Chemical Constituents from the Leaves and Stem Bark of *Garcinia dulcis*

Arun Saelee

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science in Organic Chemistry

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Thesis Title	Chemical Constituents from the Leaves and Stem Bark of *Garcinia dulcis*
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Major Program	Organic Chemistry

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The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirements for the Master of Science Degree in Organic Chemistry.

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Dean of Graduate School

This is to certify that the work here submitted is the result of the candidate's own investigations. Due acknowledgement has been made of any assistance received.

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Candidate

I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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(Mr. Arun Saelee)

Candidate

ชื่อวิทยานิพนธ์ องค์ประกอบทางเคมีจากใบและเปลือกต้นมะพูด

ผู้เขียน นายอรุณ แซ่หลี

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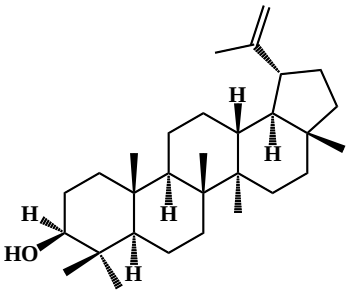
ปีการศึกษา 2556

บทคัดย่อ

การศึกษาองค์ประกอบทางเคมีจากส่วนสกัดหยาบอะซีโตนของใบมะพูดสามารถแยกสารบริสุทธิ์ได้ 9 สาร เป็นสารกลุ่ม triterpenoids 1 สาร คือ lupeol **(AS1)** สารกลุ่ม benzene derivatives 2 สาร คือ 4-hydroxy benzoic acid **(AS2)**, 4-hydroxy-3-methoxybenzoic acid **(AS3)** สารกลุ่ม biflavonoids 6 สาร คือ 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxy-3-(3-methylbut-2-enyl)phenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-6-(3-methylbut-2-enyl)-4*H*-chromen-4-one **(AS4)**, GB-2a **(AS5)**, amentoflavone **(AS6)**, morelloflavone **(AS7)**, morelloflavone-7″-sulfate **(AS8)** และ volkensiflavone **(AS9)** การศึกษาองค์ประกอบทางเคมีจากส่วนสกัดหยาบไดคลอโรมีเทนของเปลือกต้นมะพูดสามารถแยกสารบริสุทธิ์ได้ 9 สาร เป็นสารกลุ่ม triterpenoids 1 สาร คือ oleanolic acid **(AS10)** และสารกลุ่ม xanthones 8 สาร คือ garciniaxanthone C **(AS11)**, garciniaxanthone A **(AS12)**, 1,4,8-trihydroxy-6-methoxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS13)**, 12b-hydroxy-des-D-garcigerrin A **(AS14)**, 1,2,5,6-tetrahydroxy-7-(3-methylbut-2-enyl)-3-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one **(AS15)**, 1,3,5,6-tetrahydroxy-2,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS16)**, garciniaxanthone E **(AS17)** และ 1,3,5,6-tetrahydroxy-4,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS18)** ซึ่งพบว่าสาร **AS4**, **AS13**, **AS15**, **AS16** และ **AS18** เป็นสารใหม่ที่ยังไม่มีการรายงานโครงสร้าง

การศึกษาฤทธิ์ต้านแบคทีเรียของสาร **AS4**, **AS5**, **AS6**, **AS7**, **AS11**, **AS13**, **AS14** และ **AS16** พบว่า **AS5, AS7**, **AS14** และ **AS16** สามารถยับยั้งการเจริญเติบของ *Staphylococcus aureus* ATCC25923 ด้วยค่าความเข้มข้นต่ำสุด (MIC) 128, 64, 2 และ 128 μg/mL ตามลำดับ ยับยั้งการเจริญของ methicillin - resistant *Staphylococcus aureus* ด้วยค่าความเข้มข้นต่ำสุด (MIC) 64, 64, 1 และ 128 μg/mL ตามลำดับ แต่ไม่สามารถยับยั้งการเจริญของ *Escherichia coli* ATCC25922, *Pseudomonas aeruginosa* ATCC27853 สาร **AS4**, **AS6**, **AS11** และ **AS13** ไม่แสดงฤทธิ์ต้านแบคทีเรียทั้งสองที่ความเข้มข้น 200 μg/mL



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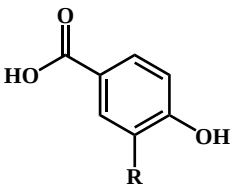

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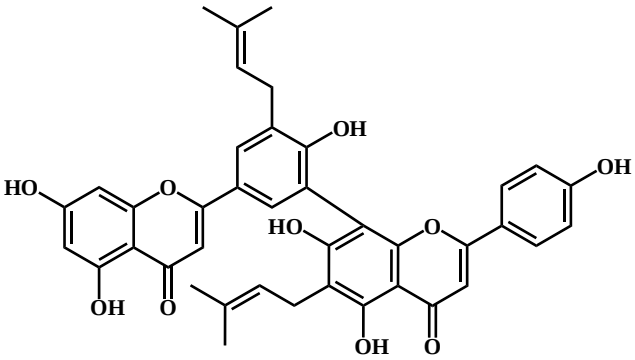

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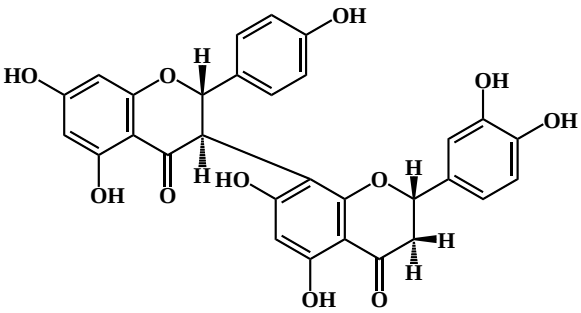

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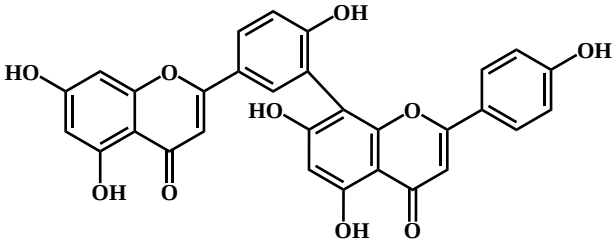

