stem	Yang *et al*., 2007
2,8-Dihydroxy-3,4,7-tri methoxyphenanthrene [**180**]	Phenanthrene	Stem	Yang *et al*., 2007
5,7-Dimethoxy phenanthrene-2,6-diol [**181**]	Phenanthrene	Stem	Hwang *et al*., 2010
Ephemeranthol A [**182**]	Phenanthrene	Stem	Yang *et al*., 2007 ; Hwang *et al*., 2010
Ephemeranthol C [**183**]	Phenanthrene	Stem	Hwang *et al*., 2010
Erianthridin [**184**]	Phenanthrene	Stem	Yang *et al*., 2007 ; Hwang *et al*., 2010
Fimbiatone [**185**]	Phenanthrene	Stem	Zhang *et al*., 2008b
Fimbriol B [**186**]	Phenanthrene	Stem	Yang *et al*., 2007 ; Hwang *et al*., 2010
Flavanthridin [**187**]	Phenanthrene	Stem	Hwang *et al*., 2010
Flavanthrinin [**188**]	Phenanthrene	Stem	Zhang *et al*., 2008b

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Gigantol [**14**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Hircinol [**77**]	Phenanthrene	Stem	Hwang *et al*., 2010
2-Hydroxy-4,7-dimethoxy-9,10-dihydrophenanthrene [**189**]	Phenanthrene	Stem	Yang *et al*., 2007
3-Hydroxy-2-oxodendrobine [**190**]	Sesquiterpene alkaloid	Stem	Wang *et al*.,1985
4-Hydroxy-3,5,3′-trimethoxybibenzyl [**191**]	Bibenzyl	Stem	Ye and Zhao, 2002
2-Hydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene [**192**]	Phenanthrene	Stem	Yang *et al*., 2007
3-Hydroxy-2,4,7-trimethoxy-9,10-dihydrophenanthrene [**193**]	Phenanthrene	Stem	Yang *et al*., 2007
3-Hydroxy-2,4,7-tri methoxyphenanthrene [**194**]	Phenanthrene	Stem	Yang *et al*., 2007
Lirioresinol A [**195**]	Lignan	Stem	Zhang *et al*., 2008b
Lusianthridin [**16**]	Phenanthrene	Stem	Yang *et al*., 2007 ; Hwang *et al*., 2010
Medioresinol [**111**]	Lignan	Stem	Zhang *et al*., 2008b
Moscatilin [**8**]	Bibenzyl	Stem	Yang *et al*., 2007 ; Hwang *et al*., 2010

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Nobilin A [**196**]	Bibenzyl	Stem	Zhang *et al*., 2006
Nobilin B [**197**]	Bibenzyl	Stem	Zhang *et al*., 2006
Nobilin C [**198**]	Bibenzyl	Stem	Zhang *et al*., 2006
Nobilin D [**199**]	Bibenzyl	Stem	Zhang *et al*., 2007a
Nobilin E [**200**]	Bisbibenzyl	Stem	Zhang *et al*., 2007a
Nobilone [**201**]	Fluorenone	Stem	Zhang *et al*., 2007a
Nudol [**202**]	Phenanthrene	Stem	Yang *et al*., 2007
Pinoresinol [**203**]	Lignan	Stem	Zhang *et al*., 2008b
Plicatol A [**204**]	Phenanthrene	Stem	Yang *et al*., 2007
Protocatechuic acid [**205**]	Phenolic compound	Stem	Ye and Zhao, 2002
Syringaresinol [**206**]	Lignan	Stem	Zhang *et al*., 2008b
10β,12,14-Trihydroxy-alloaromadendrane [**207**]	Sesquiterpene	Stem	Ye and Zhao, 2002
2,3,5-Trihydroxy-4,9-di methoxyphenanthrene [**208**]	Phenanthrene	Stem	Yang *et al*., 2007
3,4,8-Trimethoxy phenanthrene-2,5-diol [**209**]	Phenanthrene	Stem	Hwang *et al*., 2010
Dendrobium ochreatum			
Dendrosteroside [**210**]	Steroid glycoside	Whole plant	Behr and Leander, 1976

Table 1 (continued)

Plant and compound	Category	Plant part	Reference
Epi-ochreasteroside [**211**]	Steroid glycoside	Whole plant	Behr and Leander, 1976
Ochreasteroside [**212**]	Steroid glycoside	Whole plant	Behr and Leander, 1976
Dendrobium plicatile			
Batatasin [**116**]	Bibenzyl	Stem	Yamaki and Honda, 1996
2,2′-Dimethoxy-4,4′,7,7′-tetrahydroxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene [**213**]	Biphenanthrene	Stem	Yamaki and Honda, 1996
Ephemeranthoquinone [**214**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Epheranthol B [**215**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Erianthridin [**184**]	Phenanthrene	Stem	Yamaki and Honda, 1996
Lusianthridin [**16**]	Phenanthrene	Stem	Yamaki and Honda, 1996
3-*O*-Methylgigantol [**36**]	Bibenzyl	Stem	Yamaki and Honda, 1996
Plicatol A [**204**]	Phenanthrene	Stem	Honda and Yamaki, 2000
Plicatol B [**216**]	Phenanthrene	Stem	Honda and Yamaki, 2000
Plicatol C [**217**]	Phenanthrene	Stem	Honda and Yamaki, 2000

Table 1 (continued)

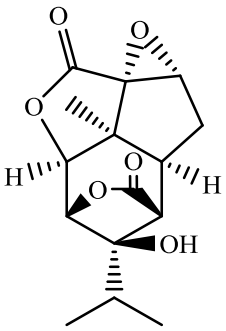
Plant and compound	Category	Plant part	Reference
Dendrobium polyanthum			
Batatasin [**116**]	Bibenzyl	Stem	Hu *et al.*, 2009
Corchoionoside C [**218**]	Sesquiterpene	Stem	Hu *et al.*, 2009
Daucosterol [**37**]	Steroid glycoside	Stem	Hu *et al.*, 2009
9,10-Dihydromoscatin [**219**]	Phenanthrene	Stem	Hu *et al.*, 2009
9,10-Dihydrophenanthrene-2,4,7-triol [**220**]	Phenanthrene	Stem	Hu *et al.*, 2009
Gigantol [**14**]	Bibenzyl	Stem	Hu *et al.*, 2009
Moscatilin [**8**]	Bibenzyl	Stem	Hu *et al.*, 2009
Moscatin [**17**]	Phenanthrene	Stem	Hu *et al.*, 2009
β-Sitosterol [**44**]	Steroid	Stem	Hu *et al.*, 2009
3,6,9-Trihydroxy-3,4-dihydroanthracen-1(2H)-one [**221**]	Anthracene	Stem	Hu *et al.*, 2009
Dendrobium rotundatum			
Batatasin III [**9**]	Bibenzyl	Whole plant	Majumder and Pal, 1992
2,7-Dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene [**222**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
2,7-Dihydroxy-3,4,6-tri-methoxyphenanthrene [**223**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Moscatin [**17**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Nudol [**202**]	Phenanthrene	Whole plant	Majumder and Pal, 1992
Rotundatin [**113**]	Phenanthrene	Whole plant	Majumder and Pal, 1992

Table 1 (continued)

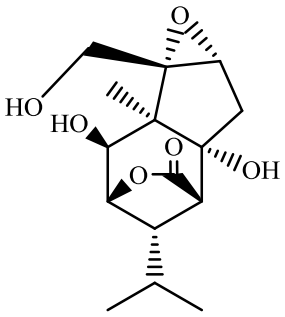
Plant and compound	Category	Plant part	Reference
Dendrobium secundum			
Brittonin A [**224**]	Bibenzyl	Stem	Sritularak *et al.*, 2011b
Ferulic acid [**225**]	Phenylpropanoid	Stem	Sritularak *et al.*, 2011b
Moscatilin [**8**]	Bibenzyl	Stem	Sritularak *et al.*, 2011b
Syringaresinol [**206**]	Lignan	Stem	Sritularak *et al.*, 2011b
4,5,4′-Trihydroxy-3,3′-dimethoxybibenzyl [**226**]	Bibenzyl	Stem	Sritularak *et al.*, 2011b
Dendrobium thyrsiforum			
Chrysophanol [**227**]	Anthraquinone	Stem	Zhang *et al*., 2005
Daucosterol [**37**]	Steroid glycoside	Stem	Zhang *et al*., 2005
Denthyrsin [**228**]	Coumarin	Stem	Zhang *et al*., 2005
Denthyrsinin [**229**]	Phenanthrene	Stem	Zhang *et al*., 2005
Denthyrsinol [**230**]	Biphenanthrene	Stem	Zhang *et al*., 2005
Denthyrsinone [**231**]	Biphenanthrene	Stem	Zhang *et al*., 2005
Emodin [**232**]	Anthraquinone	Stem	Zhang *et al*., 2005
Physcion [**233**]	Anthraquinone	Stem	Zhang *et al*., 2005
Scoparone [**73**]	Coumarin	Stem	Zhang *et al*., 2005
β-Sitosterol [**44**]	Steroid	Stem	Zhang *et al*., 2005

Table 1 (continued)

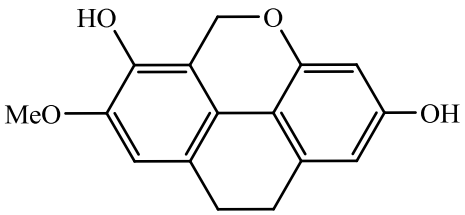
Plant and compound	Category	Plant part	Reference
Dendrobium trigonopus			
Gigantol [**14**]	Bibenzyl	Stem	Hu *et al.*, 2008b
Hircinol [**77**]	Bibenzyl	Stem	Hu *et al.*, 2008b
3-(4-Hydroxy-3-methoxy phenyl)-2-propen-1-ol [**234**]	Phenylpropanoid	Stem	Hu *et al.*, 2008b
Moscatin [**17**]	Phenanthrene	Stem	Hu *et al.*, 2008b
Naringenin [**27**]	Flavanone	Stem	Hu *et al.*, 2008b
(-)-Syringaresinol [**206**]	Lignan	Stem	Hu *et al.*, 2008b
Trigonopol A [**235**]	Bibenzyl	Stem	Hu *et al.*, 2008b
Trigonopol B [**236**]	Bibenzyl	Stem	Hu *et al.*, 2008b
Tristin [**76**]	Bibenzy	Stem	Hu *et al.*, 2008b



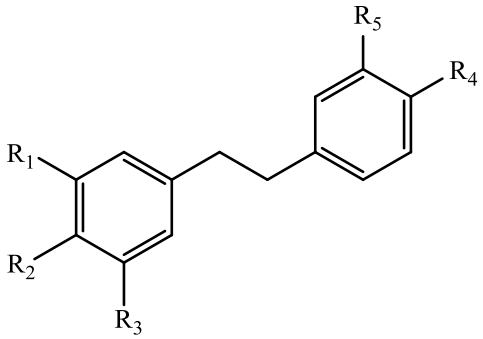
[**1**] Aduncin



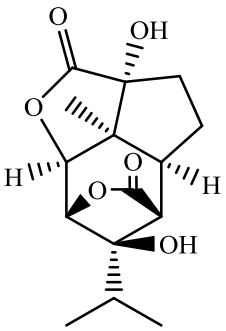
[**2**] Amoenin



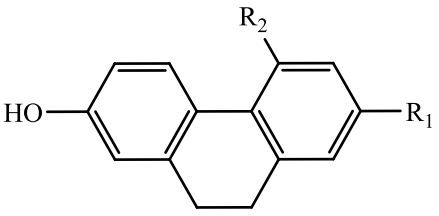
[**3**] Amoenumin



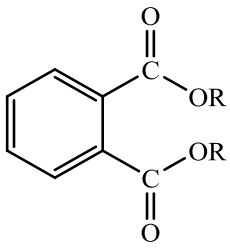
	R_1	R_2	R_3	R_4	R_5
[**4**] Amoenylin	OMe	OH	OMe	OMe	H
[**6**] 3,4′-Dihydroxy-5-methoxybibenzyl	OH	H	OMe	OH	H
[**7**] Isoamoenylin	OMe	OMe	OMe	H	OH
[**8**] Moscatilin	OMe	OH	OMe	OH	OMe
[**9**] Batatasin III	OH	H	OMe	H	OH
[**14**] Gigantol	OMe	H	H	OH	OMe



[**5**] Amotin



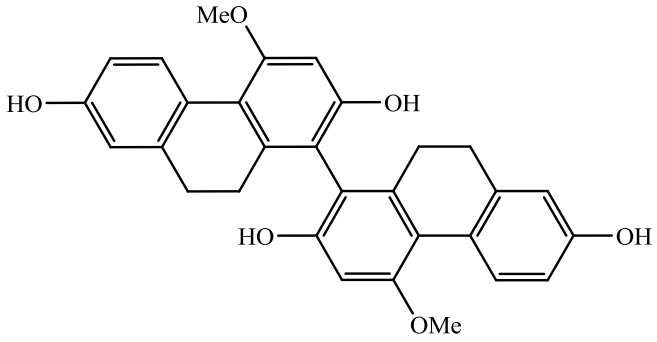
	R_1	R_2
[**10**] Coelonin	OH	OMe
[**16**] Lusianthridin	OMe	OH



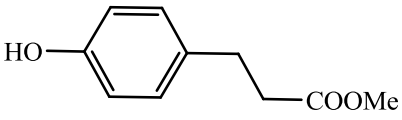
[**11**] Dibutyl phthalate: R=$(CH_2)_3CH_3$

[**12**] Diisobutyl phthalate: R=$CH_2CH(CH_3)_2$

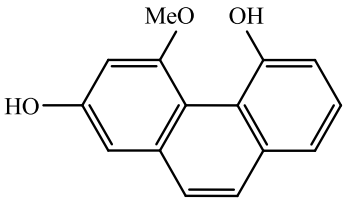
Figure 3 Structures of compounds previously isolated from *Dendrobium* species



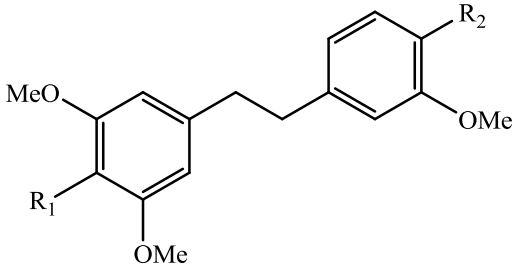
[**13**] Flavanthrin



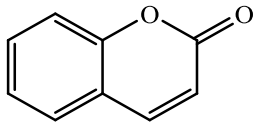
[**15**] *p*-Hydroxyphenyl propanoic methyl ester



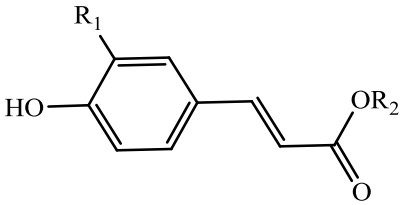
[**17**] Moscatin



	R_1	R_2
[**18**] Chrysotobibenzyl	OMe	OMe
[**19**] Chrysotoxine	OH	OMe
[**21**] Crepidatin	OMe	OH



[**20**] Coumarin

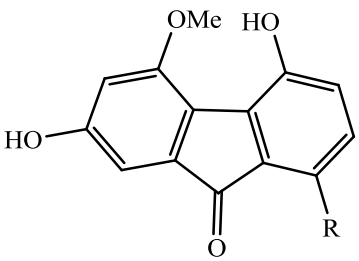


[**22**] Defuscin:

R_1=OMe, R_2= $(CH_2)_{27}CH_3$

[**28**] *n*-Octacosyl ferulate:

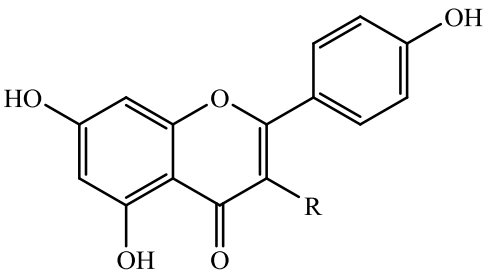
R_1=H, R_2= $(CH_2)_{29}CH_3$



[**23**] Dendroflorin: R=OH

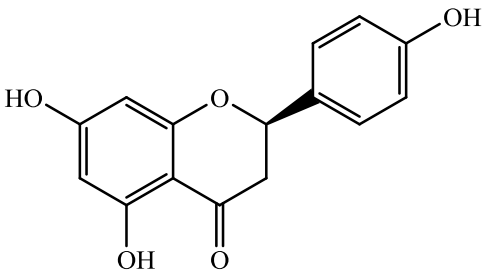
[**24**] Dengibsin: R =H

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

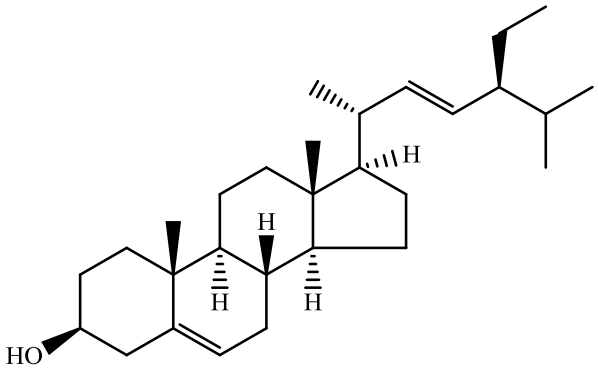


[**25**] Kaempferol: R=OH

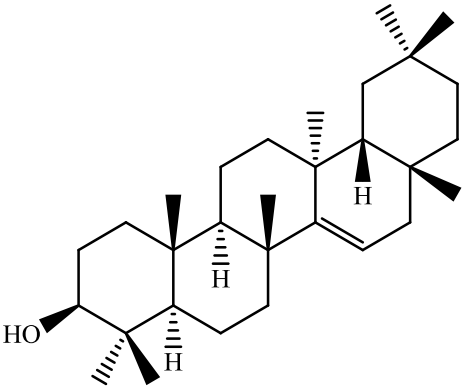
[**26**] Luteolin: R=H



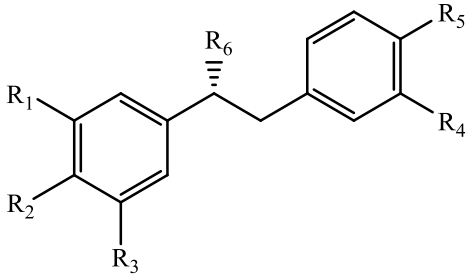
[**27**] Naringenin



[**29**] Stigmasterol

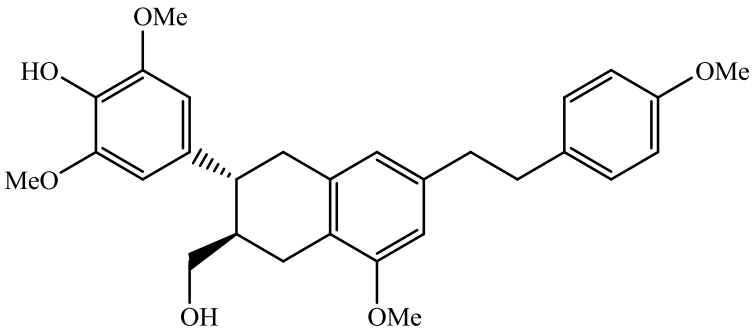


[**30**] Taraxerol

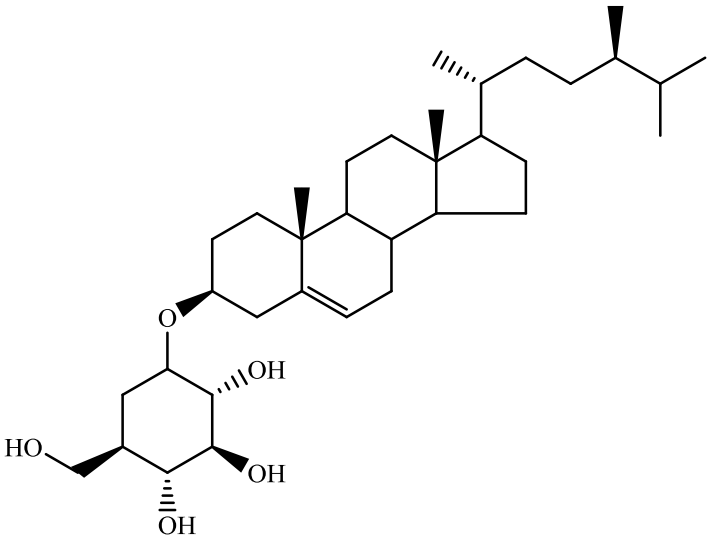


	R_1	R_2	R_3	R_4	R_5	R_6
[**31**] Dendrocandin A	OMe	OH	OH	H	OMe	OMe
[**33**] Dendrophenol	OMe	OH	OMe	OH	OH	H
[**34**] 3,4-Dihydroxy-5,4′-dimethoxybibenzyl	OH	OH	OMe	H	OMe	H
[**35**] 4,4′-Dihydroxy-3,5-dimethoxybibenzyl	OMe	OH	OMe	H	OH	H
[**36**] 3-*O*-Methylgigantol	OMe	H	OH	OMe	OMe	H

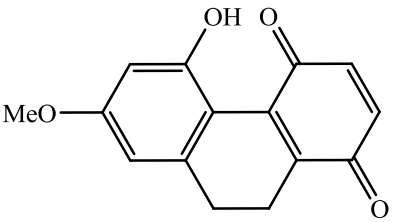
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



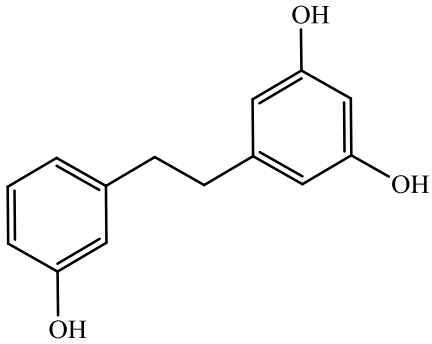
[**32**] Dendrocandin B



[**37**] Daucosterol

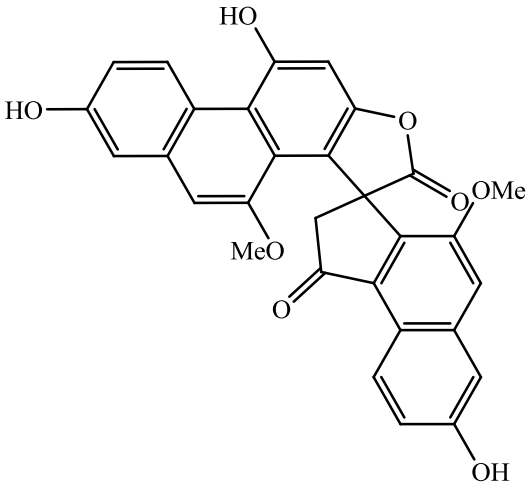


[**38**] Dendronone

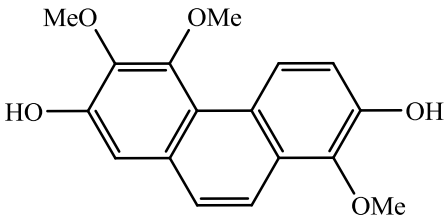


[**39**] 3,3′,5-Trihydroxybibenzyl

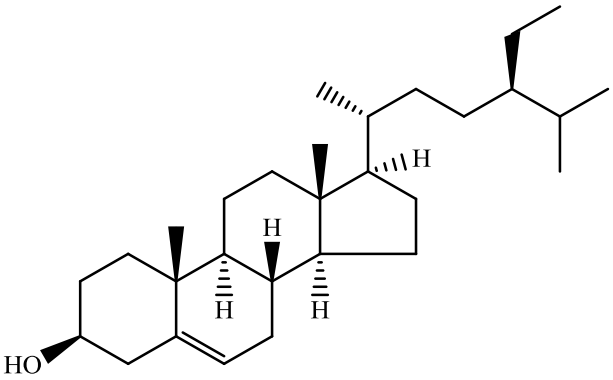
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



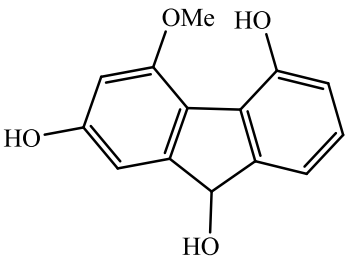
[**40**] Dendrochrysanene

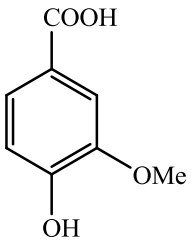


[**42**] Confusarin



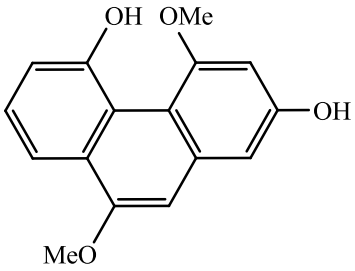
[**44**] β-Sitosterol



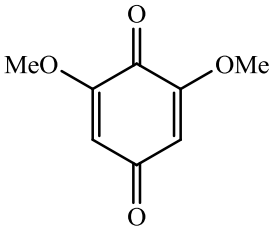


[**48**] Vanillic acid

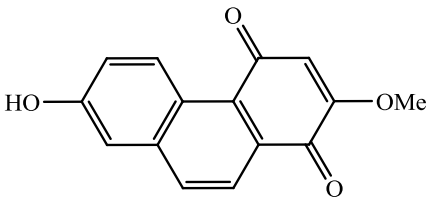
[**45**] Denchrysan B



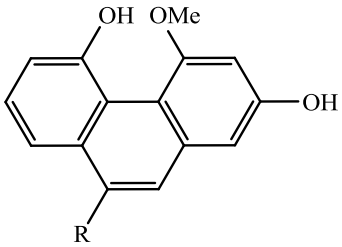
[**41**] 2,5-Dihydroxy-4,9-dimethoxylphenanthrene



[**43**] 2,6-Dimethoxybenzoquinone



[**46**] Densiflorol B



[**47**] 3,7-Dihydroxy-2,4-dimethoxyphenanthrene: R = H

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

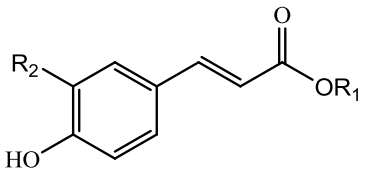
$CH_3(CH_2)_nCH_2R$

[**49**] Aliphatic acids:

R = COOH, n = 19-31

[**50**] Aliphatic alcohol:

R = OH, n = 22-32



[**51**] Alkyl 4′-hydroxy-*trans*-cinnamates:

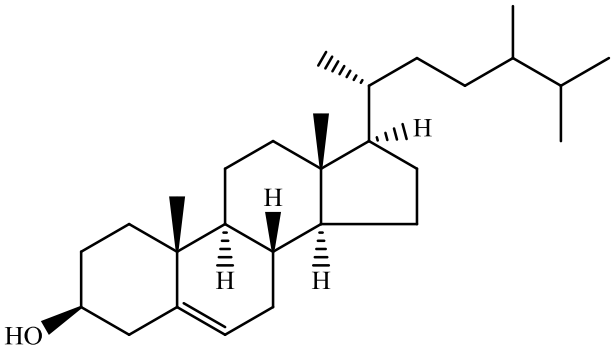
$R_1 = C_nH_{2n+1}$, n = 22-32

R_2 = H

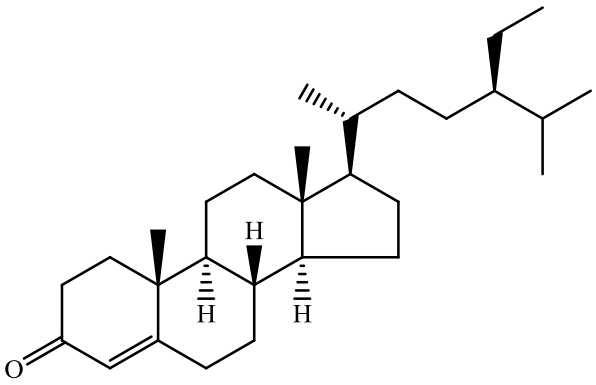
[**52**] Alkyl *trans*-ferulates :

$R_1 = C_nH_{2n+1}$, n = 18-28, 30

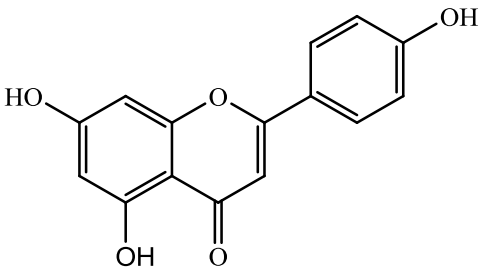
R_2 = OMe



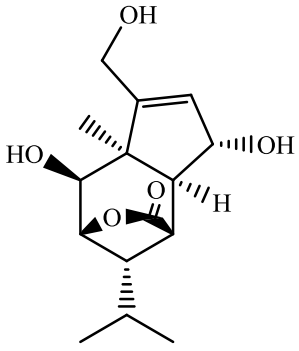
[**53**] Campesterol



[**54**] Stigmast-4-en-3-one

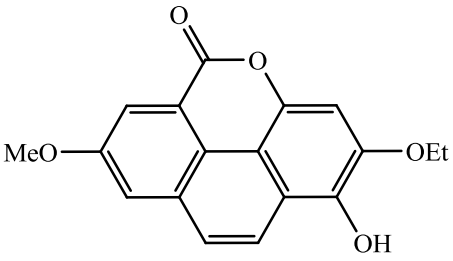


[**55**] Apigenin

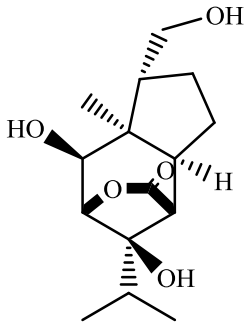


[**56**] Crystallinin

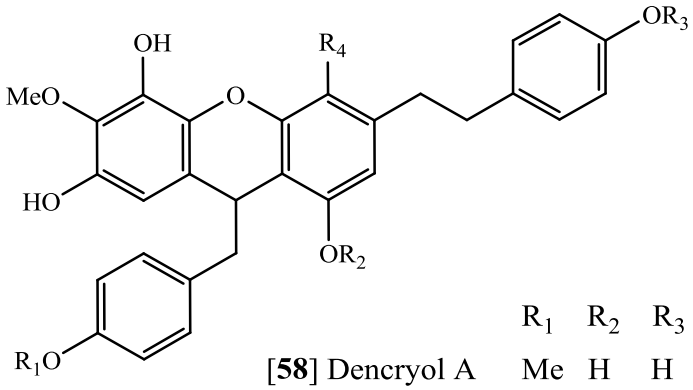
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



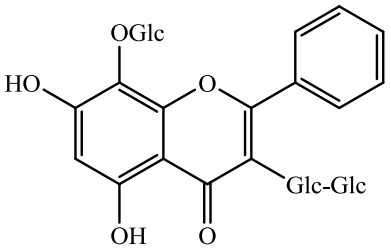
[**57**] Crystalltone



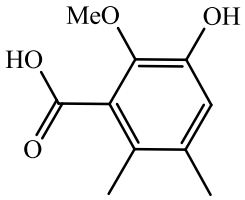
[**60**] Dendronobilin B



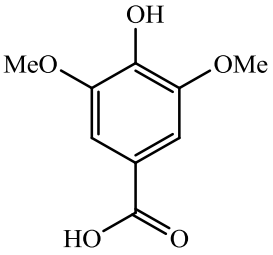
	R_1	R_2	R_3	R_4
[**58**] Dencryol A	Me	H	H	H
[**59**] Dencryol B	H	Me	Me	OH



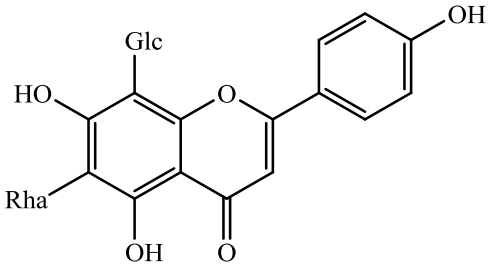
[**61**] 6‴-Glucosyl-vitexin



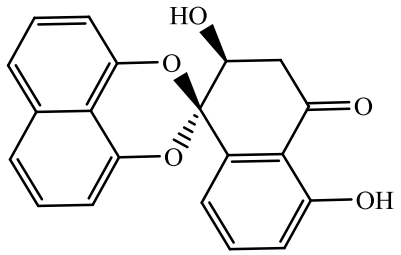
[**62**] 3-Hydroxy-2-methoxy-5,6-dimethylbenzoic acid



[**65**] Syringic acid

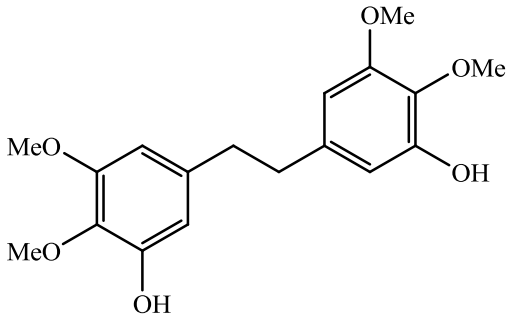


[**63**] Isoviolanthin

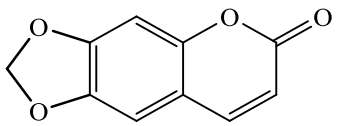


[**64**] Palmarumycin JC2

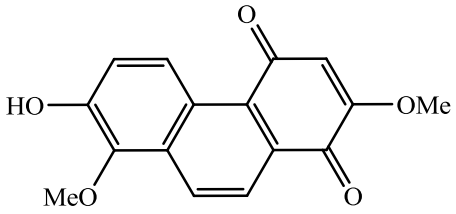
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



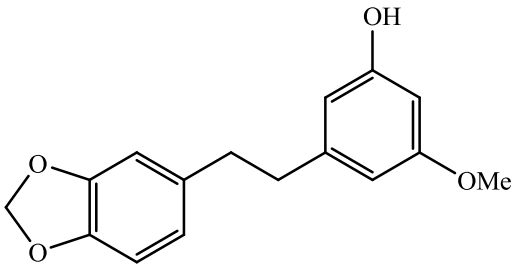
[**66**] Cumulatin



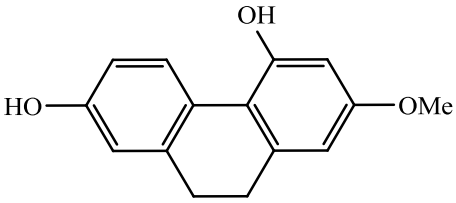
[**67**] Ayapin



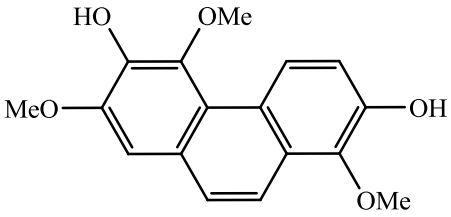
[**68**] Cypripedin



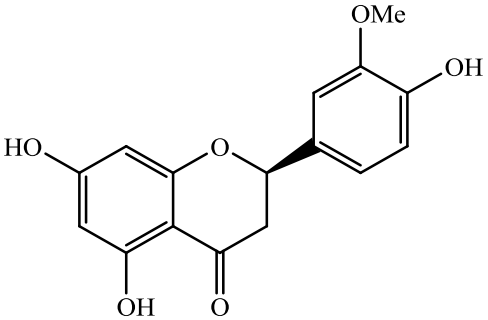
[**69**] Densiflorol A



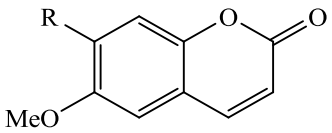
[**70**] 4,7-Dihydroxy-2-methoxy-9,10-dihydrophenanthrene



[**71**] 2,6-Dihydroxy-1,5,7-trimethoxyphenanthrene



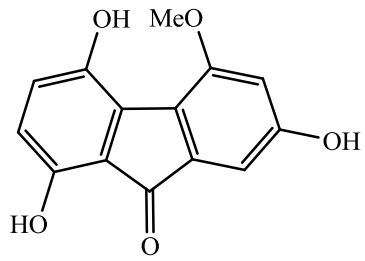
[**72**] Homoeriodictyol



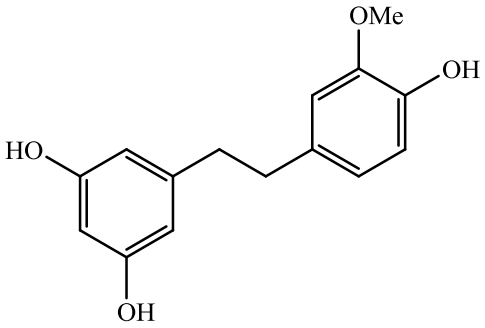
[**73**] Scoparone: R = OMe

[**74**] Scopoletin: R = H

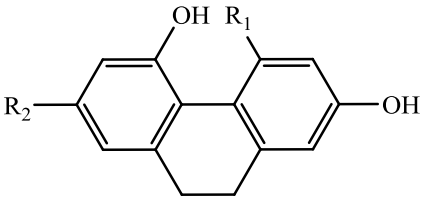
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



[**75**]1,4,7-Trihydroxy-5-methoxy-9H-fluoren-9-one

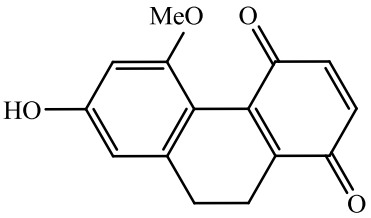


[**76**] Tristin

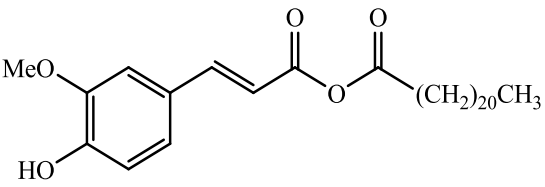


[**77**] Hircinol: R_1 = OMe, R_2 = H

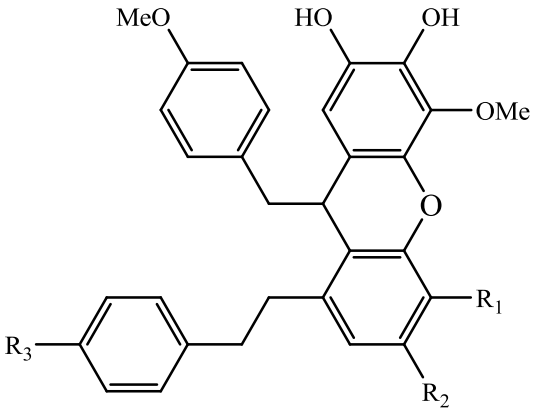
[**78**] 7-Methoxy-9,10-dihydrophenanthrene-2,4,5-triol: R_1 = OH, R_2 = OMe



[**79**] 5-Methoxy-7-hydroxy-9,10-dihydro-1,4-phenanthrenequinone



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

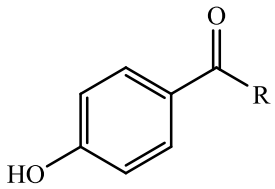


[**80**] Dendrofalconerol A:

R_1 = OH, R_2 = OMe, R_3 = OMe

[**81**] Dendrofalconerol B:

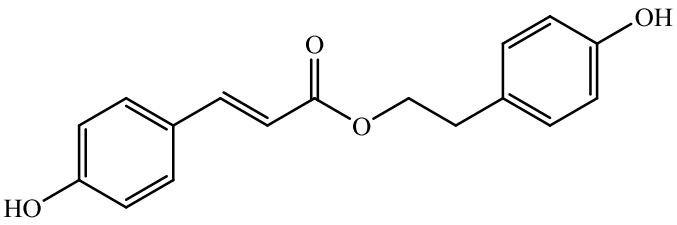
R_1 = H, R_2 = OH, R_3 = OH



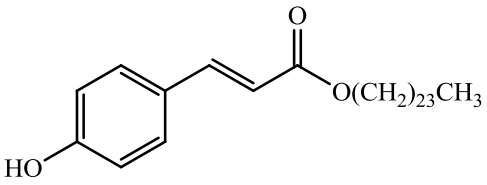
[**83**] *p*-Hydroxybenzaldehyde: R = H

[**84**] *p*-Hydroxybenzoic acid: R = OH

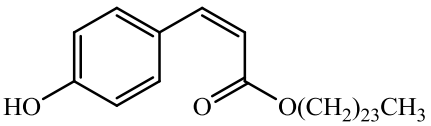
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



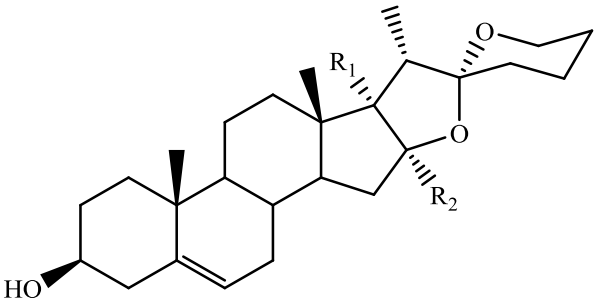
[**85**] 2-(*p*-Hydroxyphenyl) ethyl *p*-coumarate



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

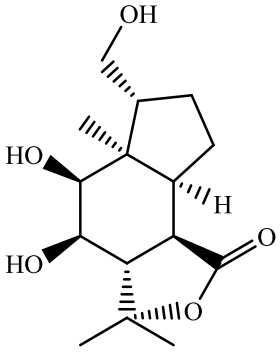


[**87**] Tetracosyl (*Z*)-*p*-coumarate

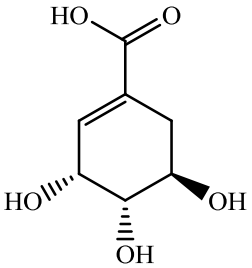


[**88**] Denfigenin: $R_1 = R_2 = OH$

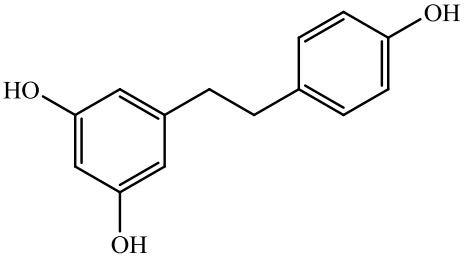
[**89**] Diosgenin: $R_1 = R_2 = H$



[**90**] Findlayanin

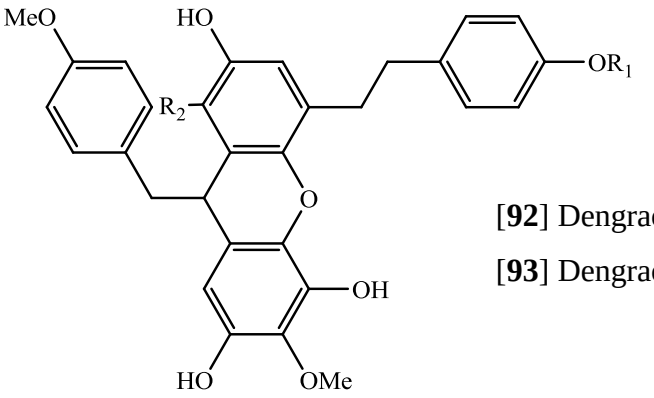


[**91**] (-)-Shikimic acid



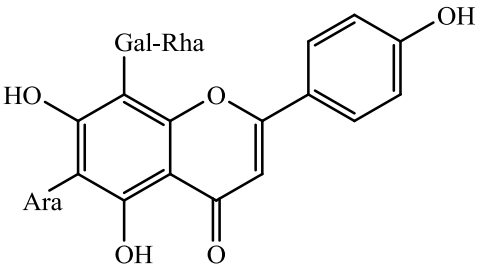
[**94**] 3,5,4′-Trihydroxybibenzyl

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

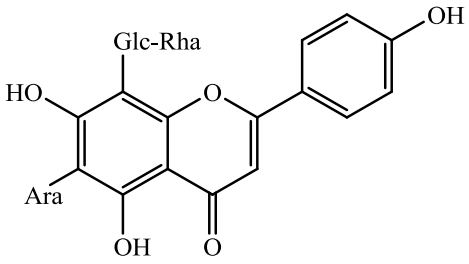


[**92**] Dengraol A: $R_1 = R_2 = H$

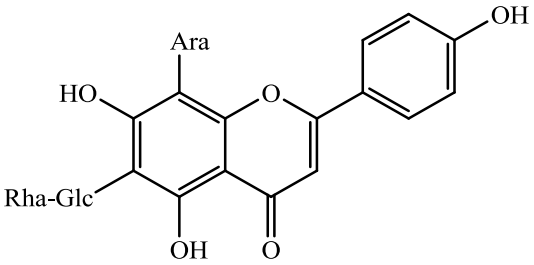
[**93**] Dengraol B: R_1 = Me, R_2 = OMe



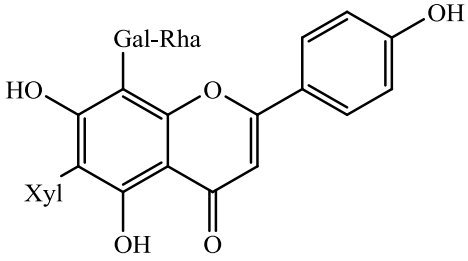
[**95**] 6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-galactopyranosyl]apigenin



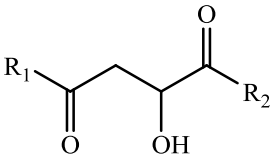
[**96**] 6-*C*-(α-Arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin



[**102**] 6-*C*-[(2-*O*-α-Rhamnopyranosyl)-β-glucopyranosyl]-8-*C*-(α-arabinopyranosyl)apigenin

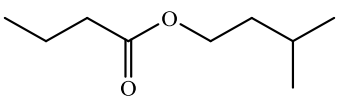


[**104**] 6-*C*-(β-Xylopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-gluco pyranosyl]apigenin



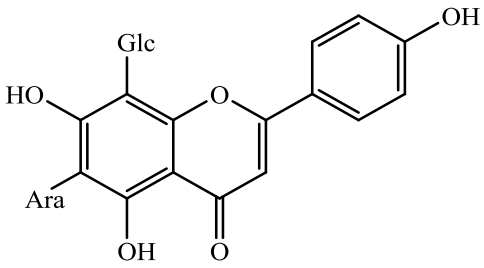
[**97**] Dimethyl malate: $R_1 = R_2$ = OMe

[**100**] Malic acid: $R_1 = R_2$ = OH

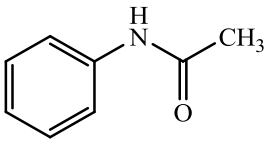


[**98**] Isopentyl butyrate

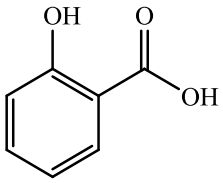
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



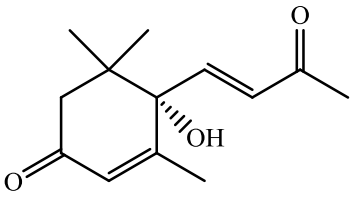
[**99**] Isoschaftoside



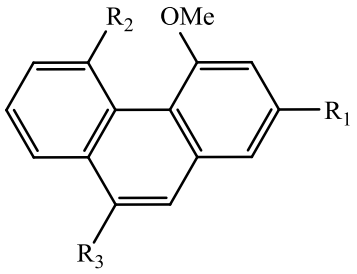
[**101**] *N*-phenylacetamide



[**103**] Salicylic acid

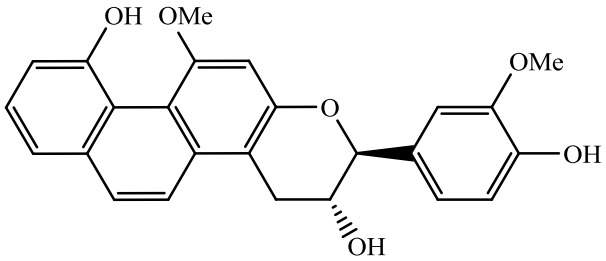


[**105**] Dehydrovomifoliol



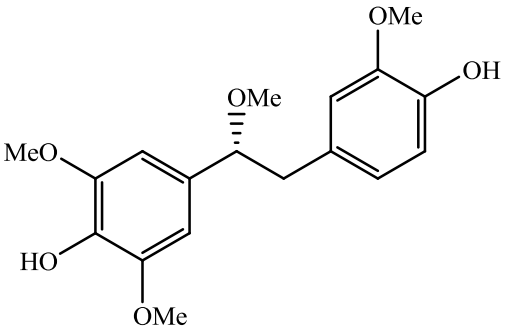
[**106**] 5-Hydroxy-2,4-dimethoxyphenanthrene:
R_1 = OMe, R_2 = OH, R_3 = H

[**107**] Loddigesiinol A: R_1 = OH, R_2 = OMe, R_3 = OH

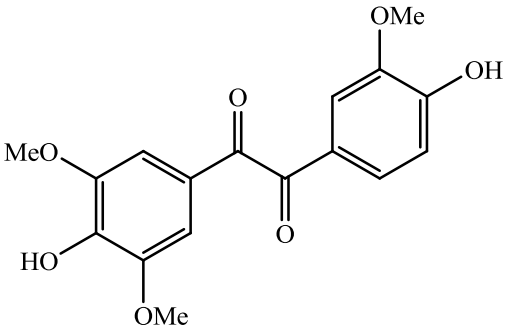


[**108**] Loddigesiinol B

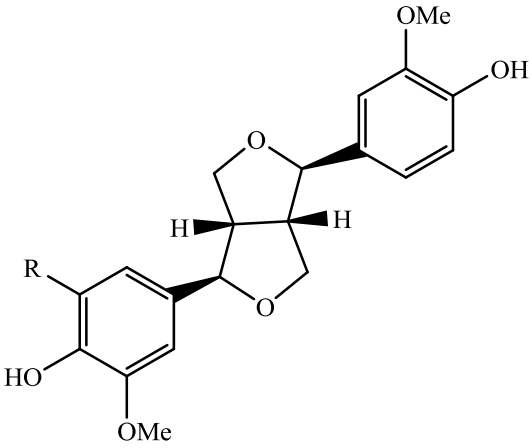
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