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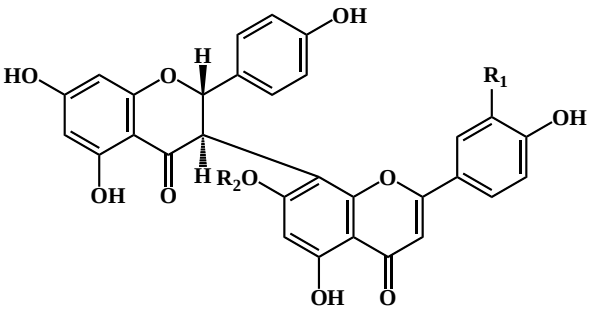

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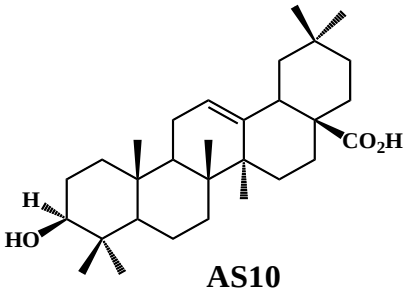
AS8 : R_1 = OH, R_2 = SO_3H
AS9 : R_1, R_2 = H



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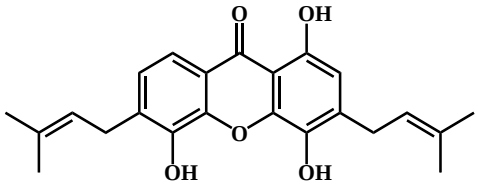

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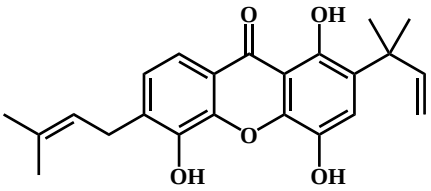

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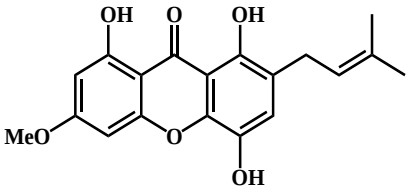

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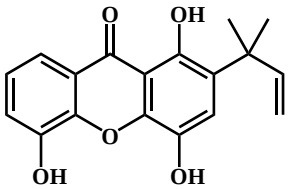

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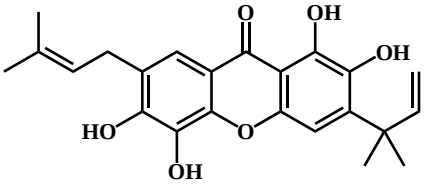

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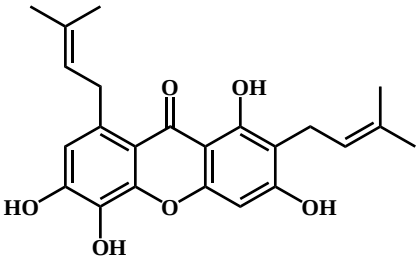

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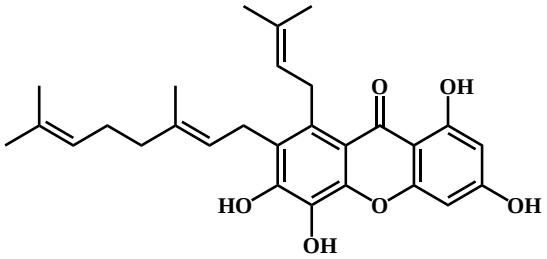

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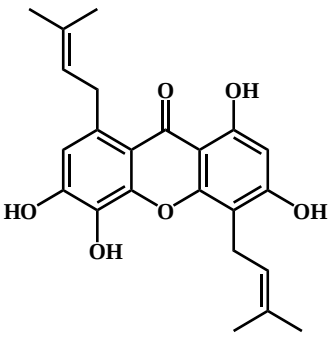


AS18

Thesis Title Chemical Constituents from the Leaves and Stem Bark of *Garcinia dulcis*

Author Mr. Arun Saelee

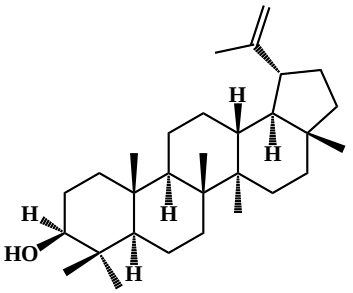
Major Program Organic Chemistry

Academic Year 2013

ABSTRACT

Study of the chemical constituents from the acetone extract of the leaves of *Garcinia dulcis*, yielded nine compounds, one triterpenoids; lupeol **(AS1)**, two benzene derivatives; 4-hydroxy benzoic acid **(AS2)**, 4-hydroxy-3-methoxybenzoic acid **(AS3)** and six biflavonoids; 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxy-3-(3-methylbut-2-enyl)phenyl)-5,7-dihydroxy-2-(4-hydroxy phenyl)-6-(3-methylbut-2-enyl)-4*H*-chromen-4-one **(AS4)**, GB-2a **(AS5)**, amentoflavone **(AS6)**, morelloflavone **(AS7)**, morelloflavone-7″-sulfate **(AS8)** and volkensiflavone **(AS9)**. Study of the chemical constituents from the dichloromethane extract of the stem bark of *G. dulcis*, yielded nine compounds, one triterpenoids; oleanolic acid **(AS10)** and eight xanthones; garciniaxanthone C **(AS11)**, garciniaxanthoneA **(AS12)**, 1,4,8-trihydroxy-6-methoxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS13)**, 12b-hydroxy-des-D-garcigerrin A **(AS14)**, 1,2,5,6-tetrahydroxy-7-(3-methylbut-2-enyl)-3-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one **(AS15)**, 1,3,5,6-tetrahydroxy-2,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS16)**, garciniaxanthone E **(AS17)**, 1,3,5,6-tetrahydroxy-4,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS18)**. Compounds **AS4**, **AS13**, **AS15**, **AS16** and **AS18** are new naturally occurrence compounds.

Compounds **AS4**, **AS5**, **AS6**, **AS7**, **AS11**, **AS13**, **AS14** and **AS16** were tested for their antibacterial activity**.** The result for the antibacterial activity **AS5**, **AS7**, **AS14** and **AS16** also showed interesting activity with MIC values of 128, 64, 2 and 128 μg/mL against *Staphylococcus aureus* ATCC25923 and 64, 64, 1 and 128 μg/mL against methicillin-resistant *Staphylococcus aureus*, respectively. They could not inhibit the growth of *Escherichia coli* ATCC25922, *Pseudomonas aeruginosa* ATCC27853 at 200 μg/mL. Compounds **AS4**, **AS6**, **AS11** and **AS13** showed no activity against four bacterial strains tested at 200 μg/mL.



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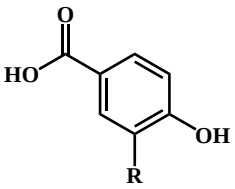

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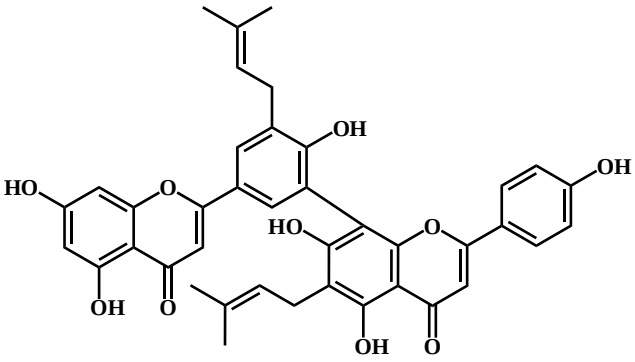

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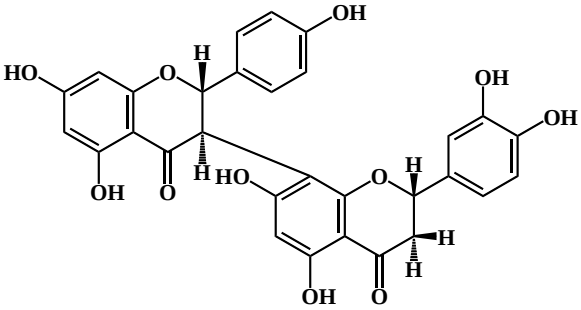

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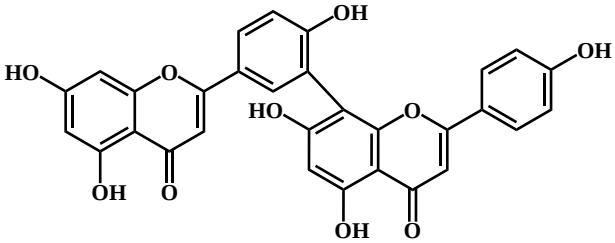

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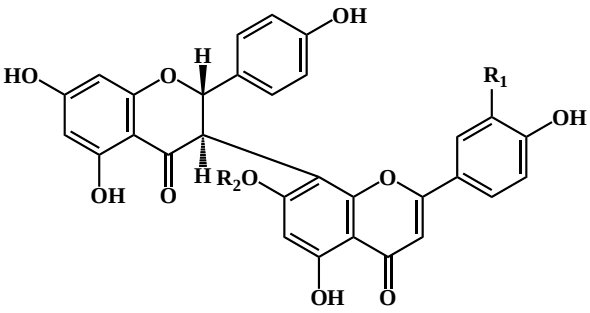

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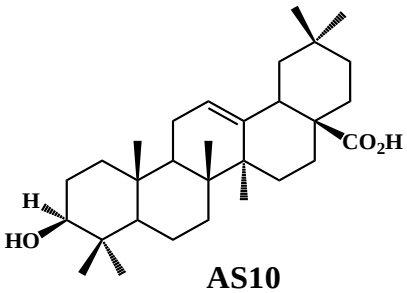

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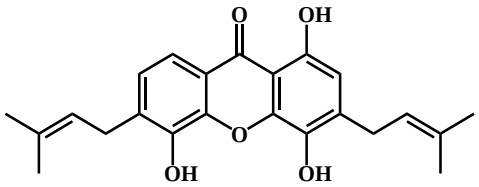

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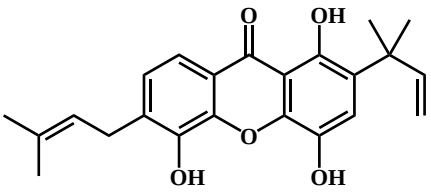

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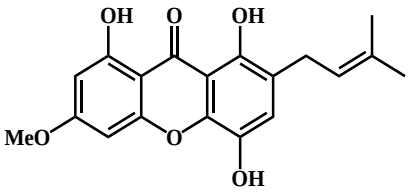

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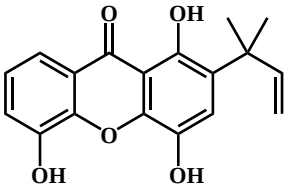

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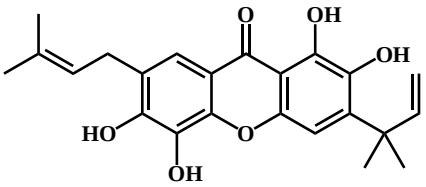

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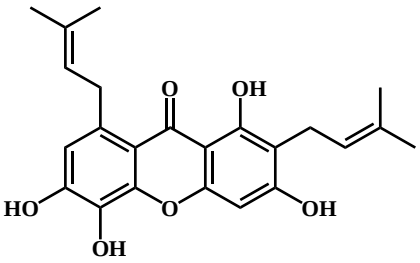

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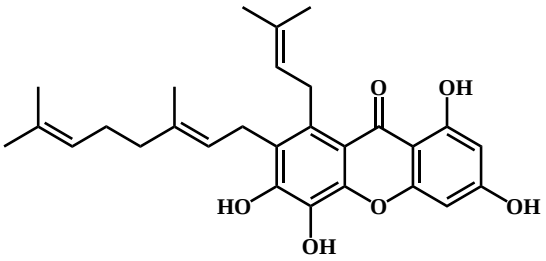

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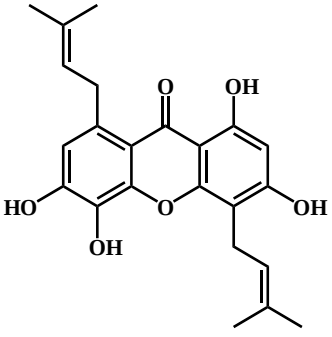

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Finally, none of this would have been possible without love and encouragement of my family and friends. I think them for their understanding during all of the times when I could not be with them and their steady love that support me. Everything will always keep in my mind.