[**109**] Loddigesiinol C

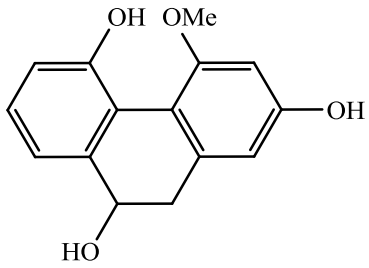


[**110**] Loddigesiinol D

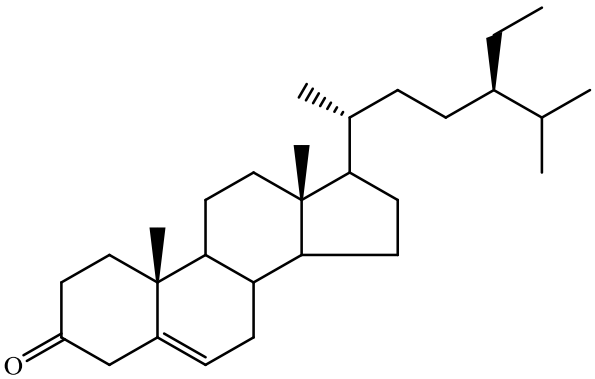


[**111**] (-)-Medioresinol: R = OMe

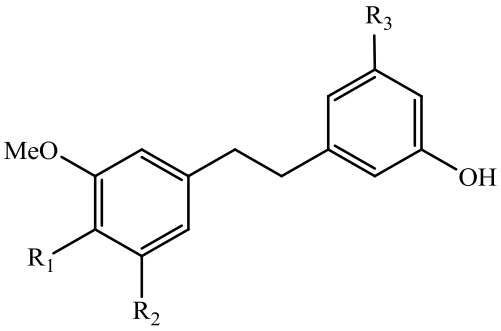
[**112**] (-)-Pinoresinol: R = H



[**113**] Rotundatin

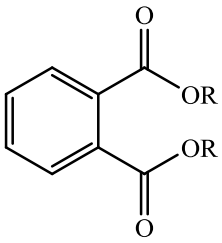


[**114**] Sitostenone

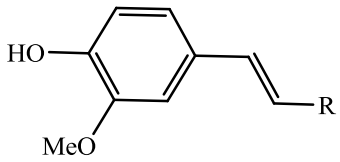


	R_1	R_2	R_3
[**115**] Aloifol I	OH	OMe	H
[**116**] Batatasin	H	H	OH

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

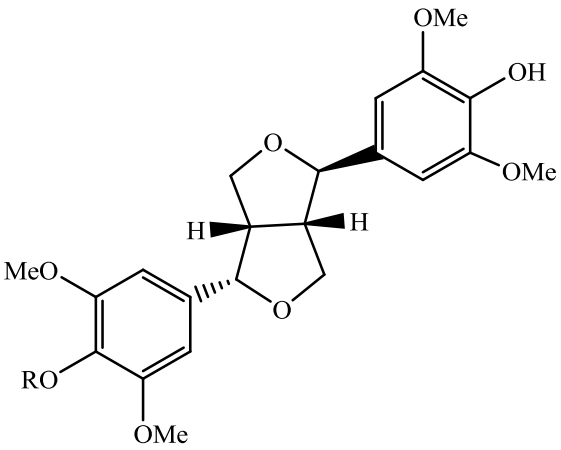


[**117**] Bis(2-ethylhexyl)phthalate:
R = $CH_2CH(C_2H_5)(CH_2)_3CH_3$



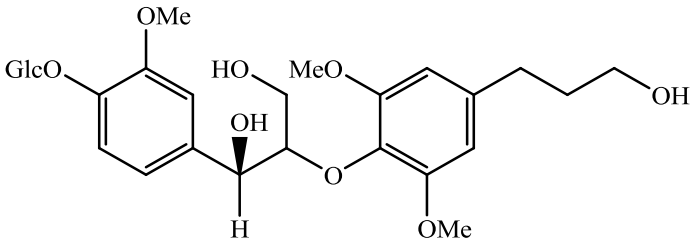
[**118**] *n*-Docosyl *trans*-ferulate:
R = $COOCH_2(CH_2)_{20}CH_3$

[**124**] Ferulaldehyde: R = CHO

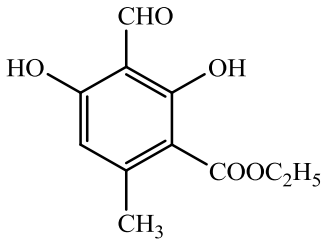


[**119**] Episyringaresinol: R = H

[**120**] Episyringaresinol 4′′-*O*-β-D-glucopyranoside: R = β-D-Glucose

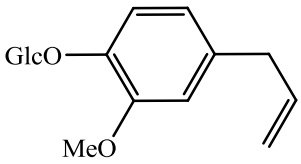


[**121**] Erythro-1-(4-*O*-β-D-glucopyranosyl-3-methoxy phenyl)-2-[4-(3-hydroxypropyl)-2,6-dimethoxy phenoxy]-1,3-propanediol

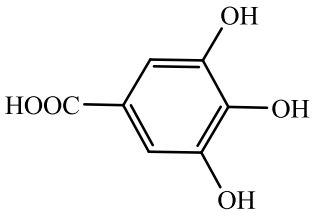


[**122**] Ethylhaematommate

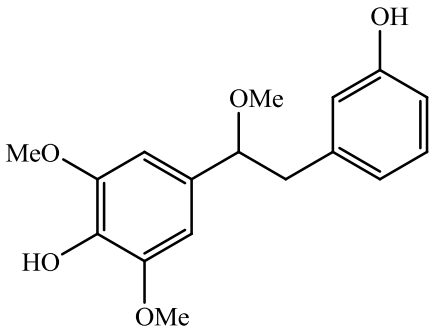
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



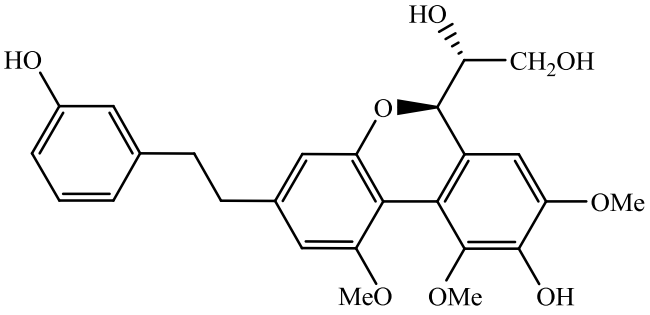
[**123**] Eugenyl -*O*-β-D-glucopyranoside



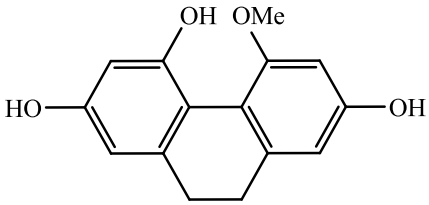
[**125**] Gallic acid



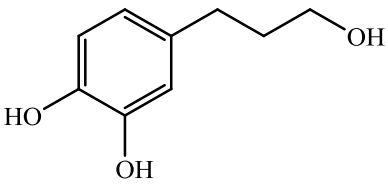
[**126**] 4-[2-(3-Hydroxyphenol)-1-methoxyl]-2,6-dimethoxyphenol



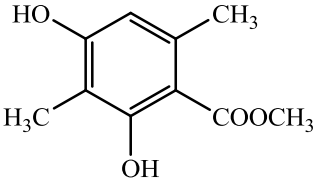
[**127**] Longicornuol A



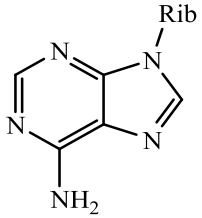
[**128**] 4-Methoxy-9,10-dihydro phenanthrene-2,5,7-triol



[**129**] 3-(3-Methoxy,4-hydroxyphenyl)-1-propanol

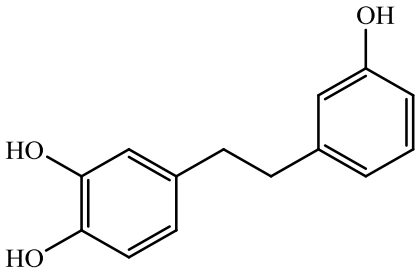


[**130**] Methyl β-orsellinate

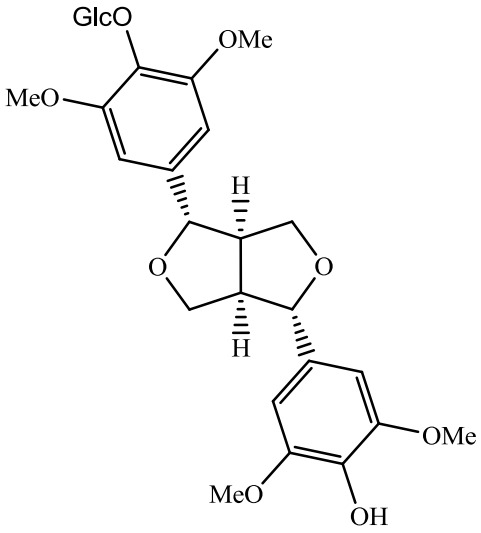


[**131**] 9-β-D-Ribofuranosyl -9H-purin-6-amine

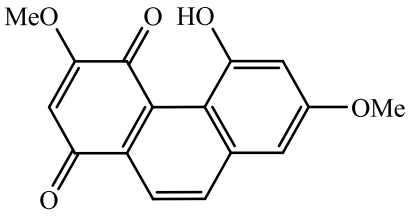
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



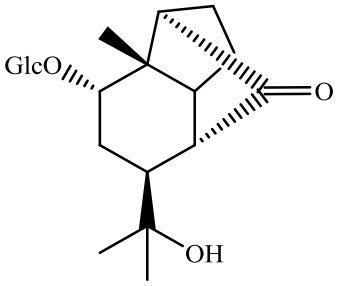
[**132**] 3,3′,4-Trihydroxybibenzyl



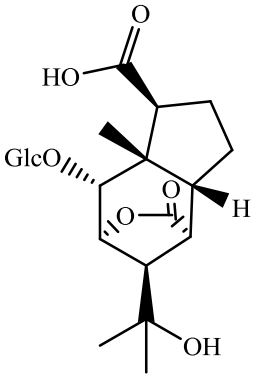
[**133**] Acanthoside B



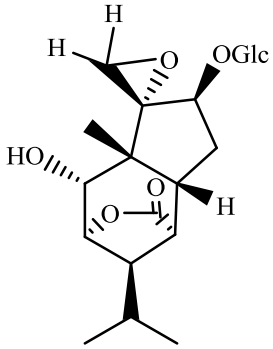
[**134**] Denbinobin



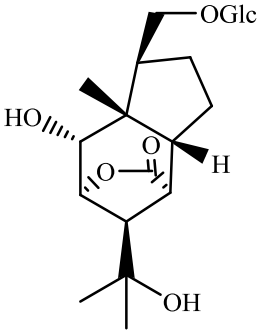
[**135**] Dendromoniliside A



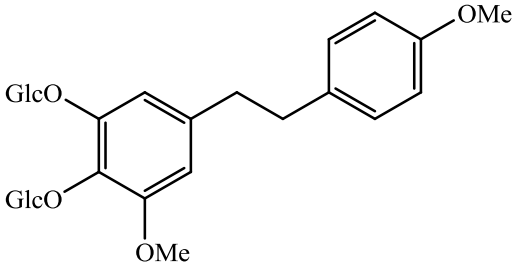
[**136**] Dendromoniliside B



[**137**] Dendromoniliside C

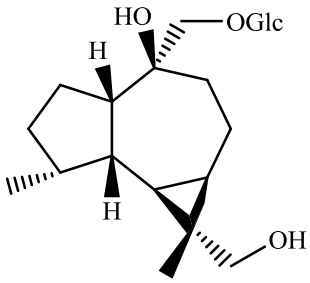


[**138**] Dendromoniliside D

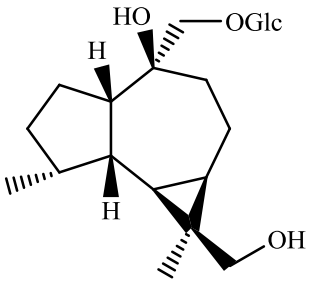


[**139**] Dendromonilisde E

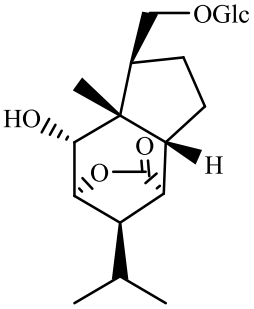
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



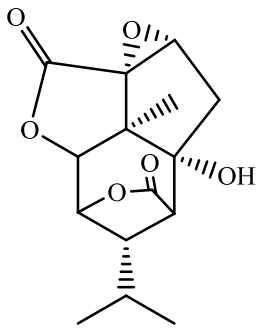
[**140**] Dendroside A



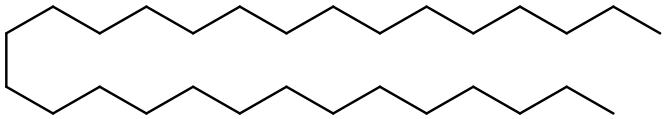
[**141**] Dendroside C



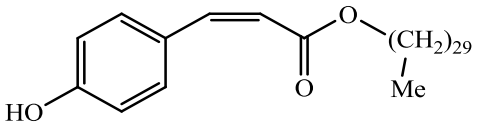
[**142**] Dendroside F



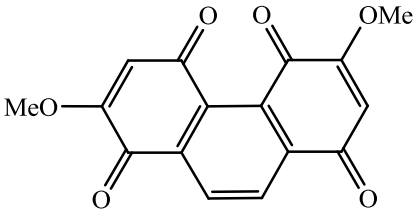
[**143**] α-Dihydropicrotoxinin



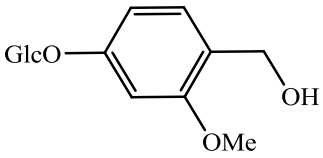
[**145**] *n*-Nonacosane



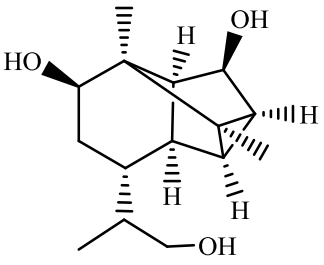
[**146**] *n*-Triacontyl *p*-hydroxy-cis-cinnamate



[**144**] Moniliformin

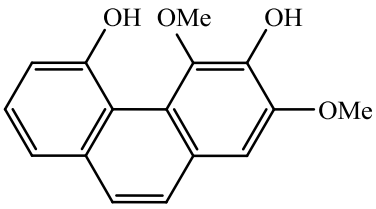


[**147**] Vanilloside

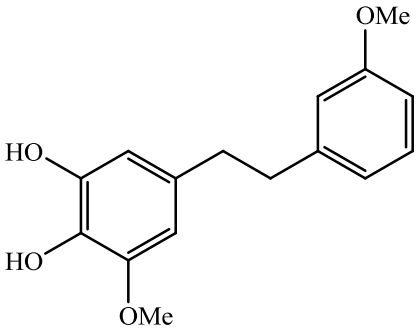


[**149**] Dendrobane A

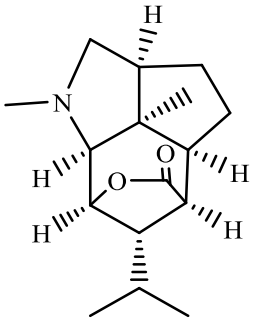
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



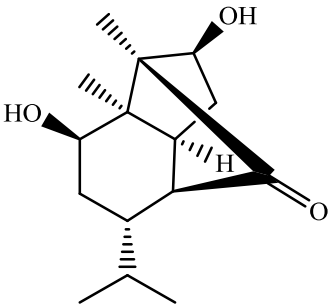
[**148**] Bulbophyllanthrin



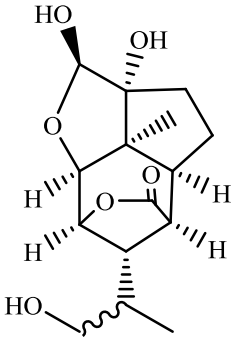
[**150**] Dendrobin A



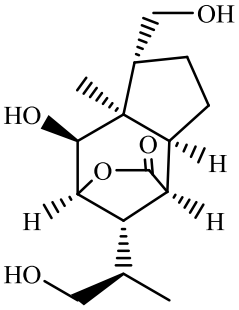
[**151**] Dendrobine



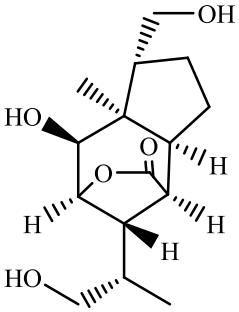
[**152**] Dendronobilin A



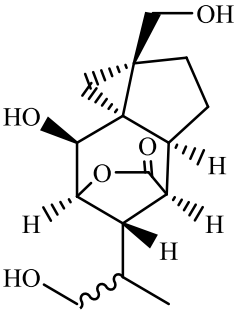
[**153**] Dendronobilin C



[**154**] Dendronobilin D

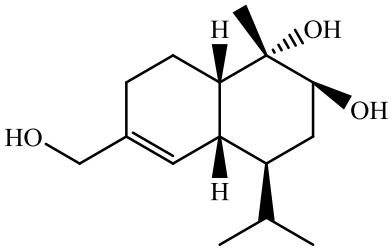


[**155**] Dendronobilin E

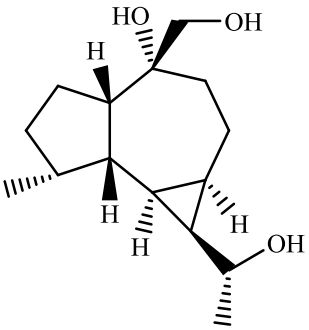


[**156**] Dendronobilin F

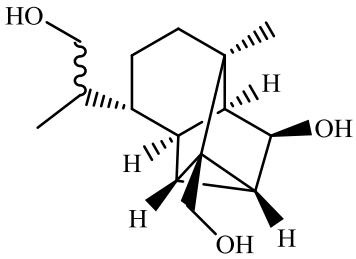
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



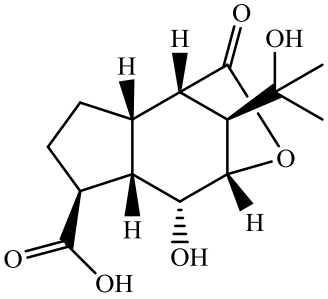
[**157**] Dendronobilin G



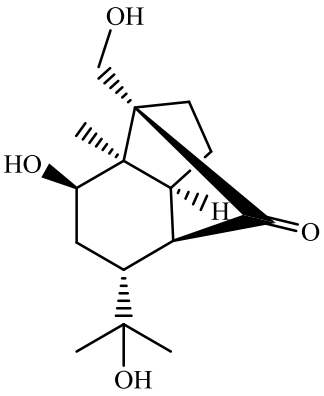
[**158**] Dendronobilin H



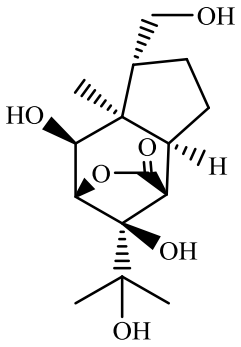
[**159**] Dendronobilin I



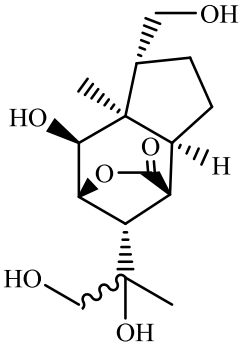
[**160**] Dendronobilin J



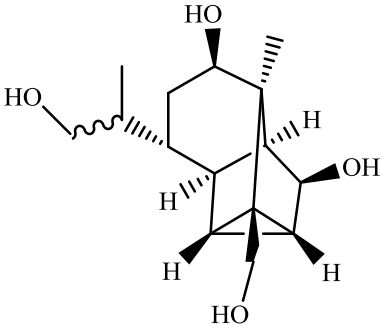
[**161**] Dendronobilin K



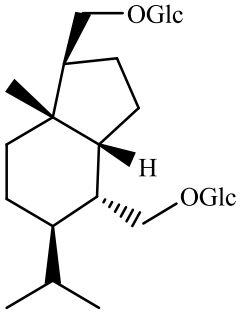
[**162**] Dendronobilin L



[**163**] Dendronobilin M

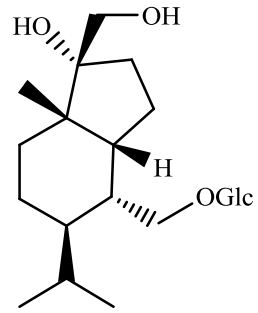


[**164**] Dendronobilin N

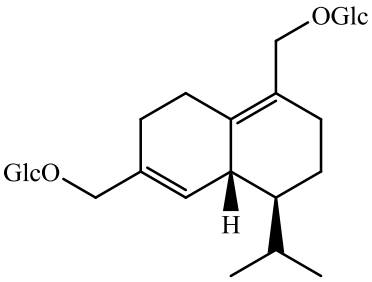


[**165**] Dendronobiloside A

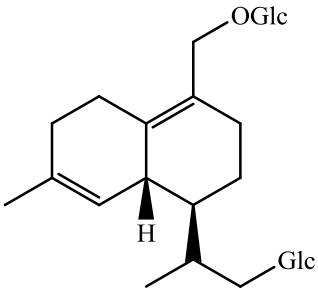
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



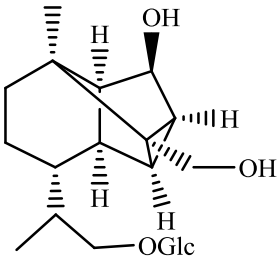
[**166**] Dendronobiloside B



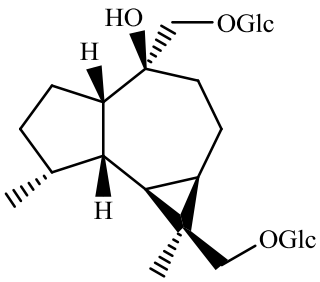
[**167**] Dendronobiloside C



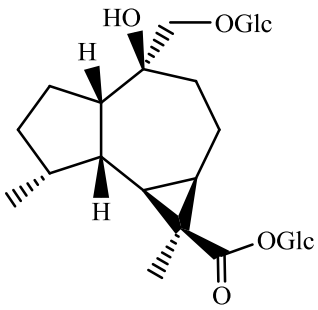
[**168**] Dendronobiloside D



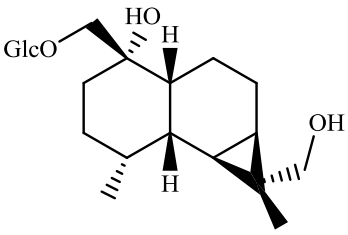
[**169**] Dendronobiloside E



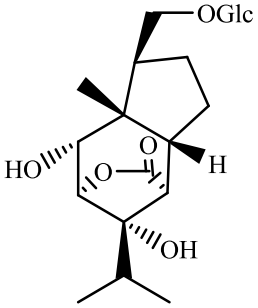
[**170**] Dendroside B



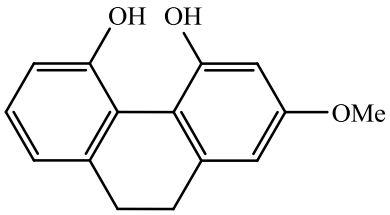
[**171**] Dendroside D



[**172**] Dendroside E

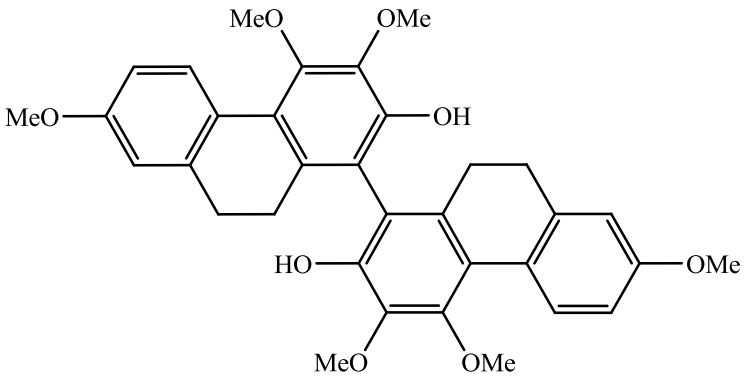


[**173**] Dendroside G

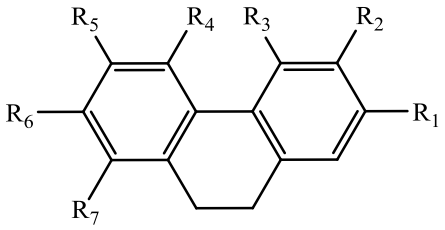


[**178**] 4,5-Dihydroxy-2-methoxy-9,10-dihydro phenanthrene

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

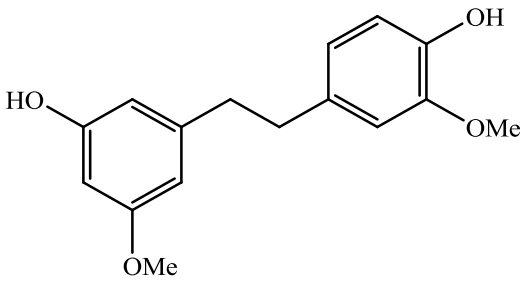


[**177**] 2,2′-Dihydroxy-3,3′,4,4′,7,7′-hexamethoxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene

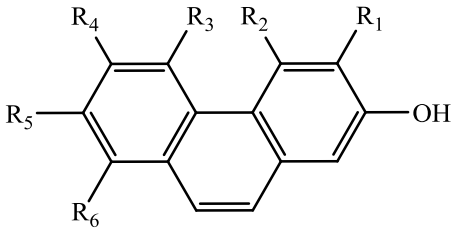


	R_1	R_2	R_3	R_4	R_5	R_6	R_7
[174] 4,5-Dihydroxy-3,7-dimethoxy-9,10-dihydrophenanthrene	H	OMe	OH	OH	H	OMe	H
[**179**] 2,8-Dihydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene	OH	OMe	OMe	H	H	OMe	OH
[**182**] Ephemeranthol A	OH	H	H	OH	OMe	OMe	H
[**183**] Ephemeranthol C	OH	OH	OMe	OH	H	H	H
[**184**] Erianthridin	OH	OMe	OMe	H	H	OH	H
[**187**] Flavanthridin	OH	H	H	OMe	OH	OMe	H

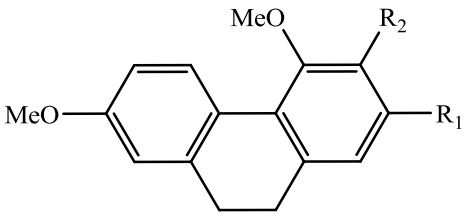
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



[**175**] 3,4′-Dihydroxy-5,5′-dimethoxydihydrostilbene

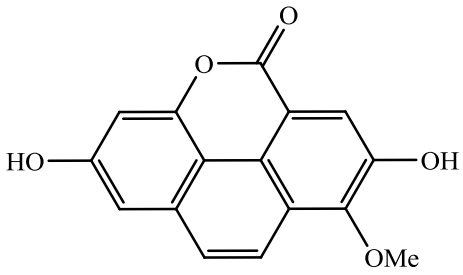


	R_1	R_2	R_3	R_4	R_5	R_6
[**176**] 2,5-Dihydroxy-3,4-dimethoxyphenanthrene	OMe	OMe	OH	H	H	H
[**180**] 2,8-Dihydroxy-3,4,7-trimethoxyphenanthrene	OMe	OMe	H	H	OMe	OH
[**181**] 5,7-Dimethoxy phenanthrene-2,6-diol	H	H	OMe	OH	OMe	H

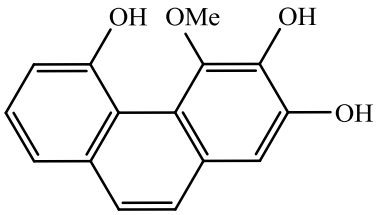


	R_1	R_2
[**189**] 2-Hydroxy-4,7-dimethoxy-9,10-dihydrophenanthrene	OH	H
[**192**] 2-Hydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene	OH	OMe
[**193**] 3-Hydroxy-2,4,7-trimethoxy-9,10-dihydrophenanthrene	OMe	OH

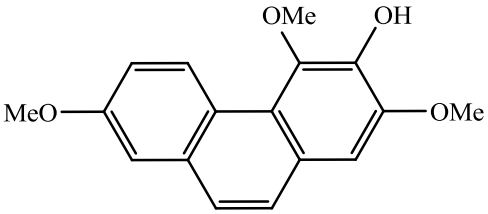
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



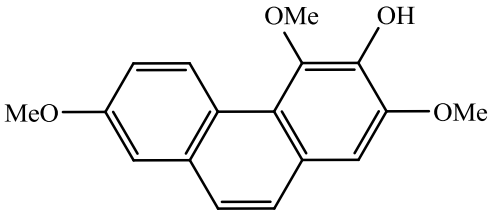
[**185**] Fimbiatone



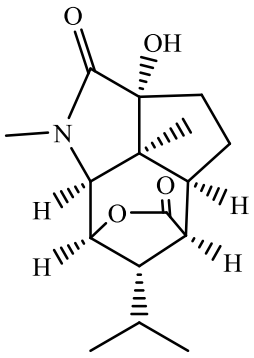
[**186**] Fimbriol B



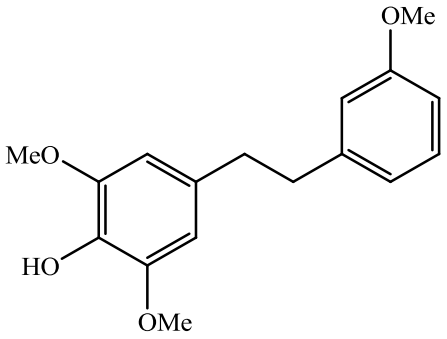
[**188**] Flavanthrinin



[**194**] 3-Hydroxy-2,4,7-trimethoxyphenanthrene

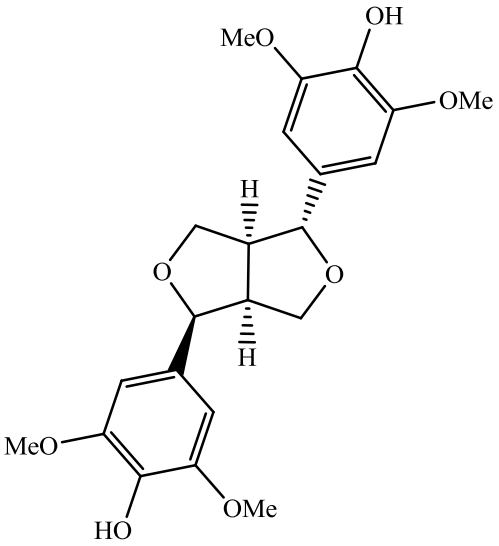


[**190**] 3-Hydroxy-2-oxodendrobine

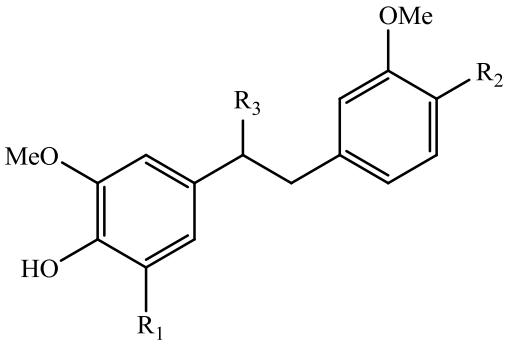


[**191**] 4-Hydroxy-3,5,3′-trimethoxybibenzyl

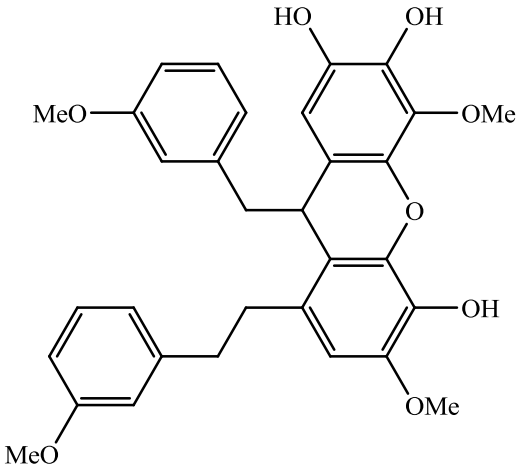
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



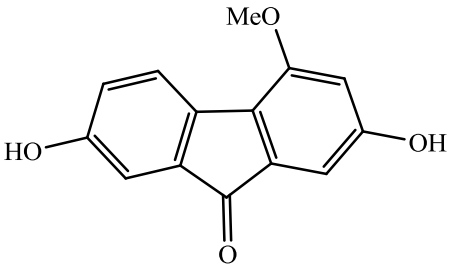
[**195**] Lirioresinol A



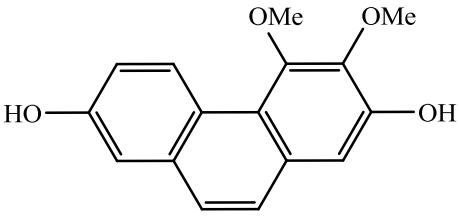
	R_1	R_2	R_3
[**196**] Nobilin A	OH	H	OMe
[**197**] Nobilin B	OMe	OH	OMe
[**198**] Nobilin C	OMe	OMe	OMe
[**199**] Nobilin D	OMe	OH	OH



[**200**] Nobilin E

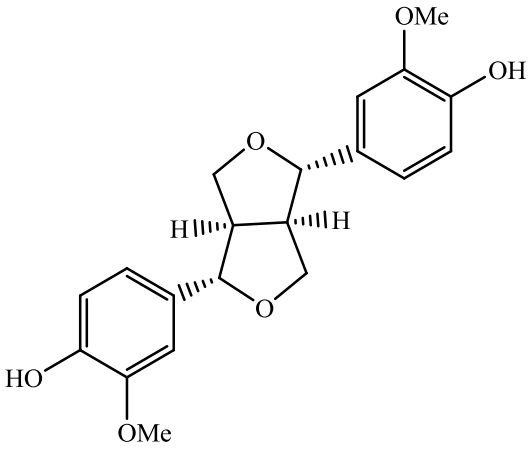


[**201**] Nobilone

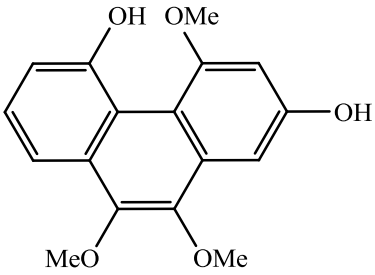


[**202**] Nudol

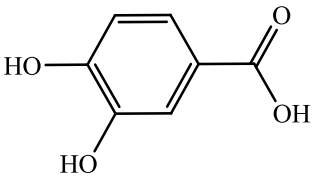
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



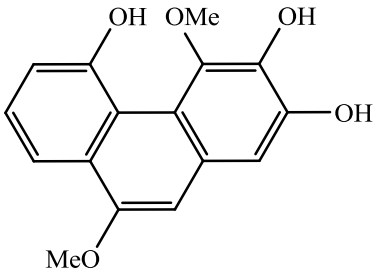
[**203**] Pinoresinol



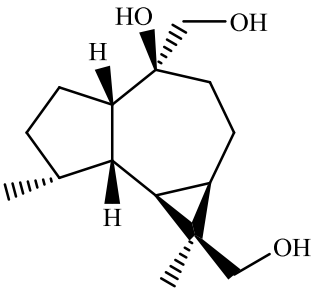
[**204**] Plicatol A



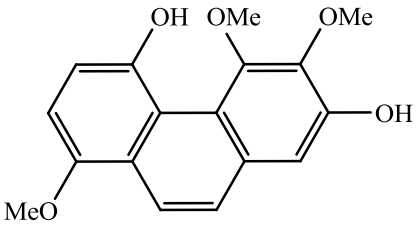
[**205**] Protocatechuic acid



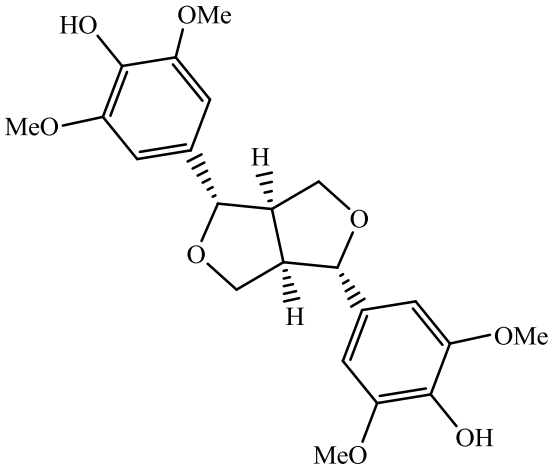
[**208**] 2,3,5-Trihydroxy-4,9-dimethoxyphenanthrene



[**207**] 10β,12,14-Trihydroxyalloaromadendrane

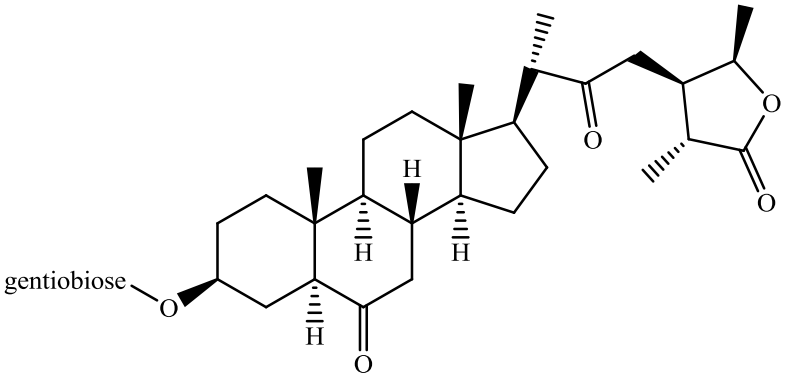


[**209**] 3,4,8-Trimethoxy phenanthrene-2,5-diol

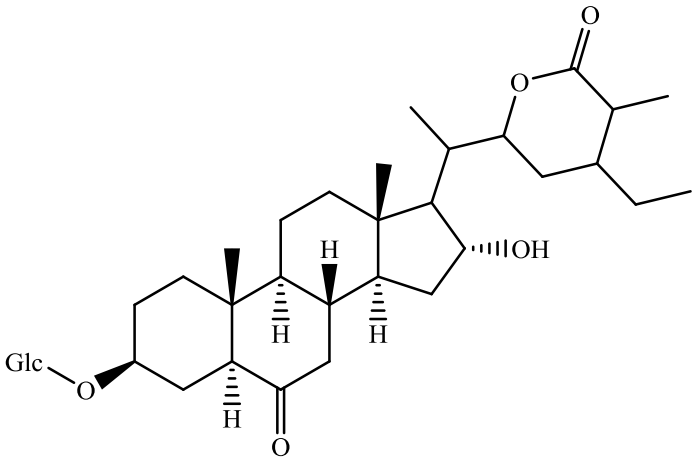


[**206**] Syringaresinol

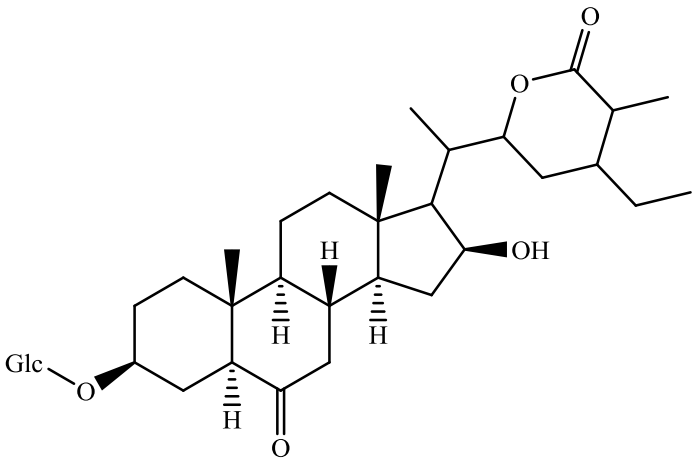
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



[**210**] Dendrosteroside

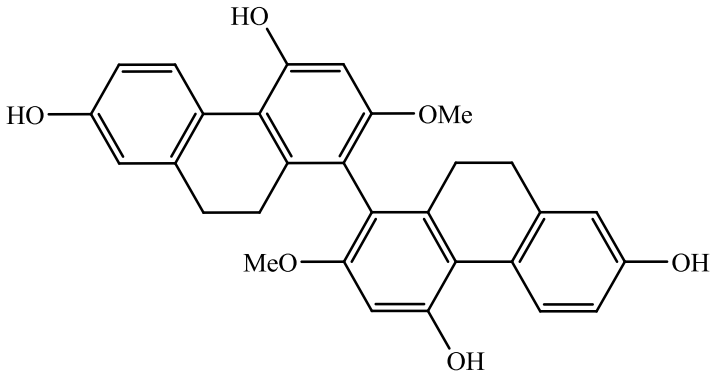


[**211**] Epi-ochreasteroside

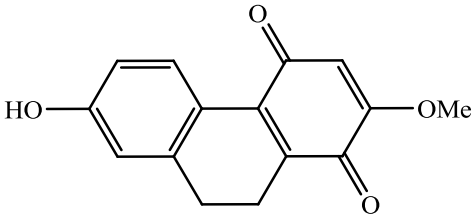


[**212**] Ochreasteroside

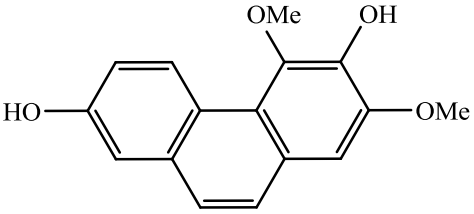
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



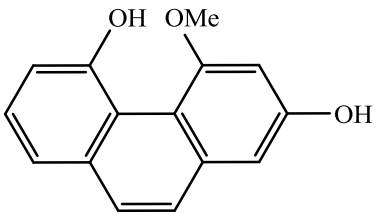
[**213**] 2,2′-Dimethoxy-4,4′,7,7′-tetrahydroxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene



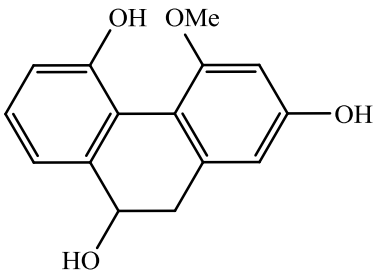
[**214**] Ephemeranthoquinone



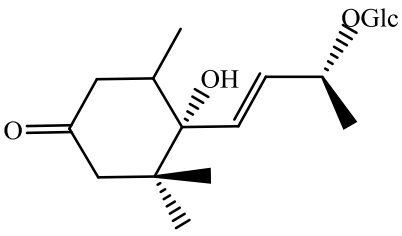
[**215**] Epheranthol B



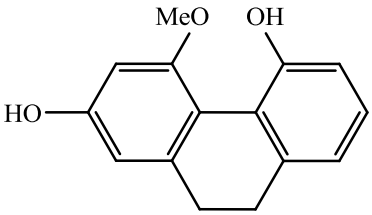
[**216**] Plicatol B



[**217**] Plicatol C

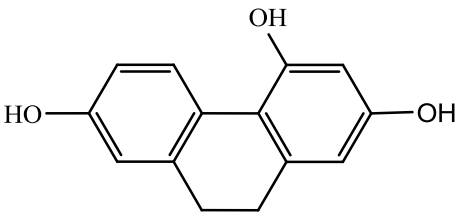


[**218**] Corchoionoside C

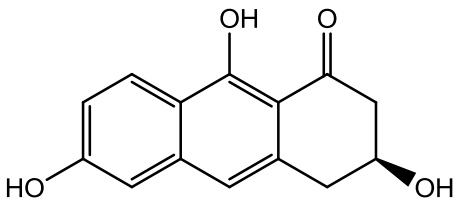


[**219**] 9,10-Dihydromoscatin

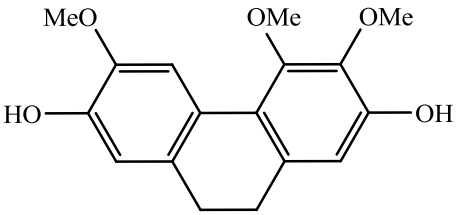
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



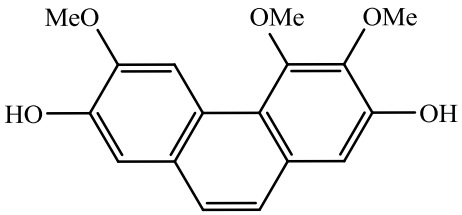
[**220**] 9,10-Dihydrophenanthrene-2,4,7-triol



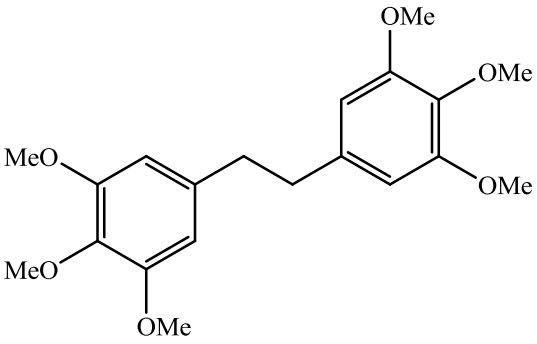
[**221**] 3,6,9-Trihydroxy-3,4-dihydroanthracen-1(2H)-one



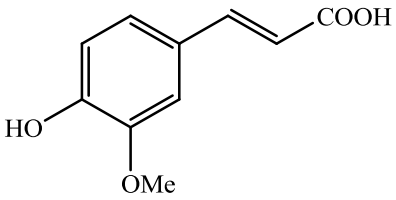
[**222**] 2,7-Dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene



[**223**] 2,7-Dihydroxy-3,4,6-trimethoxyphenanthrene

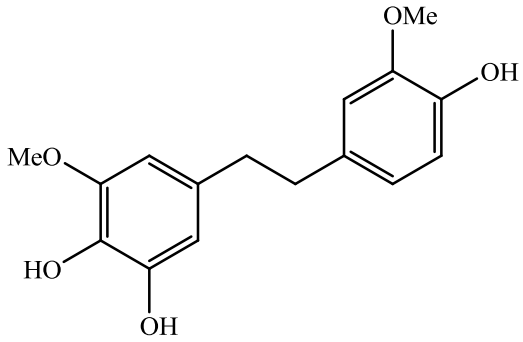


[**224**] Brittonin A

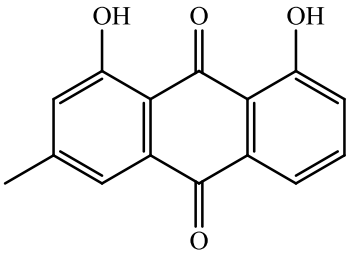


[**225**] Ferulic acid

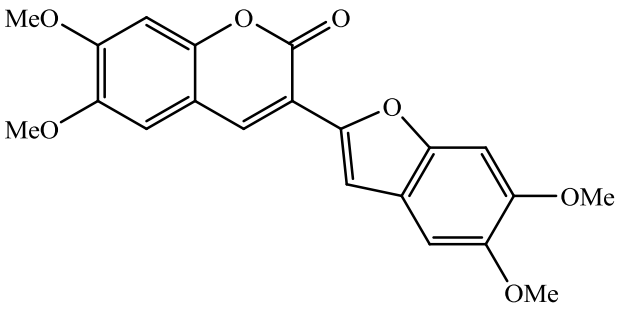
Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)



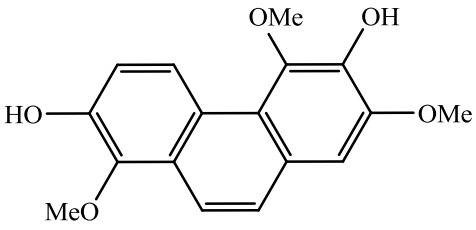
[**226**] 4,5,4′-trihydroxy-3-3′-dimethoxybibenzyl



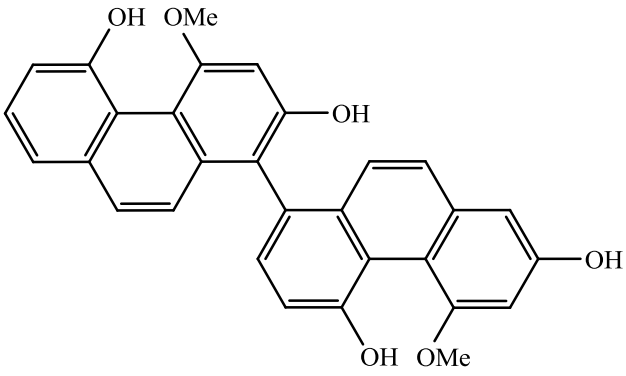
[**227**] Chrysophanol



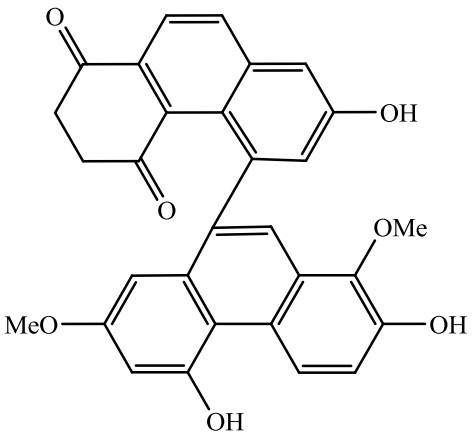
[**228**] Denthyrsin



[**229**] Denthyrsinin

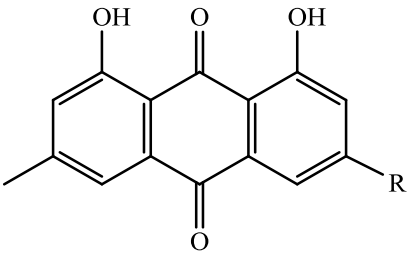


[**230**] Denthyrsinol



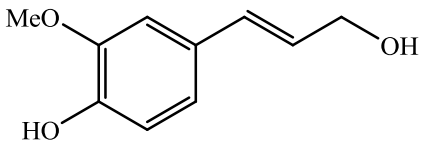
[**231**] Denthyrsinone

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

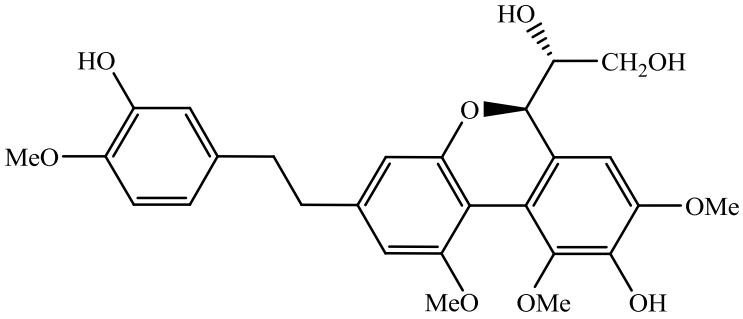


[**232**] Emodin: R = OH

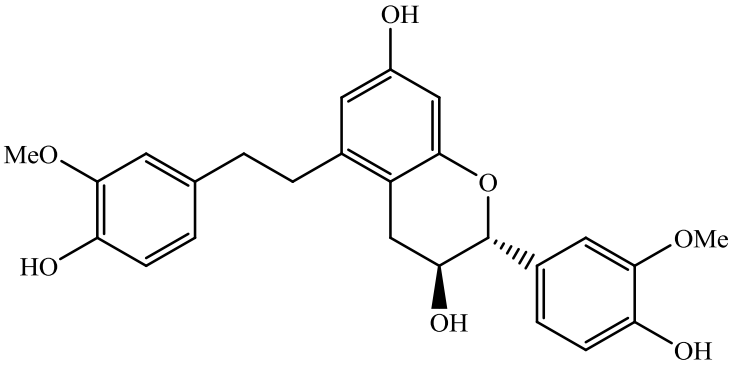
[**233**] Physcion: R = OMe



[**234**] 3-(4-Hydroxy-3-methoxyphenyl)-2-propen-1-ol



[**235**] Trigonopol A



[**236**] Trigonopol B

Figure 3 Structures of compounds previously isolated from *Dendrobium* species (continued)

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

Several plants in the genus *Dendrobium* have beautiful flowers and are widely cultivated as decorative plants. In China, these orchids are also used in traditional medicine to treat kidney, lung and stomach diseases, fever, red tongue, dry mouth, swelling, hyperglycaemia, atrophic gastritis and diabetes (Hossain, 2011). A well-known formulation, "Shi-Hu" (Herba Dendrobii), consists of dry or fresh stems of several *Dendrobium* species including *D. loddigesii*, *D. fimbriatum*, *D. chrysanthum*, *D. candidum* and *D. nobile*.