Arun Sealee

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LIST OF ILLUSTRATIONS (CONTINUED)

LIST OF ABBREVIATIONS AND SYMBOLS

s	=	Singlet
d	=	Doublet
t	=	Triplet
q	=	Quartet
m	=	Multiplet
dd	=	doublet of doublet
dt	=	doublet of triplet
br s	=	broad singlet
g	=	Gram
nm	=	Nanometer
mp	=	melting point
cm^{-1}	=	reciprocal centimeter (wave number)
δ	=	chemical shift relative to TMS
J	=	coupling constant
$[\alpha]_D$	=	specific rotation
λ_{max}	=	maximum wavelength
ν	=	absorption frequencies
ε	=	molar extinction coefficient
m/z	=	a value of mass divided by charge
^oC	=	degree celcius
MHz	=	Megahertz
ppm	=	part per million
C	=	concentration
IR	=	Infrared
UV	=	Ultraviolet

LIST OF ABBREVIATIONS AND SYMBOLS (CONTINUED)

MS	=	Mass spectroscopy
ESITOFMS	=	Electrospray Ionization Time of Flight Mass Spectroscopy
HREIMS	=	High Resolution Electron Impact Mass Spectroscopy
NMR	=	Nuclear Magnetic Resonance
1D NMR	=	One Dimensional Nuclear Magnetic Resonance
2D NMR	=	Two Dimensional Nuclear Magnetic Resonance
COSY	=	Correlation Spectroscopy
DEPT	=	Distortionless Enhancement by Polarization Transfer
HMBC	=	Heteronuclear Multiple Bond Correlation
HMQC	=	Heteronuclear Multiple Quantum Coherence
NOESY	=	Nuclear Overhauser Effect Spectroscopy
CC	=	Column Chromatography
QCC	=	Quick Column Chromatography
PLC	=	Preparative Thin Layer Chromatography
TMS	=	tetramethylsilane
Acetone-d_6	=	Deuteroacetone
DMSO-d_6	=	deuterodimethyl sulphoxide
$CDCl_3$	=	deuterochloroform
EtOAc	=	Ethyl acetate
EtOH	=	Ethanol
MeOH	=	Methanol

CHAPTER 1

INTRODUCTION

1.1 Introduction

Recently medicinal plants have been widely accepted for the international community to use for medicine, healthy diet, cosmetics as well as industrial and agriculture. Factors indicate of differences in the chemical composition of each type of plant, such as xanthones, flavonoids, alkaloids, terpeniods. There are the biological activities of their compounds, such as antioxidation, anti-inflammatory, antibacterial and cytotoxic activities. The genus *Garcinia* (Guttiferae) consists of 57 species, mostly distributed throughout the tropical countries. Many of them are used in the folk medicine in several countries. Plants in this genus have been studied for biological activity such as antioxidation, anti-inflammatory, antibacterial, anti-atherogenic and cytotoxic activities. Flavonoids, biflavonoids, xanthones and chalcones, were isolated from this plant.

Garcinia dulcis Kurz., (Guttiferae) grows widely in the tropical rain forest area in Thailand. Its local name is Ma-Phut (มะพูด) (เต็ม, 2553). *G. dulcis* is a medium-size tree about 20-40 feet tall. The trunk is simple straight, the branches 4 angled. Leaves are deep green coriaceous ovate-oblong, shortly acuminate, base rounded; nerves 10 pairs, inarching near edge, not very prominent 5-10 inches long, 1.75-4.5 inches wide; petioles 0.4-0.6 inches long stout. Flowers are greenish yellow with 0.25 inches. Fruits are 2.5-3.0 inches long globular, ovoid or pear-shaped, peduncle, pulpy yellow. Seed are 1-5 oblong. Fruits can be eaten raw or cooked.

Figure 1 *Garcinia dulcis* Kurz.

(๑๐๘ พรรณไม้ไทย, 2542)

1.2 Review of Literatures

1.2.1 The chemical constituents of *Garcinia* genus (2005-2012)

The chemical constituents which were isolated from this genus before 2005 were summarized in the thesis of Miss Suwanna Deachathai (2005). The additional constituents of *Garcinia* genus from 2005-2012, according to the information from SciFinder were summarized in **Table 1**.

Table 1 Compounds isolated from the plants of *Garcinia* genus

Scientific name (Investigated part)	**Compound**	**Reference**
G. bancana (twigs and leaves)	[1,1′-biphenyl]-2-(3-methyl-2-butenyl)-3-methoxy-4,4′,5,6-tetraol, **a1**	Rukachaisirikul *et al*., 2005
G. bracteata (stem bark)	1,4,5,6-tetrahydroxyxanthone, **d4** bracteaxanthone III, **d5** bracteaxanthone IV, **d6** bracteaxanthone V, **d7** bracteaxanthone VI, **d8**	Niu *et al*., 2012
G. cowa (fruits)	β-mangostin, **d9** α-mangostin, **d10** cowawin, **d11** cowaxanthone A, **d17** cowaxanthone B, **d18** cowaxanthone C, **d19** cowaxanthone D, **d20** cowaxanthone E, **d21**	Panthong *et al*., 2006
G. cowa (twigs)	cowaxanthone F, **d16**	Panthong *et al*., 2009

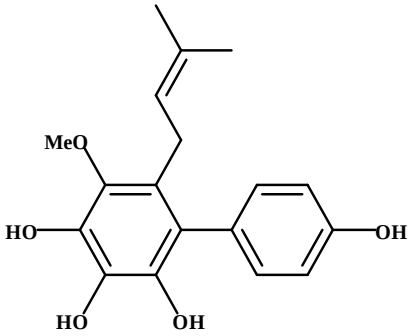
Table 1 Compounds isolated from the plant of *Garcinia* genus (continued)

Scientific name (Investigated part)	**Compound**	**Reference**
G. cowa (inflorescences)	fuscaxanthone A, **d12** 9-hydroxycalabaxanthone, **d13** garcinianone A, **d14** cowanol, **d15**	Trisuwan *et al*., 2012
G. dulcis (fruit)	dulcisisoflavone, **b1** dulcisflavan, **b2** dulcinoside, **b3** sphaerobioside acetate, **b4** dulcisxanthone A, **d1** dulcisxanthone B, **d25** isonormangostin, **d26**	Deachathai *et al*., 2005
G. dulcis (flowers)	dulcisxanthone D, **d22** dulcisxanthone E, **d23** dulcisxanthone F, **d24** dulcisxanthone C, **d42**	Deachathai *et al*., 2006
G. dulcis (seeds)	dulcisxanthone G, **d27**	Deachathai *et al*., 2008
G. hombroniana (twigs)	garcihombronane K, **c1** garcihombronane L, **c2** garcihombronone A, **d28** garcihombronone B, **d29** garcihombronone C, **d43** garcihombronone D, **d44**	Klaiklay *et al*., 2013
G.mangostana (stem)	mangosharin, **d2**	Ee *et al*., 2006

Table 1 Compounds isolated from the plant of *Garcinia* genus (continued)

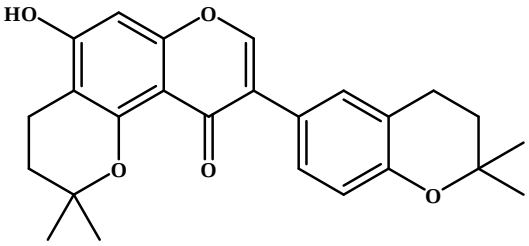
Scientific name (Investigated part)	**Compound**	**Reference**
G.mangostana (pericarp)	3-hydroxy-6-methoxy-5′-isopropyl-4′,5′-dihydrofuro[2′,3′:7,8]-6″,6″-dimethyl-4″,5″-dihydropyrano[2″,3″:1,2]xanthone, **d30** 1,6-dihydroxy-7-methoxy-8-(3-methyl but-3-enyl)-6′,6′-dimethyl-4′,5′dihydro pyrano[2′3′:3,2]xanthone, **d31**	Zhao *et al*., 2011
G. mangostana (stem bark)	11-hydroxy-3-*O*-methyl-1-isomangostin, **d32**	Han *et al*., 2009
G. nobilis (stem bark)	caroxanthone, **d3**	Fouotsa *et al*., 2012
G. nitida (stem bark)	1,6-dihydroxy-5-methoxy-6,6-dimethyl pyrano[2',3':2,3]-xanthone, **d33**	Ee *et al*., 2011
G. pedunculata (bark)	pedunxanthone A, **d34** pedunxanthone B, **d35** pedunxanthone C, **d36**	Vo *et al*., 2012
G. schomburgkiana (bark)	6-*O*-demethyloliverixanthone, **d37** schomburgxanthone, **d38**	Vo *et al*., 2012
G. smeathmannii (stem bark)	smeathxanthone A, **d39** smeathxanthone B, **d40**	Komguem *et al*., 2005
G.xipshuanbannaensis (leaves)	bannaxanthone I, **d41**	Na *et al*., 2010