Several biological activities have been reported for plants in the genus *Dendrobium*, for example, cytotoxic, antioxidative, antiinflammatory, antiplatelet aggregation and spasmolytic properties.

Examples of cytotoxic compounds from *Dendrobium* plants are coelonin [**10**] and denbinobin [**134**] from *D. nobile*, which could inhibit the proliferation of hepatic stellate cell (HSCs-T6) (Yang *et al*., 2007). Denthyrsin [**228**] from *D. thyrsiflorum* exhibited cytotoxicity against several cancer cell lines including Hela, K-562, and MCF-7 (Zhang *et al*., 2005). The bibenzyl moscatilin [**8**], isolated from several plants of this genus, showed strong cytotoxicity against several cancer cell lines. In addition, this compound was able to induce apoptosis in colorectal cancer cell lines through tubulin depolymerization and DNA damage stress. These results led to the activation of C-Jun NH_2-terminal protein kinase (JNK) and mitochondria-involved intrinsic apoptosis pathway (Chen *et al*., 2008). Moscatilin also showed anti-angiogenic effect *in vitro* and *in vivo* by inhibiting angiogenic factor signaling pathways (Tsai *et al.*, 2010).

Phenanthrenes and bibenzyls, including gigantol [**14**], crepidatin [**21**], moscatin [**17**], moscatilin [**8**] and chrysotoxine [**19**], showed stronger antioxidative activity than BHA, which was used as the positive control, in the ferric thiocyanate assay (Zhang *et al*., 2007a). Moreover, in the DPPH scavenging and ORAC assays, crepidatin [**21**], chrysotoxine [**19**] and moscatilin [**8**] showed stronger activity than or equivalent to vitamin C (Ono *et al.*, 1995).

In the antiinflammation studies, it was found that moscatin [**17**], lusianthridin [**16**], hircinol [**77**] and coelonin [**10**] could inhibit the lipopolysaccharides-induced nitric oxide secretion from macrophage cells (RAW 264.7) (Hwang *et al*., 2010).

Furthermore, denbinobin [**134**] from *D. moniliforme* showed good inhibitory activity against tumour necrosis factor α (TNF-α) and prostaglandin E2 secretion in the same macrophage cell line and in N9 (murine microglial) cell line (Lin *et al*., 2001).

The antiplatelet effects of principles from *D. loddigesii* were studied on the aggregation of washed rabbit platelets induced by thrombin, arachidonic acid (AA), collagen, and platelet activating factor (PAF), and the results revealed that moscatilin [**8**] and moscatin [**17**] strongly inhibited both AA- and collagen induced platelet aggregations (Chen *et al*., 1994). Later, the active principles isolated from *D. densiflorum*, including gigantol [**14**], moscatilin [**8**], homoeriodictyol [**72**], scoparone [**73**] and scopoletin [**74**], were found to exhibit antiplatelet aggregation activity on rat platelets *in vitro* (Fan *et al*., 2001).

In the spasmolytic effect study of stilbenoids from *Nidema boothii* (Lindl.) Schltr. (Orchidaceae), bibenzyls, such as gigantol [**14**] and batatasin III [**9**] were shown to induce notable concentration-dependent inhibition of spontaneous contractions of the guinea-pig ileum by effect on nitrergic mechanism and inhibiting CaM-mediated processes (Romero *et al*., 2007).

CHAPTER III

EXPERIMENTAL

1. Source of plant materials

The whole plants of *Dendrobium capillipes* Rchb.f. and *Dendrobium secundum* (Blume) Lindl. (Family Orchidaceae) were purchased from Jatujak market. Botanical identification was done by Associate Professor Thatree Phadungcharoen through comparison of the specimens with authentic samples (BKF No. 114946 and 110498 for *D. capillipes* and *D. secundum*, respectively) at the Department of National Park, Wildlife and Plant Conservation, Ministry of Natural Resources and Environment. Voucher specimens (DC-082553 and DS/BS-092552) have been deposited at Department of Pharmacognosy and Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University.

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 (30-35^{o}C)
Detection	:	1. Ultraviolet light at wavelengths of 254 and 365 nm 2. Spraying with 0.5% anisaldehyde reagent (0.5 mL anisaldehyde, 10 mL glacial acetic acid, 85 mL methanol, 5 mL conc sulfuric acid) and heating at 105 ^{o}C for 10 min.

2.2 Column Chromatography

2.2.1 Vacuum liquid chromatography (VLC)

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 the adsorbent, triturated, dried and then gradually placed on top of the column.
Detection	:	Each fraction was determined by TLC under UV light at the wavelengths of 254 and 365 nm.

2.2.2 Flash column chromatography (FCC)

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 of the organic solvent, mixed with a small quantity of the adsorbent, triturated, dried and then gradually distributed 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	:	Suitable organic solvent was used as the eluent. Gel filter was suspended in the eluent, left standing about 24 hours prior to use and then poured into the column and allowed to set tightly.
Sample loading	:	The sample was dissolved in a small amount of the eluent and then gradually distributed on top of the column.

Detection : Fractions were determined in the same way as described in section 2.2.1

2.2.4 Ion exchange chromatography

Adsorbent : Diaion HP20SS (Mitsubishi Chemical Co.)

Packing method : The resin was suspended in methanol, then methanol was replaced with distilled water. The mixture was stirred and then allowed to stand for 10-15 min to give resin slurry. A small amount of deionized water was added to an empty column and the resin slurry was slowly poured into the column.

Sample loading : The sample was dissolved in a small amount of the eluent and then gradually distributed on top of the column.

Detection : Fractions were examined in the same way as described in section 2.2.1

2.3 Spectroscopy

2.3.1 Mass spectra

Mass spectra were recorded either on a Bruker microTOF or Micromass LCT mass spectrometer (National Center for Genetic Engineering and Biotechnology).

2.3.2 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).

2.3.3 Infrared (IR) spectra

IR spectra were obtained on a Perkin-Elmer FT-IR 1760X spectrophotometer (Scientific and Technology Research Equipment Center, 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 with 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 (500 MHz) (Scientific and Technology Research Equipment Center, Chulalongkorn University).

Deuterated solvents for NMR spectra were used, including deuterated chloroform ($CDCl_3$), deuterated methanol (CD_3OD), deuterated dimethyl sulfoxide (DMSO- d_6). Chemical shifts were reported in ppm scale using the chemical shift of the solvent as the reference signal.

2.4 Physical property

2.4.1 Optical rotations

Optical rotations were measured on a Perkin Elmer Polarimeter 341 (Pharmaceutical Research Instrument Center, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

2.5 Solvents

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

3. Extraction and isolation

3.1 *Dendrobium capillipes*

3.1.1 Extraction

The dried whole plants (1.7 kg) were chopped, powdered and then macerated with methanol (3×5L). The methanol extract was concentrated under vacuum to give 236 g of a crude extract.

3.1.2 Separation of methanol extract

Crude extract (236 g) was subsequently separated by vacuum liquid chromatography (VLC). The procedure was performed as described in section 2.2.1. Silica gel (No.7734, 700 g) was used as the stationary phase and a step gradient of *n*-hexane-EtOAc (100:0 to 0:100) and CH_2Cl_2-MeOH (19:1 to 0:100) as the mobile phase. The eluates, about 500 mL per fraction, were collected and examined by TLC (silica gel, *n*-hexane-EtOAc = 6:4) to yield forty-four fractions. Fractions with similar chromatographic patterns were combined to give seven fractions, including fractions 1 (329 mg), 2 (13.0 g), 3 (8.2 g), 4 (2.6 g), 5 (4.7 g), 6 (40.7 g), and 7 (81.0 g).

3.1.2.1 Isolation of compound DC1 (Chrysotobibenzyl)

Fraction 4 (2.6 g) was further separated by VLC on silica gel (No. 7734) with gradient elution of *n*-hexane-EtOAc (100:0 to 0:100). Sixty-one fractions were obtained and combined according to the similarity of their TLC patterns (silica gel, *n*-hexane-EtOAc = 8:2) to give thirteen fractions: 4A (86 mg), 4B (51 mg), 4C (15 mg), 4D (7 mg), 4E (19 mg), 4F (42 mg), 4G (8 mg), 4H (48 mg), 4I (171 mg), 4J (576 mg), 4K (601 mg), 4L (97 mg), and 4M (1.4 g).

Fraction 4J (576 mg) was separated by FCC using silica gel (No. 9385) as the stationary phase with isocratic elution (pet.ether-acetone = 4:1). Fractions with similar TLC patterns (silica gel, pet.ether-acetone = 4:1) were combined to yield five fractions: 4J1 (18 mg), 4J2 (95 mg), 4J3 (77 mg), 4J4 (246 mg), and 4J5 (18 mg).

Fraction 4J3 (77 mg) was purified on a Sephadex LH-20 column, eluted with acetone, to give compound DC1 as a yellowish powder (47 mg, R_f 0.4, silica gel, pet. ether-acetone = 7:3). It was identified as chrysotobibenzyl [**18**].

3.1.2.2 Isolation of compound DC2 (Crepidatin)

Fraction 4J4 (246 mg) was purified on a Sephadex LH-20 column, eluted with CH_2Cl_2-MeOH (1:1), to give compound DC2 as a brownish powder (209 mg, R_f 0.22, silica gel, pet. ether-acetone = 7:3). It was identified as crepidatin [**21**].

3.1.2.3 Isolation of compound DC3 (Gigantol)

Fraction 4L (97 mg) was purified by FCC on silica gel (No. 9385) with isocratic elution (CH_2Cl_2-acetone = 49:1) to give compound DC3 as a dark brown amorphous solid (34 mg, R_f 0.16, silica gel, pet. ether-acetone = 7:3). It was identified as gigantol [**14**].

3.1.2.4 Isolation of compounds DC4 (Chrysotoxine) and DC5 (Moscatilin)

Fraction 5 (4.7 g) was separated by VLC on silica gel (No. 7734) with gradient elution [*n*-hexane-EtOAc (100:0 to 0:100) and then CH_2Cl_2-MeOH (100:0 to 9:1)]. After combination of the fractions with similar TLC patterns, eleven fractions were obtained: 5A (4 mg), 5B (56 mg), 5C (672 mg), 5D (188 mg), 5E (35 mg), 5F (111 mg), 5G (972 mg), 5H (522 mg), 5I (897 mg), 5J (224 mg) and 5K (976 mg)

Fraction 5I (897 mg) was separated by FCC using silica gel (No. 9385) as the stationary phase with gradient elution (CH_2Cl_2-acetone = 49:1 to 17:3) to yield nine fractions: 5I1 (84 mg), 5I2 (283 mg), 5I3 (44 mg), 5I4 (109 mg), 5I5 (17 mg), 5I6 (20 mg), 5I7 (59 mg), 5I8 (21 mg), and 5I9 (201 mg).

Fraction 5I2 (283 mg) was purified on a Sephadex LH-20 column, eluted with acetone, to give compound DC4 as a yellowish powder (122 mg, R_f 0.24, silica gel, pet. ether-acetone = 7:3). It was identified as chrysotoxine [**19**]. The same fraction also gave compound DC5 as pale yellow needle crytals (117 mg, R_f 0.14, silica gel, pet. ether-acetone = 7:3). It was identified as moscatilin [**8**].

3.1.2.5 Isolation of compound DC6 (Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside, Lysimachiin)

Fraction 7 (50 g) was divided into two partions, and each partion was then separated on a Diaion HP20SS column with gradient elution [MeOH-H_2O (0:100 to 100:0) and then EtOAc-MeOH (0:100 to 100:0)] to give eleven fractions, including 7A (19.5 g), 7B (8.5 g), 7C (11.2 g), 7D (246 mg), 7E (1.0 g), 7F (325 mg), 7G (167 mg), 7H (247 mg), 7I (289 mg), 7J (212 mg), and 7K (3.2 g).

Fraction 7I (289 mg) was separated on a Sephadex LH-20 column (MeOH) to yield three fractions (7I1-7I3): 7I1 (150 mg), 7I2 (67 mg), and 7I3 (67 mg). Fraction 7I2 (67 mg) was purified by FCC (silica gel No.9385, EtOAc-MeOH-H_2O = 96:3:1) to give compound DC6 as a yellowish amorphous solid (47 mg, R_f 0.16, silica gel, EtOAc-MeOH-H_2O = 18:1:1). It was identified as kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside or lysimachiin [**238**].

3.1.2.6 Isolation of compound DC7 (Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside)

Fraction 7J (212 mg) was further separated on a Sephadex LH-20 column (MeOH) to yield six fractions: 7J1 (25 mg), 7J2 (19 mg), 7J3 (46 mg), 7J4 (24 mg), 7J5 (82 mg), and 7J6 (16 mg).

Fraction 7J4 (24 mg) was purified by FCC (silica gel No. 9385, EtOAc-MeOH-H_2O = 37:2:1) to give compound DC7 as a yellow powder (9 mg, R_f 0.12, silica gel, EtOAc-MeOH-H_2O = 18:1:1). It was identified as kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside) [**239**].

3.1.2.7 Isolation of compound DC8 (Quercetin-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside)

Fraction 7J6 (16 mg) was further purified by FCC (silica gel No.9385, EtOAc-MeOH-H_2O = 94:3:3) to give compound DC8 as a greenish yellow amorphous solid (4 mg, R_f 0.10, silica gel, EtOAc-MeOH-H_2O = 18:1:1). It was characterized as a new compound, named quercetin-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside) [**240**]**.**

3.2 *Dendrobium secundum*

A previous study reported four known compounds and one new compound from *D. secundum* (Sritularak *et al.*, 2011b). In this study, we conducted further investigation on unstudied fractions from this plant.

3.2.1 Extraction

The dried and powdered whole plants (1.6 kg) were macerated with MeOH (3×10 L). The MeOH extract was concentrated under vacuum to give a crude extract (206 g).

3.2.2 Separation of methanol extract

The methanol extract (206 g) was separated by VLC [silica gel, gradient of *n*-hexane-EtOAc (100:0 to 0:100) and then CH_2Cl_2-MeOH (19:1 to 0:100)]. The eluates were collected 500 mL per fraction and examined by TLC (silica gel, *n*-hexane-EtOAc = 7:3) to yield forty-four fractions. Fractions with similar TLC patterns were combined to yield eight fractions: A (176 mg), B (5.6 g), C (3.6 g), D (4.5 g), E (1.6 g), F (2.3 g), G (16.8 g), H (73.7 g).

3.2.2.1 Isolation of compound DS1 (5-Hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl)

Fraction F (2.3 g) was subjected to FCC on silica gel [*n*-hexane-EtOAc gradient (4:1 to 0:100)]. After the combination of fractions with similar TLC patterns, eleven fractions were obtained: F1 (22 mg), F2 (244 mg), F3 (230 mg), F4 (208 mg), F5 (381 mg), F6 (118 mg), F7 (238 mg), F8 (298 mg), F9 (41 mg), F10 (146 mg), and F11 (39 mg).

Fraction F5 (381 mg) was further separated on a Sephadex LH-20 column (CH_2Cl_2-MeOH = 1:1) to give five fractions: F5a (6 mg), F5b (9 mg), F5c (35 mg), F5d (313 mg), and F5e (23 mg). Fraction F5d (313 mg) was further subjected to repeated FCC over silica gel (CH_2Cl_2-acetone = 49:1) to give compound DS1 as a white powder (61.0 mg, R_f 0.6, silica gel, CH_2Cl_2-acetone = 9:1). It was characterized as a new compound named 5-hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl [**241**].

3.2.2.2 Isolation of compound DS2 (Kaempferol-3,7-*O*-di-α-L-rhamnopyranoside)

Fraction H (30.0 g) was separated on a Diaion HP20SS column [MeOH-H_2O (0:100 to 100:0) and then EtOAc-MeOH (0:100 to 100:0)] to give thirteen fractions: H1 (2.0 g), H2 (400 mg), H3 (147 mg), H4 (625 mg), H5 (382 mg), H6 (191 mg), H7 (469 mg), H8 (355 mg), H9 (124 mg), H10 (2.3 g), H11 (452 mg), H12 (167 mg), and H13 (266 mg).

Fraction H7 (469 mg) was then subjected to FCC over silica gel (EtOAc-MeOH-H_2O = 48:1:1) to give ten fractions: H7a (5 mg), H7b (16 mg), H7c (8 mg), H7d (3 mg), H7e (33 mg), H7f (39 mg), H7g (21 mg), H7h (17 mg), H7i (77 mg), and H7j (250 mg).

Fraction H7e (33 mg) was purified on a Sephadex LH-20 column (MeOH) to afford compound DS2 as a yellow powder (8 mg, R_f 0.20, silica gel, EtOAc-MeOH-H_2O = 18:1:1). It was identified as kaempferol-3,7-*O*-di-α-L-rhamnopyranoside [**242**].

3.2.2.3 Isolation of compound DS3 (Quercetin-3-*O*-α-L-rhamnopyranoside)

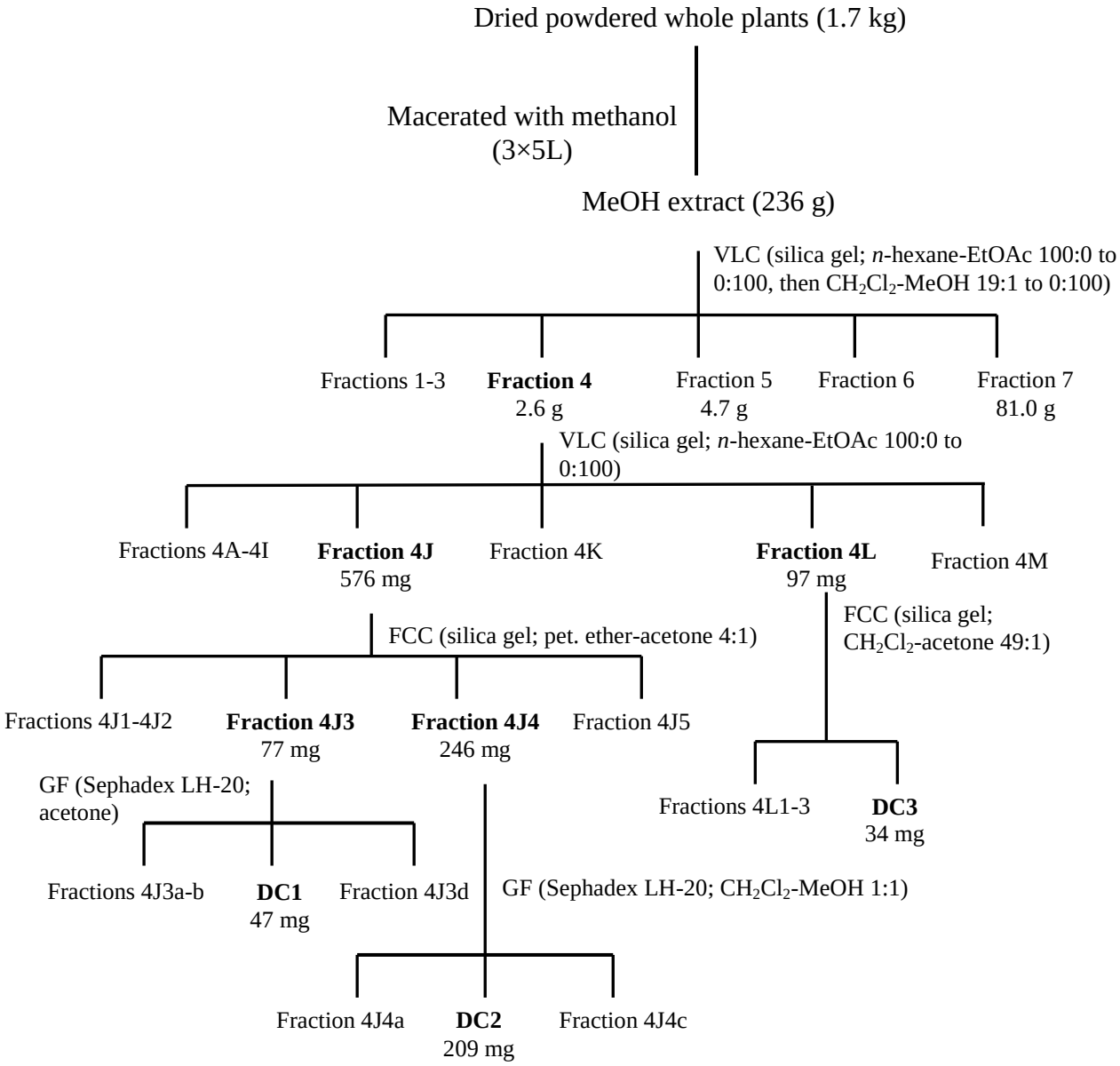
Fraction H7f (39 mg) was purified by FCC (silica gel; CH_2Cl_2-acetone = 4:1) to give three fractions: H7f1 (18 mg), H7f2 (14 mg), and H7f3 (4 mg).

Fraction H7f2 (14 mg) was further purified on a Sephadex LH-20 column (MeOH) to give compound DS3 as a greenish amorphous solid (3 mg, R_f 0.29, silica gel, EtOAc-MeOH-H_2O = 18:1:1). It was identified as quercetin-3-*O*-α-L-rhamnopyranoside [**243**].

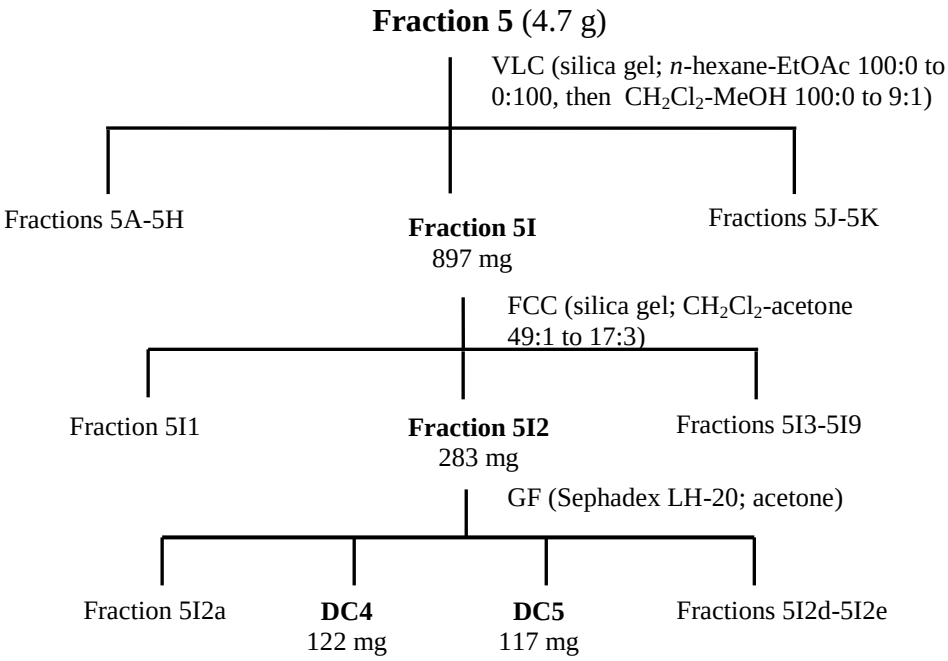
3.2.2.4 Isolation of compound DS4 (Kaempferol-3-*O*-α-L-rhamnopyranoside)

Fraction H8 (355 mg) was subjected to FCC over silica gel (CH_2Cl_2-acetone = 4:1 to 2:3) to give four fractions: H8a (4 mg), H8b (31 mg), H8c (39 mg), and H8d (251 mg).

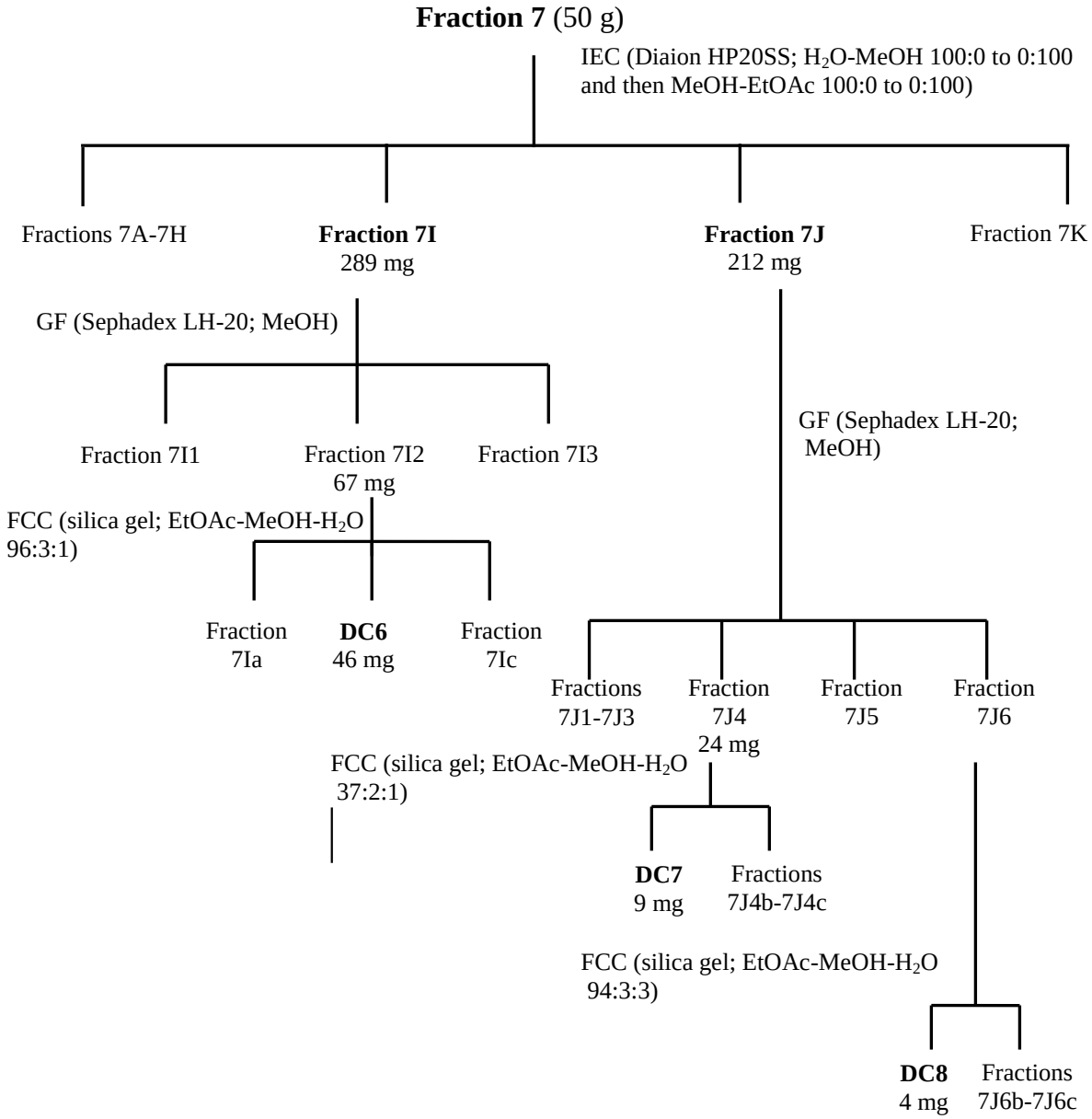
Fraction H8c (39 mg) was purified on a Sephadex LH-20 column (MeOH) to yield compound DS4 as a greenish amorphous solid (3 mg, R_f 0.38, silica gel, EtOAc-MeOH-H_2O = 18:1:1). It was identified as kaempferol-3-*O*-α-L-rhamnopyranoside [**244**].



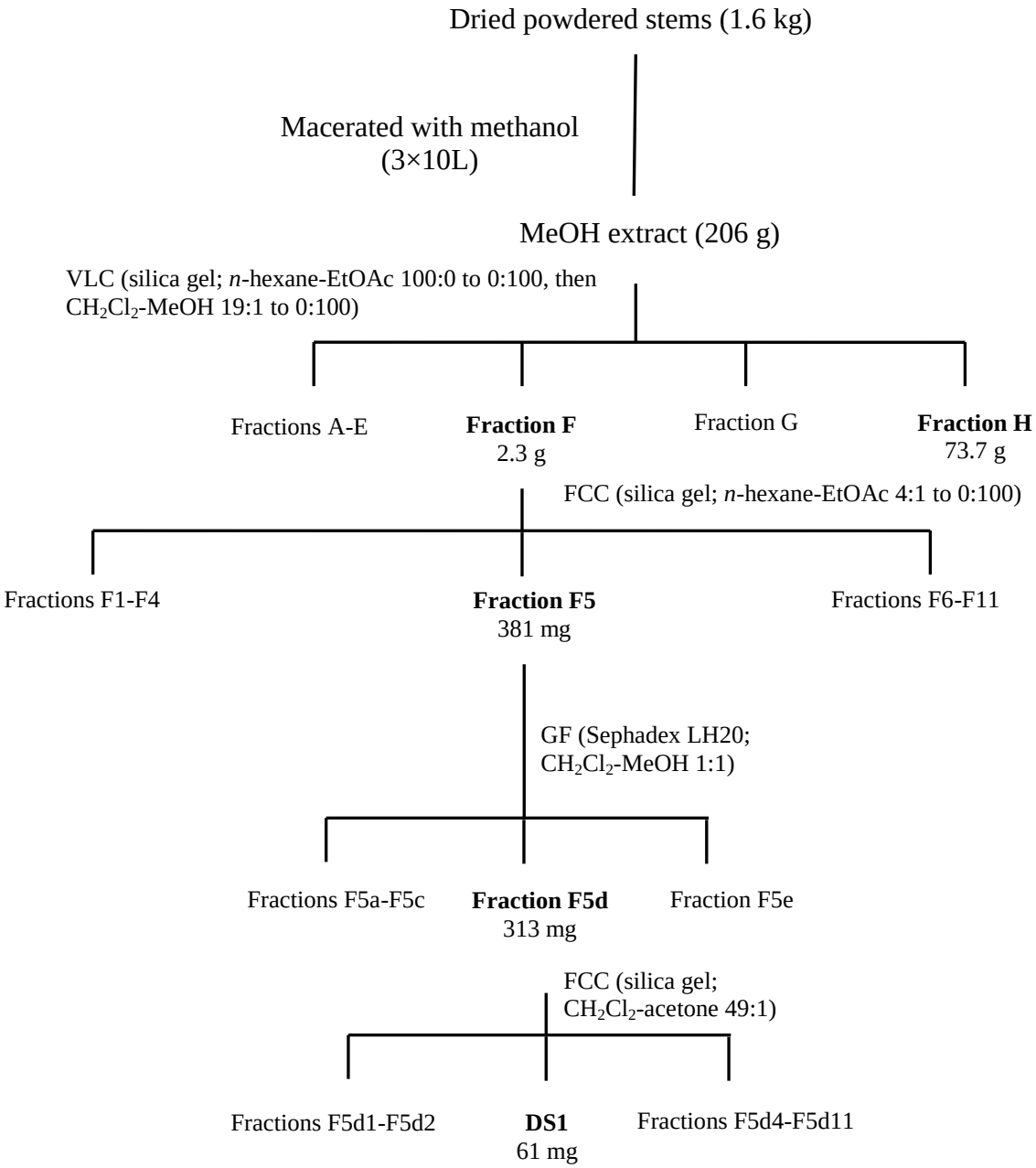
Scheme 1 Separation of the MeOH extract of *Dendrobium capillipes*



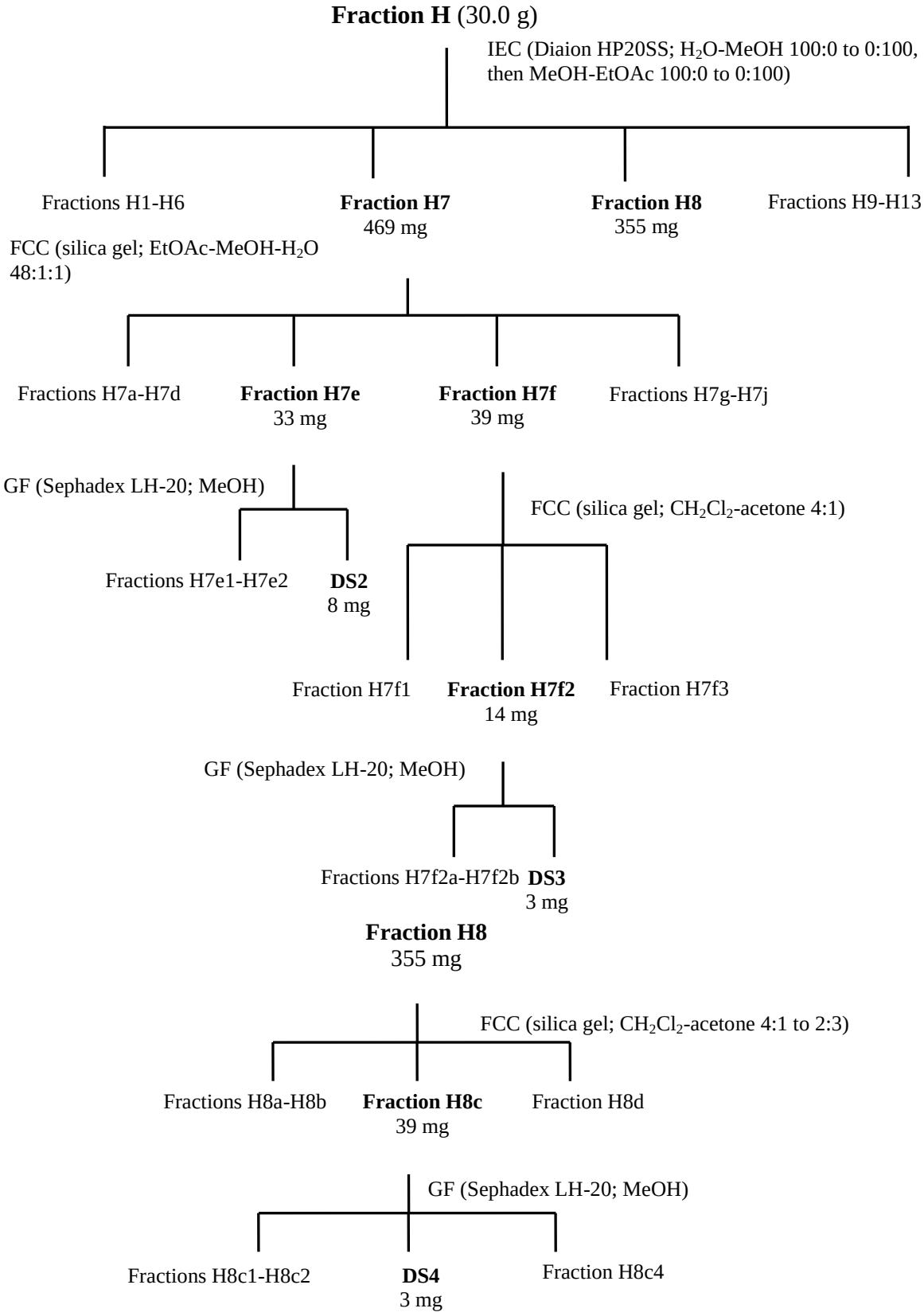
Scheme 1 Separation of the MeOH extract of *Dendrobium capillipes* (continued)



Scheme 1 Separation of the MeOH extract of *Dendrobium capillipes* (continued)



Scheme 2 Separation of the MeOH extract of *Dendrobium secundum*



Scheme 2 Separation of the MeOH extract of *Dendrobium secundum* (continued)

4. Acid hydrolysis of compound DC8

Compound DC8 (3 mg) was dissolved in 2N HCl (2 mL) and refluxed at 100 °C for 3h. After removal of the solvent, the hydrolysate was redissolved in H_2O (10 mL) and extracted with EtOAc (3×10 mL). The residue obtained from the aqueous layer after evaporation of the solvent was redissolved in methanol to give a sample solution. This sample and standards of the sugars L-arabinose, D-xylose and L-rhamnose were examined on a normal phase TLC plate, with $CHCl_3$-MeOH-H_2O (5:4:1) as the mobile phase. To visualize the spots, the TLC plate was sprayed with 0.5% anisaldehyde solution, followed by heating at 100° for 2 min.

5. Physical and spectral data of isolated compounds

5.1 Compound DC1 (Chrysotobibenzyl)

Compound DC1 was obtained as a yellowish powder, soluble in CH_2Cl_2 (47 mg, 2.8×10^{-3} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 332.87; Figure 5

FT-IR **:** υ_{max} cm^{-1}: 1589, 1510, 1463, 1232, 1128; Figure 6

UV **:** λ_{max} nm (log ε), in methanol: 214 (4.41), 280 (3.51); Figure 7

^{1}H NMR **:** δ ppm, 300 MHz, in $CDCl_3$; see Table 2, Figure 8

^{13}C NMR **:** δ ppm, 75 MHz, in $CDCl_3$; see Table 2, Figure 9

5.2 Compound DC2 (Crepidatin)

Compound DC2 was obtained as a brownish powder, soluble in CH_2Cl_2 (209 mg, 1.2×10^{-2} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 318.86; Figure 10

FT-IR **:** υ_{max} cm^{-1}: 3358, 1592, 1513, 1466, 1242, 1124; Figure 11

UV **:** λ_{max} nm (log ε), in methanol: 214 (4.25), 276 (3.30); Figure 12

^{1}H NMR **:** δ ppm, 300 MHz, in $CDCl_3$; see Table 3, Figure 13

^{13}C NMR **:** δ ppm, 75 MHz, in $CDCl_3$; see Table 3, Figure 14

5.3 Compound DC3 (Gigantol)

Compound DC3 was obtained as a dark brown amorphous solid, soluble in CH_2Cl_2 (34 mg, 2.0×10^{-3} % based on dried weight of whole plants).

ESI-MS : $[M+H]^+$ ion at *m/z* 274.88; Figure 15

FT-IR : υ_{max} cm^{-1}: 3412, 1613, 1598, 1515, 1461, 1272, 1150; Figure 16

UV : λ_{max} nm (log ε), in methanol: 210 (4.24), 281 (3.46); Figure 17

^{1}H NMR : δ ppm, 300 MHz, in $CDCl_3$; see Table 4, Figure 18

^{13}C NMR : δ ppm, 75 MHz, in $CDCl_3$; see Table 4, Figure 19

5.4 Compound DC4 (Chrysotoxine)

Compound DC4 was obtained as a yellowish powder, soluble in CH_2Cl_2 (122 mg, 7.2×10^{-3} % based on dried weight of whole plants).

ESI-MS : $[M+H]^+$ ion at *m/z* 318.85; Figure 20

FT-IR : υ_{max} cm^{-1}: 3462, 1608, 1515, 1461, 1236, 1111; Figure 21

UV : λ_{max} nm (log ε), in methanol: 213 (4.14), 279 (3.22); Figure 22

^{1}H NMR : δ ppm, 300 MHz, in $CDCl_3$; see Table 5, Figure 23

^{13}C NMR : δ ppm, 75 MHz, in $CDCl_3$; see Table 5, Figure 24

5.5 Compound DC5 (Moscatilin)

Compound DC5 was obtained as a pale yellow needle crystals, soluble in CH_2Cl_2 (117 mg, 6.9×10^{-3} % based on dried weight of whole plants).

ESI-MS : $[M+H]^+$ ion at *m/z* 304.86; Figure 25

FT-IR : υ_{max} cm^{-1}: 3429, 1613, 1516, 1468, 1217, 1114; Figure 26

UV : λ_{max} nm (log ε), in methanol: 215 (4.42), 282 (3.66); Figure 27

^{1}H NMR : δ ppm, 300 MHz, in $CDCl_3$; see Table 6, Figure 28

^{13}C NMR : δ ppm, 75 MHz, in $CDCl_3$; see Table 6, Figure 29

5.6 Compound DC6 (Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside, Lysimachiin)

Compound DC6 was obtained as a yellowish amorphous solid soluble in MeOH (47 mg, 5.4×10^{-4} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 565.16; Figure 30

FT-IR **:** υ_{max} cm^{-1}: 3399, 1658, 1609, 1507, 1449, 1205, 1178; Figure 31

UV **:** λ_{max} nm (log ε), in methanol: 215 (4.18), 267 (4.19), 346 (4.11); Figure 32

^{1}H NMR **:** δ ppm, 300 MHz, in DMSO-d_6; see Table 8, Figure 33

^{13}C NMR **:** δ ppm, 75 MHz, DMSO-d_6; see Table 8, Figure 34

$[\alpha]^{20}_D$ **:** - 123.7° (c 0.000477, MeOH)

5.7 Compound DC7 (Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside)

Compound DC7 was obtained as a yellow powder, soluble in MeOH (9 mg, 2.5×10^{-4} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 595.18; Figure 35

FT-IR **:** υ_{max} cm^{-1}: 3428, 1656, 1610, 1507, 1450, 1209, 1177; Figure 36

UV **:** λ_{max} nm (log ε), in methanol: 215 (4.12), 266 (4.11), 346 (4.03); Figure 37

^{1}H NMR **:** δ ppm, 300 MHz, in CD_3OD; see Table 9, Figure 38

^{13}C NMR **:** δ ppm, 75 MHz, in CD_3OD; see Table 9, Figure 39

$[\alpha]^{20}_D$ **:** - 112.7° (c 0.000142, MeOH)

5.8 Compound DC8 (Quercetin-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside)

Compound DC8 was obtained as a greenish yellow amorphous solid, soluble in MeOH (4 mg, 2.7×10^{-3} % based on dried weight of whole plants).

HR-ESI-MS **:** $[M+Na]^+$ ion at *m/z* 603.1388 (calcd. for $C_{26}H_{28}O_{15}Na$ 603.1326); Figure 40

FT-IR **:** υ_{max} cm^{-1}: 3349, 1660, 1607, 1504, 1446, 1200, 1125; Figure 41

UV **:** λ_{max} nm (log ε), in methanol: 215 (4.30), 256 (4.27), 346 (4.17); Figure 42

^{1}H NMR **:** δ ppm, 500 MHz, in DMSO-d_6; see Table 10, Figure 43

^{13}C NMR **:** δ ppm, 125 MHz, in DMSO-d_6; see Table 10, Figure 44

$[\alpha]^{20}_D$ **:** - 67.6° (c 0.000370, MeOH)

5.9 Compound DS1 (5-Hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl)

Compound DS1 was obtained as a white powder, soluble in CH_2Cl_2 (61 mg, 3.8×10^{-3} % based on dried weight of whole plants).

HR-ESI-MS **:** $[M+Na]^+$ ion at *m/z* 371.1469 (calcd. for $C_{19}H_{24}O_6Na$ 371.1471); Figure 47

FT-IR **:** υ_{max} cm^{-1}: 3416, 1591, 1461, 1349, 1238; Figure 48

UV **:** λ_{max} nm (log ε), in methanol: 215 (4.46), 266 (3.19); Figure 49

^{1}H NMR **:** δ ppm, 300 MHz, in $CDCl_3$; see Table 11, Figure 50

^{13}C NMR **:** δ ppm, 75 MHz, in $CDCl_3$; see Table 11, Figure 51

5.10 Compound DS2 (Kaempferol-3,7-*O*-di-α-L-rhamnopyranoside)

Compound DS2 was obtained as a yellow powder, soluble in MeOH (8 mg, 5.0×10^{-4} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 579.16; Figure 53

FT-IR **:** υ_{max} cm^{-1}: 3400, 1659, 1604, 1513, 1448, 1208, 1178; Figure 54

UV **:** λ_{max} nm (log ε), in methanol: 222 (4.02), 266 (4.09), 345 (3.96); Figure 55

^{1}H NMR **:** δ ppm, 300 MHz, in CD_3OD; see Table 12, Figure 56

^{13}C NMR **:** δ ppm, 75 MHz, in CD_3OD; see Table 12, Figure 57

$[\alpha]^{20}_D$ **:** - 100° (c 0.000271, MeOH)

5.11 Compound DS3 (Quercetin-3-*O*-α-L-rhamnopyranoside)

Compound DS3 was obtained as a greenish amorphous solid, soluble in MeOH (3 mg, 1.9×10^{-4} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 449.10; Figure 58

FT-IR **:** υ_{max} cm^{-1}: 3270, 1657, 1602, 1510, 1446, 1200, 1170; Figure 59

UV **:** λ_{max} nm (log ε), in methanol: 222 (4.15), 256 (4.21), 349 (4.08); Figure 60

^{1}H NMR **:** δ ppm, 300 MHz, in CD_3OD; see Table 13, Figure 61

^{13}C NMR **:** δ ppm, 75 MHz, in CD_3OD; see Table 13, Figure 62

$[\alpha]^{20}_D$ **:** - 107.8° (c 0.000552, MeOH)

5.12 Compound DS4 (Kaempferol-3-*O*-α-L-rhamnopyranoside)

Compound DS4 was obtained as a greenish amorphous solid, soluble in MeOH (3 mg, 1.9×10^{-4} % based on dried weight of whole plants).

ESI-MS **:** $[M+H]^+$ ion at *m/z* 433.12 ; Figure 63

FT-IR **:** υ_{max} cm^{-1}: 3334, 1656, 1609, 1510, 1454, 1209, 1176; Figure 64

UV **:** λ_{max} nm (log ε), in methanol: 224 (4.10), 266 (4.12), 345 (3.95); Figure 65

^{1}H NMR **:** δ ppm, 300 MHz, in DMSO-d_6; see Table 14, Figure 66

^{13}C NMR **:** δ ppm, 75 MHz, in DMSO-d_6; see Table 14, Figure 67

$[\alpha]^{20}_D$ **:** - 88.2° (c 0.000171, MeOH)

6. Determination of cytotoxicity

The cytotoxicity evaluations in this study were done by the Bioassay Laboratory, National Center for Genetic Engineering and Biotechnology (BIOTEC).

6.1 Cancer cell growth inhibition

The cytotoxicity assay against three cancerous human-cell lines, including KB (oral epidermal carcinoma), NCI-H187 (lung cancer) cells and MCF-7 (breast cancer) cells. The test was performed using resazurin microplate assay method (REMA) (Brien *et al.*, 2000), with ellipticine, doxorubicin and tamoxifen as positive controls, whereas 0.5% DMSO was used as negative control. The samples were diluted to 50 μg/mL for maximum final test concentration. The protocols are as follows:

1. Cells at a logarithmic growth phase were harvested and diluted to 7×10^4 cells/mL for KB and 9×10^4 cells/mL for MCF-7 and NCI-H187 cell lines in fresh medium.

2. Successively, 5 μL of test sample diluted in 5% DMSO, and 45 μL of cell suspension were added to 384-well plates, incubated at 37°C in 5% CO_2 incubator.

3. After incubation period (3 days for KB and MCF-7, and 5 days for NCI-H187), 12.5 μL of 62.5 μg/mL resazurin solution was added to each well, and the plate were then incubated at 37°C for 4 hours.

4. Fluorescence signal was measured using SpectraMax M5 multi-detection microplate reader (Molecular Devices, USA) at the excitation and emission wavelengths of 530 nm and 590 nm, respectively. Percent inhibition of cell growth was calculated using the following equation:

$$\% \text{ Inhibition} = [1-(FU_T/FU_C) \times 100]$$

whereas, FU_T and FU_C are the mean fluorescent unit from treated and untreated conditions, respectively. Dose response curves were plotted from 6 concentrations of 2-fold serially diluted test compounds and the sample concentrations that inhibit cell growth by 50% (IC_{50}) can be derived using the SOFTMax Pro software (Molecular Devices, USA).

The criteria of interpretation are shown below:

Inactive = % inhibition < 50

Active (reported as IC_{50} value) = % inhibition ≥ 50

6.2 Cytotoxic against primate cell line

The cytotoxicity assay against normal cell (Vero cell) was evaluated using Green fluorescence protein (GFP) based assay. The drug, ellipticine, and 0.5% DMSO were used as positive and negative controls, respectively. The samples were diluted to 50 μg/mL for maximum final test concentration. The protocols are as follows:

1. The GFP-expressing Vero cell line was generated in-house by stably transfecting the African green monkey cell line (Vero, ATCC CCL-81), with pEGFP-N1 plasmid (Clontech). The cell line was maintained in minimal essential medium supplemented with 10% heat-activated fetal bovine serum, 2 mM L- glutamine, 1 mM sodium pyruvate, at 37 °C in a humidified incubator with 5% CO_2.

2. The assay was carried out by adding 45 mL of cell suspension at 3.3×10^4 cells/mL to each well plates containing 5 μL of test compounds previously diluted in 0.5% DMSO, and then incubating for 4 days at 37 °C incubator with 5% CO_2.

3. Fluorescence signal was measured by using SpectraMax M5 microplate reader (Molecular Devices, USA) in the bottom reading mode with excitation and emission wavelengths of 485 nm and 535 nm. Fluorescence signal at day 4 was

subtracted with background fluorescence at day 0. The percentage of cytotoxic was calculated using the following equation, where FU_T and FU_C represent the fluorescence units of cells treated with test compound and untreated cells, respectively.

$$\% \text{ cytotoxicity} = [1-(FU_T/FU_C) \times 100]$$

IC_{50} values are derived from dose-response curves, using 6 concentrations of 2-fold serially diluted samples, by the SOFTMax Pro software (Molecular Devices, USA).

The criteria of interpretation are shown below:

Non-cytotoxic = % cell growth > 50

Cytotoxic (IC_{50} included) = % cell growth $\leq$ 50

CHAPTER IV

RESULTS AND DISCUSSION

In this study, the dried and powdered whole plants of *Dendrobium capillipes* (1.7 kg) was macerated with methanol to give a crude extract which showed a positive result for inhibiting KB cancer cells with an IC_{50} value of 16.67 μg/mL. The extract was separated by vacuum liquid chromatography to yield seven fractions. Fractions 4 and 5 showed cytotoxicity against KB cell line (74.86 and 74.93% inhibition at 50 μg/mL, respectively), and were chromatographed to give five pure compounds [**DC1-DC5**]. An inactive fraction, Fraction 7, was also separated to give three pure compounds [**DC6-DC8**]. In addition, chemical re-examination of *D. secundum* led to the isolation of four polyphenolic compounds [**DS1-DS4**]. The structures of these compounds were characterized by spectroscopic means, including UV, IR, NMR and MS. In addition, they were evaluated for their cytotoxicity against three types of cancer cells.

1. Structure characterization of isolated compounds

1.1 Structure determination of compound DC1

Compound DC1 was obtained as a yellowish powder. The ESI mass spectrum (Figure 5) showed a pseudomolecular ion $[M+H]^+$ at *m/z* 332.87, suggesting the molecular formula $C_{19}H_{24}O_5$**.** The IR spectrum (Figure 6) showed absorption peaks at 1589, 1510, 1463, 1232, 1128 cm^{-1}, indicating the presence of the aromatic rings and C-O stretching of ether functionality. The UV spectrum (Figure 7) of this compound showed maximal absorptions at 214 and 280 nm**,** characteristic of bibenzyl skeleton (Zhang *et al*., 2008a).