a. Biphenyl derivative

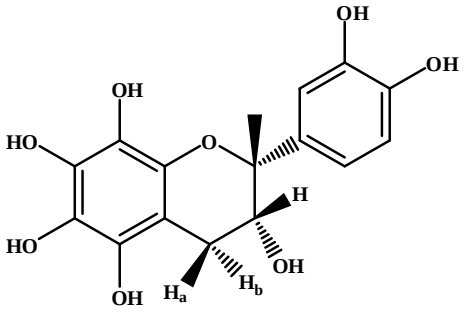


[1,1′-biphenyl]-2-(3-methyl-2-butenyl)-3-methoxy-4,4′,5,6-tetraol, **a1**

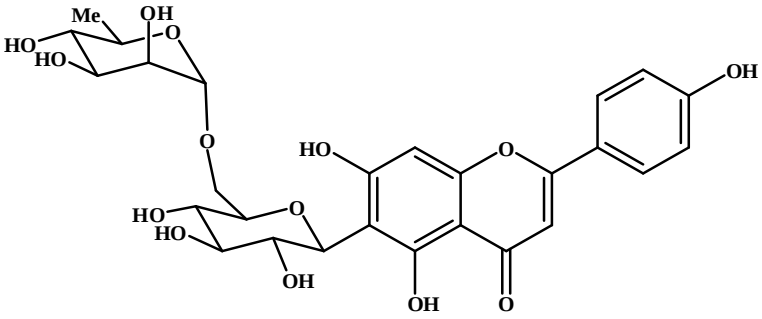
b. Flavonoids



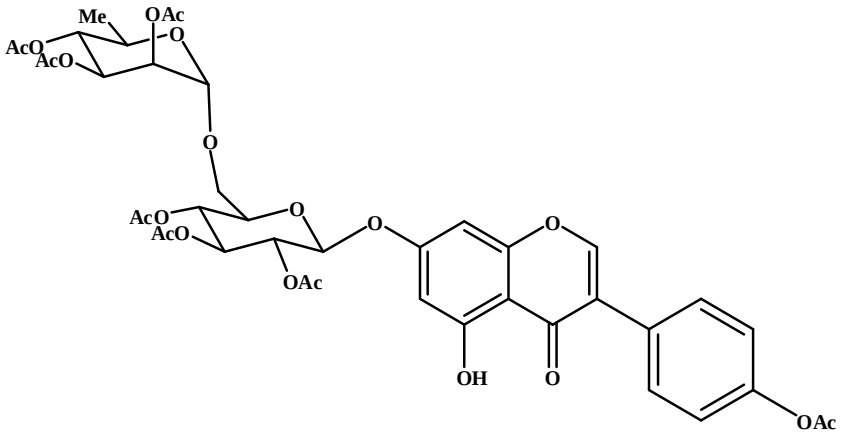
dulcisisoflavone, **b1**



dulcisflavan, **b2**

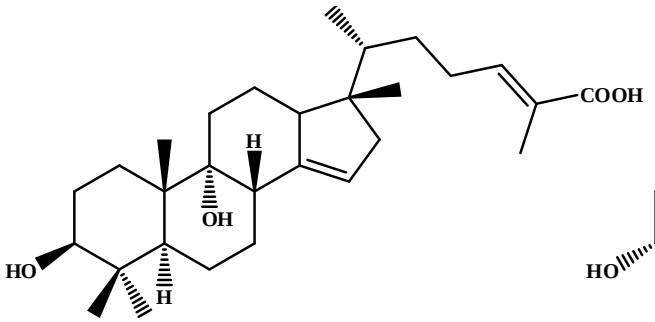


dulcinoside, **b3**

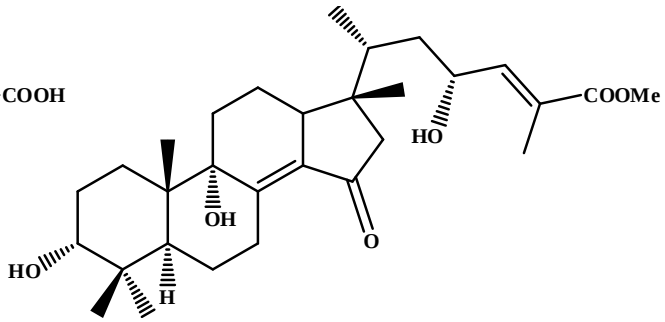


sphaerobioside acetate, **b4**

c. Steroids



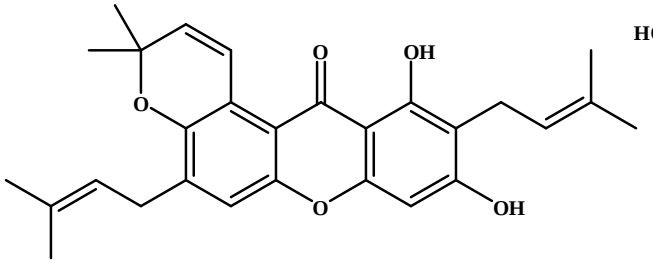
garcihombronane K, **c1**



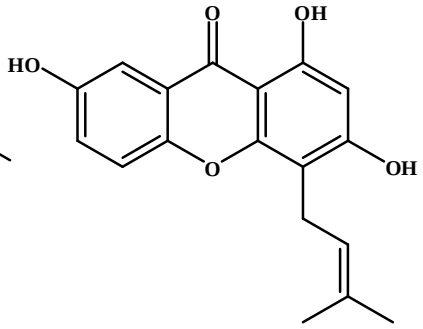
garcihombronane L, **c2**

d. Xanthones

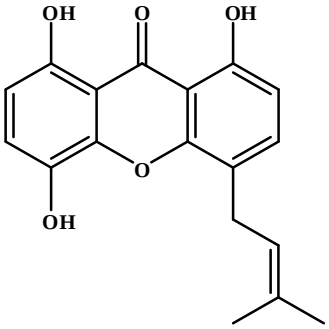
- **Trioxygenated xanthones**



dulcisxanthone A, **d1**

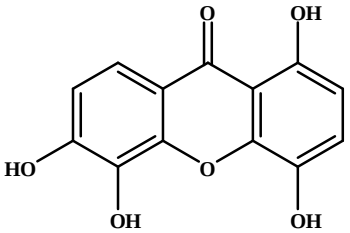


mangosharin, **d2**

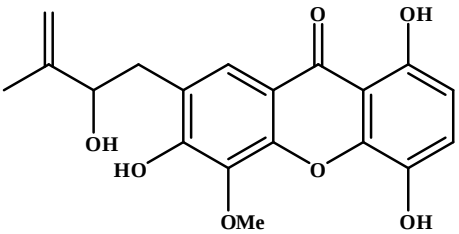


caroxanthone, **d3**

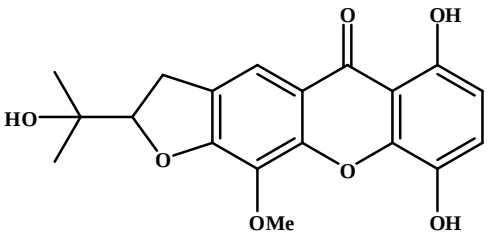