The NMR data (Figures 8 and 9, and Table 2) showed a characteristic proton signal for a bibenzyl structure at δ_H 2.82 (4H, br s, α,α′) which could be correlated to the carbon signals at δ_C 37.5 and 38.5. Moreover, the ^{1}H NMR spectrum showed four signals (5H) in the aromatic region at δ_H 6.77 (1H, d, *J* = 8.4 Hz, H-5), 6.69 (1H, br d, *J* = 8.4 Hz, H-6), 6.64 (1H, br s, H-2) and 6.34 (2H, s, H-2′ and H-6′). These spectral

properties indicated the presence of five substituents on the two aromatic rings, with one ring symmetrically substituted.

There were five methoxyl groups which appeared as singlets at δ_H 3.79, 3.81 and 3.83 (15H, 3,4,3′,4′,5′-OMe) in the ^{1}H NMR spectrum. The structure was confirmed by the ^{13}C NMR spectrum (Figure 9) which exhibited sixteen peaks, including ten peaks for twelve aromatic carbons, two peaks for two methylene carbons and four peaks for five methoxyl groups. The four peaks representing five methoxyl groups resonated at δ_C 55.7, 55.8, 55.9 and 60.7 ppm. It should be noted that the 4′-OMe carbon had the highest chemical shift when compared with the other methoxyl groups in the molecule. This signal is the characteristic peak when ring B has two identical substituents (methoxyl or hydroxyl group) on the *o*-positions of the 4′-OMe group.

By comparing the ^{1}H NMR, ^{13}C NMR, UV, IR and molecular formula of this compound with previously published data (Bi *et al*., 2001; Li *et al*., 2011), compound DC1 was identified as chrysotobibenzyl [**18**].

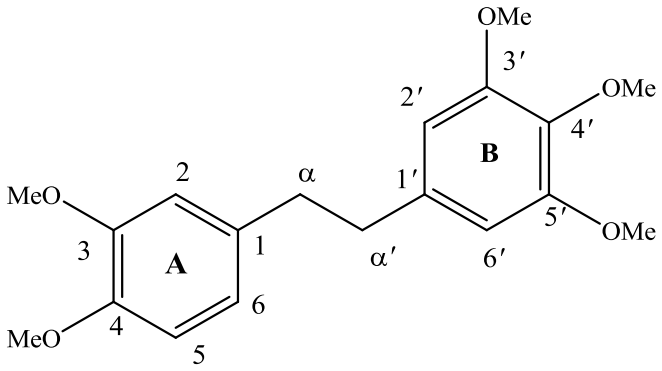
Chrysotobibenzyl was also named aloifol II dimethyl ether and amoenylinin, found in several plants in genus *Dendrobium*, including *D. aurantiacum* var. *denneanum, D. chrysanthum, D. chryseum, D. chrysotoxum, D. fimbriatum* and *D. nobile* (Ma *et al*., 1998; Yang *et al*., 2006a; Yang *et al.*, 2006b; Bi *et al*., 2001; Li *et al*., 2011).

Table 2 NMR spectral data of compound DC1 (in $CDCl_3$) and chrysotobibenzyl (in $CDCl_3$)

Position	Compound DC1		Chrysotobibenzyl[a]	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	-	134.2	-	134.3
2	6.64 (br s)	112.0	6.66 (d , 1.85)	112.0
3	-	148.7	-	148.8
4	-	147.3	-	147.4
5	6.77 (d, 8.4)	111.3	6.80 (d, 8.4)	111.3
6	6.69 (br d, 8.4)	120.3	6.72 (dd, 8.4, 1.85)	120.4
α	2.82 (br s)	37.5*	2.85 s	37.6*
α′	2.82 (br s)	38.5*	2.85 s	38.5*
1′	-	137.4	-	137.5
2′	6.34 s	105.5	6.37 s	105.6
3′	-	153.0	-	153.1
4′	-	136.2	-	136.3
5′	-	153.0	-	153.1
6′	6.34 s	105.5	6.37 s	105.6
3-OMe	3.81 s	55.7	3.84 s	55.8
4-OMe	3.83 s	55.8	3.86 s	56.0
3′,5′-OMe	3.79 s	55.9	3.82 s	56.1
4′-OMe	3.79 s	60.7	3.82 s	60.8

*Values are exchangeable within vertical column.

[a] ^{1}H NMR data from Li *et al*., 2011. ^{13}C NMR data from Bi *et al*., 2001.



Chrysotobibenzyl [**18**]

1.2 Structure determination of compound DC2

Compound DC2 was obtained as a brownish powder. Its ESI mass spectrum (Figure 10) showed a pseudomolecular ion $[M+H]^+$ at *m/z* 318.86, suggesting the molecular formula $C_{18}H_{22}O_5$**.**

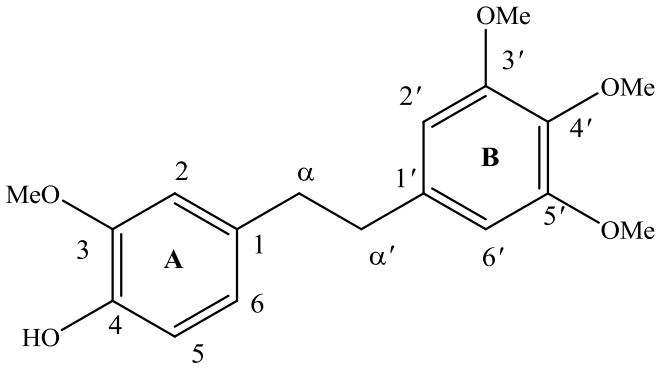
The IR spectrum (Figure 11) showed absorption bands at 3358 cm^{-1} for hydroxyl group, at 1592, 1513, 1466 cm^{-1} for aromatic ring and at 1242, 1124 cm^{-1} for C-O stretching of ether group. Its UV spectrum (Figure 12) was similar to that of compound DC1, showing absorption maxima at λ_{max} 214 and 276 nm. The ^{1}H NMR data showed a characteristic bibenzyl signal of two adjacent methylene protons at δ_H 2.79 (4H, br s, α,α′), and ^{13}C NMR data revealed the presence of methylene carbons at δ_C 38.0 and 39.0**.**

Furthermore, the ^{1}H NMR spectrum (Figure 13) showed signals for five aromatic protons at δ_H 6.80 (1H, d, *J* = 8.1 Hz, H-5), 6.66 (1H, br d, *J* = 8.1 Hz, H-6), 6.58 (1H, d, *J* = 0.9 Hz, H-2) and 6.33 (2H, s, H-2′ and H-6′). These spectral data indicated the presence of five substituents on the two aromatic rings, with symmetrical substitution on one ring. The ^{1}H NMR spectrum also disclosed the presence of four methoxyl groups as singlets at δ_H 3.72 (3H), 3.75 (6H) and 3.79 (3H) and a hydroxyl proton signal at δ_H 5.95 (1H, br s, 4-OH).

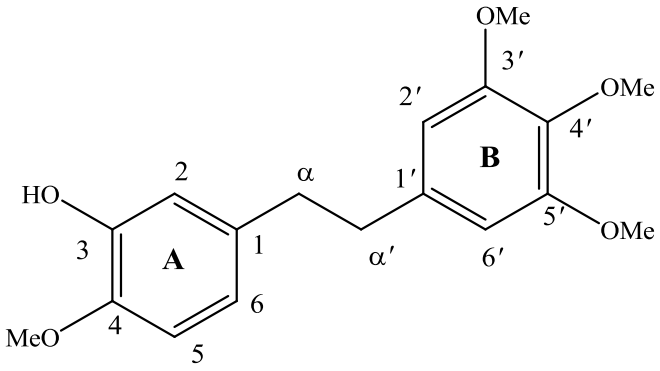
The ^{13}C NMR spectrum (Figure 14) exhibited three peaks for four methoxyl groups at δ_C 56.2, 56.5 and 61.2 ppm. It also showed a characteristic peak of 4′-OMe as found in DC1. Close examination of the ^{1}H and ^{13}C NMR data indicated that the B ring of DC2 was identical to that of DC1.

From the above data and through comparison with previously reported data (Ono *et al*., 1995), DC2 was identified as crepidatin [**21**]. In addition, the probability of DC2 as erianin, the isomer of crepidatin, was rejected after comparison with the NMR data of bibenzyls that had the identical structure of A ring, including gigantol, moscatilin and tristin, and previously reported values of erianin (Li *et al*., 2011).

Crepidatin was firstly isolated and reported as a bibenzyl derivative from the orchid *D. crepidatum*. Moreover, it was also found in several *Dendrobium* species, including *D. aurantiacum* var. *denneanum*, *D. chrysanthum* and *D. nobile* (Yang *et al*., 2006b; Zhang *et al*., 2007a; Lui *et al*., 2009a).



Crepidatin [**21**]



Erianin [**237**]

Table 3 NMR spectral data of compound DC2 (in $CDCl_3$), crepidatin (in $CDCl_3$) and erianin (in $CDCl_3$)

Position	Compound DC2		Crepidatin[a]		Erianin[b]	
	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., J in Hz)	δ_C
1	-	133.9	-	133.5	-	136.5
2	6.58 (d, 0.9)	111.9	6.6 (d, 1.9)	111.2	6.81 (d , 2.0)	110.7
3	-	146.9	-	146.3	-	145.6
4	-	144.4	-	143.8	-	144.9
5	6.80 (d, 8.1)	114.8	6.84 (d, 8)	114.2	6.76 (d, 8.4)	114.8
6	6.66 (br d, 8.1)	121.4	6.69 (dd, 8, 1.9)	121.0	6.64 (dd, 8.4, 2.0)	119.8
α	2.79 (br s)	39.0*	2.82 (s)	38.6*	2.82 s	37.3*
α′	2.79 (br s)	38.0*	2.82 (s)	37.7*	2.82 s	38.4*
1′	-	138.0	-	137.6	-	135.1
2′	6.33 (s)	106.1	6.36 (s)	105.5	6.38 s	105.7
3′	-	153.4	-	153.0	-	153.1
4′	-	136.7	-	136.2	-	137.4
5′	-	153.4	-	153.0	-	153.1
6′	6.33 (s)	106.1	6.36 (s)	105.5	6.38 s	105.7
3-OMe	3.72 (s)	56.2	3.81 (s)	55.9	3.87 s	-
4-OMe	-	-		-		56.1
4′-OMe	3.79 (s)	61.2	3.83 (s)	60.8	3.83 s	60.8
3′, 5′ -OMe	3.75 (s)	56.5		56.0	3.83 s	56.1
4-OH	5.95 (s)		5.47 (s)		-	

* Values in the same column are interchangeable.

[a] Ono *et al*., 1995.; [b] Li *et al*., 2011.

1.3 Structure determination of compound DC3

Compound DC3 was obtained as a dark brown amorphous solid. The ESI mass spectrum **(**Figure 15**)** showed a quasimolecular ion $[M+H]^+$ at *m/z* 274.88, suggesting the molecular formula $C_{16}H_{18}O_4$**.** The IR spectrum (Figure 16) showed absorption bands for hydroxyl (3412 cm^{-1}), aromatic (1613, 1598, 1515, 1461 cm^{-1}) and C-O of ether (1272, 1150 cm^{-1}) functionalities. Its UV spectrum (Figure 17) showed absorption maxima at 210 and 281 nm.

The ^{1}H NMR spectrum (Figure 18 and Table 4) showed a characteristic proton signal for a bibenzyl skeleton at δ_H 2.78 which could be correlated to two methylene carbons at δ_C 37.1 and 38.2 ppm in the ^{13}C NMR spectrum. Moreover, the ^{1}H NMR data revealed signals for six aromatic protons at δ_H 6.82 (1H, d, *J* = 8.0 Hz, H-5), 6.66 (1H, br d, *J* = 8.0 Hz, H-6), 6.61 (1H, br s, H-2), and 6.24 (2H, s, H-2′ and H-6′), 6.30 (1H, s, H-4′). The ^{1}H NMR spectrum also exhibited the presence of two methoxyl groups at δ_H 3.73 (3H) and 3.81 (3H) and revealed two hydroxyl proton signals at δ_H 5.54 and 5.95 (2H, br s each, 4- and 5′-OH).

The ^{13}C NMR and DEPT spectra (Figure 19 and Table 4) exhibited sixteen carbon signals, including six aromatic quaternary carbon signals, which supported the presence of four substituents on the bibenzyl skeleton. Six methine carbon signals, two methylene carbon signals and two methyl carbon signals were also observed.

Based on the above spectral evidence and through comparison with previously reported data (Juneja, Sharma and Tandon, 1985; Ono *et al*., 1995), DC3 was identified as gigantol [**14**].

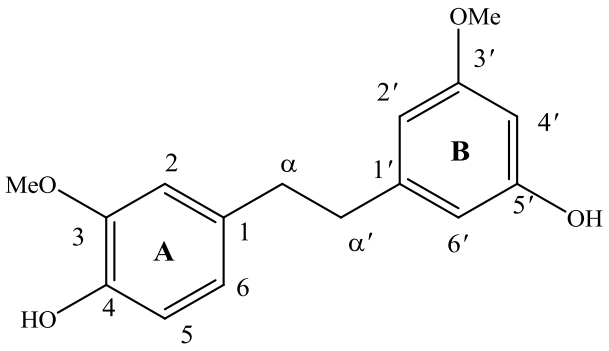
Gigantol was isolated and reported firstly in 1985 from the orchid *Cymbidium giganteum* (Juneja *et al*., 1985). Besides, this compound was also found in several genera of the Orchidaceae family such as *C. aloifolium* (Juneja *et al*., 1987), *Epidendrum rigidum, Scaphyglottis livida* (Hossain, 2011), *Nidema boothii* (Romero *et al*., 2007) and *Dendrobium* species, including *D. aphyllum, D. aurantiacum* var. *denneanum, D. candidum, D. cariniferum, D. chrysanthum, D. chrysotoxum, D. densiflorum, D. draconis, D. gratiotissimum, D. loddigesii, D. longicornu, D. nobile, D. polyanthum* and *D. trigonopus***.** (Fan *et al*., 2001; Yang *et al*., 2006b; Zhang *et al*., 2007a; Chen *et al*., 2008a; Chen *et al*., 2008b; Hu *et al*., 2008a; Hu *et al*., 2008b ; Li *et al*., 2008; Zhang *et al*., 2008a; Hu *et al*., 2009; Li *et al*., 2009a; Lui *et al*., 2009a; Ito *et al*., 2010; Sritularak *et al*., 2001a).

Table 4 NMR spectral data of compound DC3 (in $CDCl_3$) and gigantol (in $CDCl_3$)

Position	Compound DC3		Gigantol[a]	
	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C
1	-	133.7	-	133.7
2	6.61 (br s)	111.2	6.65 (d, 2)	111.2
3	-	146.3	-	146.3
4	-	143.6	-	143.7
5	6.82 (d, 8.0)	114.2	6.81 (d, 9)	114.2
6	6.66 (br d, 8.0)	121.0	6.77 (dd, 9, 2)	121.0
α	2.78 (br s)	37.1*	2.83	37.2*
α′	2.78 (br s)	38.2*	2.83	38.2*
1′	-	144.5	-	144.5
2′	6.24 (s)	108.1	6.29 (br s)	108.1
3′	-	156.7	-	156.6
4′	6.30 (s)	99.1	6.29 (br s)	99.1
5′		160.7	-	160.8
6′	6.24 (s)	106.7	6.29 (br s)	106.8
3, 3′-OMe	3.81	55.2	3.85	55.3
	3.73	55.8	3.77	55.9
4, 5′-OH	5.54, 5.59		5.57	

*Values are interchangeable within vertical column.

[a] ^{1}H NMR data from Juneja *et al*, 1985. ^{13}C NMR data from Ono *et al*., 1995.



Gigantol [**14**]

1.4 Structure determination of compound DC4

Compound DC4 was obtained as a yellowish powder. The ESI mass spectrum (Figure 20) showed a pseudomolecular ion $[M+H]^+$ at *m/z* 318.85, suggesting the molecular formula $C_{18}H_{22}O_5$ and indicating that DC4 was a structural isomer of DC2

The IR spectrum (Figure 21) showed absorption bands at 3462 (hydroxyl), at 1608, 1515, 1461 (aromatic) and at 1236, 1111 (C-O) cm^{-1}. Its UV spectrum (Figure 22) exhibited characteristic absorptions for a bibenzyl skeleton at λ_{max} 213 and 279 nm. The ^{1}H NMR data (Figure 23 and Table 5) also displayed a characteristic signal for a bibenzyl at δ_H 2.79 (4H, br s, α,α′) and ^{13}C NMR data (Figure 24 and Table 5) revealed signals for methylene carbons at δ_C 37.4 and 37.9**.**

The ^{1}H NMR spectrum (Figure 23 and Table 5) also exhibited signals for five aromatic protons with splitting patterns similar to those of DC1 and DC2, including δ_H 6.75 (1H, d, *J* = 8.1 Hz, H-5), 6.66 (1H, br d, *J* = 8.1 Hz, H-6), 6.63 (1H, br s, H-2) and 6.33 (2H, s, H-2′ and H-6′). These spectral data indicated the presence of five substituents on the two aromatic rings, with one ring symmetrically substituted. The ^{1}H NMR spectrum also showed the presence of four methoxyl groups as a singlet at δ_H 3.79 (12H), and a hydroxyl proton at δ_H 5.45 (1H, br s, 4′-OH).

The structure of DC4 was further studied for ^{13}C NMR properties (Figure 24 and Table 5), which exhibited fifteen carbon peaks, comprising ten peaks for twelve aromatic carbons, three peaks for four methoxyl groups and two peaks for methylene carbons. The four methoxyl carbons resonated at δ_C 55.5, 55.8 and 56.0. Comparison of the ^{13}C NMR data of DC4 with those of DC2, indicated that the hydroxyl group should be at 4′-position.

From the above data and through comparison with previously reported data (Ono *et al*., 1995), DC4 was identified as chrysotoxine [**19**].

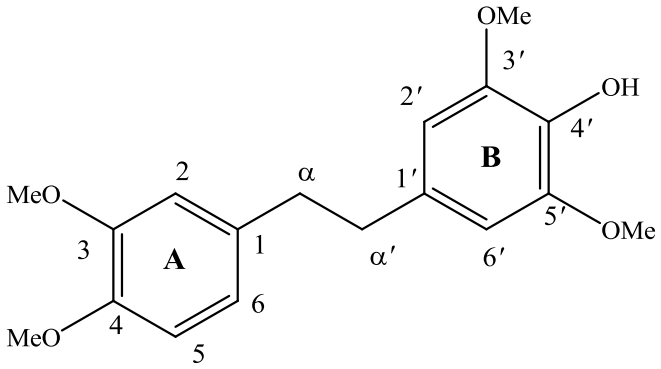
A recent study reported that chrysotoxine or chrysotoxin showed neuroprotective activity, and was suggested as a drug candidate for the further evaluation for the treatment of Parkinson's disease. (Song *et al*, 2010). This compound was also found in several *Dendrobium* species, including *D. aurantiacum* var. *denneanum, D. chrysanthum, D. chryseum* and *D. nobile* (Ma *et al*., 1998; Yang *et al*., 2006a; Yang *et al*., 2006b; Zhang *et al*., 2007a).

Table 5 NMR spectral data of compound DC4 (in $CDCl_3$) and chrysotoxine (in $CDCl_3$)

Position	Compound DC4		Chrysotoxine[a]	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	-	134.1	-	134.3
2	6.63 (br s)	111.8	6.66 (d, 1.8)	111.9
3	-	147.0	-	147.2
4	-	148.5	-	148.7
5	6.75 (d, 8.1)	111.1	6.79 (d, 8.1)	111.2
6	6.66 (br d, 8.1)	120.1	6.70 (dd, 8.1, 1.8)	120.4
α	2.79 (br s)	37.9*	2.83 (s)	38.3*
α′	2.79 (br s)	37.4*	2.83 (s)	37.8*
1′	-	132.5	-	132.8
2′	6.33 (s)	105.0	6.36 (s)	105.2
3′	-	146.6	-	146.8
4′	-	132.7	-	132.8
5′	-	146.6	-	146.8
6′	6.33 (s)	105.0	6.36 (s)	105.2
3-OMe	3.79 (s)	56.0**	3.84 (s), 3.85 (s)	55.9**
4-OMe	-	55.5**	-	55.8**
3′,5′-OMe	-	55.8	-	56.2
4′-OH	5.45 (br s)		5.40 (br s)	

*,** Value in the same column are interchangeable.

[a] Ono *et al*., 1995.



Chrysotoxine [**19**]

1.5 Structure determination of compound DC5

Compound DC5 was obtained as pale yellow needle crystals. The ESI mass spectrum (Figure 25) showed a pseudomolecular ion $[M+H]^+$ at *m/z* 304.86, suggesting the molecular formula $C_{17}H_{20}O_5$**.**

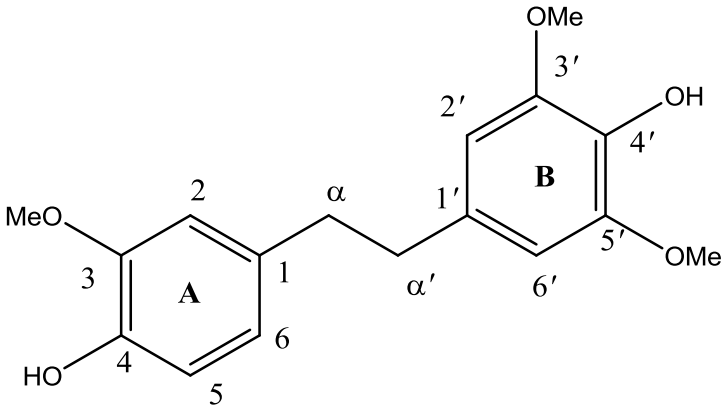
The IR spectrum (Figure 26) showed absorption bands at 3429 (hydroxyl), 1613, 1516 (aromatic) and at 1217, 1114 (C-O) cm^{-1}. The UV spectrum (Figure 27) exhibited the absorption peaks at λ_{max} 213 and 279 nm, which were similar to those of DC1, DC2, DC3 and DC4.

By comparing the NMR data of DC5 with DC1-DC4, it was found that the splitting patterns of aromatic protons of compound DC5 were similar to those of DC1, DC2 and DC4. The ^{1}H NMR spectrum (Figure 28 and Table 6) showed four signals for five aromatic protons at δ_H 6.82 (1H, d, *J* = 8.1 Hz, H-5), 6.66 (1H, dd, *J* = 8.1, 1.2 Hz, H-6), 6.60 (1H, br s, H-2) and 6.34 (2H, s, H-2′ and H-6′). These spectral data indicated the presence of five substituents on the two aromatic rings, with one ring symmetrically substituted. Moreover, the ^{1}H NMR spectrum showed the presence of three methoxyl groups coincidentally appearing as a singlet at δ_H 3.82 (9H).

The ^{13}C NMR spectrum (Figure 29 and Table 6) showed only two signals for three methoxyl groups at δ_C 55.8 and 56.2, indicated that two methoxyl groups were symmetrically substituted on one aromatic ring. By comparing ^{13}C NMR data of DC5 with those of DC1 and DC4, it was found that compound DC5 also lacked the characteristic peak for 4′-OMe, suggesting that the B ring of DC5 was similar to that of DC4 and A ring was similar to that of DC2.

Through comparison of its ^{1}H, ^{13}C NMR, MS, IR and UV data with reported values (Majumder and Sen, 1987), DC5 was identified as moscatilin [**8**].

Moscatilin was a bibenzyl derivative originally isolated from *D. moscatum*. This compound was found not only in *D. moscatum*, but also in *D. amoenum*, *D. aurantiacum* var. *denneanum*, *D. chrysanthum*, *D. densiflorum*, *D. gratiotissimum*, *D. loddigesii*, *D. longicornu* and *D. secundum* (Majumder and Sen 1987; Majumder *et al*., 1999; Fan *et al*., 2001; Yang *et al*., 2006a; Yang *et al*., 2006b; Hu *et al*., 2008a; Zhang *et al*., 2008a; Ito *et al*., 2010).



Moscatilin [**8**]

Table 6 NMR spectral data of compound DC5 (in $CDCl_3$) and moscatilin (in $CDCl_3$)

Position	Compound DC5		Moscatilin[a]	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
1	-	132.8	-	132.8
2	6.60 (br s)	111.2	6.60 (d, 2)	111.2
3	-	146.2	-	146.1
4	-	143.7	-	143.7
5	6.82 (d, 8.1)	114.1	6.77(d, 8)	114.1
6	6.66 (dd, 8.1, 1.2)	121.0	6.74 (dd, 8, 2)	121.0
α	2.80 (br s)	38.4*	2.79 (s)	38.8*
α′	2.80 (br s)	37.8*	2.79 (s)	37.8*
1′	-	132.9	-	132.8
2′	6.34 (s)	105.2	6.30 (s)	105.2
3′	-	146.8	-	146.8
4′	-	133.6	-	133.5
5′	-	146.8	-	146.8
6′	6.34 (s)	105.2	6.30 (s)	105.2
3-OMe	3.82 (s)	55.8	3.81 (s)	55.8
3′, 5′-OMe	3.82 (s)	56.2	3.81 (s)	56.2
4,4′-OH	-		5.30, 5.39	

* Values in the same column are interchangeable.

[a] Majumder and Sen, 1987.

1.6 Structure determination of compound DC6

Compound DC6 was obtained as a yellowish amorphous solid. The ESI mass spectrum **(**Figure 30**)** showed a pseudomolecular ion $[M+H]^+$ at *m/z* 565.16, suggesting the molecular formula $C_{26}H_{28}O_{14}$**.**

The IR spectrum (Figure 31) showed absorption bands at 3399 (hydroxyl), 1658 (conjugated carbonyl), 1609, 1570 (aromatic) and 1205, 1178 (C-O) cm^{-1}. The UV spectrum showed absorption maxima at 215, 267 and 346 nm**,** characteristic of flavonoids (Figure 32). The presence of a conjugated carbonyl carbon was indicated by the ^{13}C NMR resonance at δ 177.3 (Figure 34).

The ^1H NMR spectrum (Figure 33 and Table 8) of DC6 exhibited signals for A ring protons [H-6 at δ_H 6.19 (1H, d, *J* = 1.5 Hz) and H-8 at δ_H 6.43 (1H, d, *J* = 1.5 Hz)] and B ring protons [H-2′ and H-6′ at δ_H 8.03 (2H, d, *J* = 8.7 Hz), and H-3′ and H-5′ at 6.90 (2H, d, *J* = 8.7 Hz)]. The ^{13}C NMR spectrum of DC6 showed signals for A ring carbons at δ_C 161.3 (C-5), 98.9 (C-6), 164.6 (C-7), 93.8 (C-8), 156.4 (C-9), and 103.9 (C-10), B ring carbons at δ_C 120.8 (C-1′), 130.7 (C-2′ and C-6′), 115.4 (C-3′ and C-5′), and 160.2 (C-4′), and C ring carbons at δ_C 156.1 (C-2), 132.8 (C-3), and 177.3 (C-4 carbonyl). Moreover, the ^1H NMR spectrum showed a chealated proton resonance at δ_H 12.59, which supported the presence of a hydroxyl group at C-5. Therefore, the aglycone of DC6 was identified as kaempferol (Itoh *et al.*, 2009).

Two anomeric protons of sugar units were observed at δ_H 5.09 (1H, br s, Rhamnose 1′′′) and 5.53 (1H, d, *J* = 7.2, Xylose 1′′). In addition, the ^1H NMR spectrum displayed a proton signal at δ_H 0.89 (3H, d, *J* = 6.3 Hz, Rhamnose 6′′′), belonging to the methyl protons of rhamnose.

The ^{13}C NMR and DEPT spectra (Figure 34 and Table 8) displayed twenty-four signals for twenty-six carbons, comprising one methyl, one methylene, thirteen methines and nine quaternary carbons. By comparing the ^{13}C NMR data with previously published values (Table 7) it was found that the two sugar units were β-D-xylopyranose and α-L-rhamnopyranose. The β-anomeric configuration for the xylose unit was determined from its large $^3J_{H1,\ H2}$ coupling constant (7.2 Hz). The anomeric proton of α-L-rhamnopyranose was linked to C-2′′ of β-D- xylopyranose because the ^{13}C chemical shift at C-2′′ of β-D- xylopyranose was shifted downfield about 2 ppm.

Through comparison of its ^{1}H, ^{13}C NMR, MS, IR and UV data with reported values (Cui *et al.*, 2003), DC6 was identified as kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside or lysimachiin [**238**]. It should be noted that this study is the second report of lysimachiin, a flavonol glycoside firstly found in *Lysimachia christinae* Hance. (Primalaceae).

Table 7 ^{13}C NMR data for glycopyranoses and methyl glycopyranosides[a]

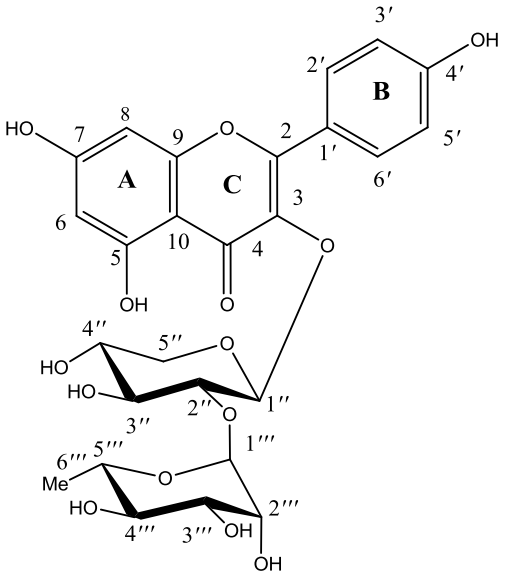
Sugar	**C-1**	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**
Glycopyranoses						
β-D-Glc	96.8	75.2	76.7	70.7	76.7	61.8
α-D-Glc	93.0	72.4	73.7	70.7	72.3	61.8
β-L-Rha	94.4	72.2	73.8	72.8	72.8	17.6
α-L-Rha	94.8	71.8	71.0	73.2	69.1	17.7
β-D-Xyl	97.5	75.1	76.8	70.2	66.1	-
α-D-Xyl	93.1	72.5	73.9	70.4	61.9	-
Methyl glycopyranosides						
β-D-Glc	104.0	74.1	76.8	70.6	76.8	61.8
α-D-Glc	100.0	72.2	74.1	70.6	72.5	61.6
β-L-Rha	102.4	71.8	74.1	73.4	73.4	17.9
α-L-Rha	102.1	71.2	71.5	73.3	69.5	17.9

[a] Agrawal, 1992.

Table 8 NMR spectral data of compound DC6 (in DMSO-d_6) and kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside or lysimachiin (in DMSO-d_6)

Position	**Compound DC6**		**Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside or lysimachiin[a]**	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
2	-	156.1	-	156.2
3	-	132.8	-	132.8
4	-	177.3	-	177.3
5	-	161.3	-	161.3
6	6.19 (d, 1.5)	98.9	6.20 (d, 2.0)	98.9
7	-	164.6	-	164.3
8	6.43 (d, 1.5)	93.8	6.43 (d, 2.0)	93.8
9	-	156.4	-	156.4
10	-	103.9	-	104.0
1′	-	120.8	-	120.8
2′	8.03 (d, 8.7)	130.7	8.05 (d, 8.8)	130.8
3′	6.90 (d, 8.7)	115.4	6.09 (d, 8.8)	115.4
4′	-	160.2	-	160.2
5′	6.90 (d, 8.7)	115.4	6.09 (d, 8.8)	115.4
6′	8.03 (d, 8.7)	130.7	8.05 (d, 8.8)	130.8
Xyl 1″	5.53 (d, 7.2)	99.5	5.52 (d, 7.6)	99.5
Xyl 2″	3.48 (m)	77.3	3.47 (m)	77.3
Xyl 3″	3.34 (m)	76.8	3.33 (m)	76.8
Xyl 4″	3.48 (m)	70.7	3.49 (m)	70.7
Xyl 5″-H_a	2.97 (m)	66.0	2.97 (m)	66.0
Xyl 5″-H_b	3.61 (m)		3.58 (m)	
Rha 1‴	5.09 (brs)	100.8	5.08 (s)	100.8
Rha 2‴	3.34 (m)	69.8	3.33 (m)	69.8
Rha 3‴	3.79 (m)	70.7	3.77 (m)	70.7
Rha 4‴	3.17 (m)	72.0	3.16 (m)	72.0
Rha 5‴	3.79 (m)	68.5	3.77 (m)	68.5
Rha 6‴	0.89 (d, 6.3)	17.5	0.88 (d, 6.0)	17.5

[a] Cui *et al*., 2003**.**



Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside [**238**]

1.7 Structure determination of compound DC7

Compound DC7 was obtained as a yellow powder. The ESI mass spectrum **(**Figure 35**)** showed a pseudomolecular ion $[M+H]^+$ at *m/z* 595.18, suggesting the molecular formula $C_{27}H_{30}O_{15}$**.**

The IR spectrum (Figure 36) was similar to that of compound DC6, exhibiting absorption bands for hydroxyl groups at 3428 cm^{-1}, for a conjugated carbonyl group at 1656 cm^{-1}, for aromatic rings at 1610, 1507, 1450 cm^{-1} and for C-O stretching at 1209, 1177 cm^{-1}. The UV spectrum (Figure 37) exhibited absorption peaks at λ_{max} 215, 256 and 346 nm, which were similar to those of DC6.

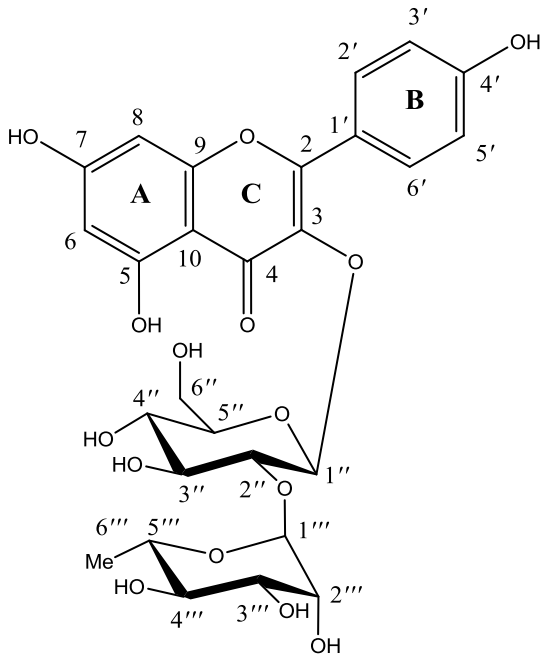
The ^1H and ^{13}C NMR (Figures 38 and 39, and Table 9) data of DC7 apparently displayed patterns similar to those of DC6, but the ^{13}C NMR spectrum of DC7 had one more carbon signal in sugar region. Its ^1H NMR spectra exhibited the presence of six aromatic protons at δ 6.15 (1H, d, *J* = 1.5 Hz, H-6), 6.34 (1H, d, *J* = 1.5 Hz, H-8), 6.86 (2H, d, *J* = 8.7 Hz, H-3′ and H-5′) and 8.01 (2H, d, *J* = 8.7 Hz, H-2′ and H-6′). These spectral data suggested that DC6 should have kaempferol as the aglycone.

Two anomeric proton signals were observed at δ_H 5.20 (1H, br s, Rha 1‴) and 5.70 (1H, d, *J* = 7.2, Glc 1′), indicating the presence of two sugar units in the structure. The methyl doublet at δ_H 0.93 (3H, *J* = 6.3 Hz, Rha 6‴) was characteristic of rhamnose.

The ^{13}C NMR and DEPT spectra (Figure 39) exhibited twenty-five signals for twenty-seven carbons, including one methyl, one methylene, fourteen methines and nine quaternary carbons. By comparing its ^{13}C NMR data with previously published values (Table 7), the sugar unit connected through *O*-glycosidic linkage to C-3 of the kaempferol aglycone was identified as β-D-glucose ($^3J_{H1,\ H2}$ = 7.2 Hz). Rhamnose was connected to C-2 of glucose unit, as indicated by the downfield shift of about 5 ppm of the C-2″ signal of the glucose.

Through comparison of its ^{1}H, ^{13}C NMR, MS, IR and UV data with reported values (Wu *et al.*, 2009), DC7 was identified as kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside [**239**].

This compound was also called kaempferol 3-*O*-β-neohesperidoside, previously isolated from *Cyathea phalerata* (Cyatheaceae) and *Acer mandshuricum* (Aceraceae). It showed an insulin-like activity and significantly increased the function of osteoblastic cells (Zanatta *et al*., 2008; Ding *et al.*, 2010).



Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside [**239**]

Table 9 NMR spectral data of compound DC7 (in CD_3OD) and kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside (in CD_3OD)

Position	Compound DC7		Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside[a]	
	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C
2	-	158.4	-	158.2
3	-	134.4	-	134.4
4	-	179.4	-	179.2
5	-	163.2	-	163.0
6	6.15 (d, 1.5)	99.7	5.97 (br s)	99.8
7	-	165.7	-	165.6
8	6.34 (d, 1.5)	94.6	6.08 (br s)	94.7
9	-	158.5	-	158.5
10	-	106.0	-	105.8
1′	-	123.1	-	123.1
2′	8.01 (d, 8.7)	132.1	7.98 (d, 8.4)	132.1
3′	6.86 (d, 8.7)	116.1	6.80 (d, 8.4)	116.1
4′	-	161.3	-	161.1
5′	6.86 (d, 8.7)	116.1	6.80 (d, 8.4)	116.1
6′	8.01 (d, 8.7)	132.1	7.98 (d, 8.4)	132.1
Glc 1″	5.70 (d, 7.2)	100.3	5.62 (d, 7.8)	100.3
Glc 2″	3.53 (m)	80.1	3.53 (m)	79.8
Glc 3″	3.58 (t, 8.3)	78.9	3.64 (t, 9)	78.8
Glc 4″	3.53 (m)	71.9	3.53 (m)	71.7
Glc 5″	3.22 (m)	78.3	3.19 (br dd, 9, 6)	78.0
Glc 6″-H_a	3.70 (m)	62.6	3.70 (br d, 12)	62.6
Glc 6″-H_b	3.47 (m)		3.52 (br d, 12)	
Rha 1‴	5.20 (br s)	102.6	5.24 (br s)	102.5
Rha 2‴	4.00 (m)	72.4	4.00 (m)	72.3
Rha 3‴	3.75 (dd, 9.6, 3.3)	72.3	3.82 (m)	72.2
Rha 4‴	3.29 (m)	74.1	3.32 (m)	74.0
Rha 5‴	4.00 (m)	69.9	4.09 (m)	69.9
Rha 6‴	0.93 (d, 6.3)	17.5	1.02 (d, 6.6)	17.6

[a] Wu *et al.*, 2009.

1.8 Structure elucidation of compound DC8

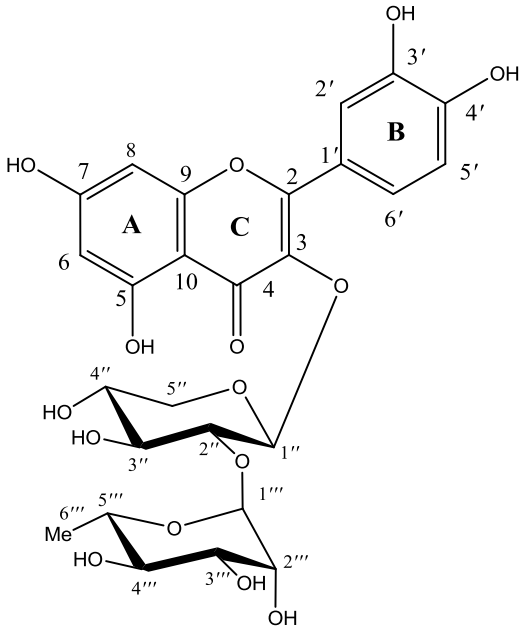
Compound DC8 was obtained as a greenish yellow amorphous solid. The positive HR-ESITOF mass spectrum (Figure 40) exhibited an $[M+Na]^+$ ion at *m/z* 603.1388 (calcd. 603.1326), suggesting the molecular formula $C_{26}H_{28}O_{15}$. The UV spectrum (Figure 42) showed three absorption maxima of flavonoids at 215, 256 and 346 nm, as found in DC6 and DC7. The IR spectrum (Figure 41) demonstrated peaks at 3349 (hydroxyl), 1660 (keto-carbonyl) and 1025-1303 (C-O) cm^{-1}.

The NMR spectra of compounds DC6 and DC8 shared some similarity. From ^{13}C NMR data, it could be assumed that compound DC8 had the same sugar units as DC6, but it had a different aglycone. To prove our assumption, we used 2D-NMR techniques, including HSQC (Figures 45a-45e) and HMBC (Figures 46a-46e) to analyse the structure of DC8, and the data are shown in Table 10. The ^1H NMR spectrum displayed characteristic signals for quercetin moiety at δ_H 6.18 (1H, d, *J* = 2.0 Hz, H-6), 6.39 (1H, d, *J* = 2.0 Hz, H-8), 7.53 (1H, d, *J*= 2.0 Hz, H-2′), 6.84 (1H, d, *J* = 8.5 Hz, H-5′) and 7.57 (1H, dd, *J* = 8.5, 2.0 Hz, H-6′). This was supported by the ^{13}C NMR signals for the A ring at δ_C 161.2 (C-5), 98.7 (C-6), 164.3 (C-7), 93.5 (C-8), 156.2 (C-9) and 103.8 (C-10), and for the B ring at δ_C 120.9 (C-1′), 115.9 (C-2′), 145.0 (C-3′), 148.6 (C-4′), 115.2 (C-5′) and 121.5 (C-6′). The ^{13}C NMR spectrum showed seven oxygenated carbon signals at δ_C 164.3 (C-7), 161.2 (C-5), 156.2 (C-9), 156.0 (C-2), 148.6 (C-4′), 145.0 (C-3′) and 132.8 (C-3) ppm. The carbon signals for C-2, C-5, C-7, C-9, C-3′ and C-4′ were assigned by HMBC data, leaving the resonance at δ 132.8 to be assigned to C-3. Furthermore, the ^1H NMR spectrum showed two anomeric protons at δ_H 5.51 (1H, d, *J* = 7.5 Hz) and 5.08 (1H, br s) which were correlated to the carbon signals at δ_C 99.4 and 100.6 in the HSQC spectrum, respectively.

These NMR data suggested the presence of two sugar units in the structure, and they were identified as β-xylopyranose and α-rhamnopyranose by comparison of their NMR data with previously reported values (Table 7). The carbon signals at C-2″ and C-3″ of β-xylose appeared at nearly the same position, but the latter carbon could be distinguished by the HMBC correlation from the attached H-3″ (δ_H 3.32) of xylose to C-5″ (δ_C 66.0) of xylose. The HMBC spectrum showed cross peaks between C-3 (δ_C 132.8) of the quercetin aglycone and H-1″ (δ_H 5.51) of xylose; C-2″ (δ_C 76.9) of xylose and H-1‴ (δ_H 5.08) of rhamnose; C-1‴ (δ_C 100.6) of rhamnose and

H-2″ (δ_H 3.54) of xylose. Therefore, the β-xylopyranose unit should be attached at C-3 of quercetin, and the α-rhamnopyranose unit was connected to the C-2 position of the β-xylopyranose unit. The downfield shift (about 2 ppm) of this position also supported that α-rhamnopyranose unit was attached to C-2″ of β-xylopyranose. In addition, acid hydrolysis of compound DC8 yielded D-xylose and L-rhamnose, as shown in Figure 4. It was concluded that compound DC8 was quercetin-3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranoside [**240**]. This structure was unknown prior to this study.

Figure 4 Acid hydrolysis of compound DC8 [TLC conditions: silica gel 60 F_{254} plate (Merck) [using $CHCl_3$-MeOH-H_2O (5:4:1)]; Lane 1: R_f 0.44 (L-arabinose), Lane 2: R_f 0.38 (D-xylose), Lane 3: Hydrolysate from aqueous layer, Lane 4: R_f 0.58 (L-rhamnose)]



Quercetin-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside [**240**]

Table 10 ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data of compound DC8 (in DMSO-d_6)

Position	δ_H (mult., *J* in Hz)	δ_C	HMBC (correlation with ^{1}H)
2		156.0	H-2′, H-6′
3		132.8	H-1″
4		177.1	-
5		161.2	H-6*
6	6.18 (d, 2.0)	98.7	H-8
7		164.3	H-6*, H-8*
8	6.39 (d, 2.0)	93.5	H-6
9		156.2	H-8*
10		103.8	H-6, 8
1′		120.9	H-5′
2′	7.53 (d, 2.0)	115.9	H-6′
3′		145.0	H-2′, H-5′
4′		148.6	H-2′, H-5′*, H-6′
5′	6.84 (d, 8.5)	115.2	-
6′	7.57 (dd, 8.5, 2.0)	121.5	H-2′
Xyl 1″	5.51 (d, 7.5)	99.4	H-2″*, H-5″
Xyl 2″	3.54 (t, 8.0)	76.9	H-1‴
Xyl 3″	3.32	76.8	H-2″*, H-4″*, H-5″
Xyl 4″	3.34	69.6	H-3″*, H-5″*
Xyl 5″	2.95 (m), 3.59 (dd, 11.0, 4.0)	66.0	H-1″, H-3″
Rha 1‴	5.08 (br s)	100.6	H-2″
Rha 2‴	3.48 (dd, 9.0, 3.0)	70.5	H-1‴*, H-3‴*, H-4‴
Rha 3‴	3.73	70.6	H-1‴, H-4‴*
Rha 4‴	3.15 (m)	71.8	H-2‴, H-3‴*
Rha 5‴	3.78 (m)	68.3	H-1‴, H-4‴*
Rha 6‴	0.87 (d, 6.5)	17.4	H-4‴, H-5‴*

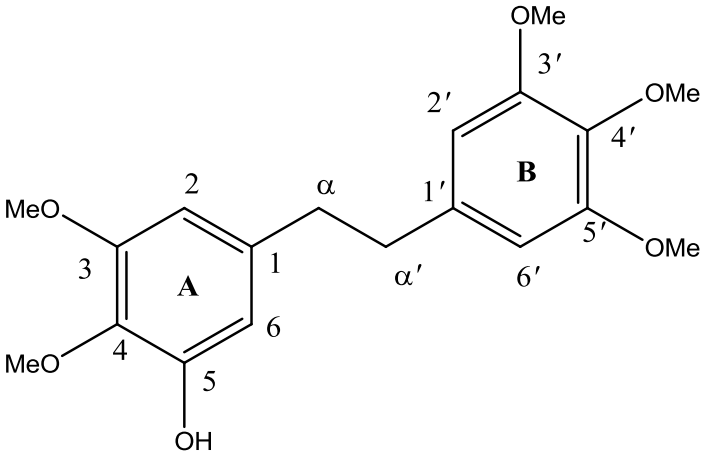
* Two-bond coupling.

1.9 Structure elucidation of compound DS1

Compound DS1 was obtained as a white powder, and had the molecular formula of $C_{19}H_{24}O_6$, as indicated by an $[M+Na]^+$ ion at *m/z* 371.1469 (calcd. for $C_{19}H_{24}O_6Na$ 371.1471) in the HRESI mass spectrum (Figure 47). The UV spectrum (Figure 49) showed typical benzenoid absorptions at 215 and 266 nm, similar to those of bibenzyl derivatives (DC1-DC5). The IR spectrum (Figure 48) exhibited peaks at 3416 (hydroxyl), 1591 and 1461 (aromatic ring), and 1333, 1349, 1238 (ether) cm^{-1}. The ^1H NMR spectrum (Figure 50 and Table 11) showed resonances for two pairs of benzylic protons at δ 2.80 (4H, br s, H_2-α and H_2-α′), five methoxy groups at δ 3.79 (3H, s), 3.80 (3H, s), 3.81 (6H, s) and 3.84 (3H, s) and four aromatic protons at δ 6.21 (1H, s, H-2) and 6.46 (1H, s, H-6) and 6.35 (2H, s, H-2′ and H-6′). From these ^1H NMR data, it could be inferred that DS1 was a hexa-oxygenated bibenzyl containing a hydroxy and five methoxy substituents. The ^{13}C NMR resonances (Figure 51 and Table 11) at δ 153.0 (C-3′ and C-5′) and 136.3 (C-4′) suggested that ring B of DS1 was tri-methoxylated at *m*- and *p*-positions to the ethane bridge, similar to that of brittonin A [**224**] (Sritularak *et al*., 2011b). Thus, two methoxy groups and a hydroxyl group remained to be placed on ring A. The structure of ring A was unsymmetrical, as evidenced by the different chemical shifts of the aromatic protons at δ 6.21 (1H, s, H-2) and 6.46 (1H, s, H-6). Therefore, the two methoxy groups should be adjacent and located at *m*- and *p*-positions of the ethane bridge, leaving the hydroxy group to be placed at the other *m*-position of ethane bridge. The proposed structure of DS1, was confirmed by the NOESY correlations observed between 5-OH and 4-OMe, and between H-2 and 3-OMe protons (Figures 52a and 52b). Thus, the structure of DS1 was determined as a new bibenzyl, namely, 5-hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl [**241**].

Table 11 ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectral data of compound DS1 (in $CDCl_3$)

Position	δ_H (mult., *J* in Hz)	δ_C
1		137.8
2	6.21 (s)	107.9
3		149.1
4		133.7
5		152.0
6	6.46 (s)	104.5
α	2.80 (br s)	38.1
α′	2.80 (br s)	38.1
1′		137.3
2′	6.35 (s)	105.5
3′		153.0
4′		136.3
5′		153.0
6′	6.35 (s)	105.5
5-OH	5.76 (s)	-
3-OMe	3.79 (s)	55.7
4-OMe	3.84 (s)	60.8
3′,5′-OMe	3.81 (s)	56.0
4′-OMe	3.80 (s)	60.8



5-Hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl [**241**]

1.10 Structure determination of compound DS2

Compound DS2 was obtained as a yellow powder. The ESI mass spectrum **(**Figure 53**)** showed a pseudomolecular ion $[M+H]^+$ at *m/z* 579.16, suggesting the molecular formula $C_{27}H_{29}O_{14}$**.** Its UV spectrum (Figure 55) showed maximal absorptions at 222, 266 and 345 nm, which were similar to those of DC6-DC8, indicating a flavonoid structure. The IR spectrum (Figure 54) exhibited absorption bands due to hydroxyl (3400 cm^{-1}), carbonyl (1659 cm^{-1}), aromatic (1604, 1513, 1448 cm^{-1}) and C-O ether (1208, 1178 cm^{-1}) functionalities.

The ^1H NMR spectrum (Figure 56) showed the presence of four signals for six aromatic protons. Four aromatic protons resonated at δ_H 6.92 (2H, d, *J* = 8.7 Hz, H-3′ and H-5′) and 7.77 (2H, d, *J* = 8.7 Hz, H-2′ and H-6′), representing an AA′BB′ system of the B ring. Two aromatic protons resonating at δ_H 6.44 (1H, br s) and 6.70 (1H, br s,) were assigned to H-6 and H-8 protons, respectively. The spectral data indicated that DS2 had kaempferol as the aglycone, similar to DC6 and DC7. In addition, two anomeric proton signals were observed at δ_H 5.38 (1H, br s, Rha 1′′) and 5.54 (1H, br s, Rha 1′′′), indicating the presence of two sugar units. The ^1H NMR spectrum also showed the characteristic methyl doublets for rhamnose at δ_H 0.91 (*J* = 4.8 Hz, Rha 6′′) and 1.24 (*J* = 6.3 Hz, Rha 6′′′). It was then confirmed by comparing the ^{13}C NMR data (Figure 57 and Table 12) with previously published values (Table 7).

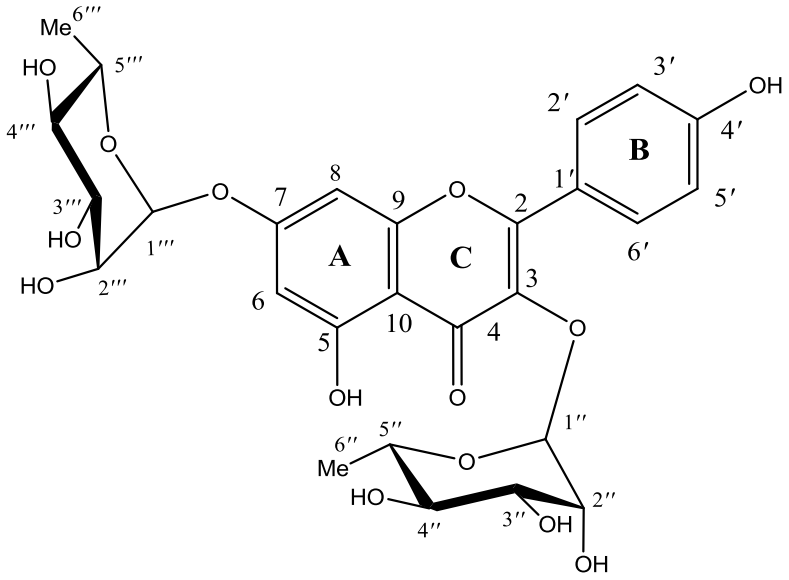
From the above data and through comparison with previously reported data (Toker *et al*., 2004), DS2 was identified as kaempferol-3,7-*O*-di-α-L-rhamnopyranoside [**242**].

This compound was also known as kaempferitrin, found in several plants such as *Lotus corniculatus* (Fabaceae), and exhibited antimicrobial activity comparable to several antibiotics against Gram positive and Gram negative bacteria (Abdel-Ghani *et al*., 2001). It was also found in *Bauhinia forficate* (Leguminosae), and was reported to have a significant hypoglycemic effect in diabetic rat and showed antioxidative property comparable to those of quercetin (De Sousa *et al*., 2004).

Table 12 NMR spectral data of compound DS2 (in CD_3OD) and kaempferol-3,7-*O*-di-α-L-rhamnopyranoside (in CD_3OD)

Position	Compound DS2		Kaempferol-3,7-*O*-di-α-L-rhamnopyranoside[a]	
	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C
2	-	159.8	-	159.8
3	-	136.5	-	136.5
4	-	179.8	-	179.8
5	-	163.0	-	163.0
6	6.44 (br s)	99.9	6.46 (d, 2.4)	99.9
7	-	163.6	-	163.6
8	6.70 (br s)	95.6	6.71 (d, 2.4)	95.6
9	-	158.1	-	158.1
10	-	107.6	-	107.6
1′	-	122.4	-	122.4
2′	7.77 (d, 8.7)	132.0	7.78 (d, 9.2)	132.0
3′	6.92 (d, 8.7)	116.6	6.93 (d, 9.2)	116.6
4′	-	161.8	-	161.8
5′	6.92 (d, 8.7)	116.6	6.93 (d, 9.2)	116.7
6′	7.77 (d, 8.7)	132.0	7.78 (d, 9.2)	132.0
Rha 1″	5.38 (br s)	103.5	5.40 (d, 1.8)	103.8
Rha 2″	4.20 (br s)	71.9	4.22 (dd, 3.3, 1.8)	71.9
Rha 3″	3.69 (m)	72.1	3.71 (dd, 9.0, 3.1)	72.2
Rha 4″	3.29-3.33 (m)	73.2	3.33-3.34 (m)	73.2
Rha 5″	3.29-3.33 (m)	72.2	3.33-3.36 (m)	72.1
Rha 6″	0.91 (d, 4.8)	17.7	0.93 (d, 5.6)	17.8
Rha 1‴	5.54 (br s)	100.6	5.55 (d, 1.7)	100.0
Rha 2‴	4.00 (br s)	71.7	4.02 (dd, 4.1, 1.8)	71.7
Rha 3‴	3.81 (dd, 9.3, 3.0)	72.1	3.83 (dd, 9.5, 3.1)	72.2
Rha 4‴	3.46 (t, 9.3)	73.6	3.46-3.50 (t, 9.8, 9.2)	73.6
Rha 5‴	3.59 (m)	71.3	3.59-3.62 (m)	71.3
Rha 6‴	1.24 (d, 6.3)	18.1	1.26 (d, 6.1)	18.0

[a] Toker *et al*., 2004.



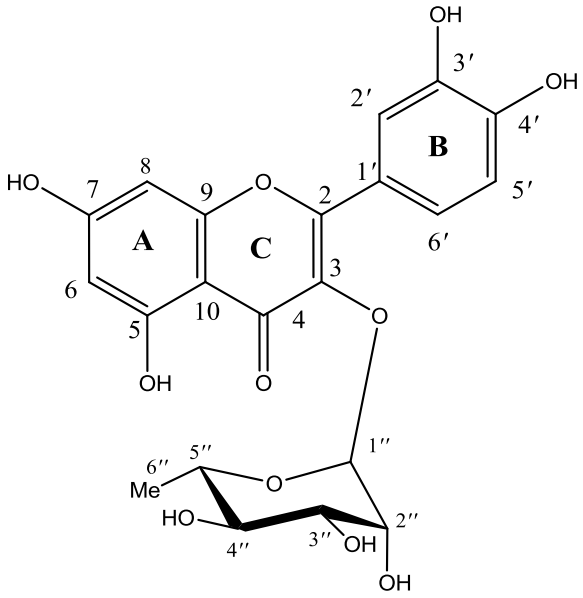
Kaempferol-3,7-*O*-di-α-L-rhamnopyranoside [**242**]

1.11 Structure determination of compound DS3

Compound DS3 was obtained as a greenish amorphous solid. The IR spectrum (Figure 59) showed absorption peaks at 3270 (hydroxyl), 1657 (conjugated carbonyl), 1602, 1510 and 1446 (aromatic), and 1200, 1170 (C-O) cm^{-1}. Its ESI mass spectrum (Figure 58) exhibited a protonated molecular ion peak at *m/z* 449.10 $[M+H]^+$, providing the formula $C_{21}H_{20}O_{11}$. Absorption bands were observed at λ_{max} 222, 256 and 349 nm in its UV spectrum (Figure 60), indicating the flavonoid as basic skeleton**.** The ^1H NMR spectrum (Figure 61 and Table 13) showed the presence of a quercetin aglycone as identified by ABM splitting patterns on the B ring, including signals at δ_H 6.83 (1H, d, *J* = 8.4 Hz, H-5′), 7.21 (1H, d, *J* = 1.8 Hz, H-2′) and 7.25 (1H, m, H-6′), and two aromatic protons of the A ring at δ_H 6.12 (1H, d, *J* = 1.5 Hz, H-6) and 6.29 (1H, br s, H-8), which were similar to those of DC8. The presence of the rhamnosyl unit was indicated by a characteristic methyl doublet at δ_H 0.86 (3H, *J* = 6.0 Hz, Rha 6″) and a broad singlet of anomeric proton at δ_H 5.27. The ^{13}C NMR and DEPT spectra (Figure 62 and Table 13) showed twenty-one signals, comprising one methyl, ten methines and ten quaternary carbons, corresponding to quercetin aglycone (15C) and rhamnosyl unit (6C).

Based on the above spectral evidence and through comparison with previously reported data (Olszewska and Wolbis, 2002), DS3 was identified as quercetin-3-*O*-α-L-rhamnopyranoside [**243**].

Quercetin-3-*O*-α-L-rhamnoside or quercitrin is the most common flavonol glycoside in the nature with several biological activities, including antidiarrhoeic (Galvez *et al.*, 1993), sedative (Kang *et al*., 2000), antifungal (Lu *et al.*, 2002) and anti-inflammatory (Manga *et al*., 2004) activities.



Quercetin-3-*O*-α-L-rhamnopyranoside [**243**]

Table 13 NMR spectral data of compound DS3 (in CD_3OD) and quercetin-3-*O*-α-L-rhamnopyranoside (in DMSO-d_6)

Position	Compound DS3		Quercetin-3-*O*-α-L-rhamnopyranoside[a]	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
2	-	158.5	-	156.4
3	-	136.3	-	134.2
4	-	179.7	-	177.8
5	-	163.2	-	161.3
6	6.12 (d, 1.5)	99.8	6.20 (d, 1.8)	98.7
7	-	165.9	-	164.1
8	6.29 (br s)	94.7	6.39 (d, 1.8)	93.6
9	-	159.3	-	157.3
10	-	105.9	-	104.0
1′	-	123.0	-	120.7
2′	7.21 (d, 1.8)	116.4	7.29 (d, 1.9)	115.4
3′	-	146.4	-	145.2
4′	-	149.8	-	148.4
5′	6.83 (d, 8.4)	117.0	6.86 (d, 8.2)	115.6
6′	7.25 (m)	122.9	7.25 (dd, 8.2, 1.9)	121.1
Rha 1″	5.27 (br s)	103.6	5.25 (br s)	101.8
Rha 2″	4.12 (d, 1.2)	72.0	3.97 (br s)	70.3
Rha 3″	3.67 (dd, 9.3, 3.0)	72.2	3.50 (dd, 9.1, 3.0)	70.6
Rha 4″	3.22-3.30 (m)	73.3	3.12-3.17 (m)	71.2
Rha 5″	3.34 (m)	71.9	3.21 (dd, 9.5, 6.1)	70.0
Rha 6″	0.86 (d, 6.0)	17.6	0.81 (d, 6.1)	17.8

[a] Olszewska and Wolbis, 2002.

1.12 Structure determination of compound DS4

Compound DS4 was obtained as a greenish amorphous solid. The ESI mass spectrum **(**Figure 63**)** showed a pseudomolecular ion $[M+H]^+$ at *m/z* 433.12, suggesting the molecular formula $C_{21}H_{20}O_{10}$**.** The IR spectrum (Figure 64) showed absorption bands at 3334 (hydroxyl), 1656 (conjugated carbonyl), 1609, 1510 and 1454 (aromatic) and 1209, 1176 (C-O) cm^{-1}. The UV spectrum showed absorptions at 224, 266 and 345 nm (Figure 65). By comparing the ^1H and ^{13}C NMR spectra (Figures 66 and 67, and Table 14) of DS4 with those of DS3, it was found that DS4 had the same sugar unit as DS3 but it had a different aglycone. The ^1H NMR spectrum displayed four signals for six aromatic protons, including δ 6.18 (1H, br s, H-6), 6.37 (1H, br s, H-8), 7.74 (2H, d, *J* = 8.1 Hz, H-2′ and H-6′) and 6.90 (2H, d, *J* = 8.1 Hz, H-3′ and H-5′). In addition, the ^1H NMR spectrum displayed a chealated proton resonance at δ_H 12.61, which supported the presence of a hydroxyl group at C-5. It could be inferred that the aglycone part of DS4 was kaempferol, similar to those of compounds DC6, DC7 and DS2. Moreover, the presence of the rhamnosyl unit, as found in DS3, was supported by a characteristic methyl doublet at δ_H 0.78 (3H, *J* = 4.8 Hz, Rha 6″) and a broad singlet corresponding to the anomeric proton at δ_H 5.28.

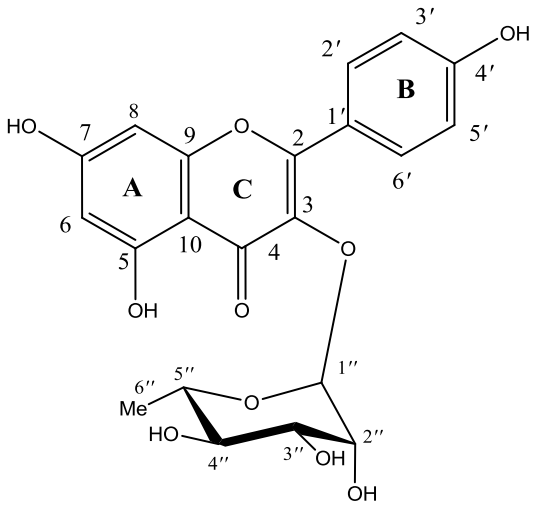
From the above data and through comparison with previously reported data (Bilia *et al*, 1996), DS4 was identified as kaempferol-3-*O*-α-L-rhamnopyranoside [**244**].

Kaempferol-3-*O*-α-L-rhamnopyranoside was also named afzelin. In previous studies, this compound was isolated from the leaves of *Erythroxylum laurifolium* (Erythroxylaceae), and showed interesting angiotensin converting enzyme (ACE) inhibitory activity (Hansen *et al*., 1996), and was also found in the antiviral fractions of *Persea Americana* (Lauraceae) leaf (Almeida *et al*., 1998).

Table 14 NMR spectral data of compound DS4 (in DMSO-d_6) and kaempferol-3-*O*-α-L-rhamnopyranoside (in CD_3OD)

Position	Compound DS4		Kaempferol-3-*O*-α-L-rhamnopyranoside[a]	
	δ_H (mult., *J* in Hz)	**δ_C**	**δ_H (mult., *J* in Hz)**	**δ_C**
2	-	157.1	-	158.7
3	-	134.2	-	133.9
4	-	177.7	-	179.1
5	-	162.0	-	162.2
6	6.18 (br s)	98.9	5.98 (d, 2.2)	99.8
7	-	165.0	-	165.3
8	6.37 (br s)	93.9	6.28 (d, 2.2)	94.5
9	-	156.6	-	158.3
10	-	101.8	-	104.2
1′	-	120.6	-	122.5
2′	7.74 (d, 8.1)	130.6	7.35 (d, 8.7)	132.2
3′	6.90 (d, 8.1)	115.4	6.83 (d, 8.7)	116.0
4′	-	160.1	-	159.4
5′	6.90 (d, 8.1)	115.4	6.83 (d, 8.7)	116.0
6′	7.74 (d, 8.1)	130.6	7.35 (d, 8.74)	132.2
Rha 1″	5.28 (br s)	101.8	5.43 (d, 2.1)	102.5
Rha 2″	3.08-3.97 (m)	70.4	3.20-4.42 (m)	71.7
Rha 3″	3.08-3.97 (m)	70.6	3.20-4.42 (m)	72.3
Rha 4″	3.08-3.97 (m)	71.2	3.20-4.42 (m)	73.2
Rha 5″	3.08-3.97 (m)	70.1	3.20-4.42 (m)	71.4
Rha 6″	0.78 (d, 4.8)	17.5	0.89 (d, 6.4)	17.5

[a] Bilia *et al*., 1996.



Kaempferol-3-*O*-α-L-rhamnopyranoside [**244**]

2. Cytotoxic activity

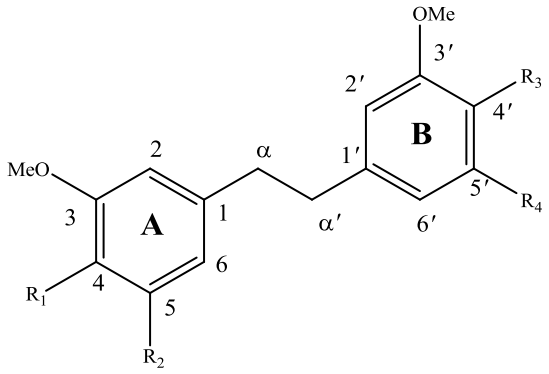
Evaluation for cytotoxicity was done on the compounds isolated in sufficient quantity. Cytotoxicity assays against three human cancer cell lines including KB (oral human epidermal carcinoma), NCI-H187 (human lung cancer) cells and MCF-7 (breast cancer) cells, and normal cells (Vero cells) were provided by the bioassay laboratory of National Center for Genetic Engineering and Biotechnology (BIOTEC). The results are summarized in Table 15.

Table 15 IC_{50} Values (μM) for cytotoxicity of isolated compounds and positive controls.

Compound	KB	NCI-H187	MCF-7	Vero cell
Chrysotobibenzyl [**DC1**]	132.4	123.7	Inactive[a]	0.06
Crepidatin [**DC2]**	14.4	13.7	inactive	0.08
Gigantol [**DC3**]	61.9	71.6	67.8	0.10
Chrysotoxine [**DC4**]	60.5	65.6	inactive	Non-cytotoxic[b]
Moscatilin [**DC5**]	2.2	10.5	inactive	0.04
Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside [**DC6**]	inactive	inactive	inactive	Non-cytotoxic
Kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside [**DC7**]	inactive	inactive	inactive	Non-cytotoxic
5-Hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl [**DS1**]	inactive	87.8	inactive	0.12
Brittonin A	inactive	inactive	inactive	Non-cytotoxic
4,5,4′-Trihydroxy-3,3′-dimethoxybibenzyl	48.3	63.8	62.6	Non-cytotoxic
Ellipticine	1.8	1.4	-	0.006
Doxorubicin	0.6	0.08	11.2	-
Tamoxifen	-	-	14.0	-

[a]Less than 50% inhibition at concentration of 50 μg/mL.

[b]More than 50% cell growth at concentration of 50 μg/mL.



	R_1	**R_2**	**R_3**	**R_4**
Chrysotobibenzyl [**DC1**]	OMe	H	OMe	OMe
Crepidatin [**DC2]**	OH	H	OMe	OMe
Gigantol [**DC3**]	H	OH	OH	H
Chrysotoxine [**DC4**]	OMe	H	OH	OMe
Moscatilin [**DC5**]	OH	H	OH	OMe
5-Hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl [**DS1**]	OMe	OH	OMe	OMe
Brittonin A	OMe	OMe	OMe	OMe
4,5,4′-Trihydroxy-3,3′-dimethoxybibenzyl	OH	OH	OH	H

The compounds studied for their cytotoxicity include five bibenzyls [DC1-DC5] and two flavonol glycosides [DC6-DC7] from *D. capillipes*, and three bibenzyls [DS1, brittonin A and 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl] from *D. secundum*. Brittonin A and 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl, isolated and reported previously (Sritularak *et al.*, 2011b), were included in this study for evaluation structure activity relation (SAR) of bibenzyls and their cytotoxicity.

In this study, all bibenzyls, except brittonin A, exhibited inhibitory activity against cancer cell lines tested. The flavonol glycosides, which were isolated from the inactive fraction, were devoid of cytotoxicity as expected. It was found that DC5 (moscatilin) was the most potent compound, inhibiting both KB (oral human epidermal carcinoma) and NCI-H187 (human lung cancer) cells with IC_{50} of 2.2 and 10.5 μM, respectively. However, the compound was not active against MCF-7 (breast cancer) cells. DC3 (gigantol) and 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl showed weak cytotoxicity against all three cancer cell lines. In addition, DC4

(chrysotoxine), brittonin A and 4,5,4′-trihydroxy-3,3′-dimethoxybibenzyl showed non-cytotoxicity against Vero cell.

It appeared that both the number and position of hydroxyl and methoxyl groups on the aromatic rings played an important role on the cytotoxic activity of bibenzyls. It seemed that the presence of 4-OH group might be important for the activity, and substituting this group with a methoxy group decreased the activity significantly. In moscatilin (DC5), where optimal activity was obtained, the bibenzyl is penta-oxygenated, with two OH groups placed at the 4- or 4′-position and three OMe groups at either the 3-/3′- or 5-/5′-positions of the aromatic rings. Any deviation from this structural arrangement seems to result in the decrease of activity.

CHAPTER V

CONCLUSION

In this study, eight compounds were isolated from *Dendrobium capillipes* and four compounds were obtained from *Dendrobium secundum.* Five of them were known bibenzyls, including chrystobibenzyl [**18**], crepidatin [**21**], gigantol [**14**], chrysotoxine [**19**], moscatilin [**8**], in addition to five known flavonol glycosides, comprising kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside [**238**], kaempferol-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside [**239**], kaempferol-3,7-*O*-di-α-L-rhamnopyranoside [**242**], quercetin-3-*O*-α-L-rhamnopyranoside [**243**] and kaempferol-3*O*-α-L-rhamnopyranoside [**244**]. A new flavonol glycoside named quercetin-3-*O*-α-L-rhamnopyranosyl (1→2)-β-D-xylopyranoside [**240**] and a new bibenzyl, namely, 5-hydroxy-3,4,3′,4′,5′-pentamethoxybibenzyl [**241**] were characterized in this study. The present results agree with previously published data in that bibenzyls were most commonly found in plants of this genus (Chen *et al*., 2008a). Flavonoid glycosides were also reported in *Dendrobium* plants (Wang *et al.*, 2009; Chang *et al.*, 2010). The bibenzyls showed cytotoxicity against various types of cancer cells. It could be proposed that both the number and the position of the OH and OMe groups on the aromatic rings were critical for these bibenzyls to exert their cytotoxicity.

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APPENDIX

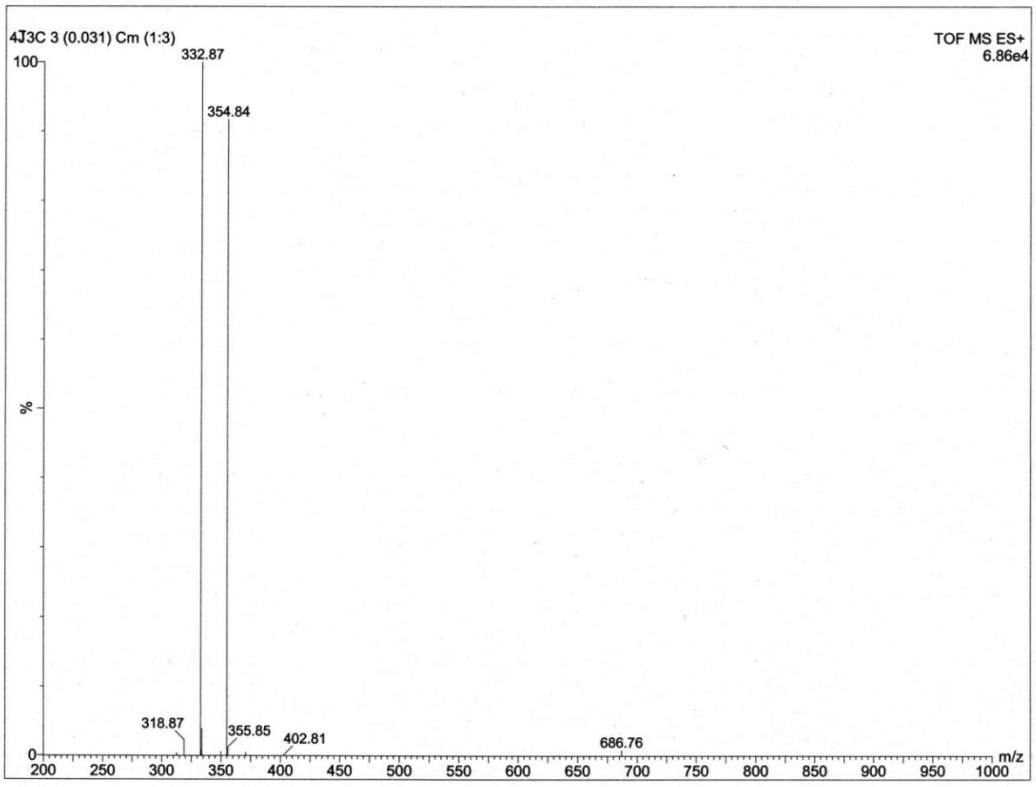

Figure 5 Mass spectrum of compound DC1

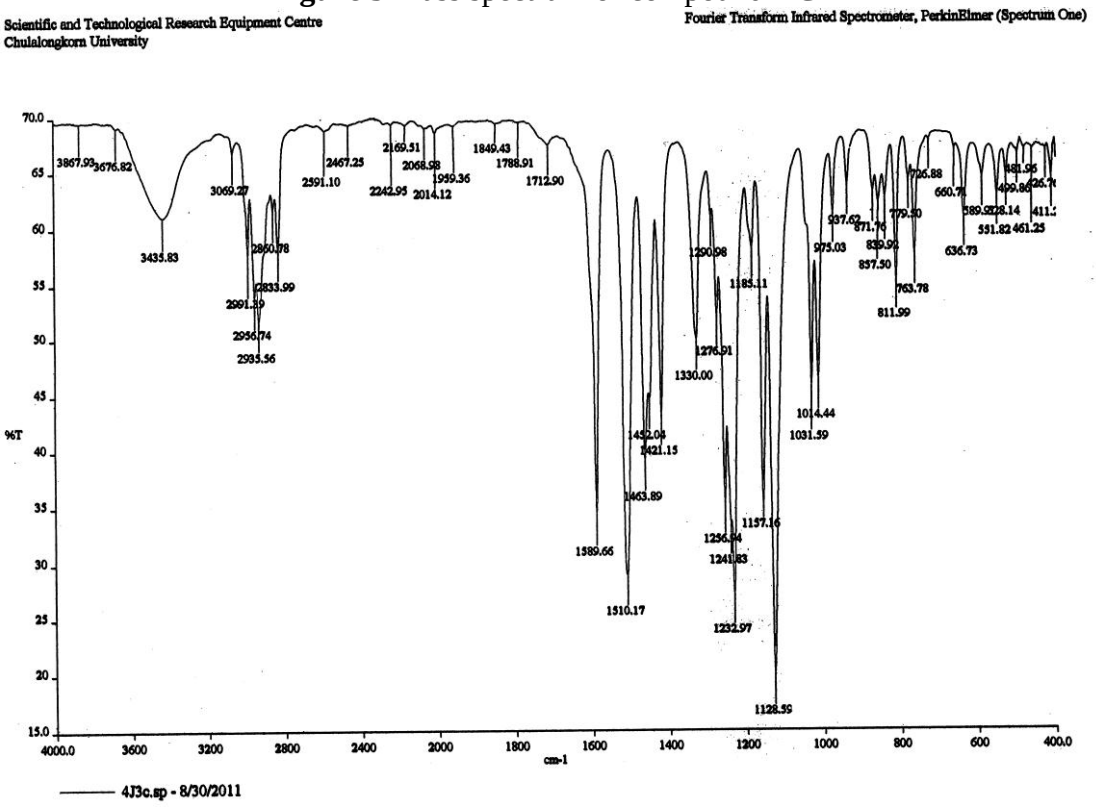

Figure 6 IR spectrum of compound DC1

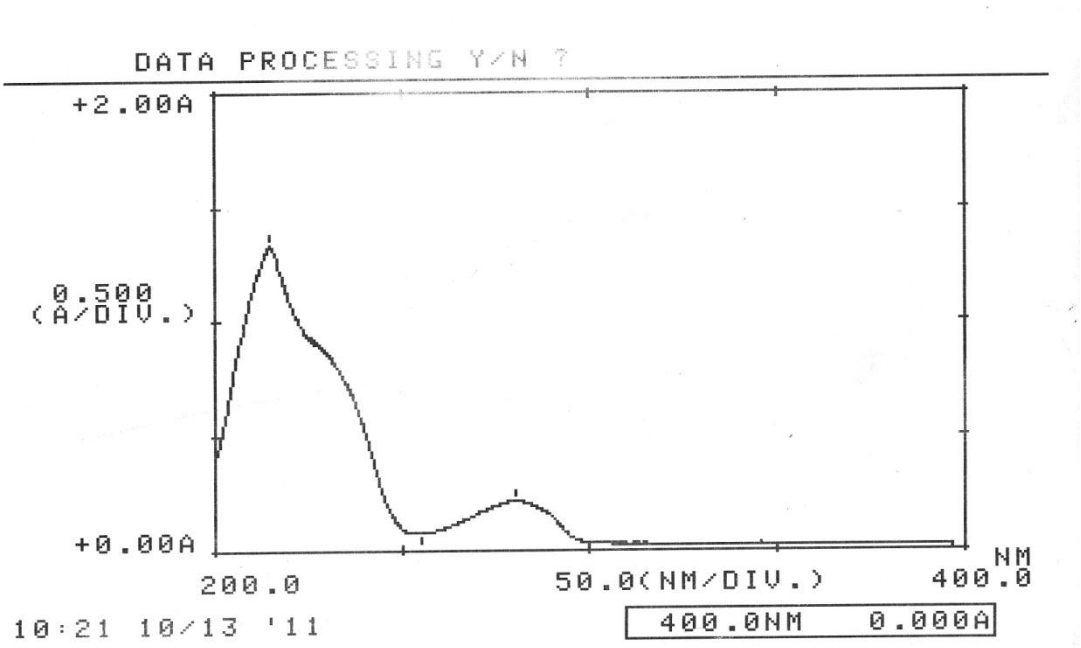

Figure 7 UV spectrum of compound DC1

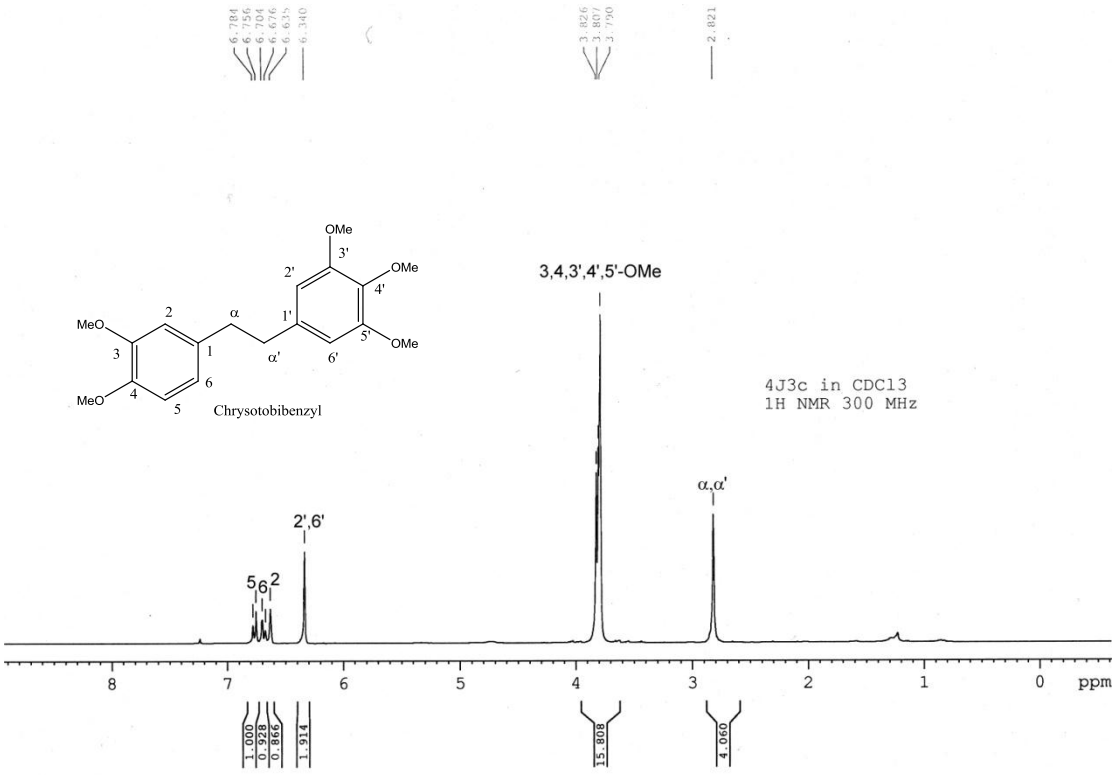

Figure 8 ^{1}H-NMR (300 MHz) spectrum of compound DC1 ($CDCl_3$)

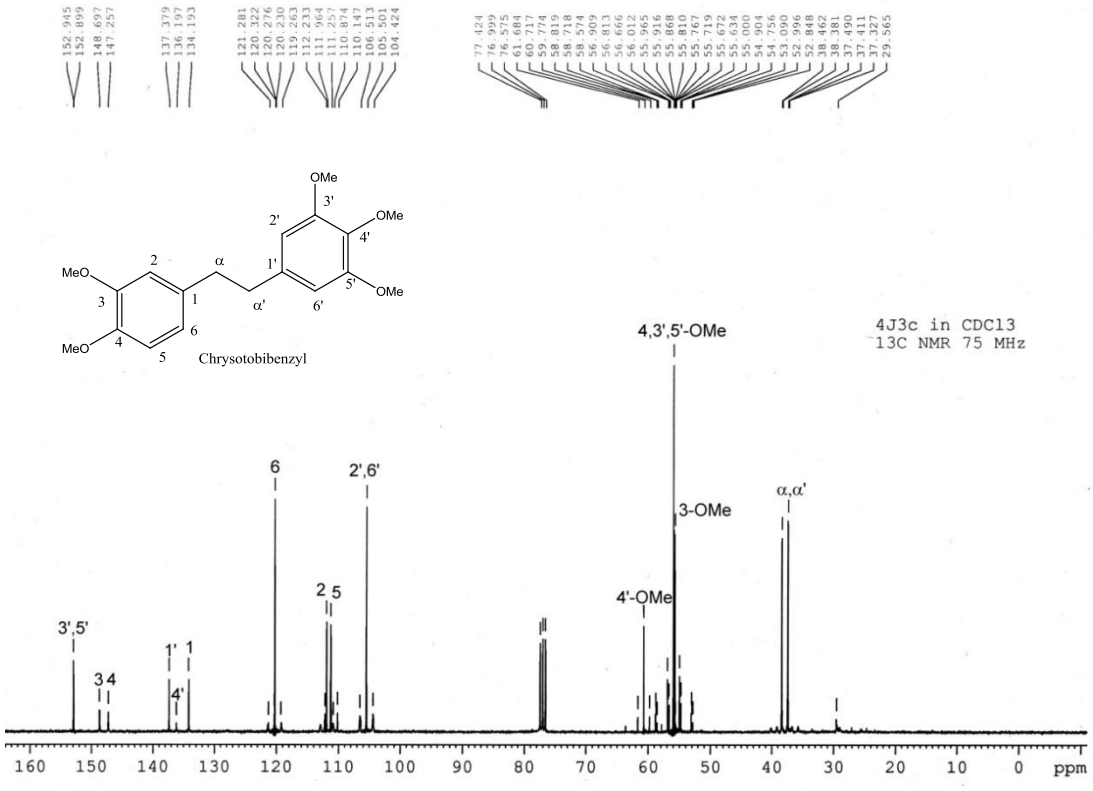

Figure 9 ^{13}C-NMR (75 MHz) spectrum of compound DC1 ($CDCl_3$)

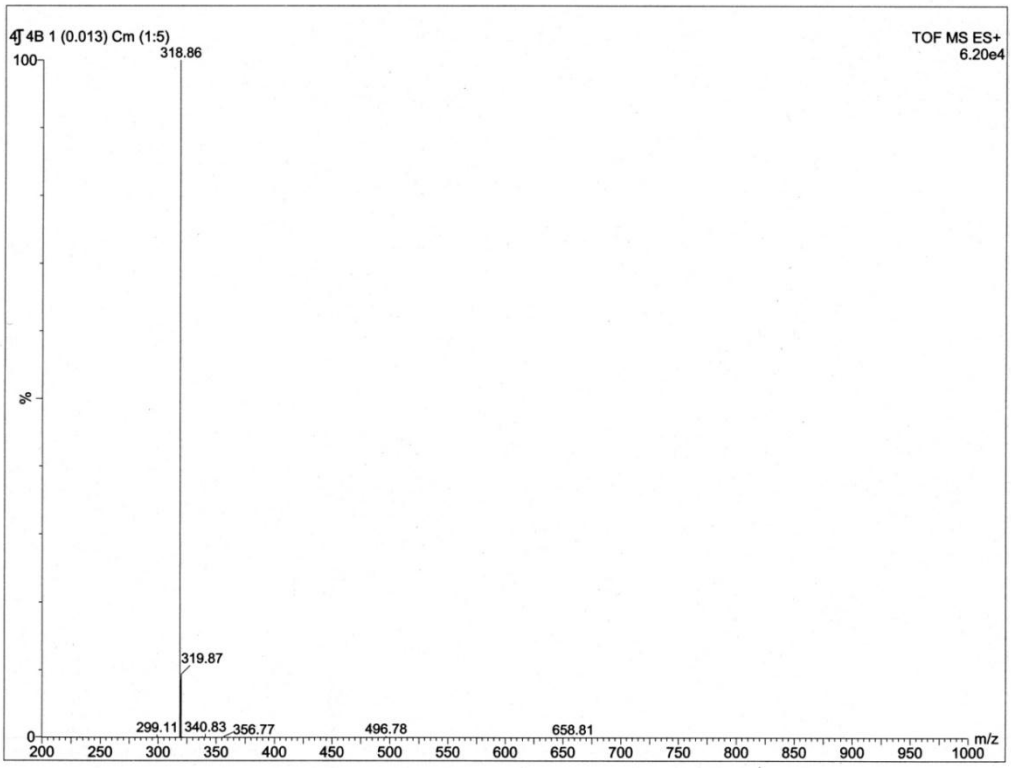

Figure 10 Mass spectrum of compound DC2

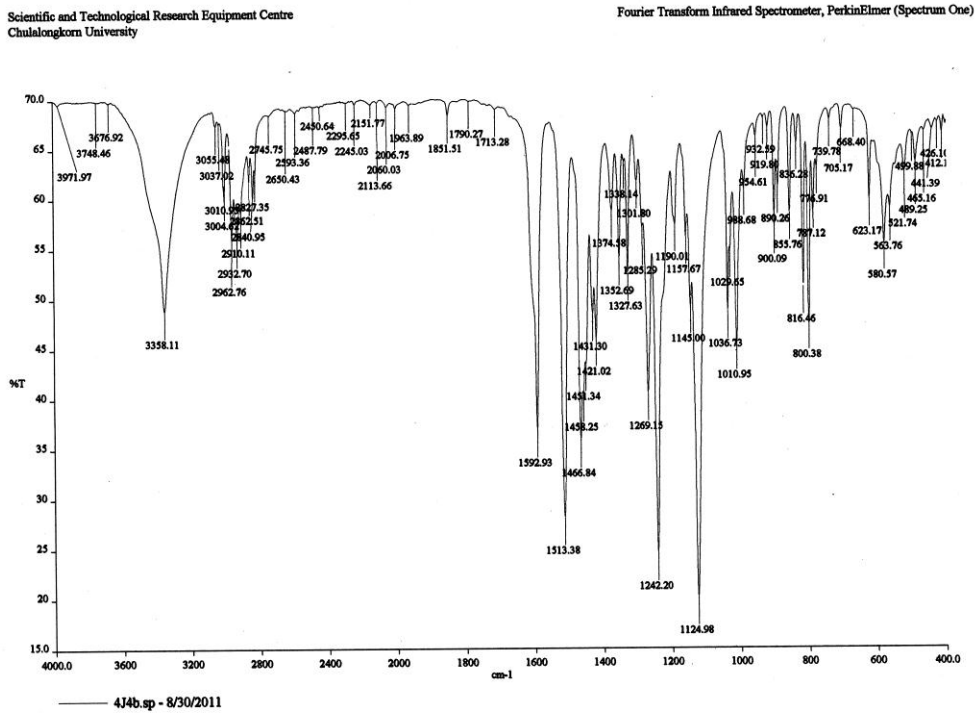

Figure 11 IR spectrum of compound DC2

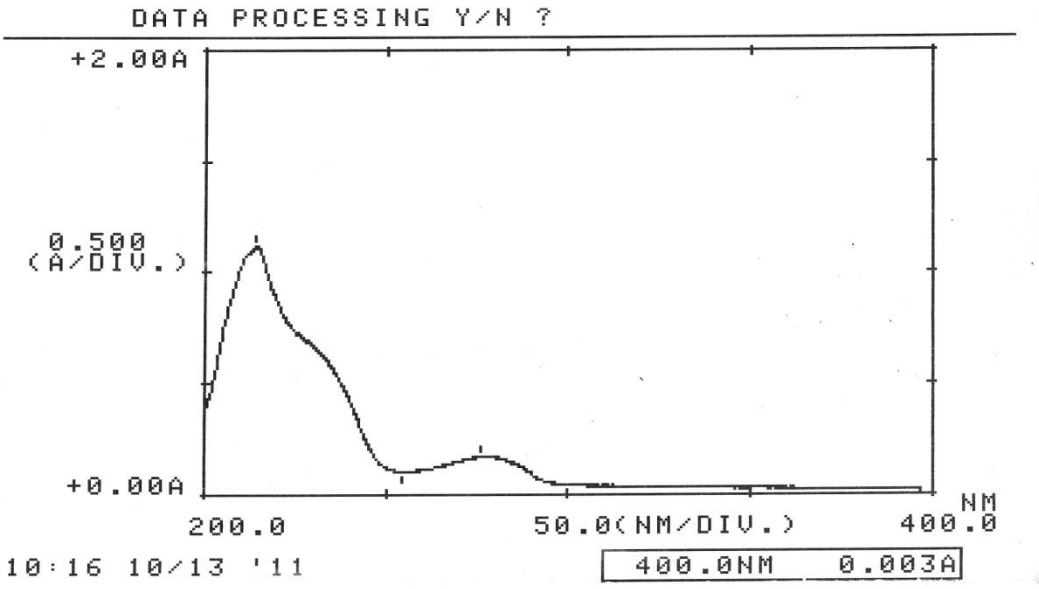

Figure 12 UV spectrum of compound DC2

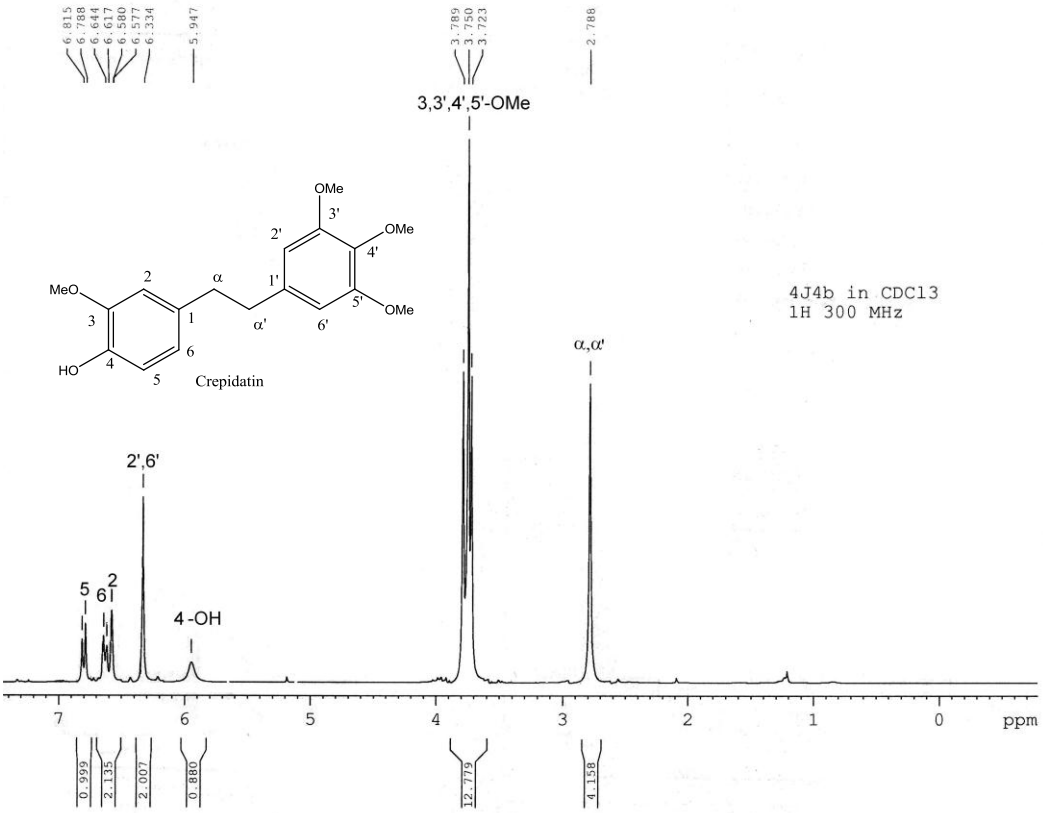

Figure 13 ^{1}H-NMR (300 MHz) spectrum of compound DC2 ($CDCl_3$)

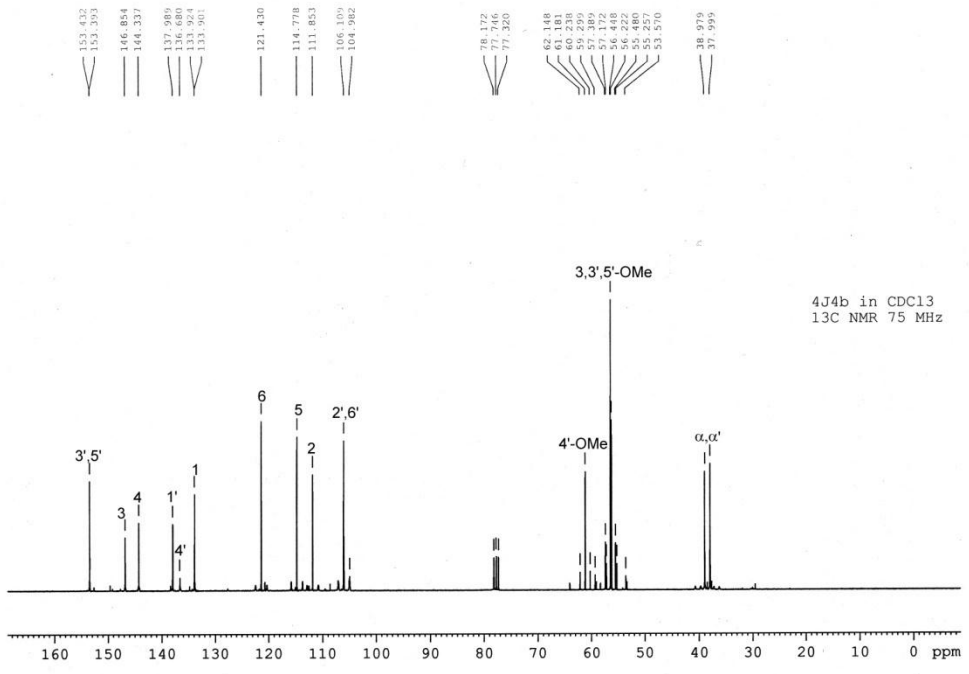

Figure 14 ^{13}C-NMR (75 MHz) spectrum of compound DC2 ($CDCl_3$)