- **Tetraoxygenated xanthones**



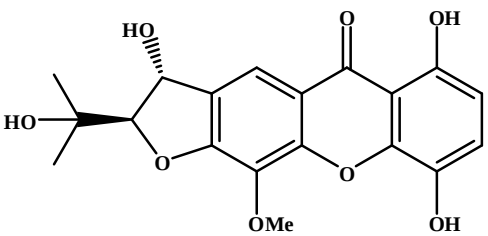
1,4,5,6- tetrahydroxyxanthone, **d4**



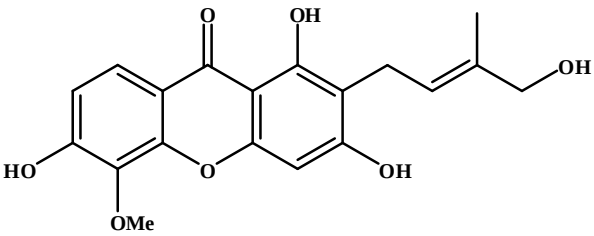
bracteaxanthone III, **d5**



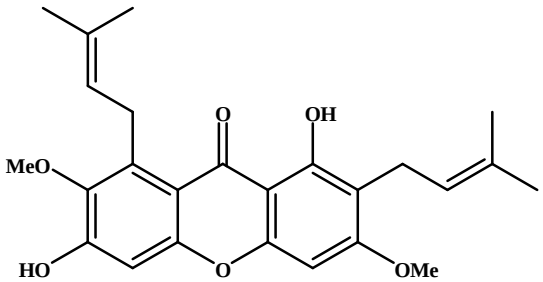
bracteaxanthone IV, **d6**



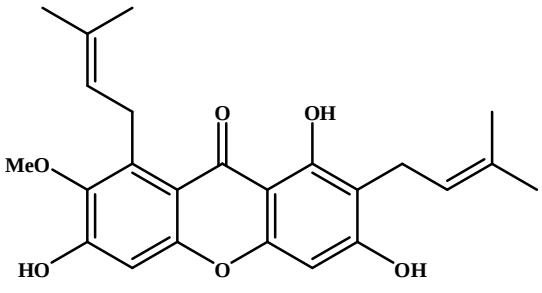
bracteaxanthone V, **d7**



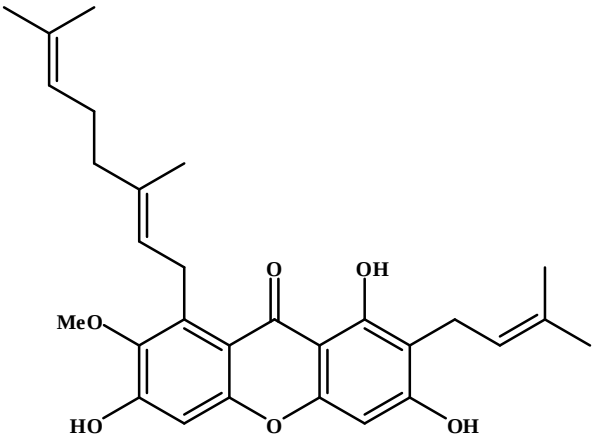
bracteaxanthone VI, **d8**



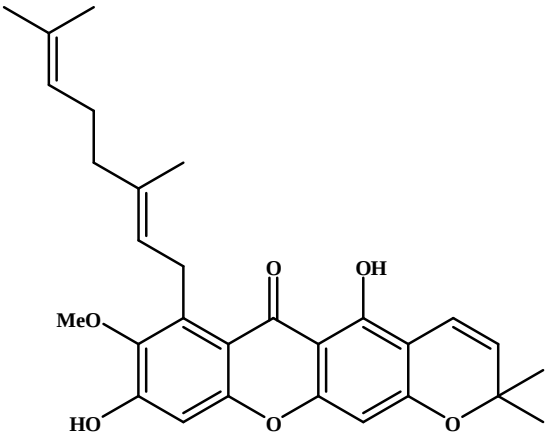
β-mangostin, **d9**



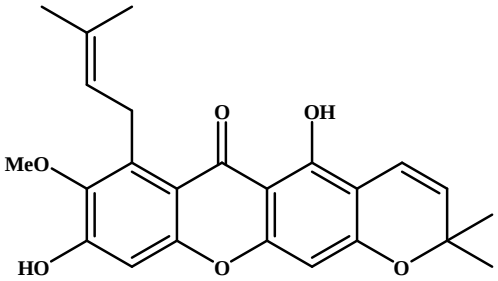
α-mangostin, **d10**



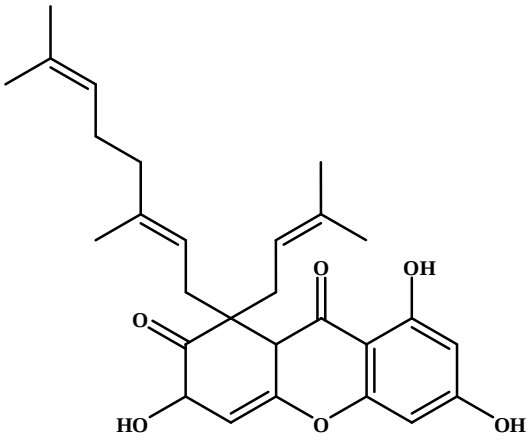
cowawin, **d11**



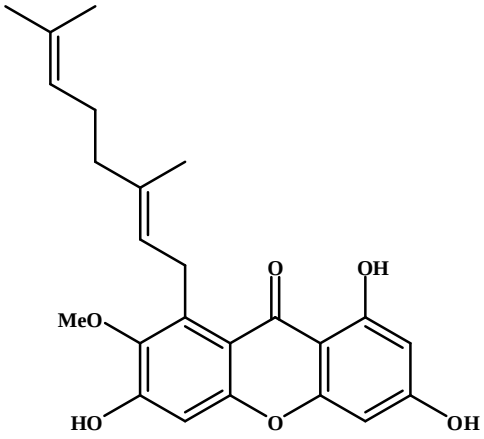
fuscaxanthone A, **d12**



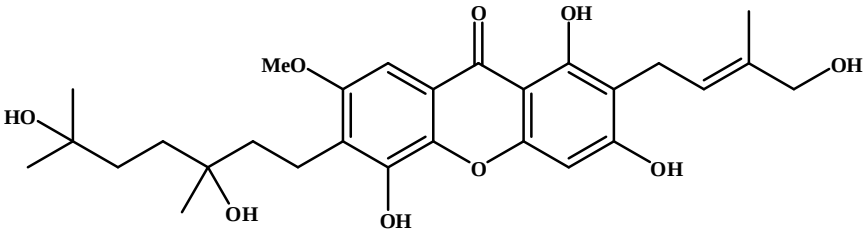
9-hydroxycalabaxanthone, **d13**



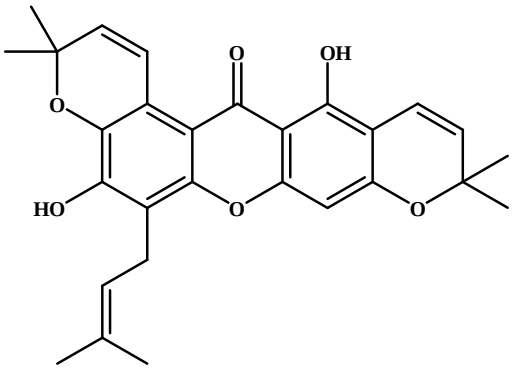
garcinianone A, **d14**



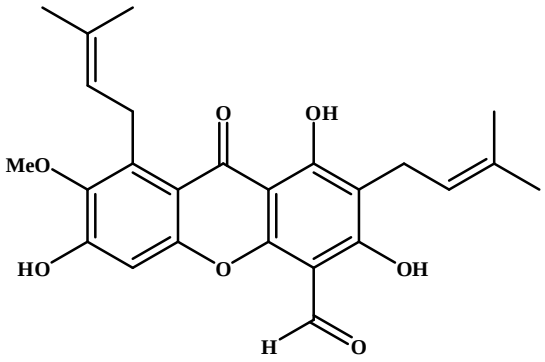
cowanol, **d15**



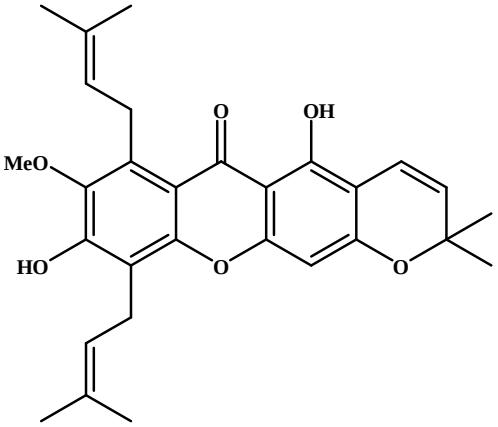