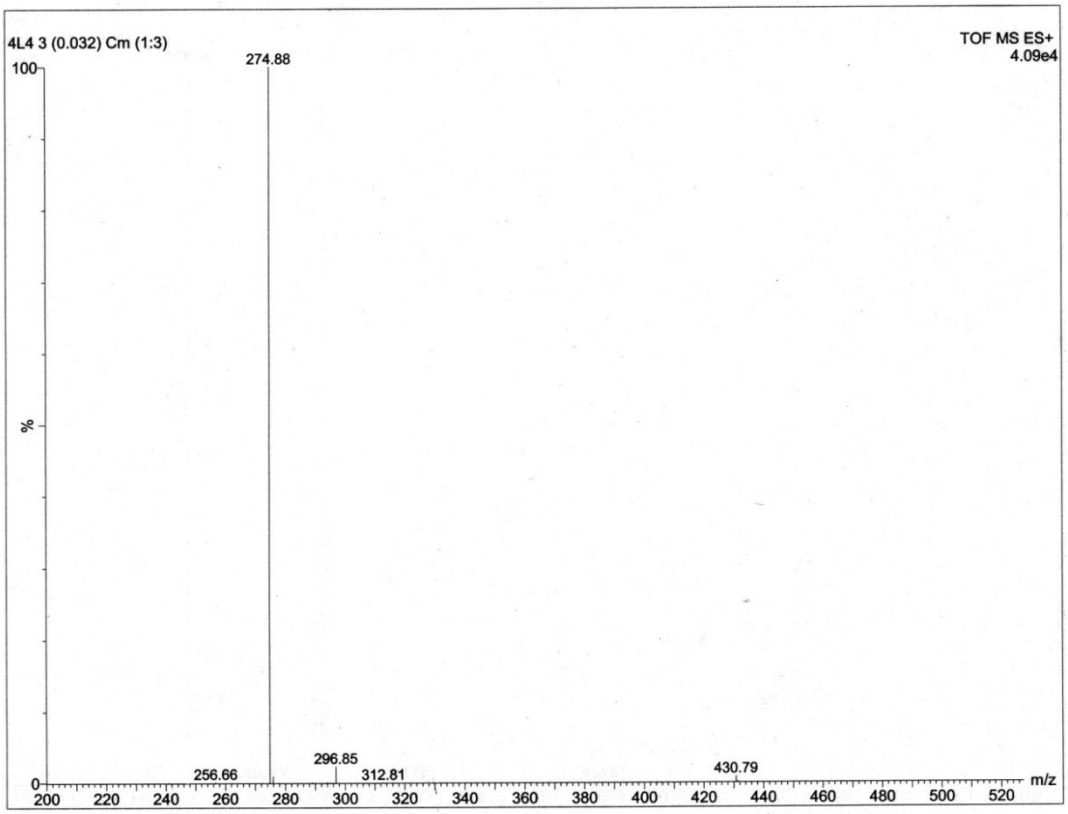

Figure 15 Mass spectrum of compound DC3

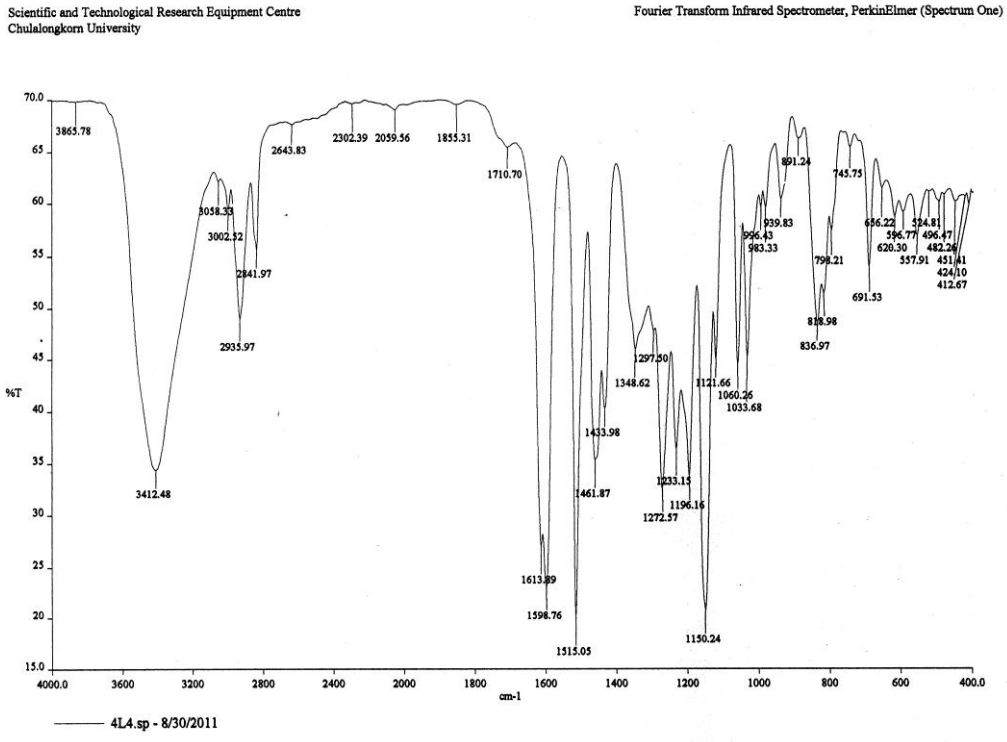

Figure 16 IR spectrum of compound DC3

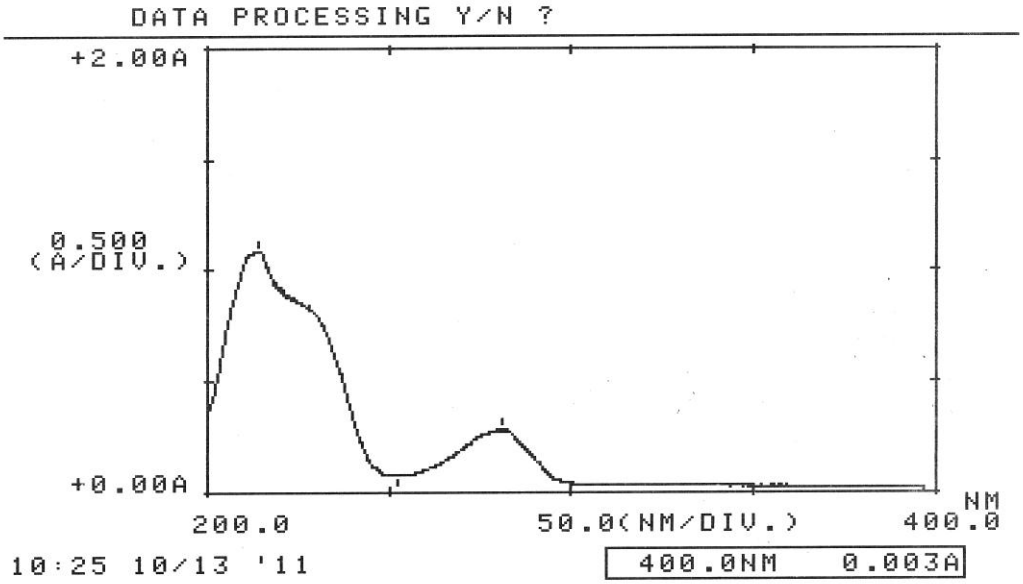

Figure 17 UV spectrum of compound DC3

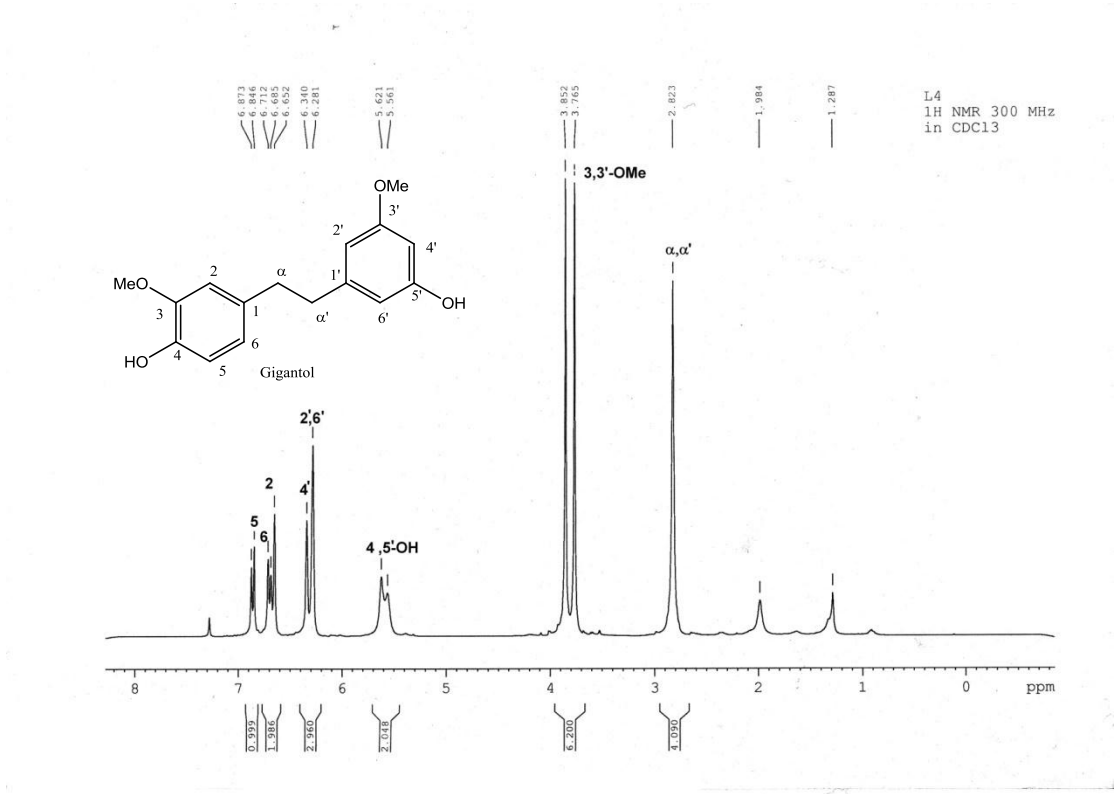

Figure 18 ^{1}H-NMR (300 MHz) spectrum of compound DC3 ($CDCl_3$)

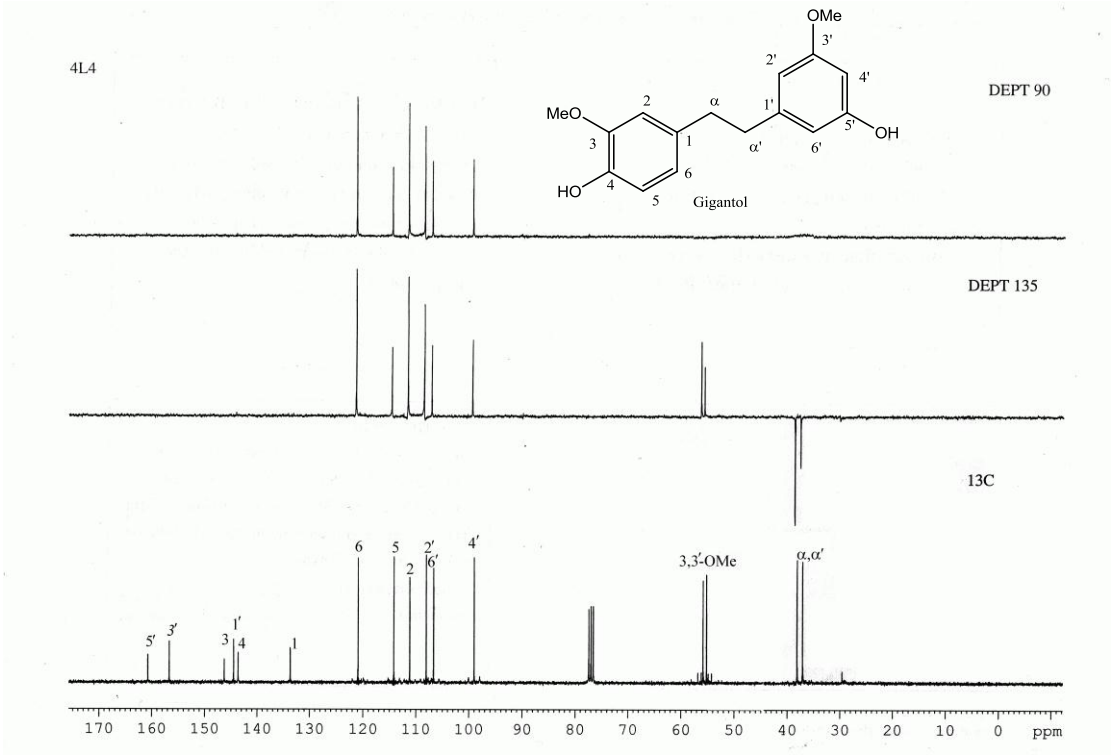

Figure 19 ^{13}C-NMR (75 MHz) and DEPT spectra of compound DC3 ($CDCl_3$)

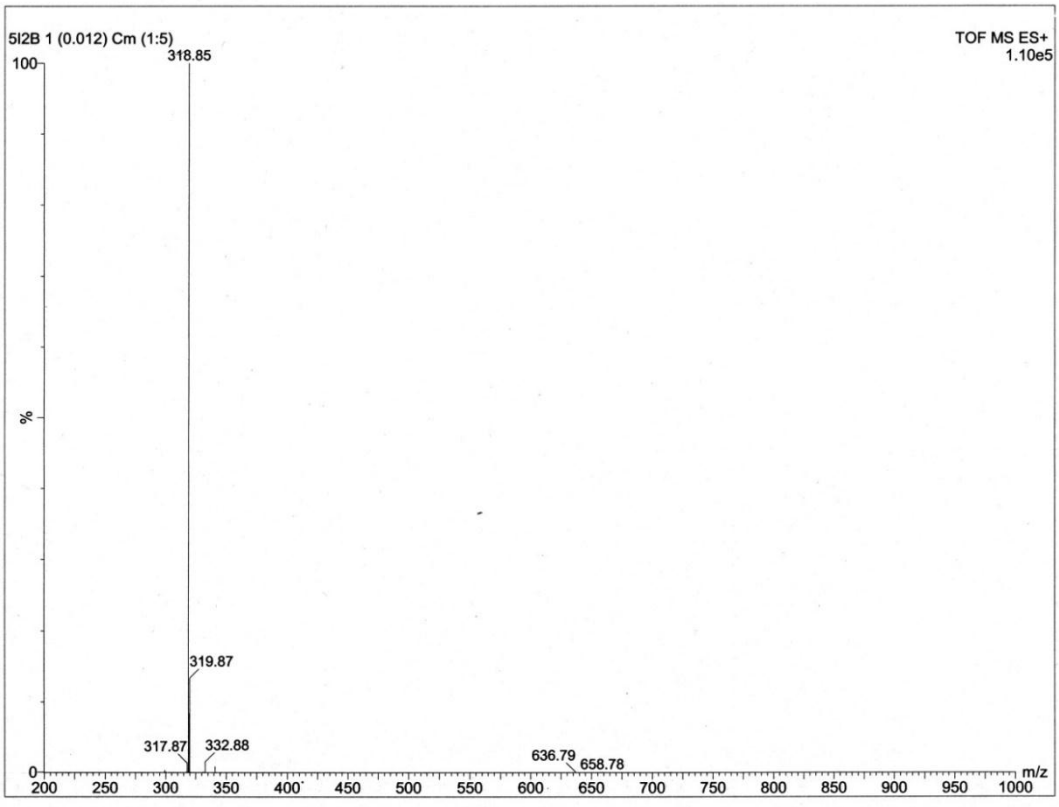

Figure 20 Mass spectrum of compound DC4

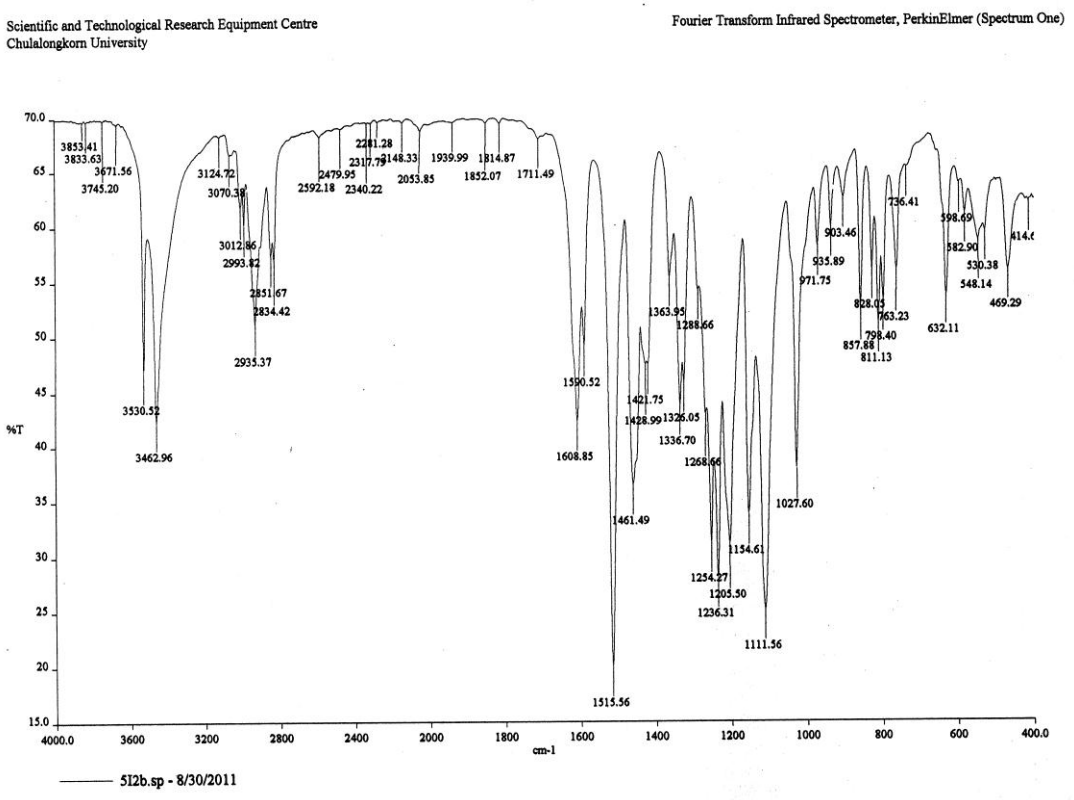

Figure 21 IR spectrum of compound DC4

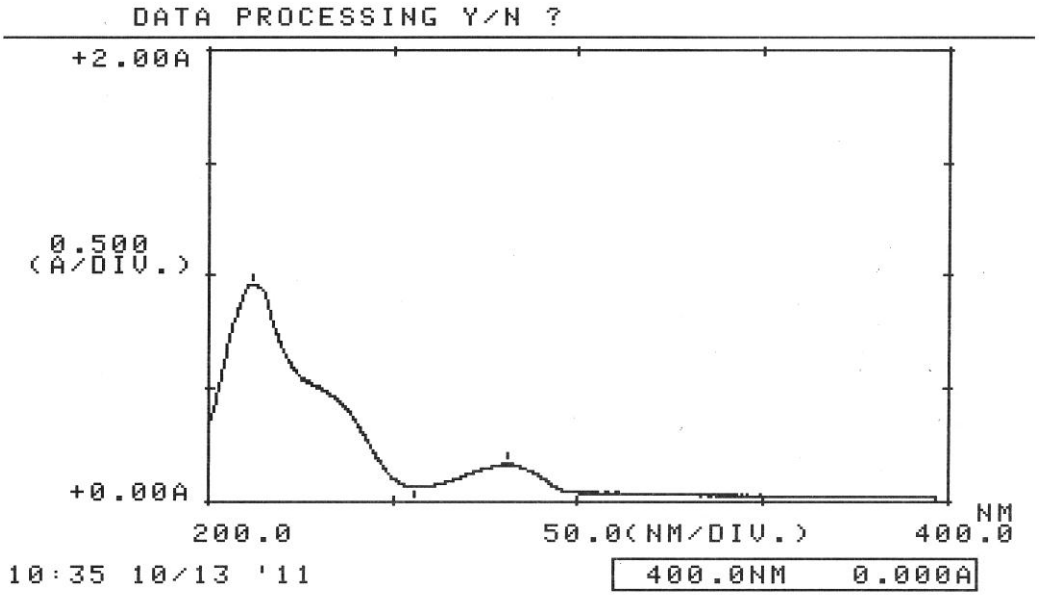

Figure 22 UV spectrum of compound DC4

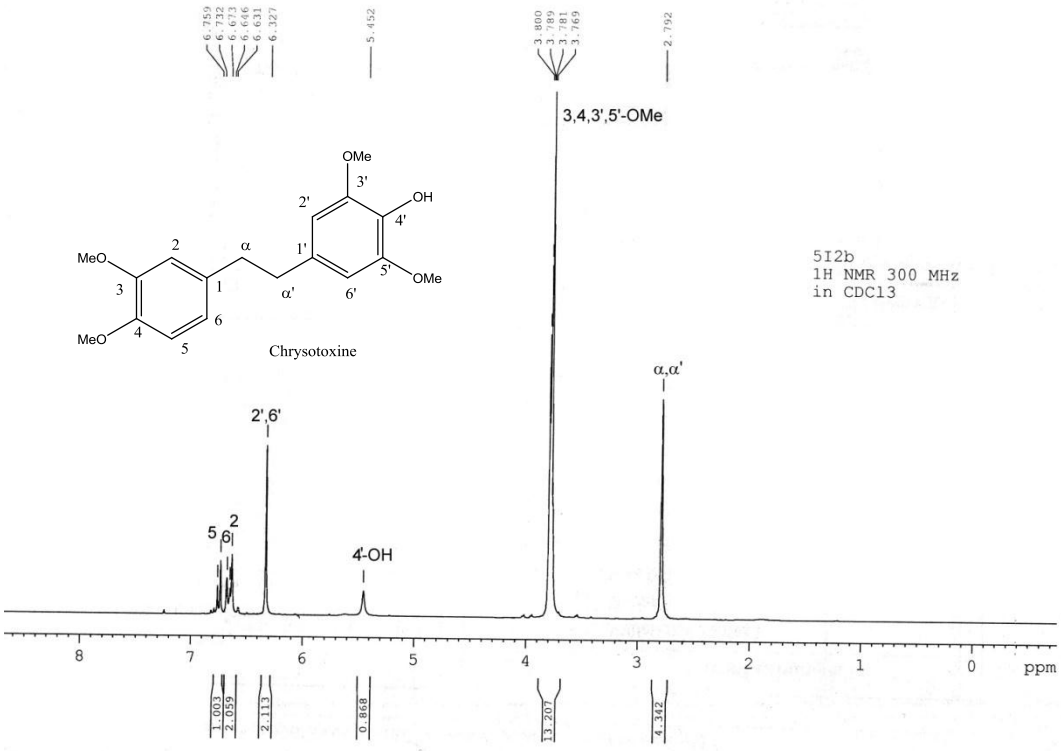

Figure 23 ^{1}H-NMR (300 MHz) spectrum of compound DC4 ($CDCl_3$)

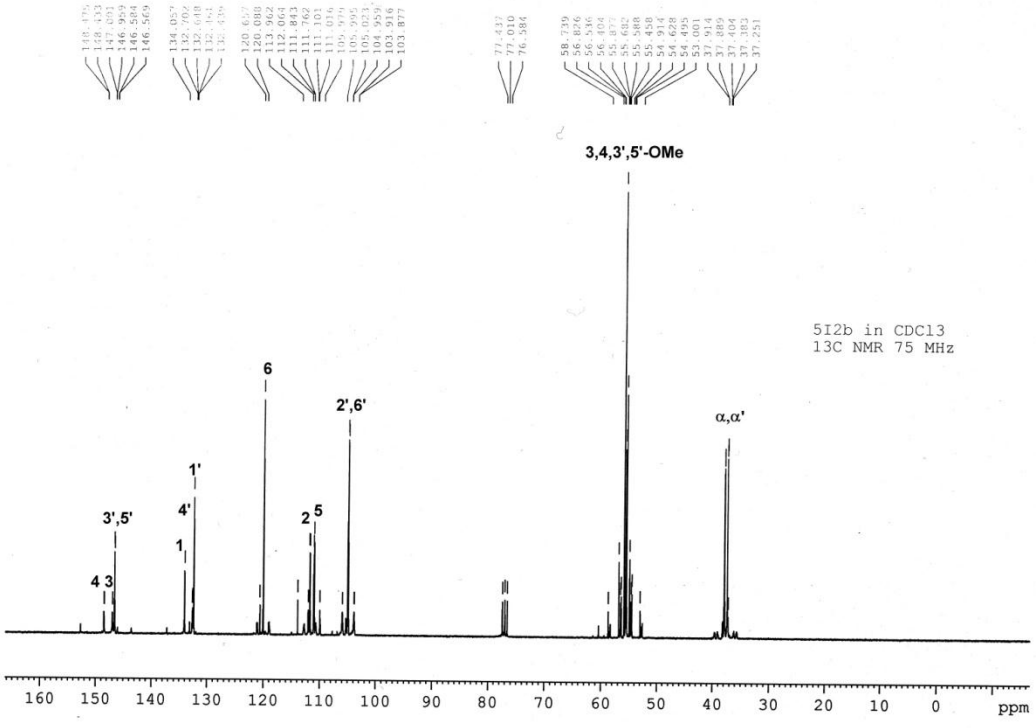

Figure 24 ^{13}C-NMR (75 MHz) spectrum of compound DC4 ($CDCl_3$)

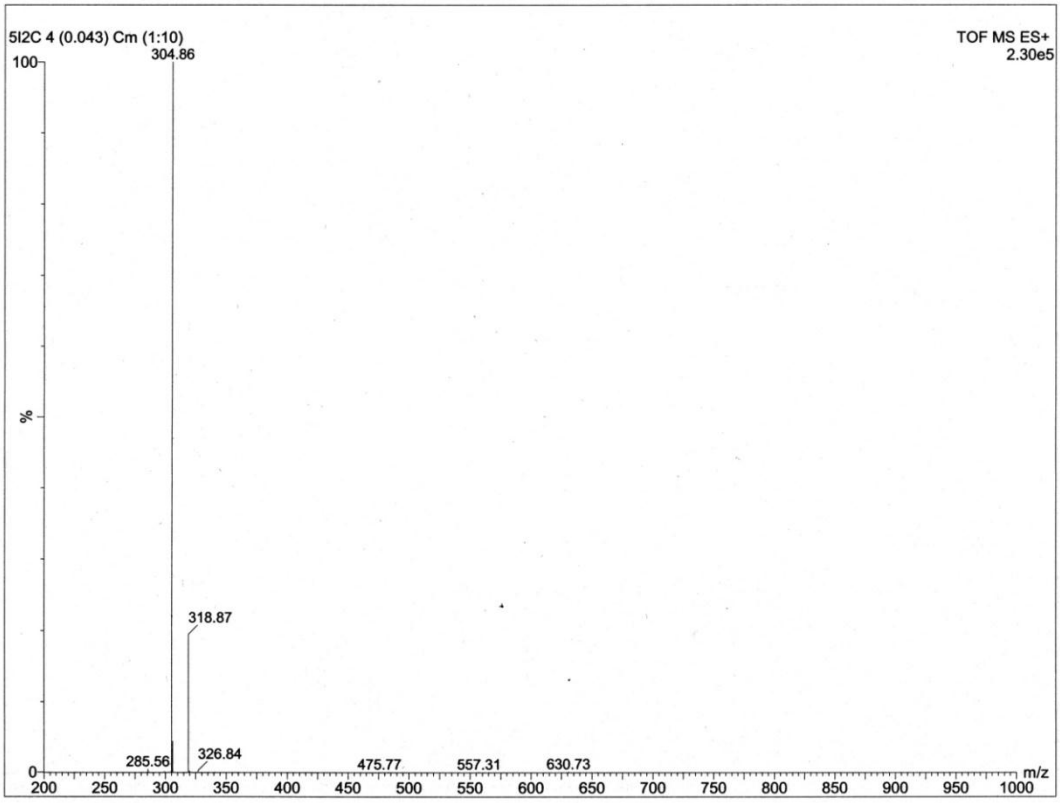

Figure 25 Mass spectrum of compound DC5

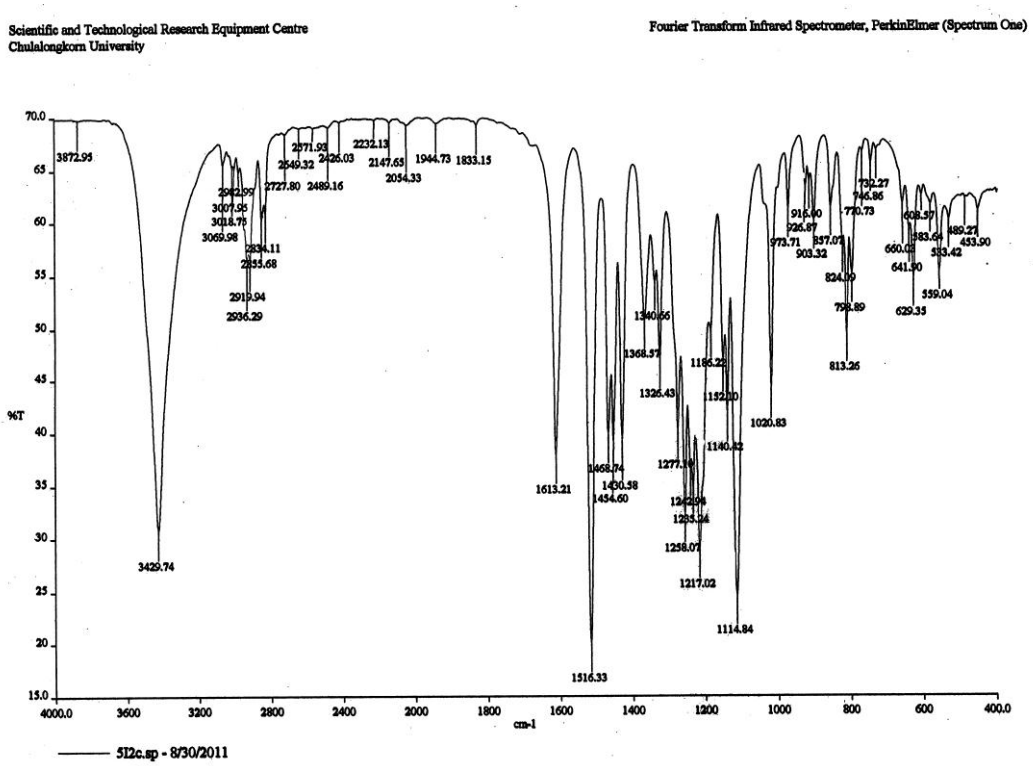

Figure 26 IR spectrum of compound DC5

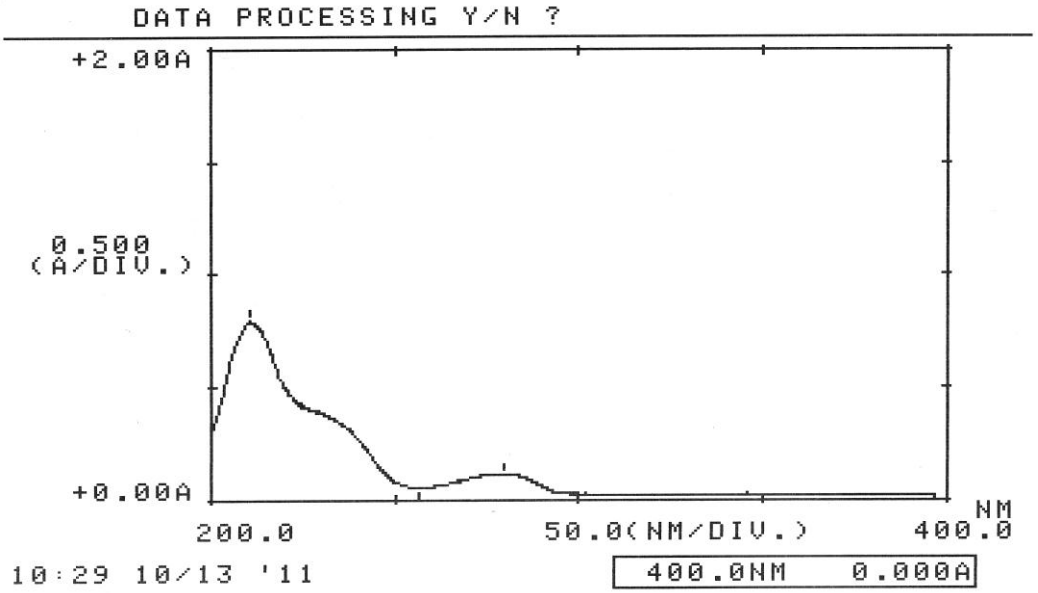

Figure 27 UV spectrum of compound DC5

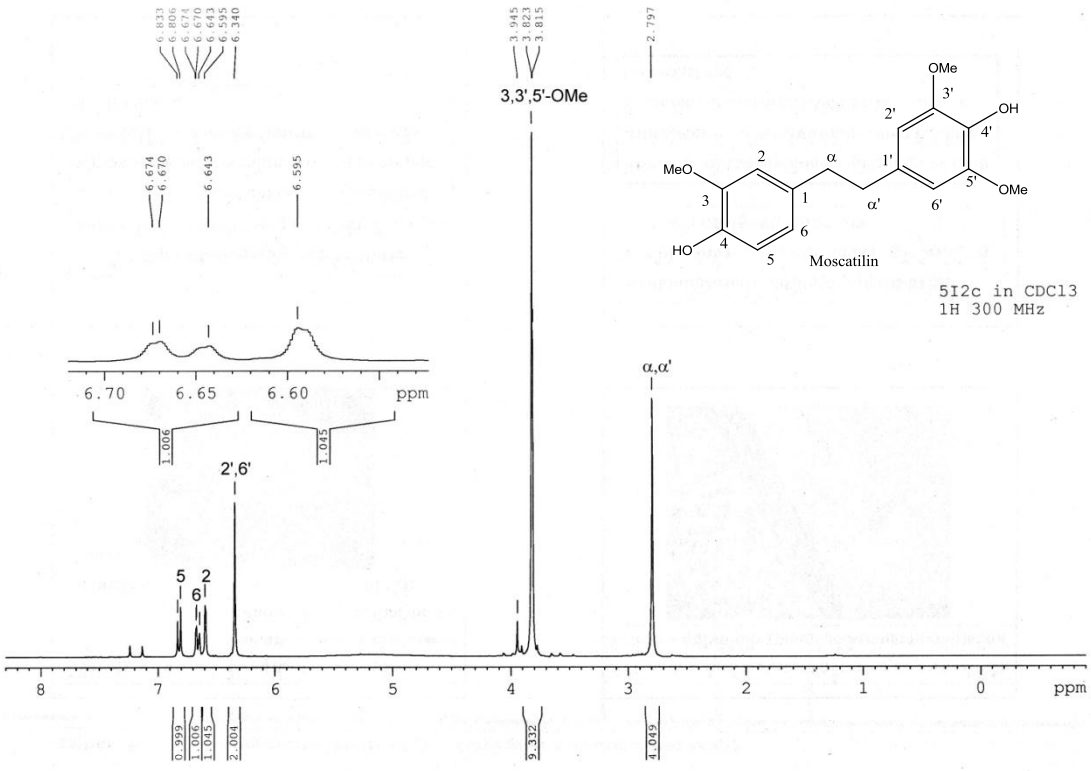

Figure 28 ^{1}H-NMR (300 MHz) spectrum of compound DC5 ($CDCl_3$)

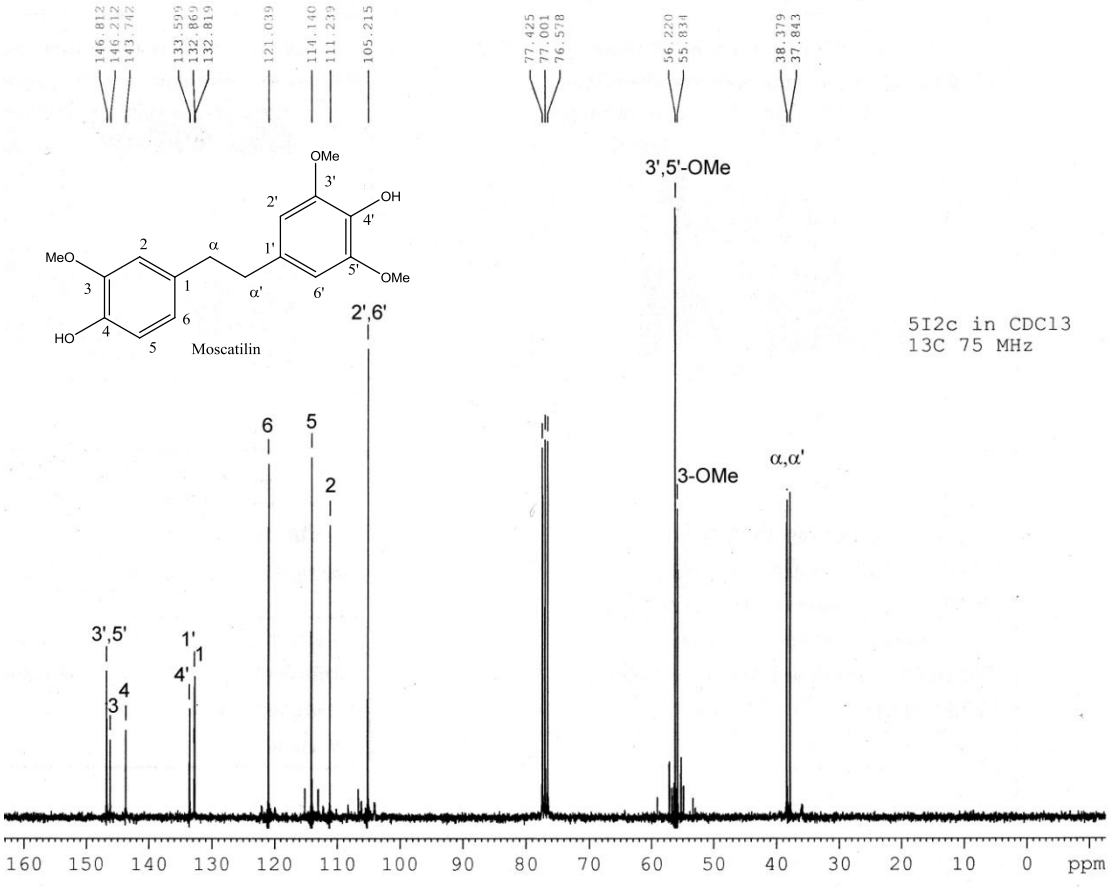

Figure 29 ^{13}C-NMR (75 MHz) spectrum of compound DC5 ($CDCl_3$)

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High resolution report

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Sample Name 7K12B

Operator Sutichai Ext: 3560
Instrument micrOTOF Bruker
Calibrate by Sodium Formate

Acquisition Parameter

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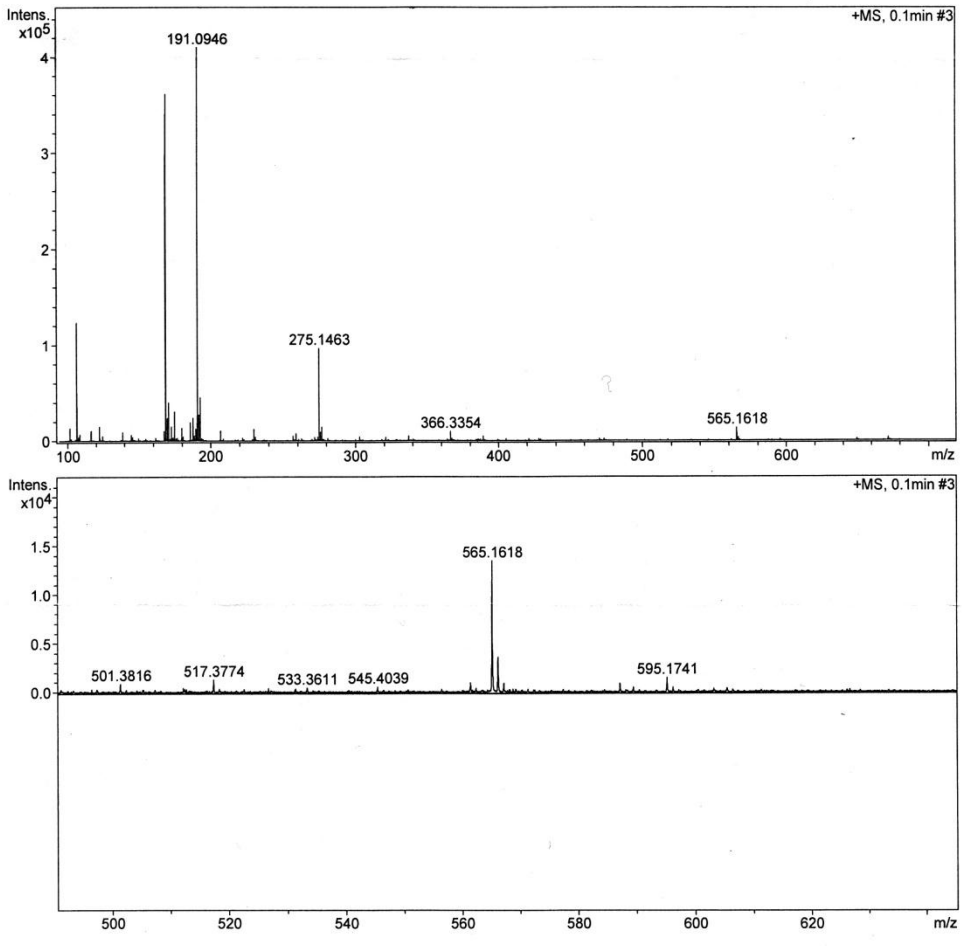

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Figure 30 Mass spectrum of compound DC6

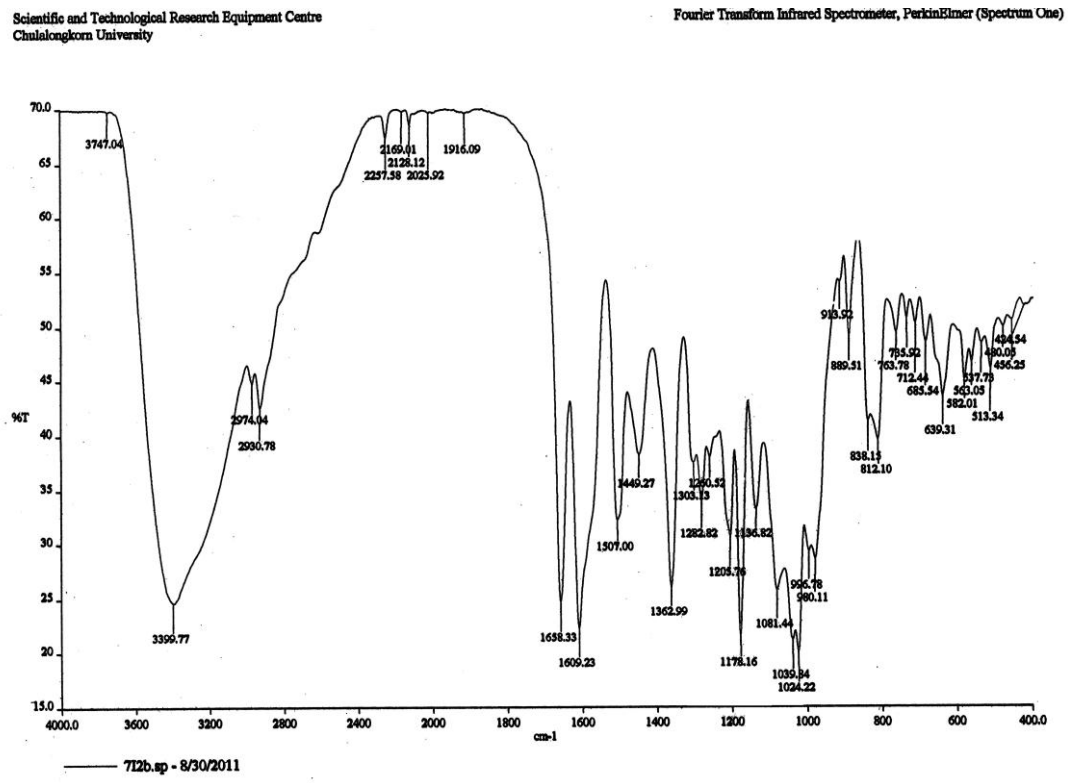

Figure 31 IR spectrum of compound DC6

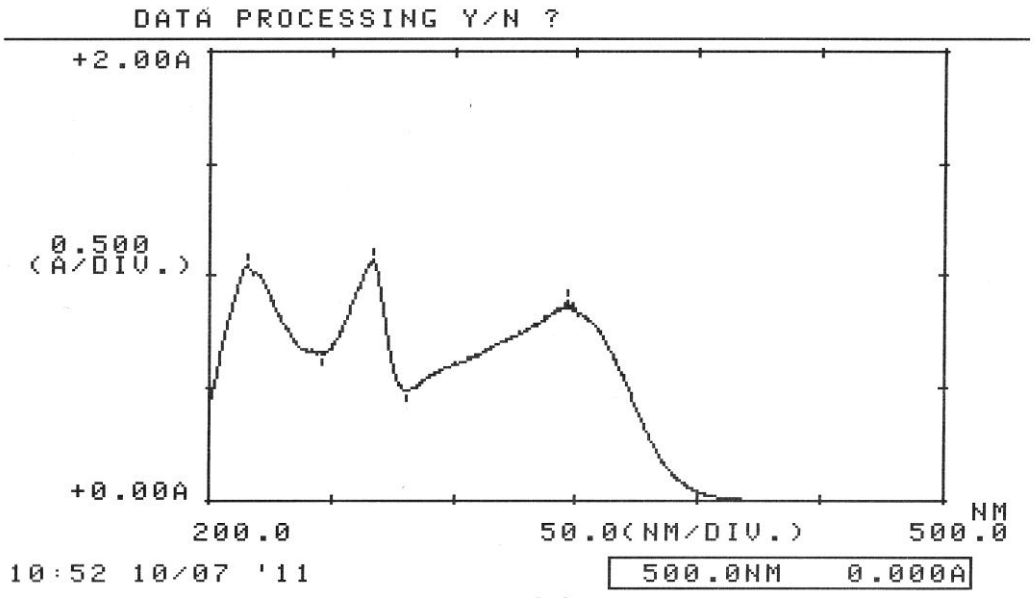

Figure 32 UV spectrum of compound DC6

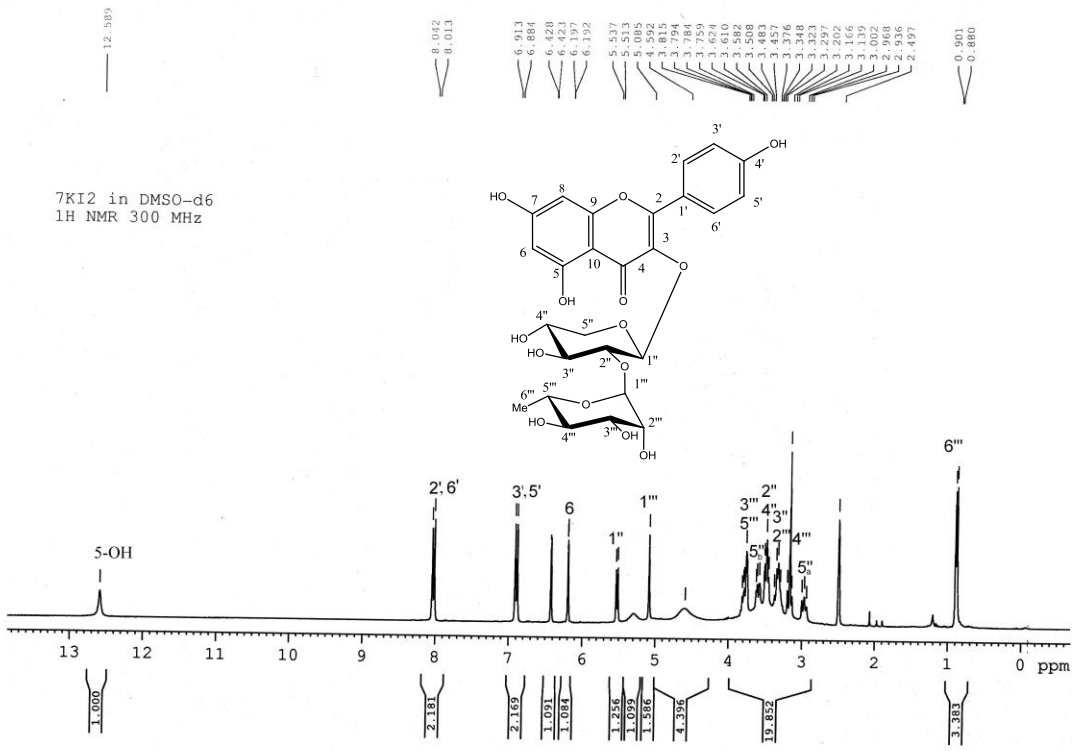

Figure 33 ^{1}H-NMR (300 MHz) spectrum of compound DC6 (DMSO-d_6)

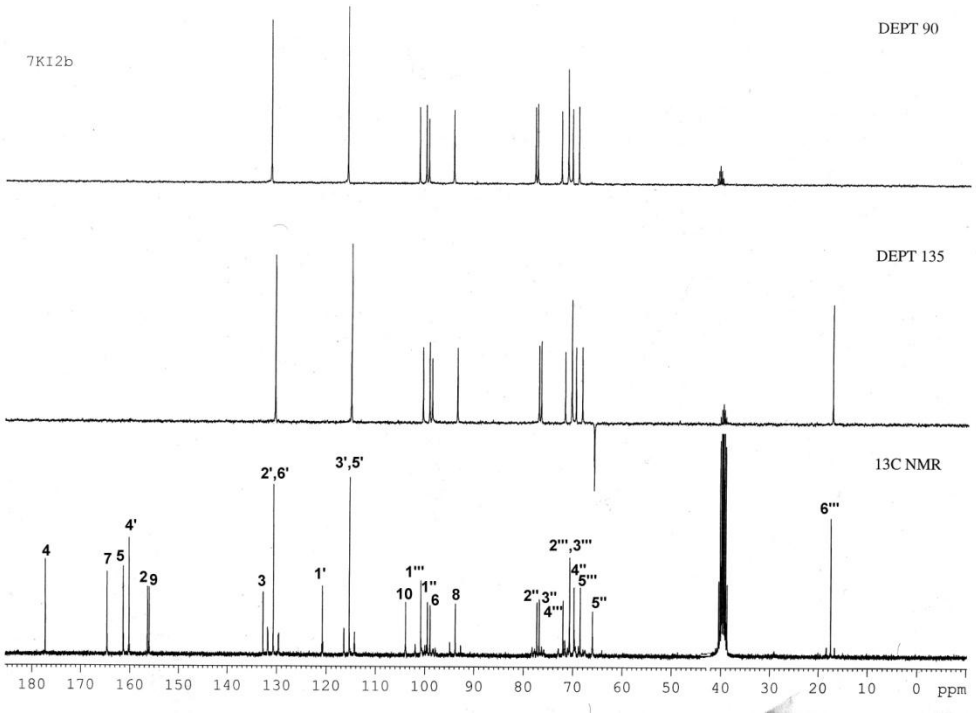

Figure 34 ^{13}C-NMR (75 MHz) and DEPT spectra of compound DC6 (DMSO-d_6)

BIORESOURCES RESEARCH UNIT

High resolution report

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Sample Name 7J4B

Operator Sutichai Ext: 3560
Instrument micrOTOF Bruker
Calibrate by Sodium Formate

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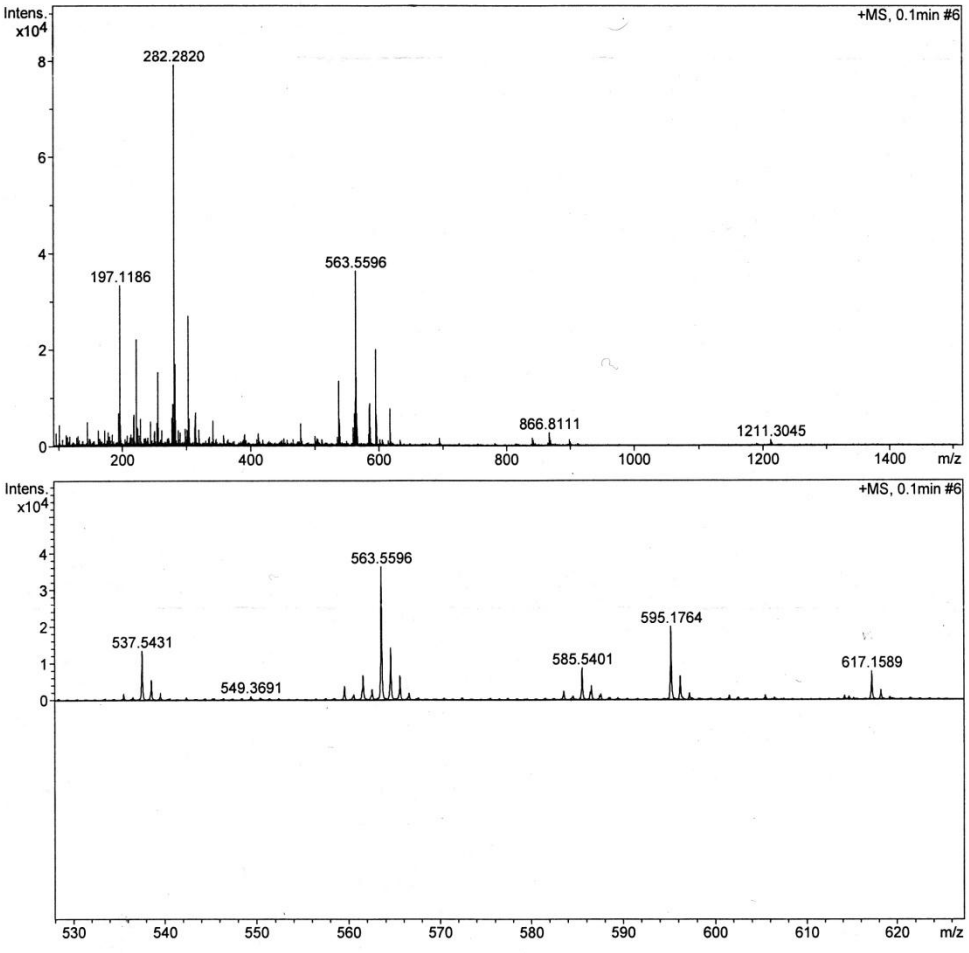

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Figure 35 Mass spectrum of compound DC7

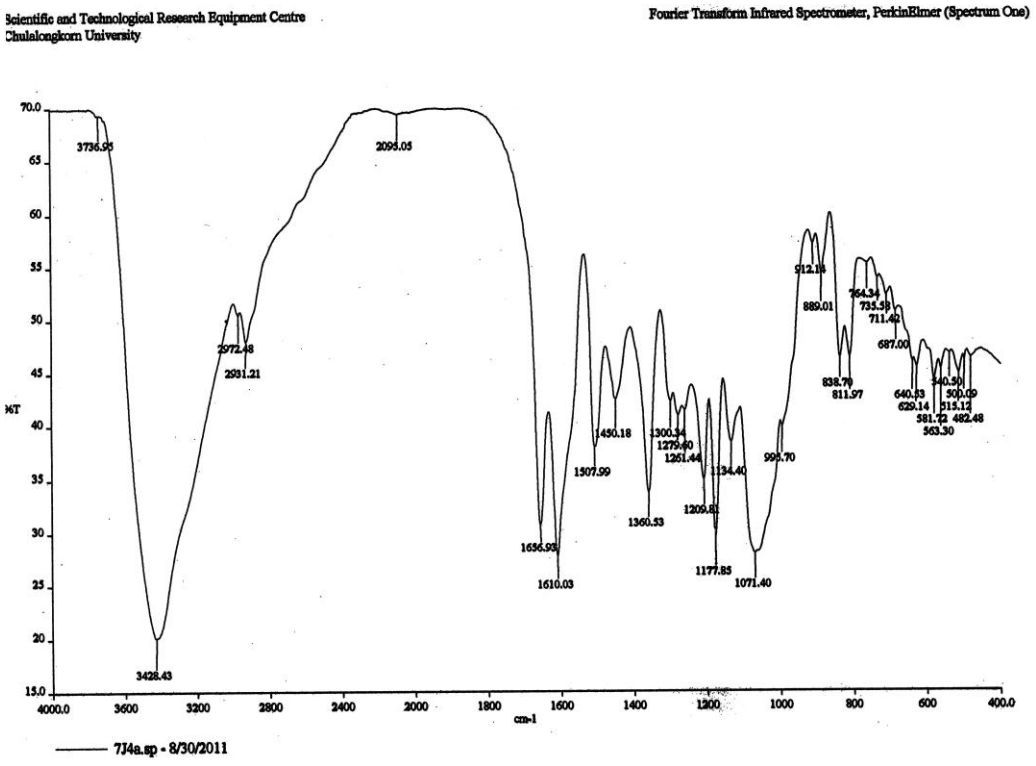

Figure 36 IR spectrum of compound DC7

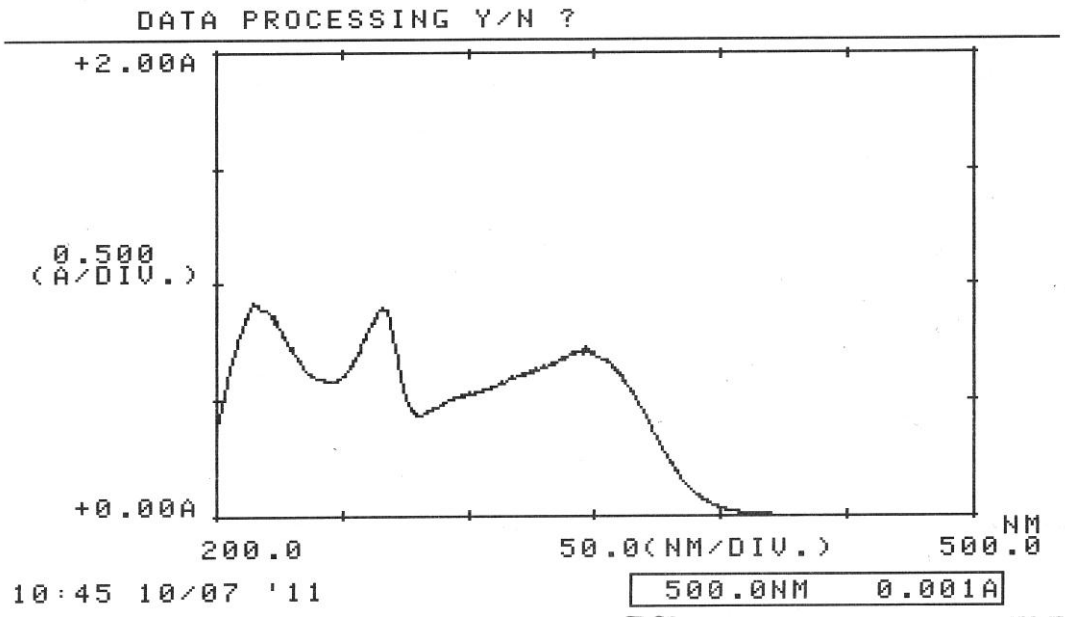

Figure 37 UV spectrum of compound DC7

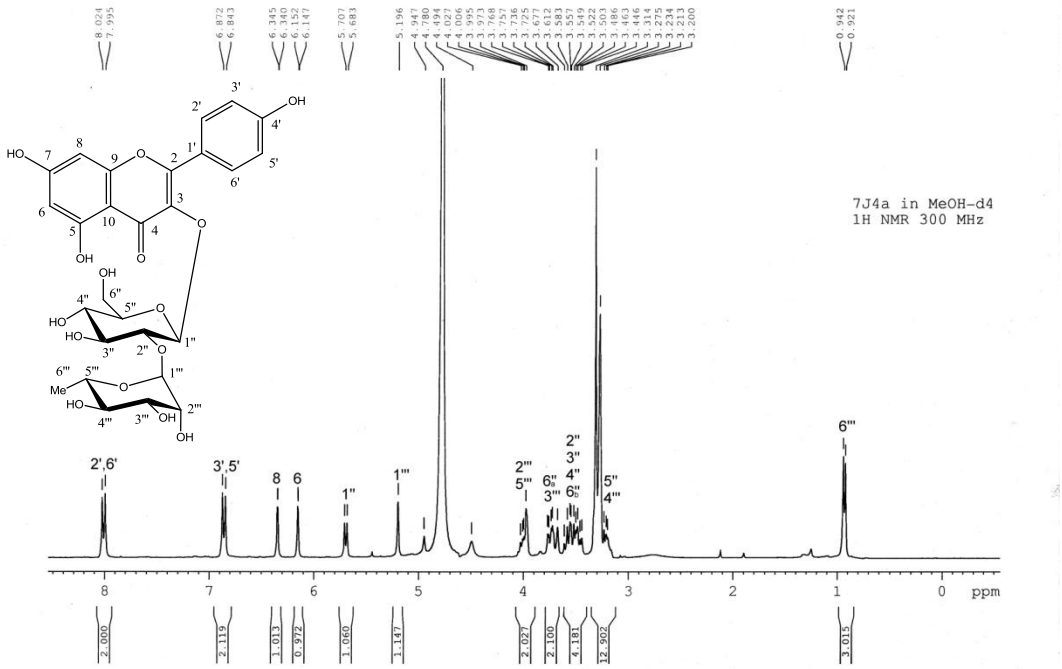

Figure 38 ^{1}H-NMR (300 MHz) spectrum of compound DC7 (CD_3OD)

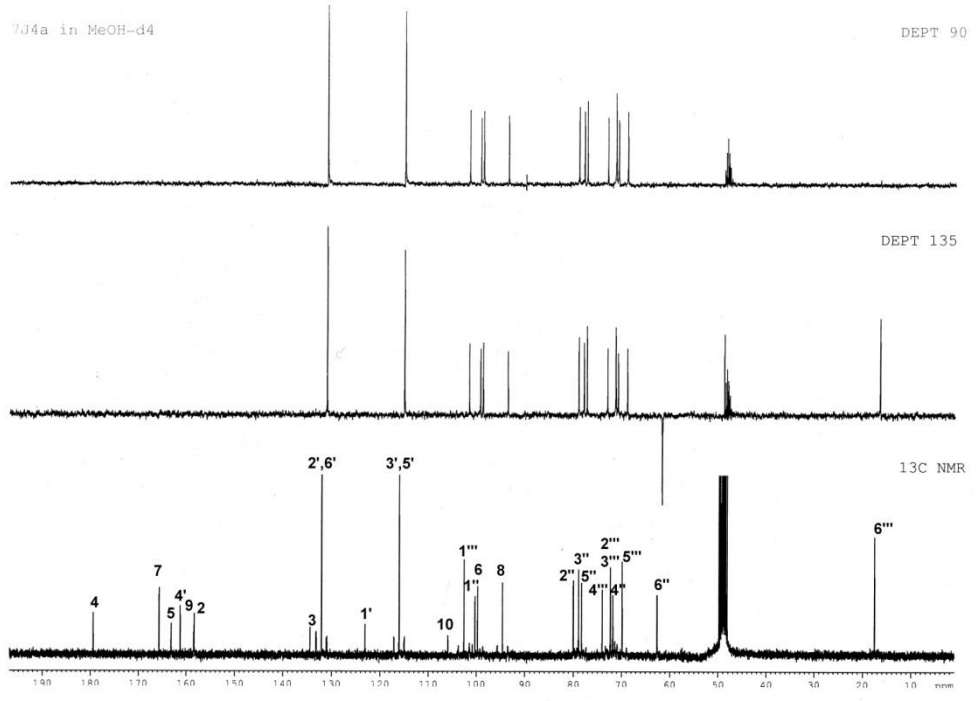

Figure 39 ^{13}C-NMR (75 MHz) and DEPT spectra of compound DC7 (CD_3OD)

BIORESOURCES RESEARCH UNIT

High resolution report

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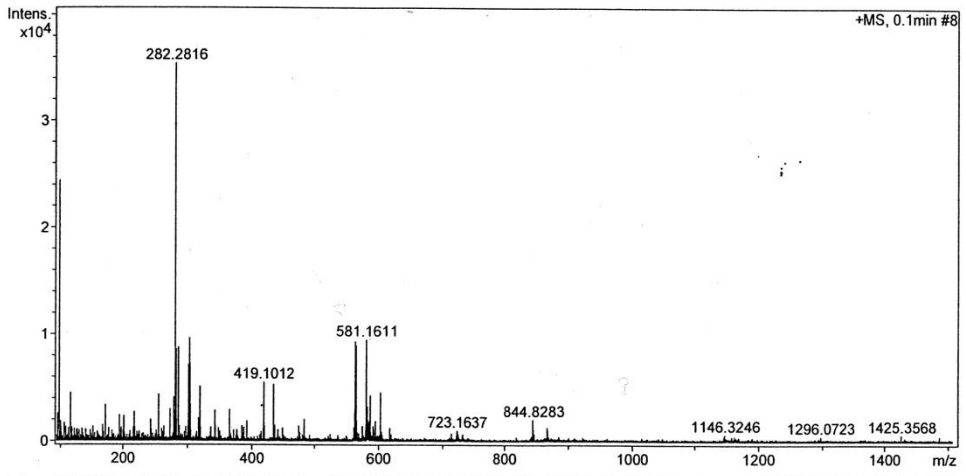

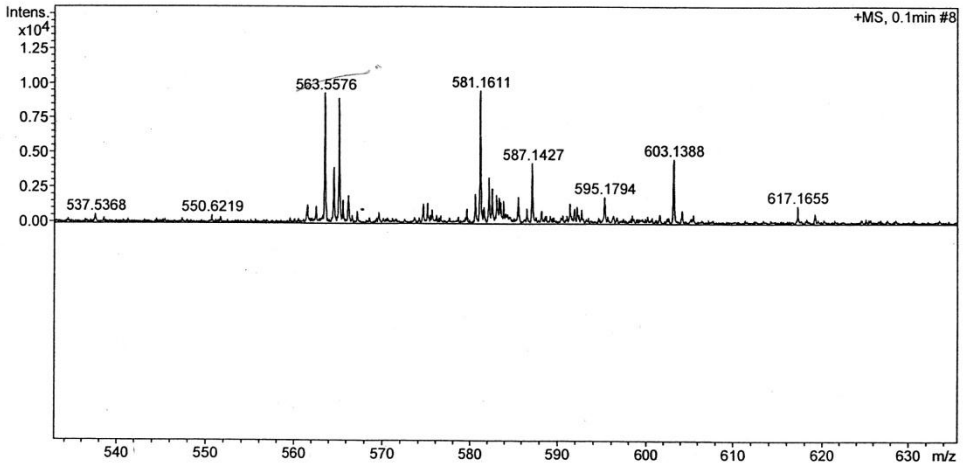

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Figure 40 Mass spectrum of compound DC8

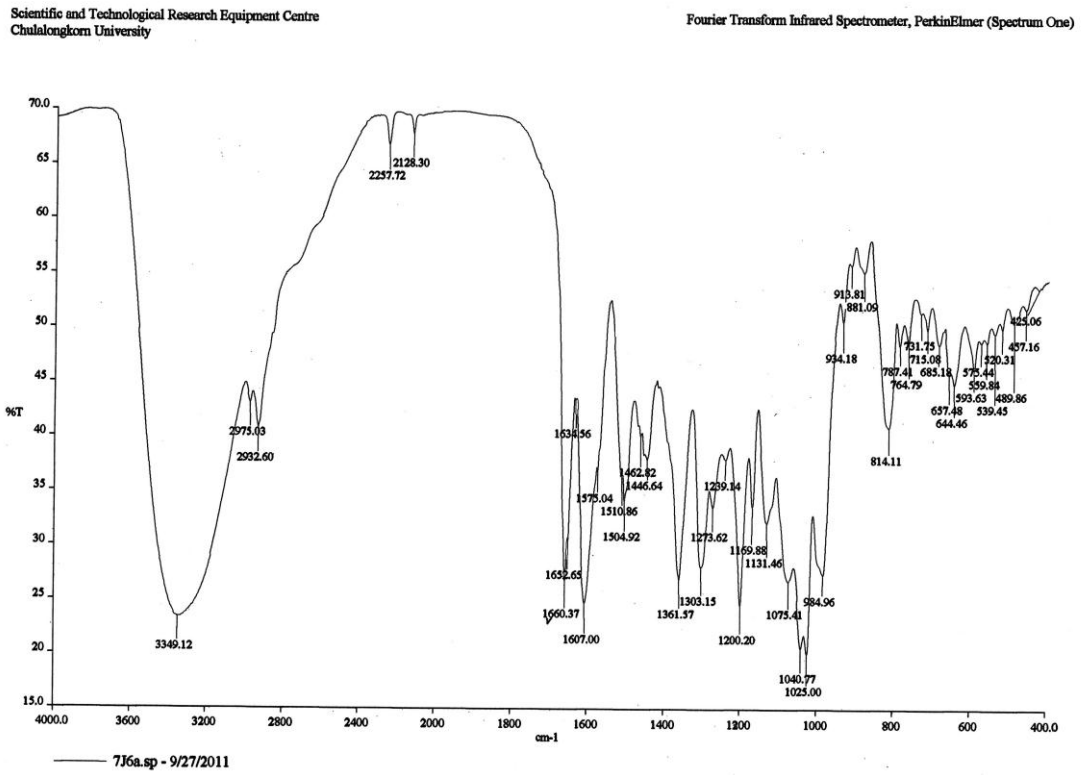

Figure 41 IR spectrum of compound DC8

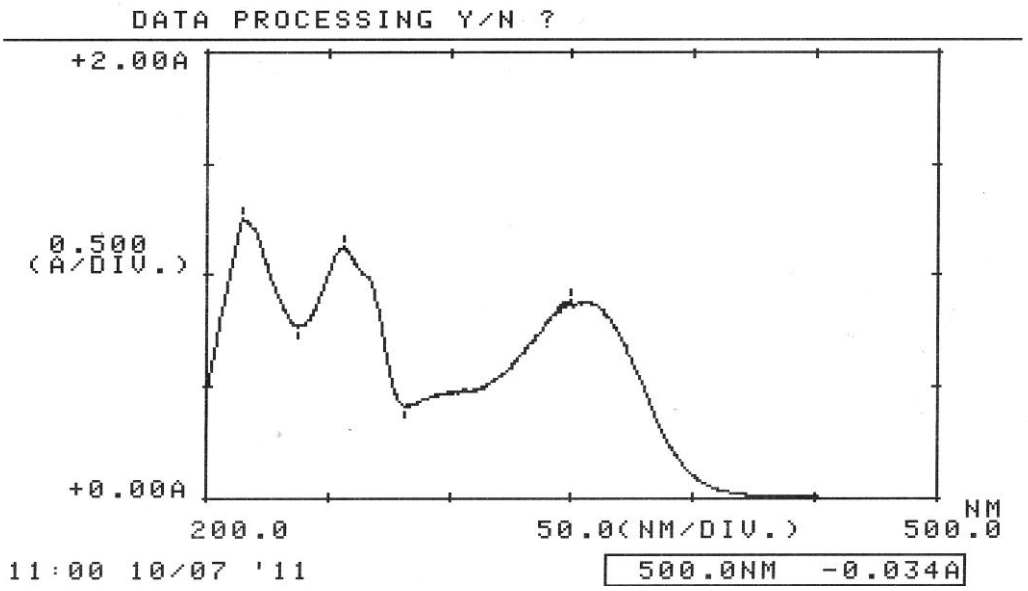

Figure 42 UV spectrum of compound DC8

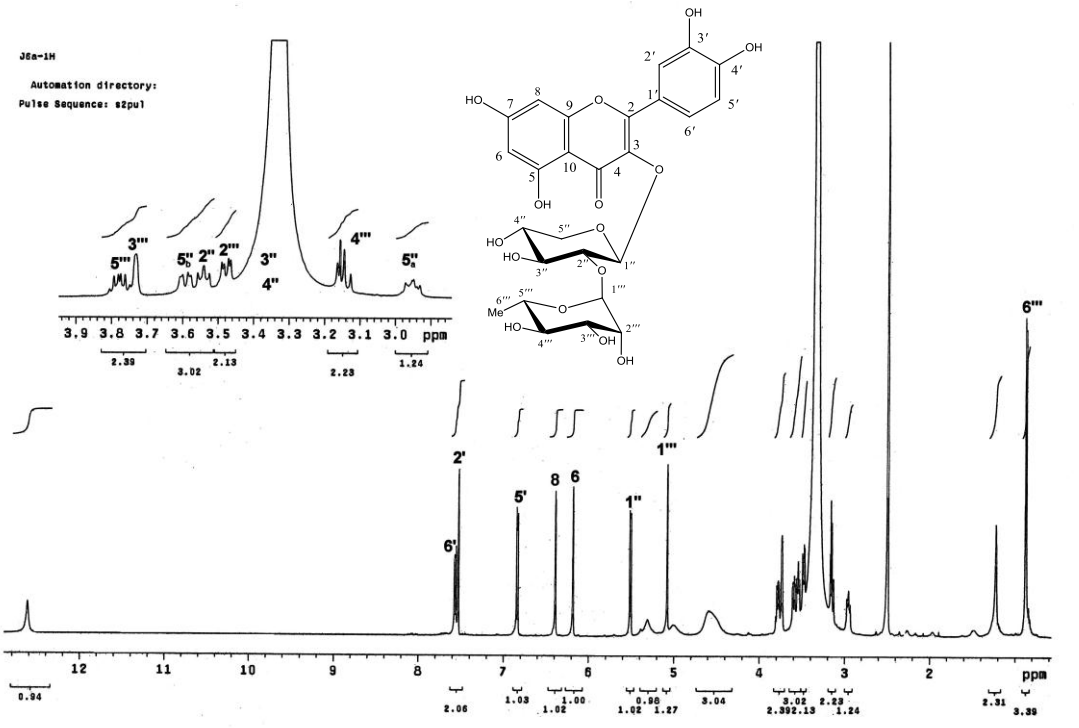

Figure 43 ^{1}H-NMR (500 MHz) spectrum of compound DC8 (DMSO-d_6)

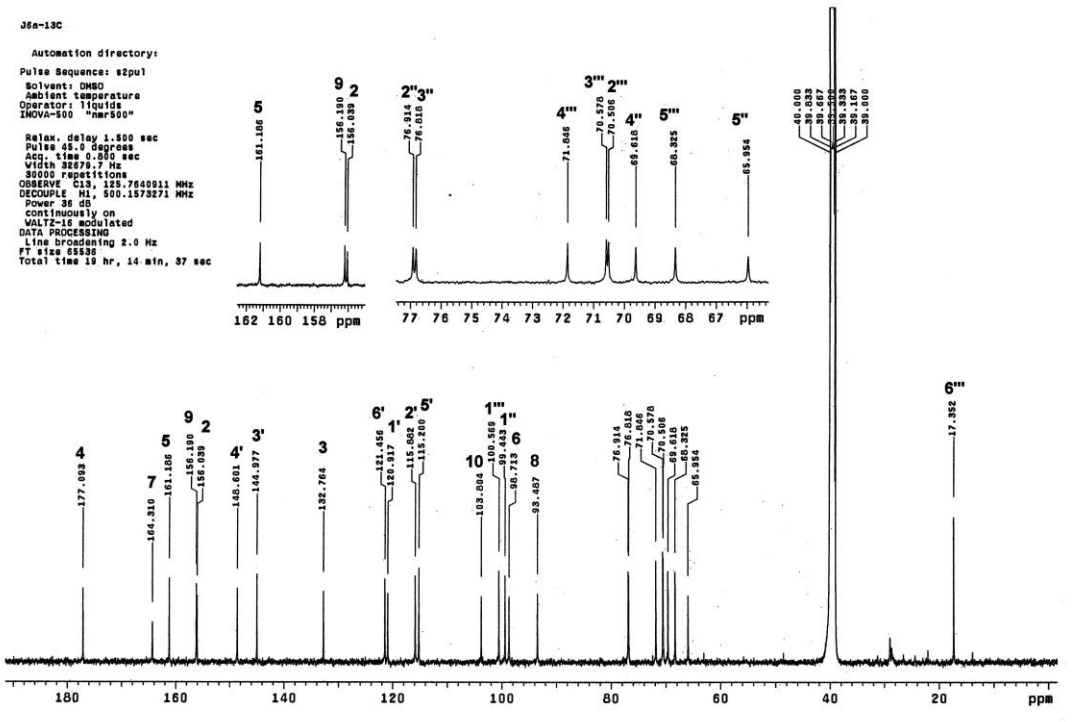

Figure 44 ^{13}C-NMR (125 MHz) spectrum of compound DC8 (DMSO-d_6)

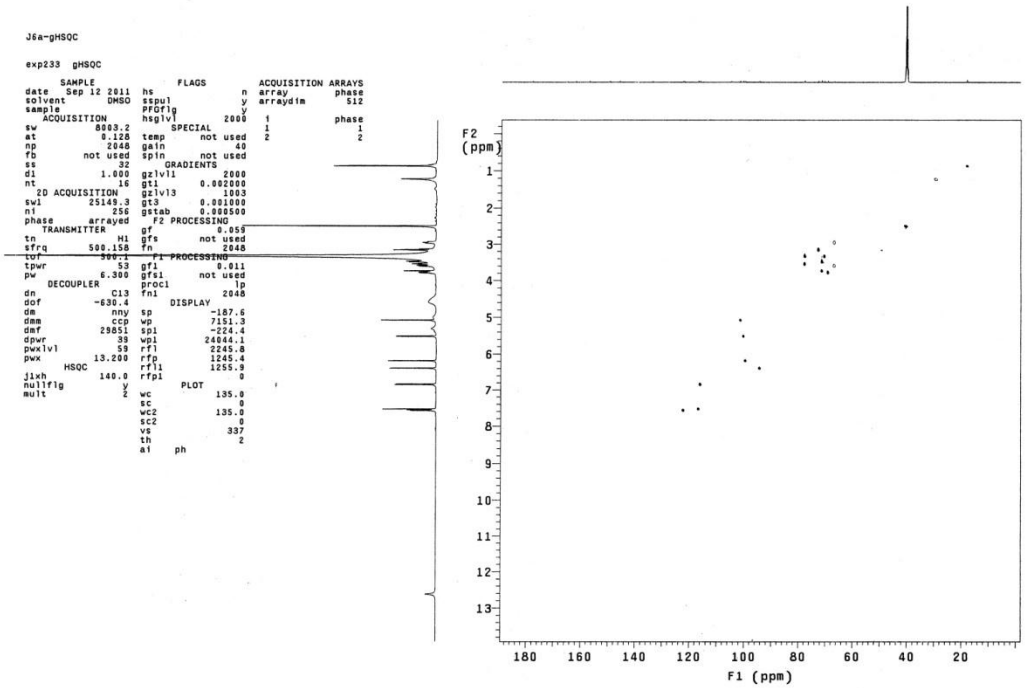

Figure 45a HSQC spectrum of compound DC8 (DMSO-d_6)

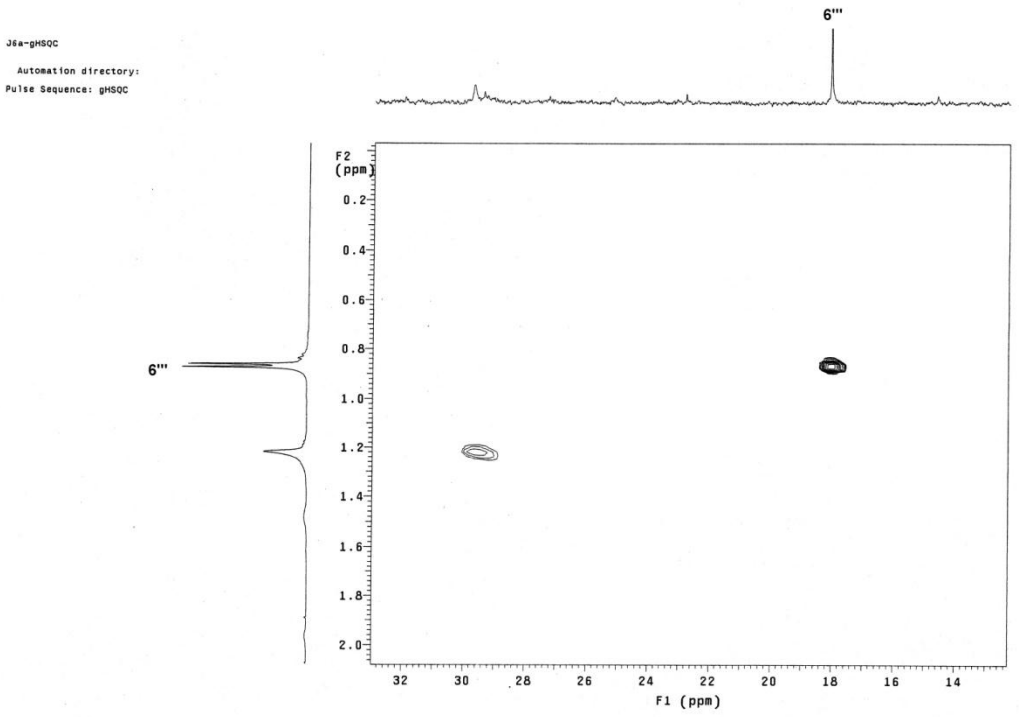

Figure 45b HSQC spectrum of compound DC8 (DMSO-d_6)
(δ_H 0.2-2.0, δ_C 12-32 ppm)

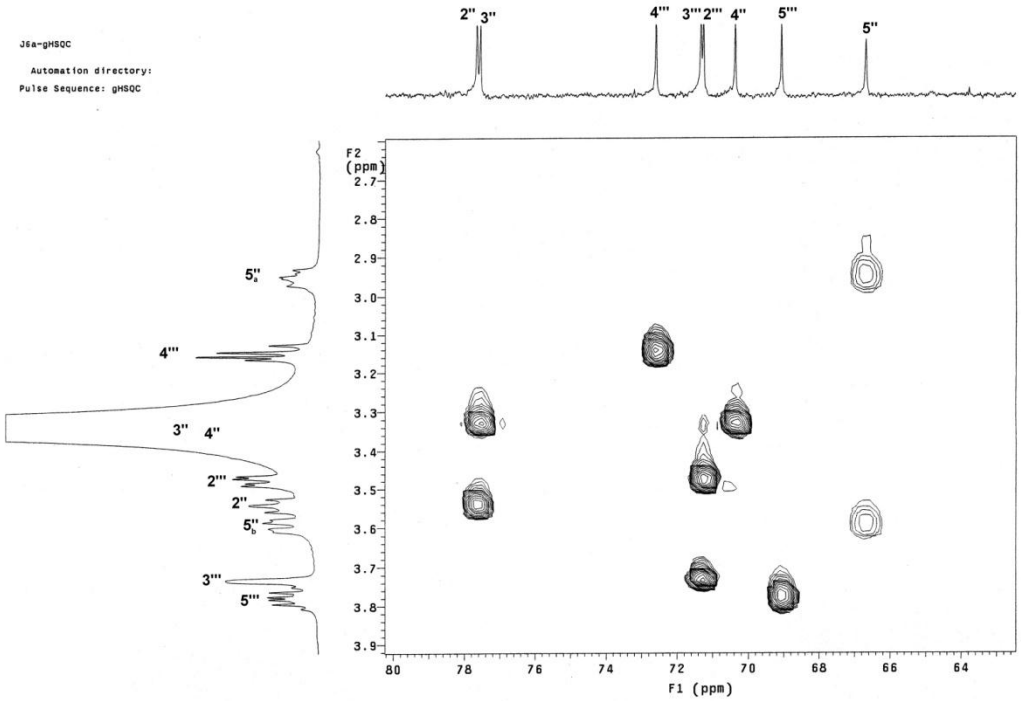

Figure 45c HSQC spectrum of compound DC8 (DMSO-d_6)
(δ_H 2.7-3.9, δ_C 64-80 ppm)

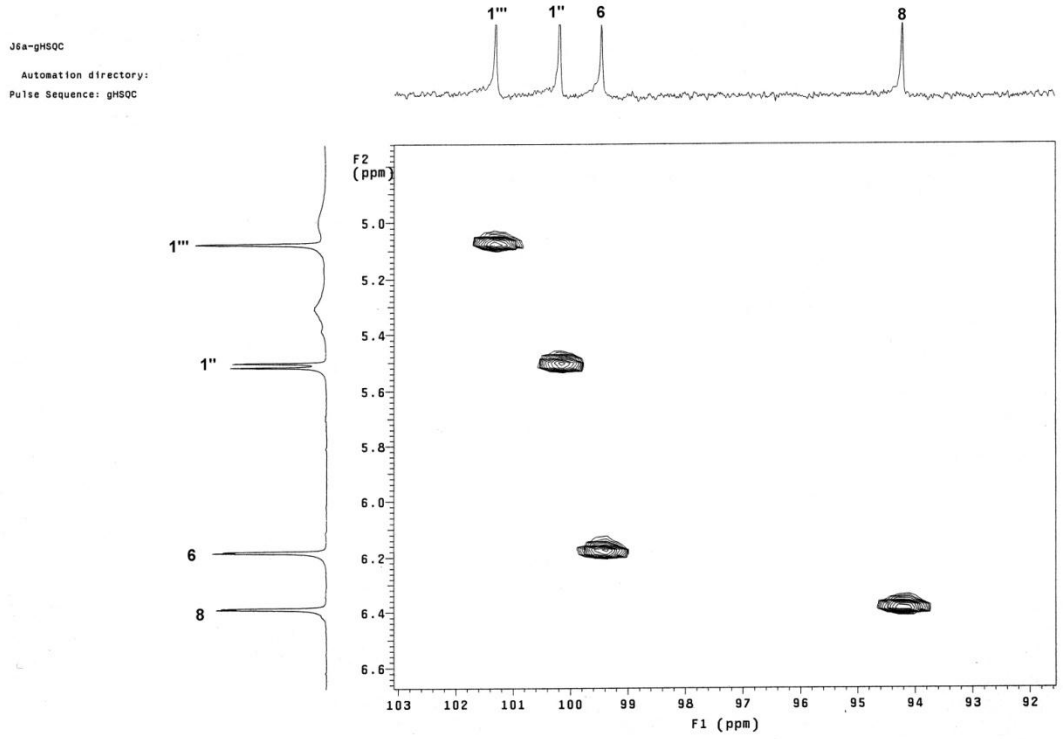

Figure 45d HSQC spectrum of compound DC8 (DMSO-d_6)
(δ_H 5.0-6.6, δ_C 92-103 ppm)

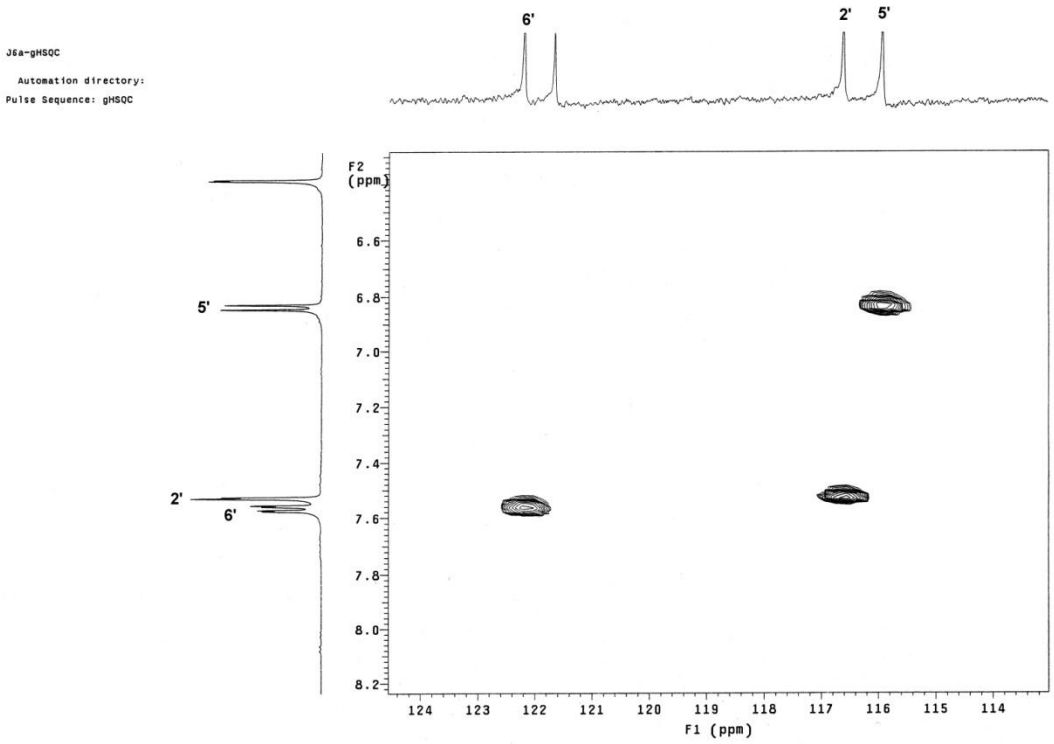

Figure 45e HSQC spectrum of compound DC8 (DMSO-d_6)
(δ_H 6.4-8.2, δ_C 114-124 ppm)

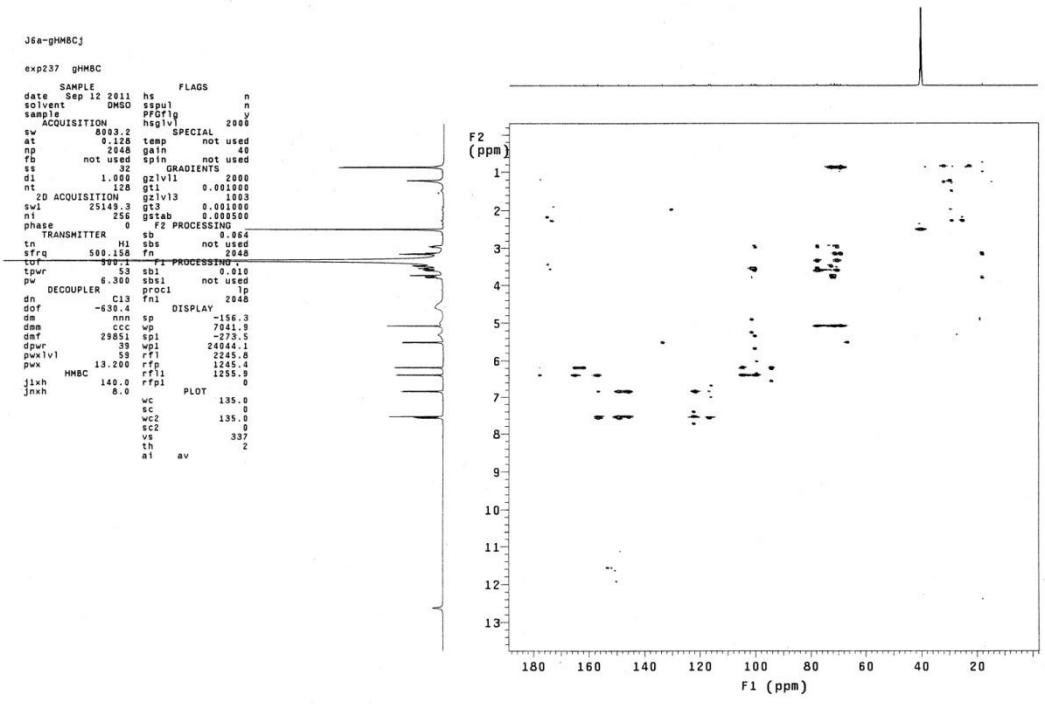

Figure 46a HMBC spectrum of compound DC8 (DMSO-d_6)

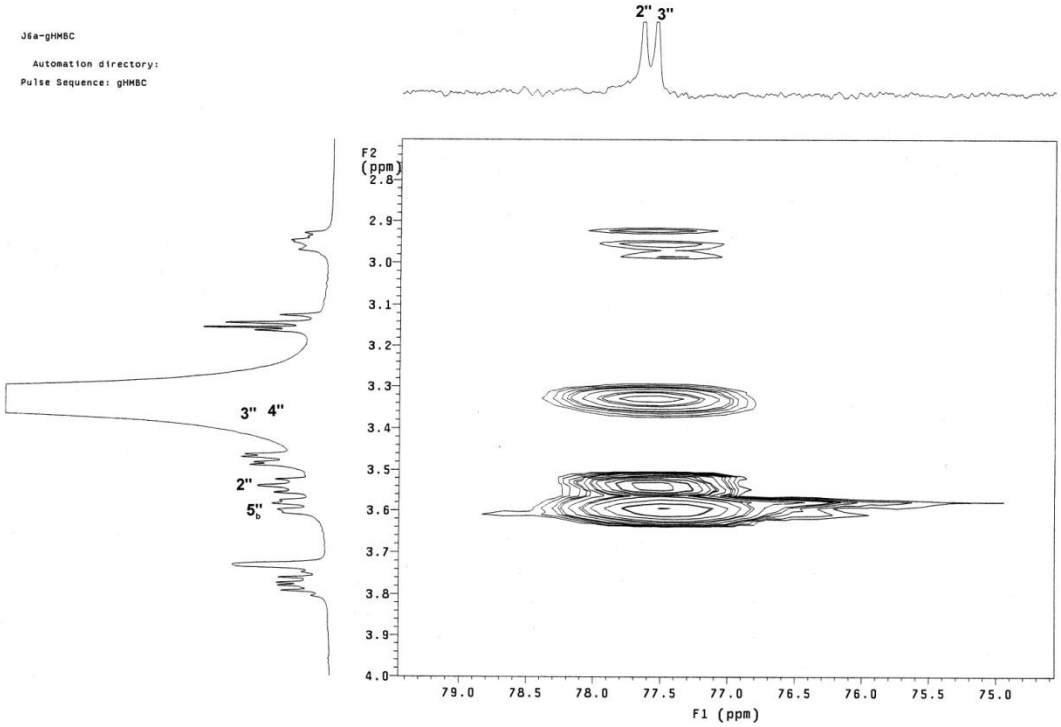

Figure 46b HMBC spectrum of compound DC8 (DMSO-d_6)
(δ_H 2.8-4.0, δ_C 75-79 ppm)

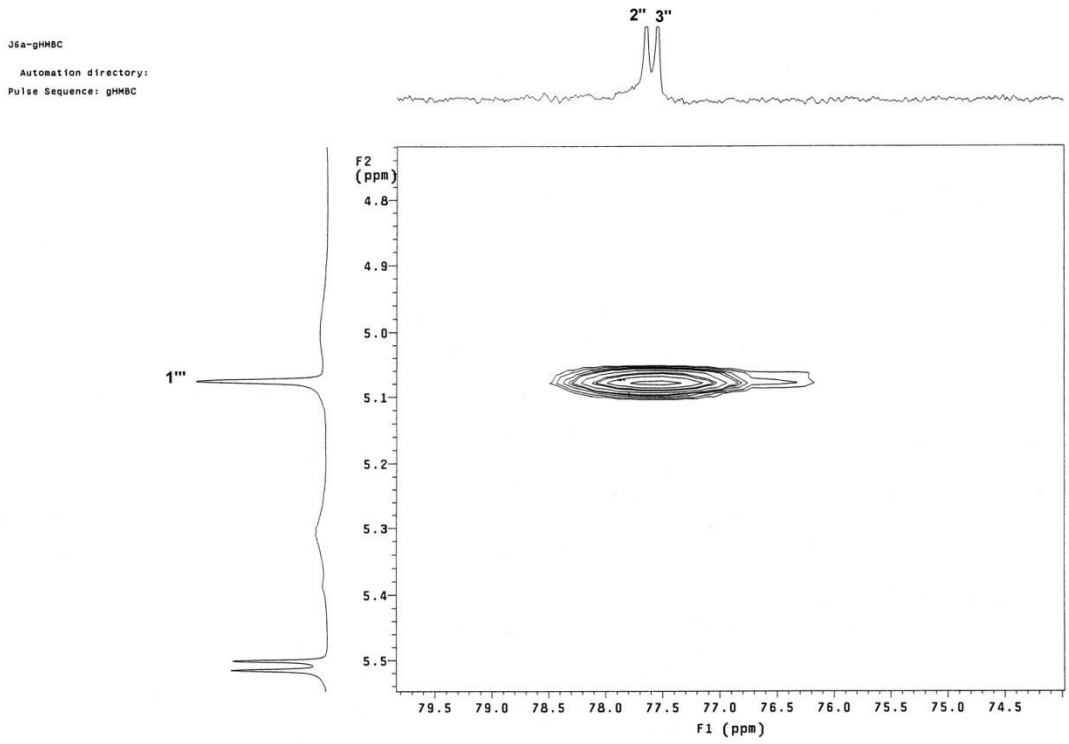

Figure 46c HMBC spectrum of compound DC8 (DMSO-d_6)
(δ_H 4.8-5.5, δ_C 74.5-79.5 ppm)

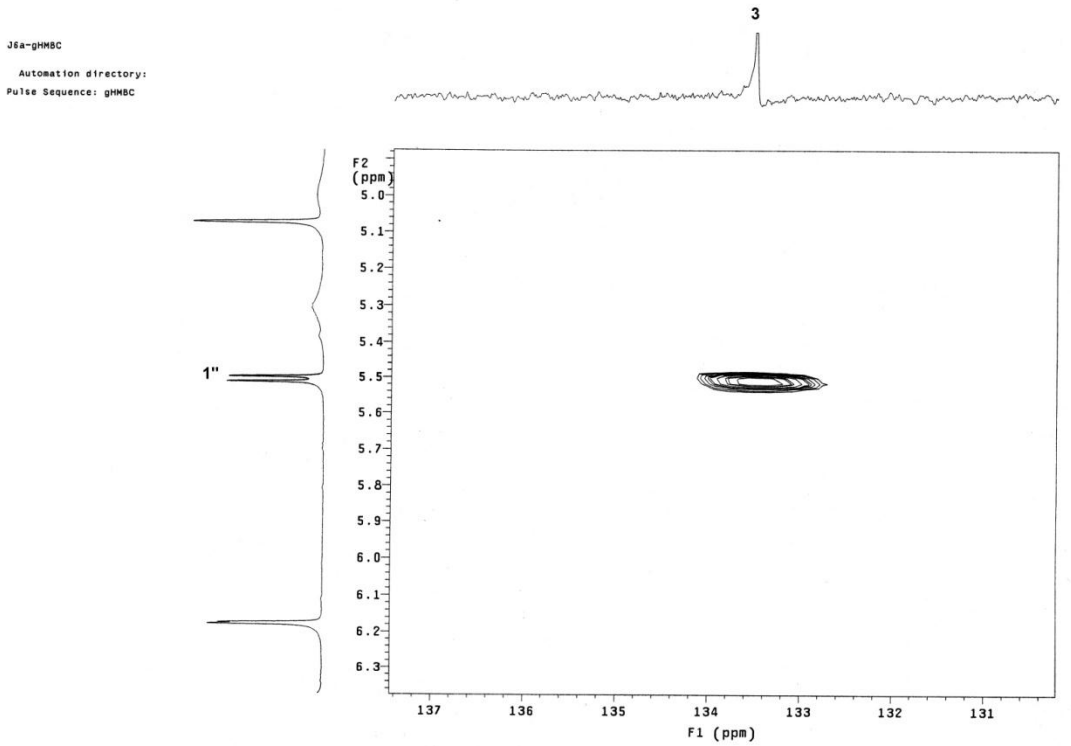

Figure 46d HMBC spectrum of compound DC8 (DMSO-d_6)
(δ_H 5.0-6.3, δ_C 131-137 ppm)

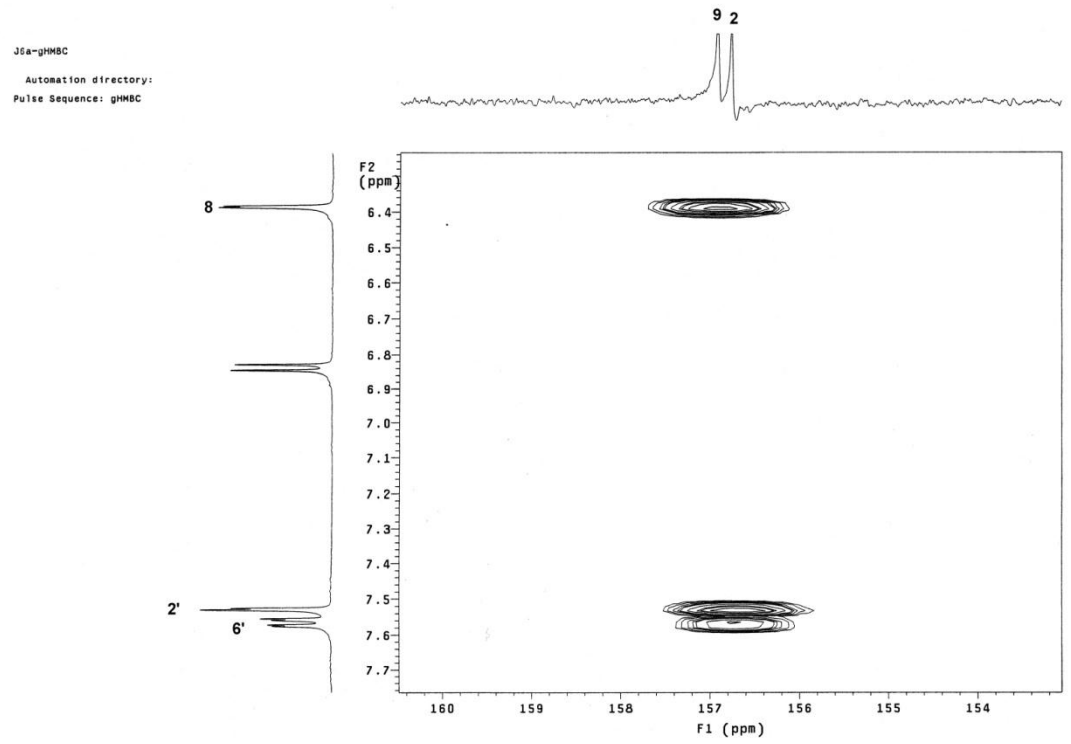

Figure 46e HMBC spectrum of compound DC8 (DMSO-d_6)
(δ_H 6.3-7.7, δ_C 154-160 ppm)

BIORESOURCES RESEARCH UNIT

High resolution report

		Acquisition Date	2/15/2011 2:02:34 PM
Analysis Name	D:\Data\customer\DS19 High.d		
Method	NaFormate_pos_infusion.m	Operator	Sutichai Ext: 3560
Sample Name	DS19 High	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

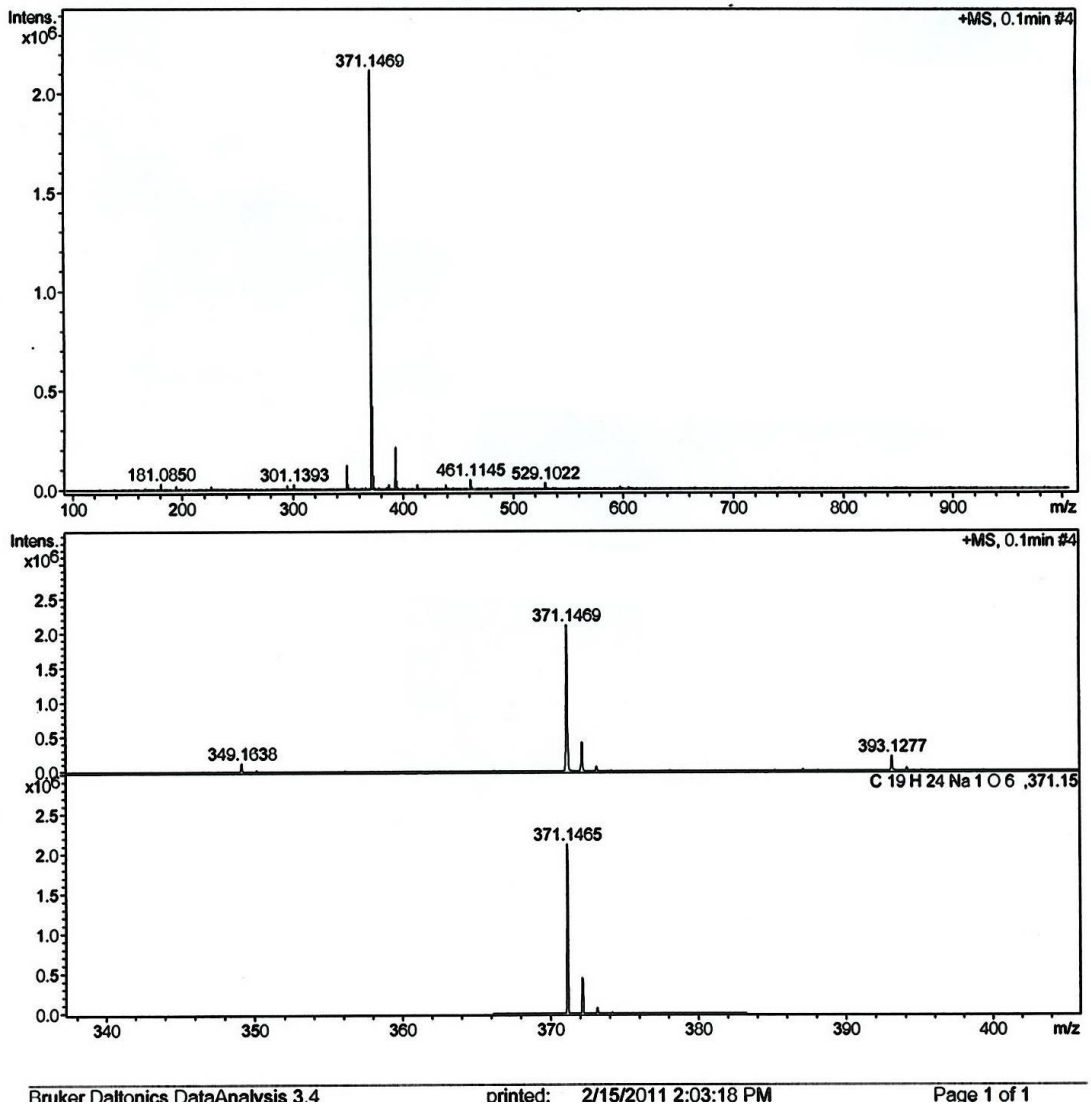

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Figure 47 Mass spectrum of compound DS1

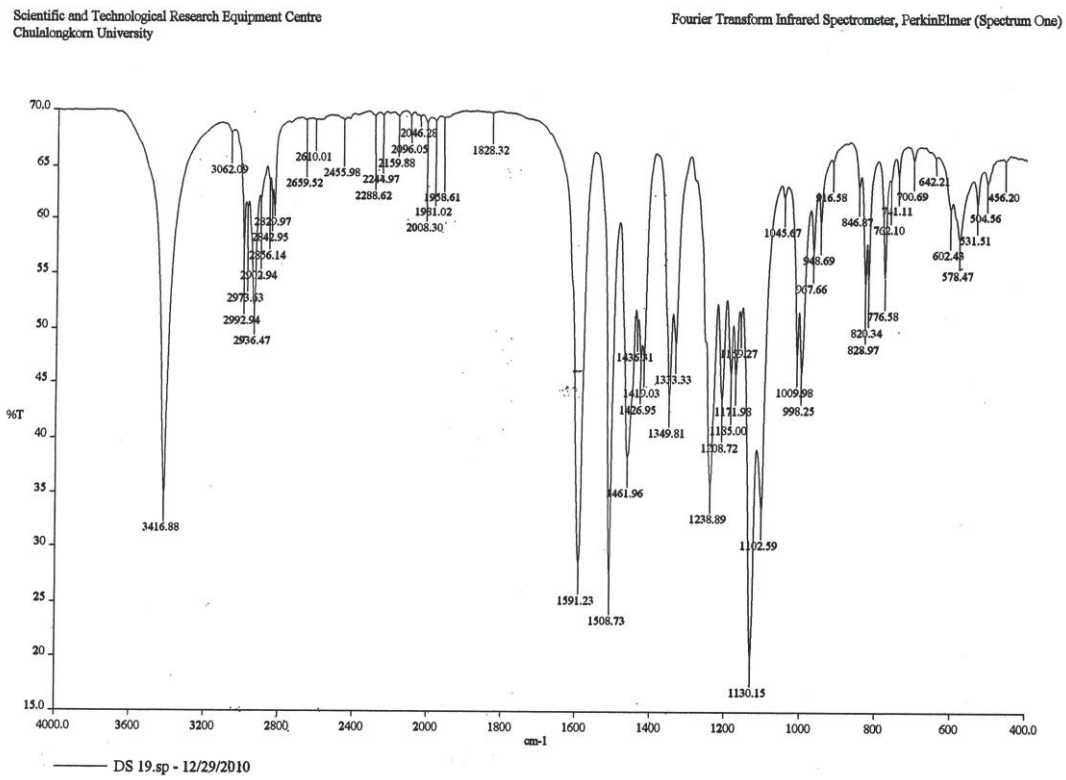

Figure 48 IR spectrum of compound DS1

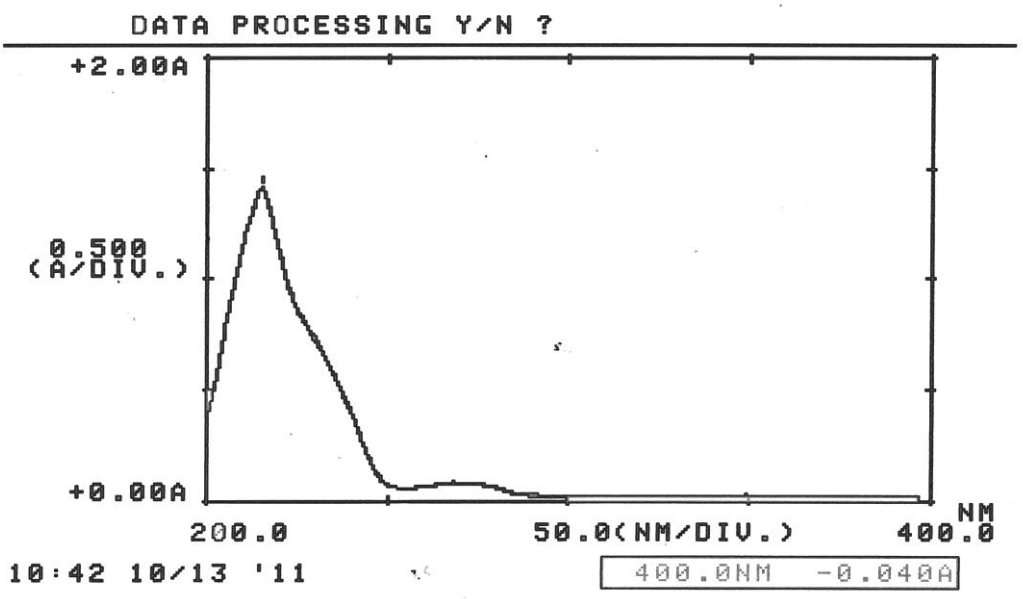

Figure 49 UV spectrum of compound DS1

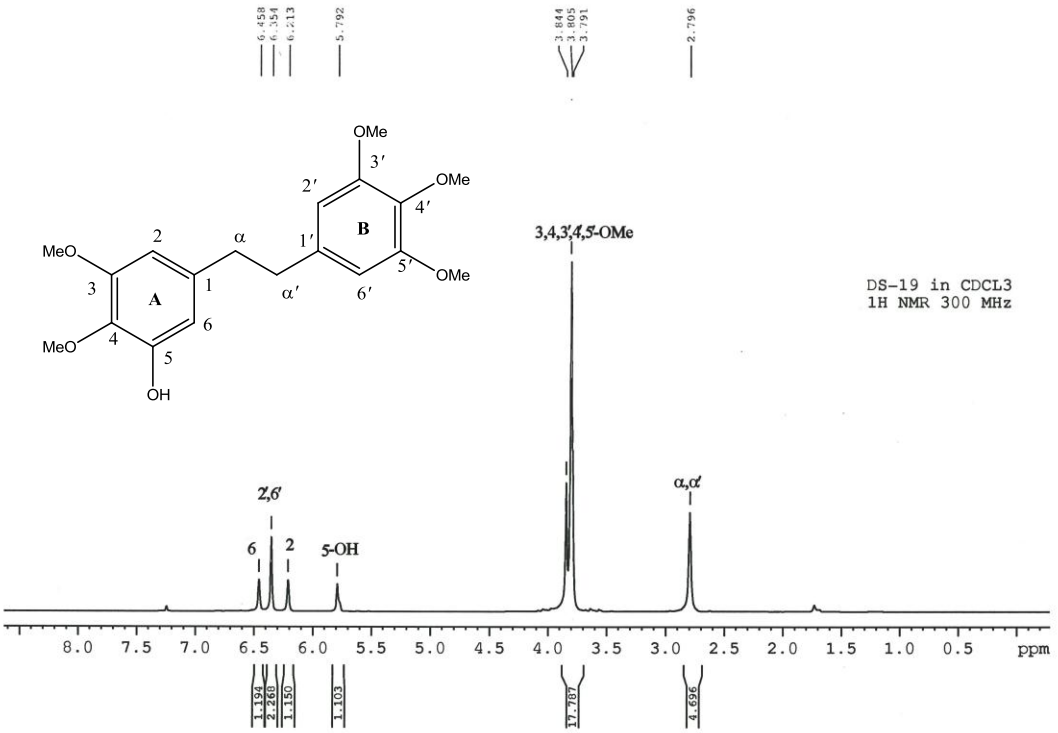

Figure 50 ^{1}H-NMR (300 MHz) spectrum of compound DS1 ($CDCl_3$)

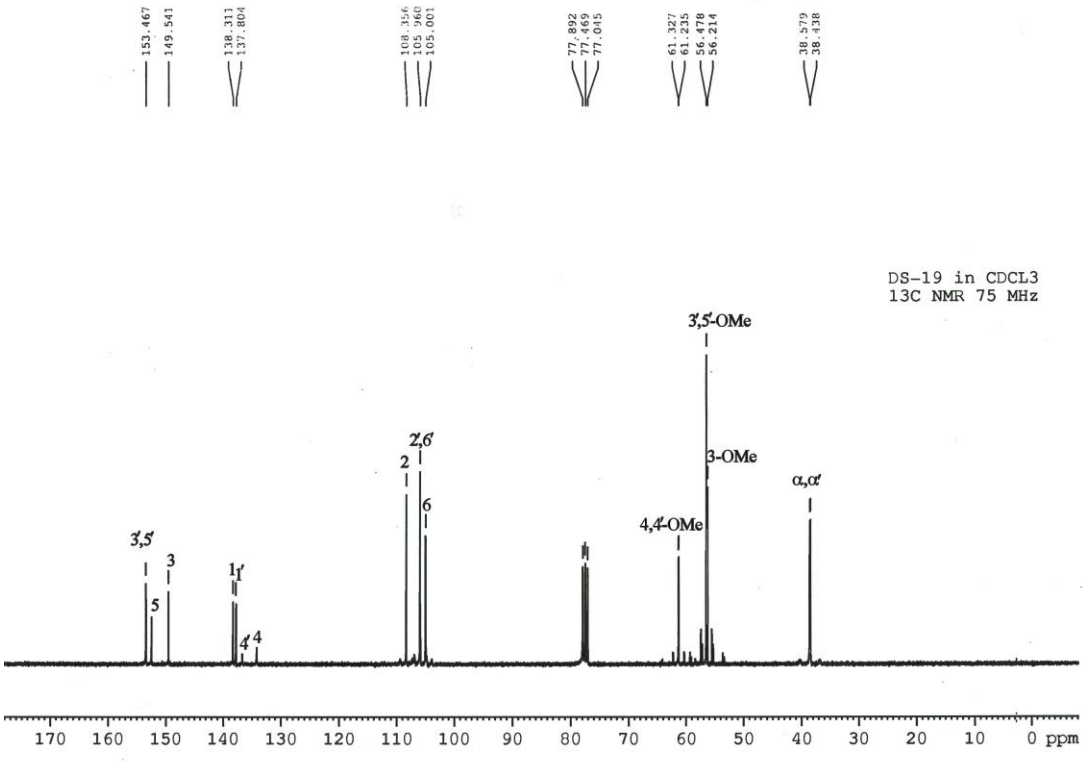

Figure 51 ^{13}C-NMR (75 MHz) spectrum of compound DS1 ($CDCl_3$)

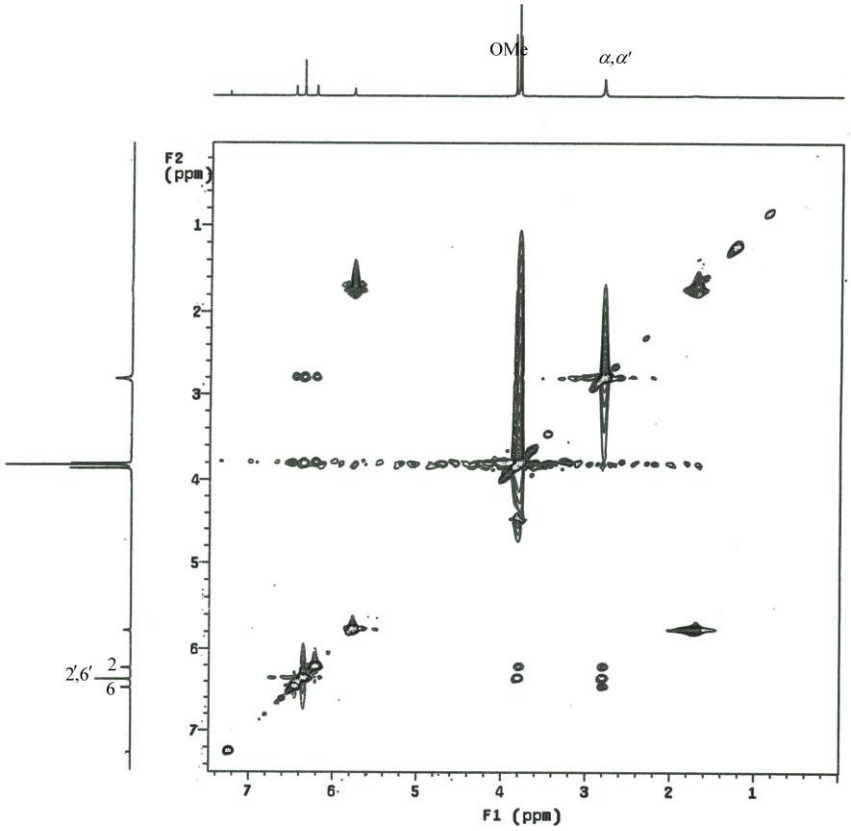

Figure 52a NOESY spectrum of compound DS1 ($CDCl_3$)

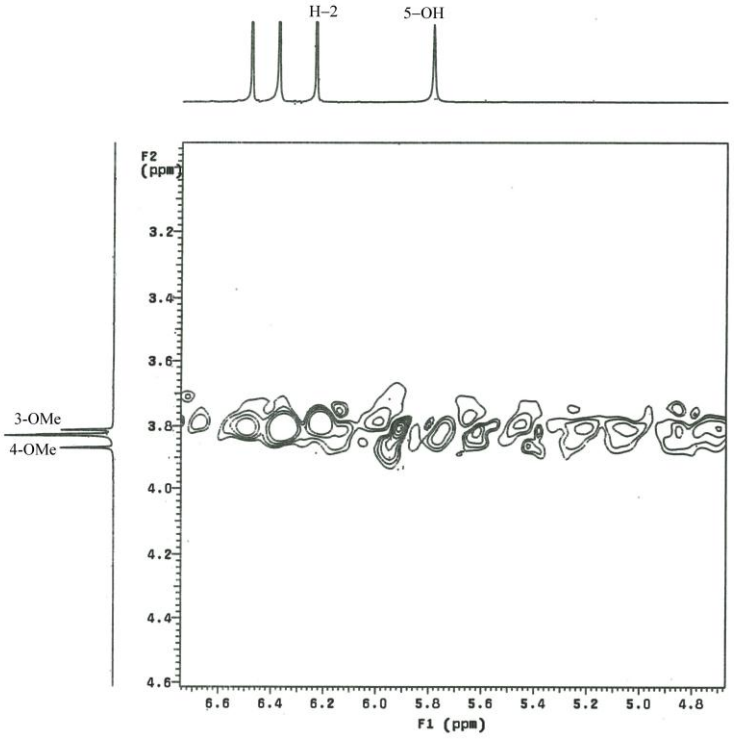

Figure 52b NOESY spectrum of compound DS1 ($CDCl_3$)
(δ_H 4.8-6.6, δ_H 3.2-4.6 ppm)

BIORESOURCES RESEARCH UNIT

Low resolution report

		Acquisition Date	3/5/2012 2:19:55 PM
Analysis Name	D:\Data\customer\DS_M2.d		
Method	NaFormate_pos_infusion .m	Operator	Sutichai Ext: 3560
Sample Name	DS_M2	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	5000 V	Set Dry Gas	2.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

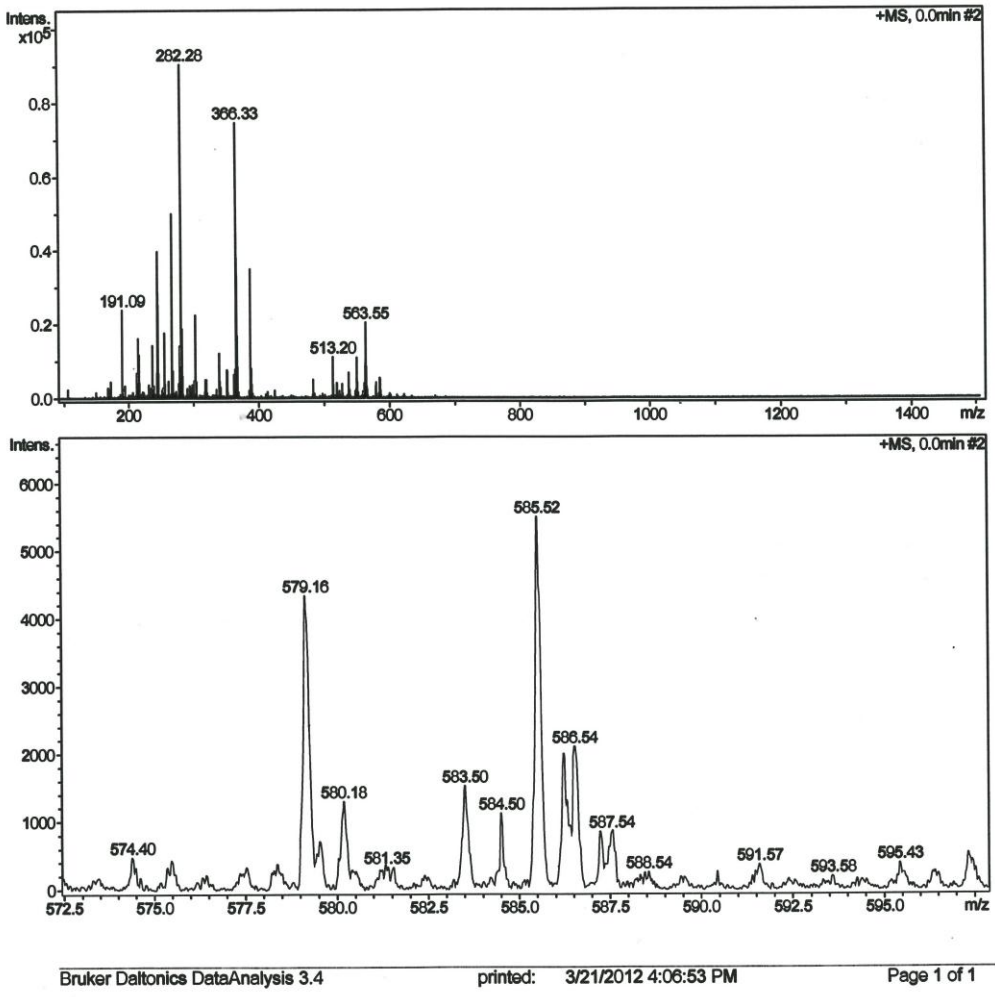

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Figure 53 Mass spectrum of compound DS2

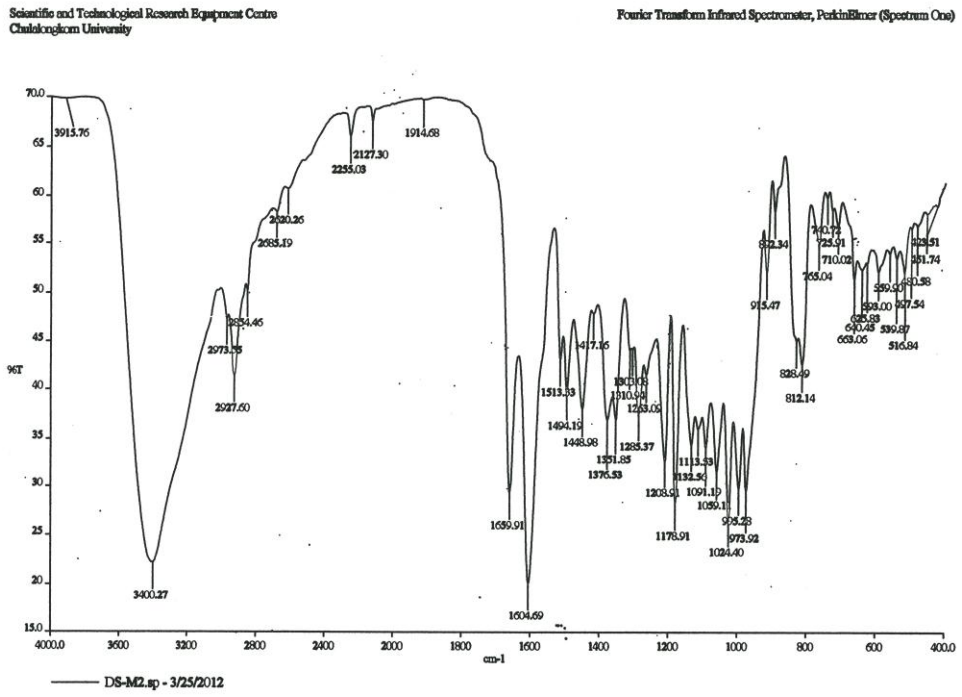

Figure 54 IR spectrum of compound DS2

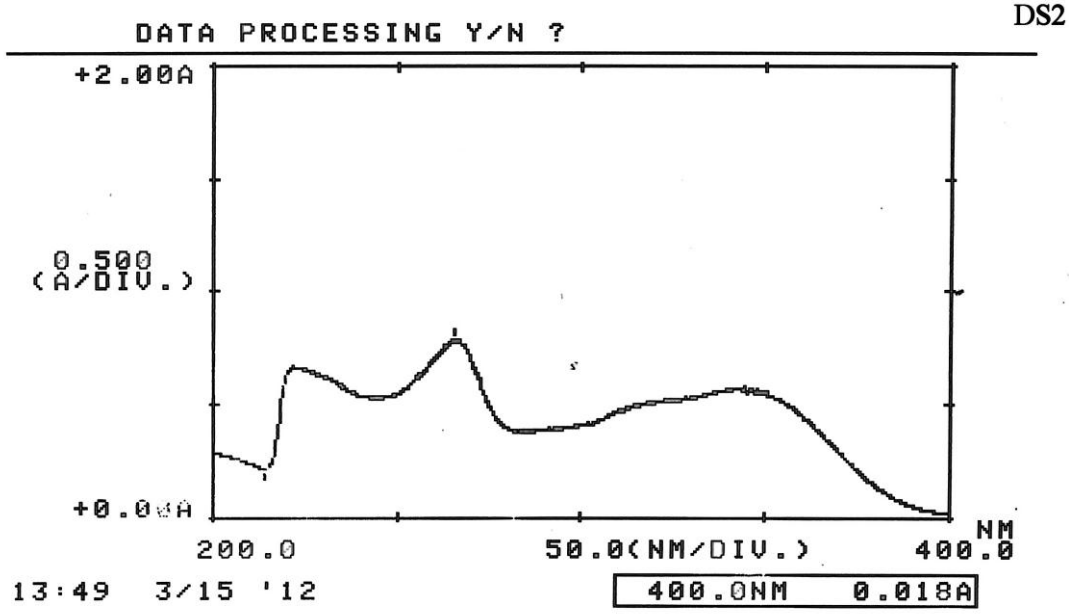

Figure 55 UV spectrum of compound DS2

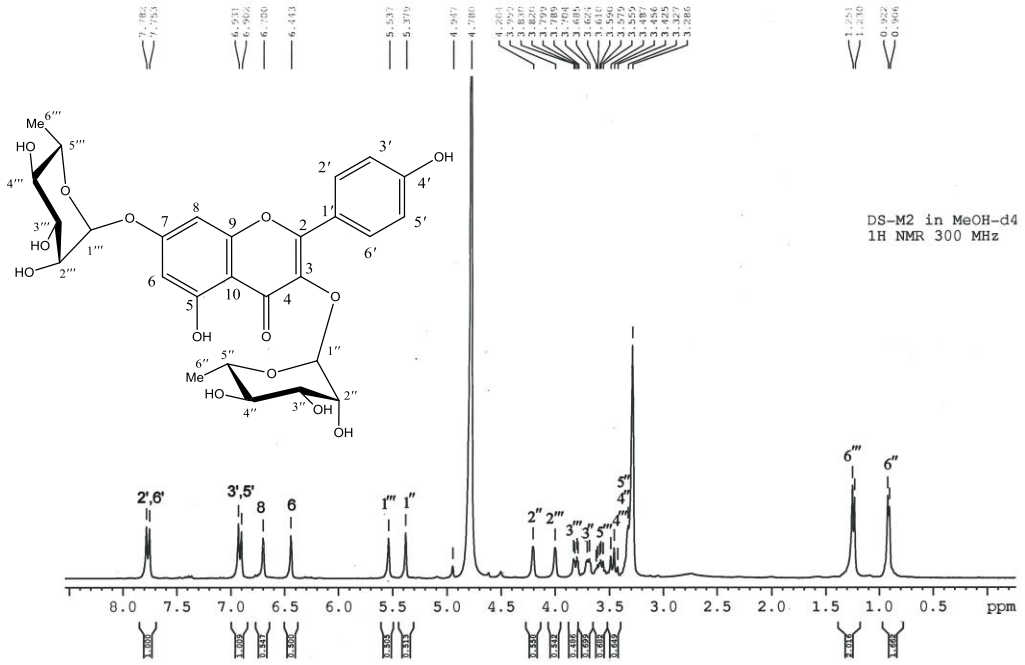

Figure 56 ^{1}H-NMR (300 MHz) spectrum of compound DS2 (CD_3OD)

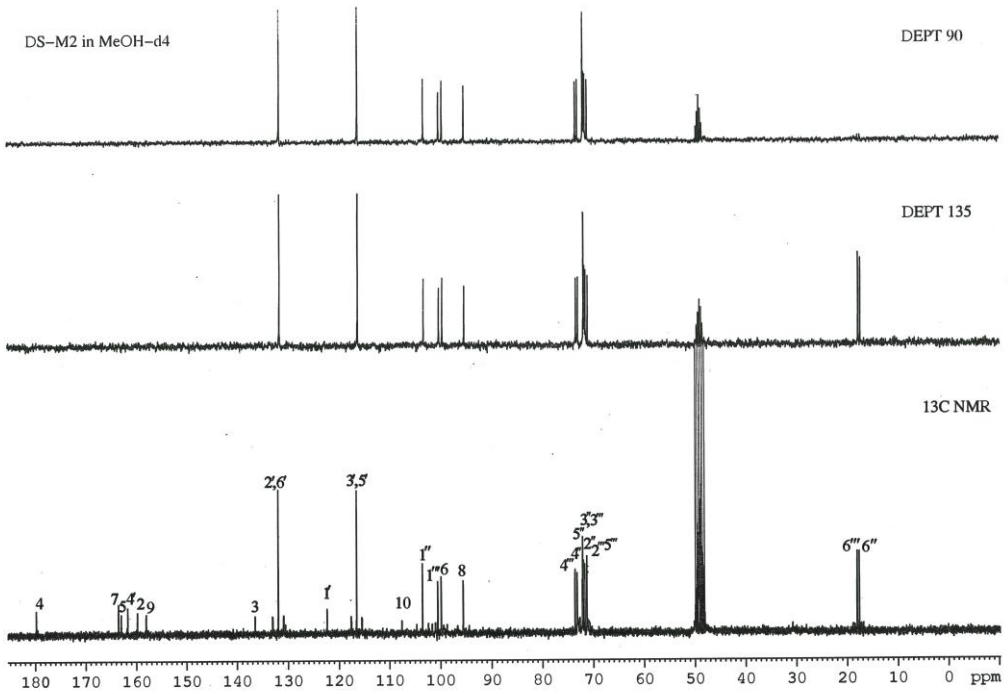

Figure 57 ^{13}C-NMR (75 MHz) and DEPT spectra of compound DS2 (CD_3OD)

BIORESOURCES RESEARCH UNIT

Low resolution report

Analysis Name	D:\Data\customer\DS_M3.d	Acquisition Date	3/5/2012 2:24:35 PM
Method	NaFormate_pos_infusion .m	Operator	Sutichai Ext: 3560
Sample Name	DS_M3	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	5000 V	Set Dry Gas	2.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

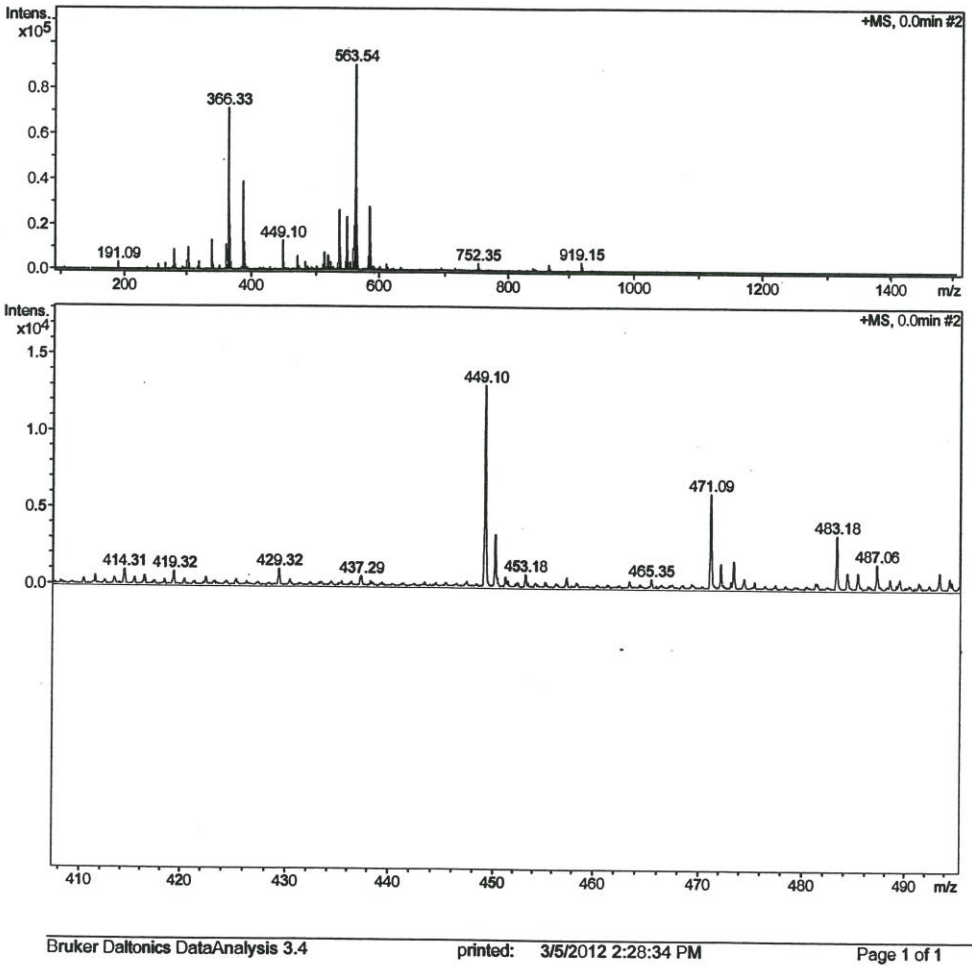

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Figure 58 Mass spectrum of compound DS3

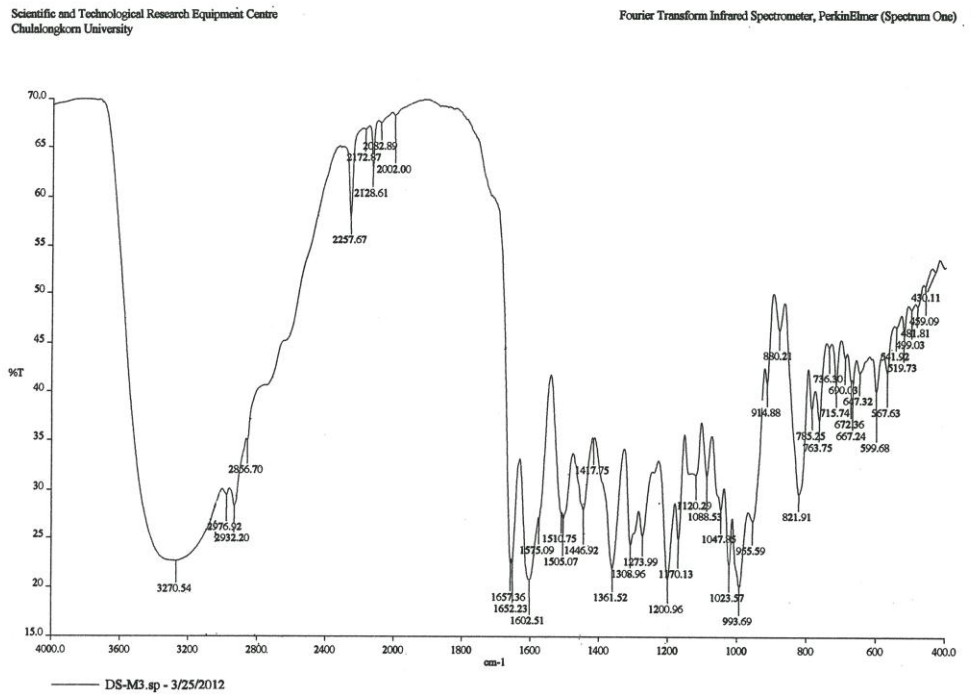

Figure 59 IR spectrum of compound DS3

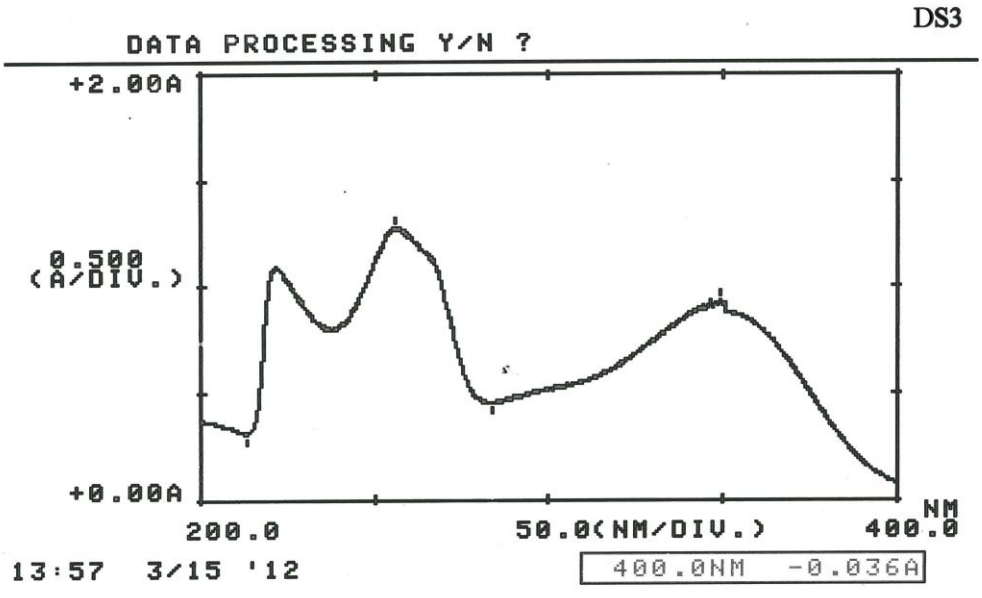

Figure 60 UV spectrum of compound DS3

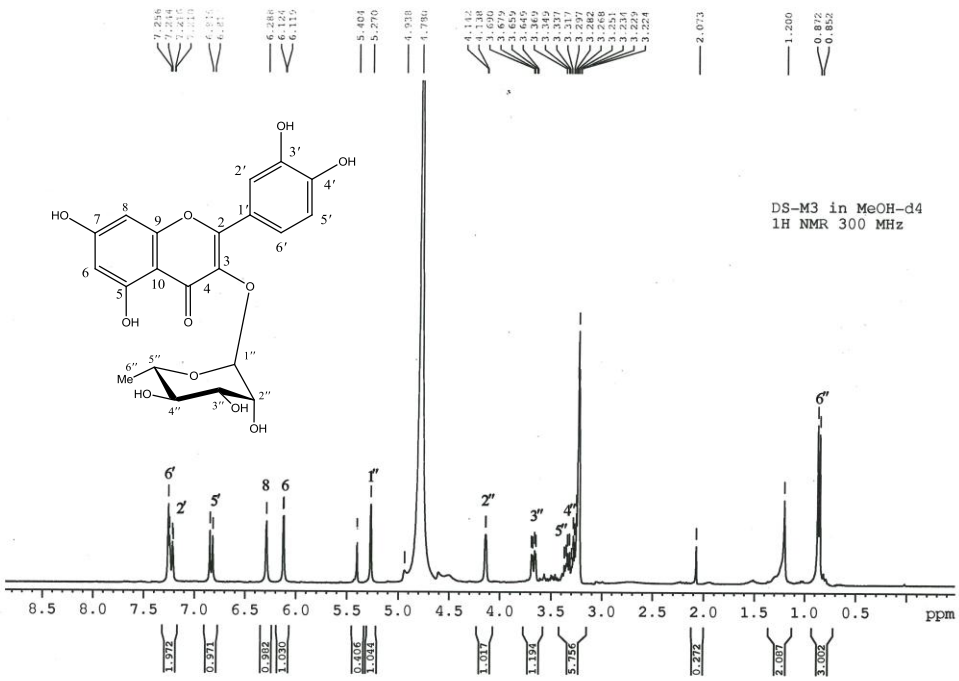

Figure 61 ^{1}H-NMR (300 MHz) spectrum of compound DS3 (CD_3OD)

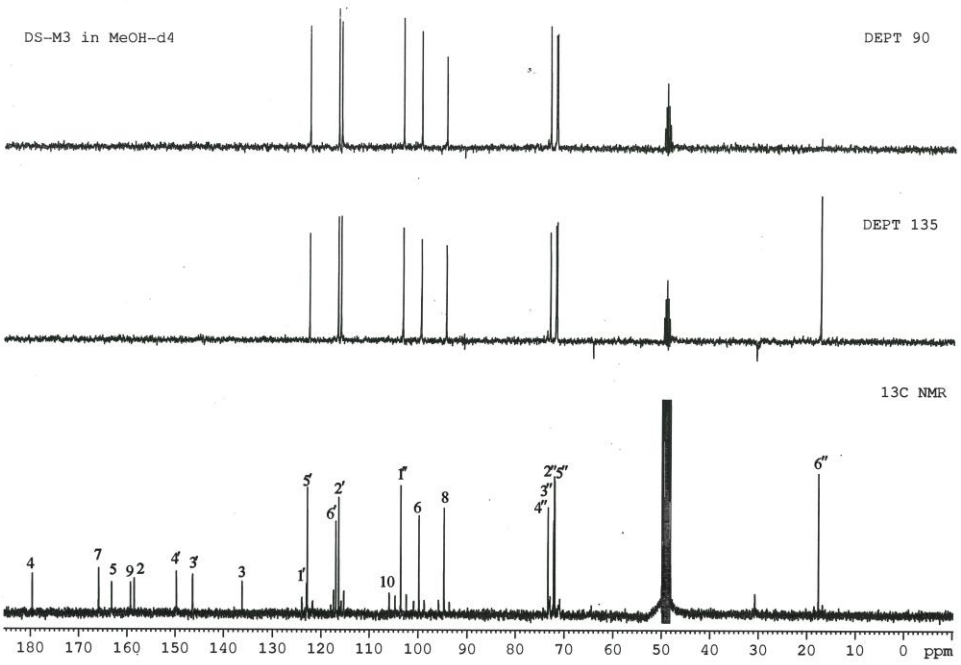

Figure 62 ^{13}C-NMR (75 MHz) and DEPT spectra of compound DS3 (CD_3OD)

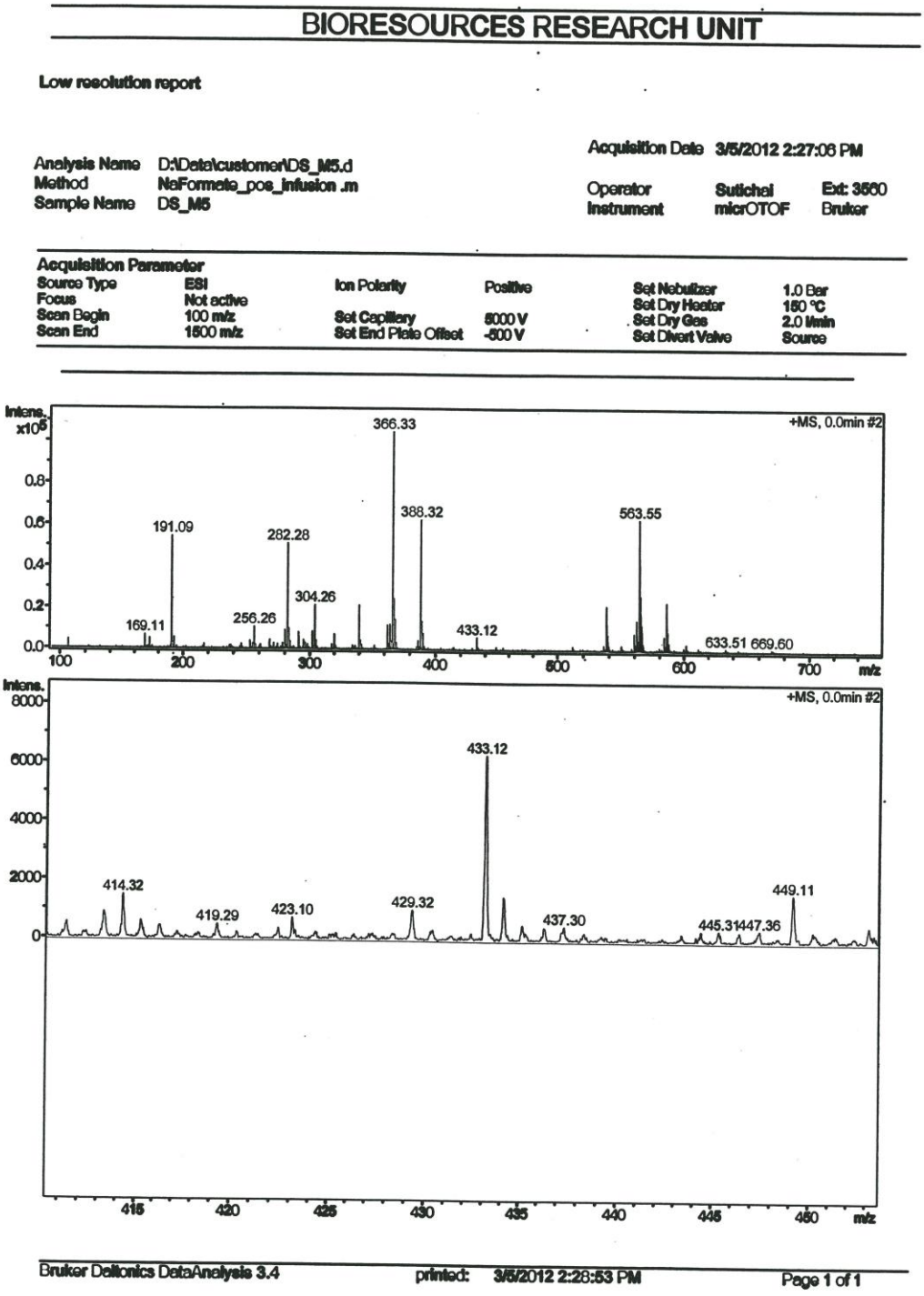

Figure 63 Mass spectrum of compound DS4

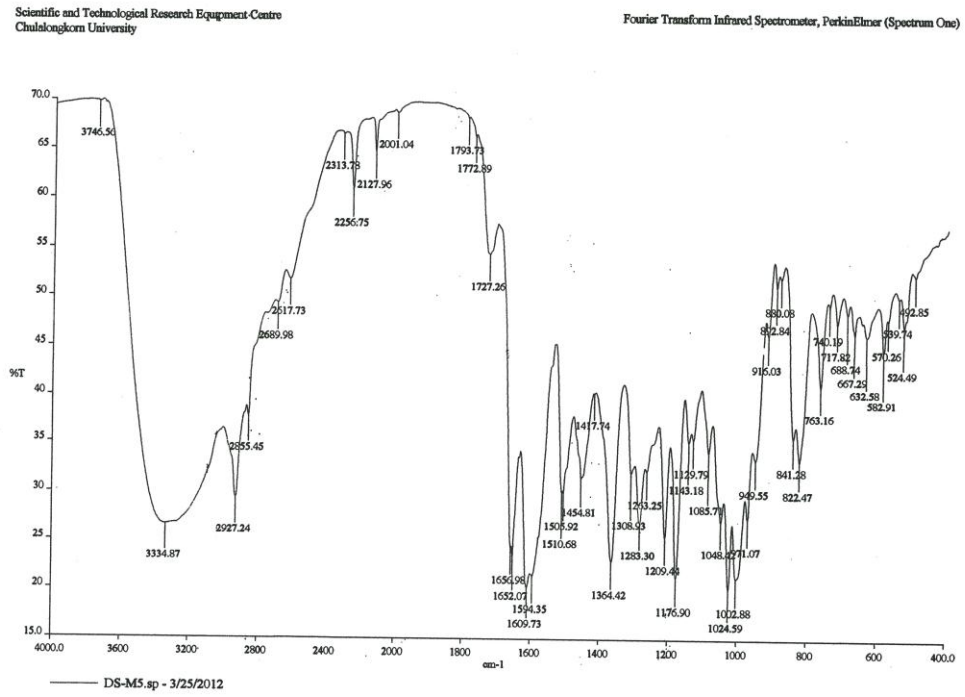

Figure 64 IR spectrum of compound DS4

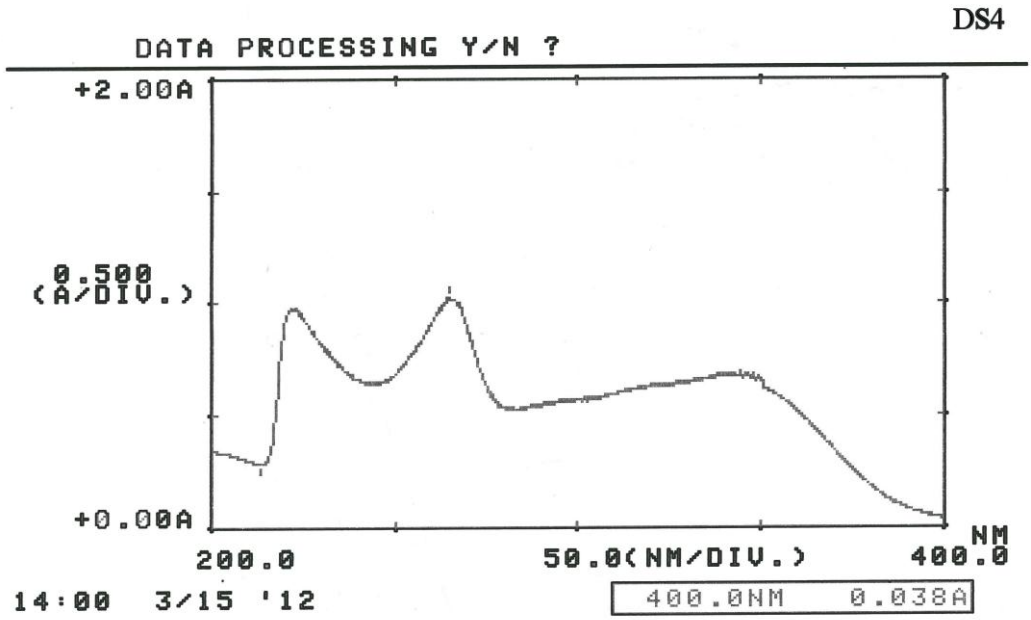

Figure 65 UV spectrum of compound DS4

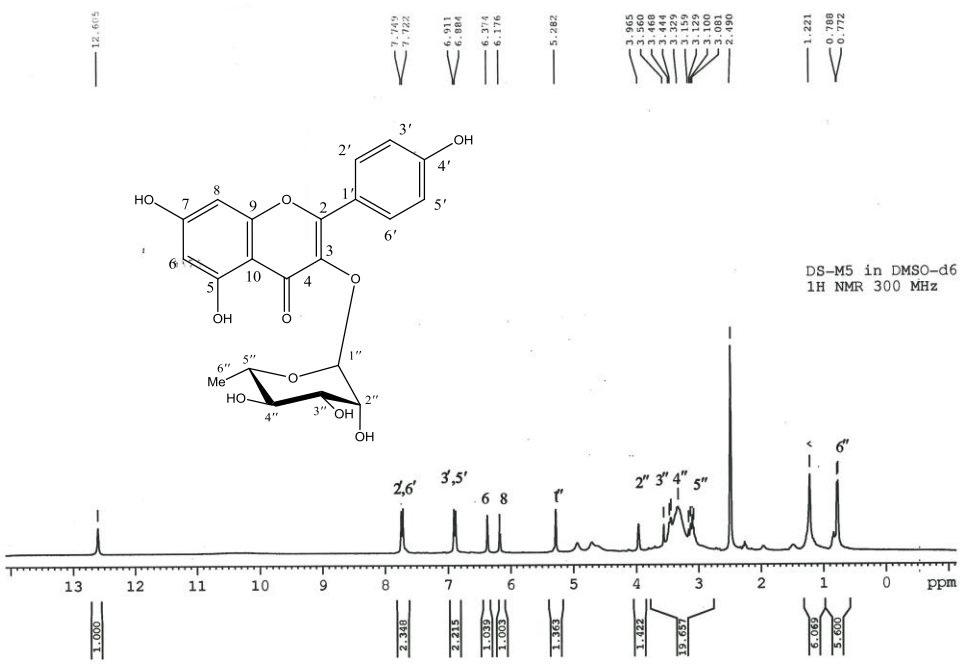

Figure 66 ^{1}H-NMR (300 MHz) spectrum of compound DS4 (DMSO-d_6)

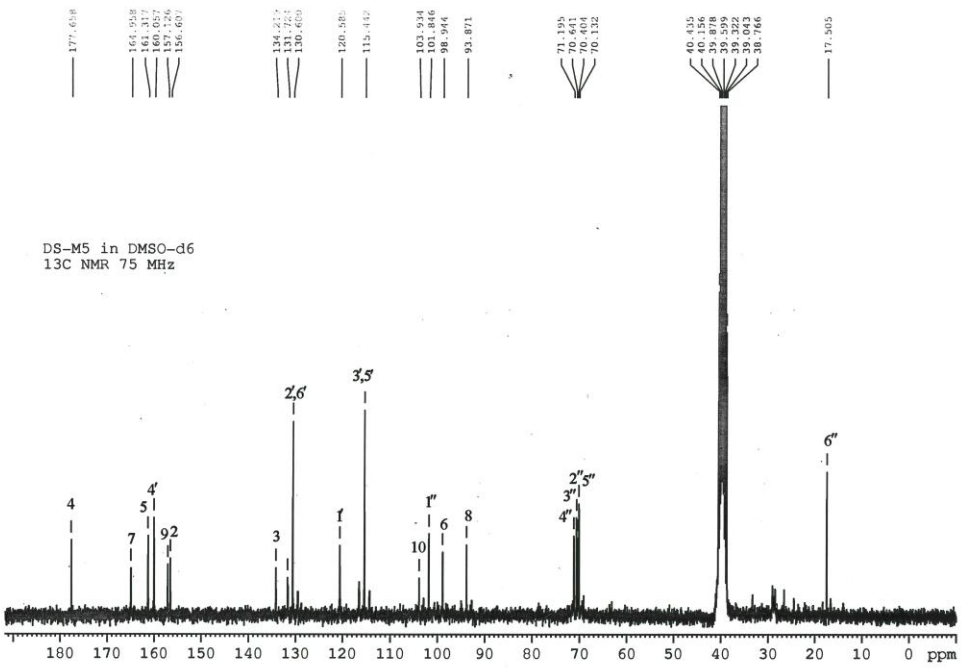

Figure 67 ^{13}C-NMR (75 MHz) spectrum of compound DS4 (DMSO-d_6)

VITA

Mr. Thanawuth Phechrmeekha was born on December 29, 1984 in Phatthalung, Thailand. He received his B. Pharm. in 2008 from the Faculty of Pharmaceutical Sciences, Prince of Songkla University, Thailand.

Poster presentation

Thanawuth Phechrmeekha, Boonchoo Sritularak and Kittisak Likhitwitayawuid. Cytoxic constituents from *Dendrobium capillipes*. Proceedings of the 28th Annual Research conference in Pharmaceutical Sciences, January 20, 2012. Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand. p. 4-5.

Publication

Thanawuth Phechrmeekha, Boonchoo Sritularak and Kittisak Likhitwitayawuid. New phenolic compounds from *Dendrobium capillipes* and *D. secundum*. Journal of Asian Natural Products Research (in press).