cowaxanthone F, **d16**



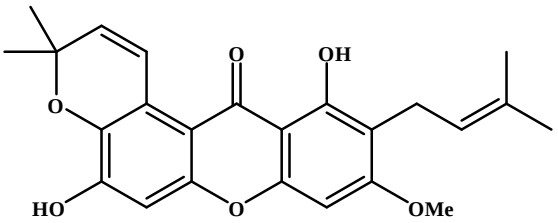
cowaxanthone A, **d17**



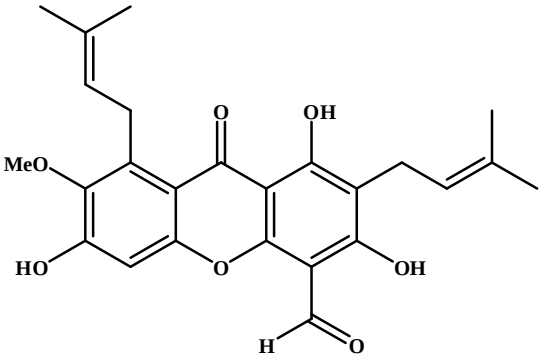
cowaxanthone B, **d18**



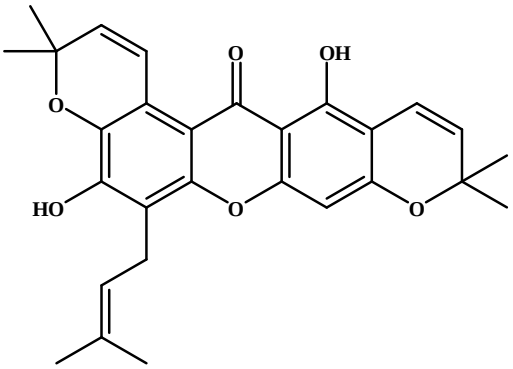
cowaxanthone C, **d19**



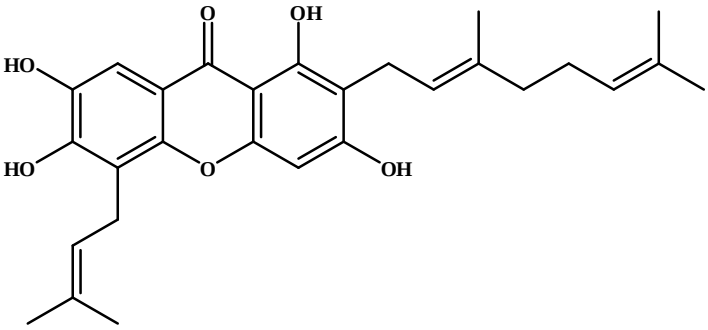
cowaxanthone D, **d20**



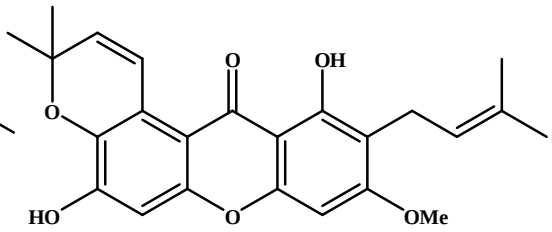
cowaxanthone E, **d21**



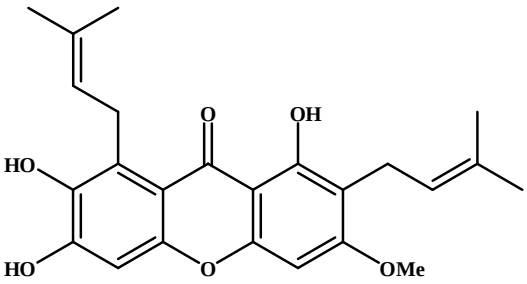
dulcisxanthone D, **d22**



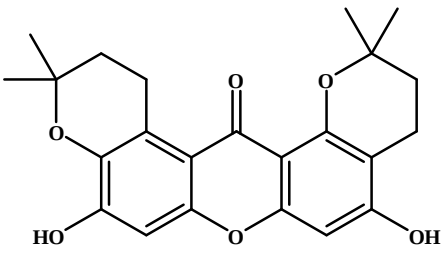
dulcisxanthone E, **d23**



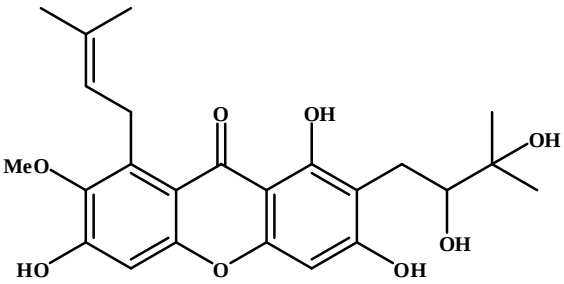
dulcisxanthone F, **d24**



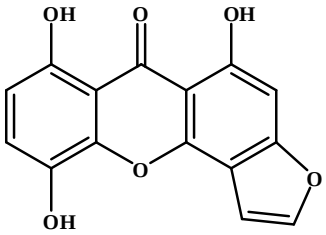
dulcisxanthone B, **d25**



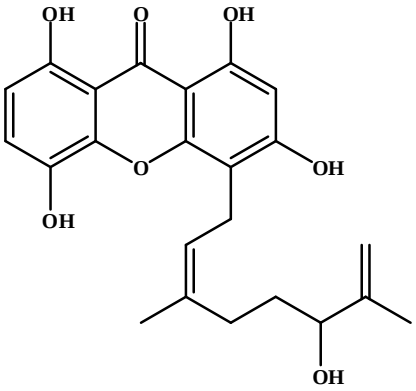
isonormangostin, **d26**



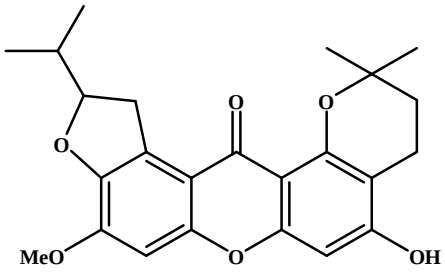
dulcisxanthone G, **d27**



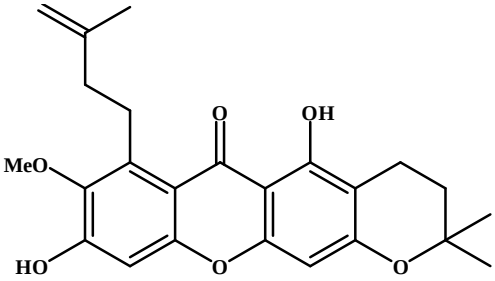
garcihombronone A, **d28**



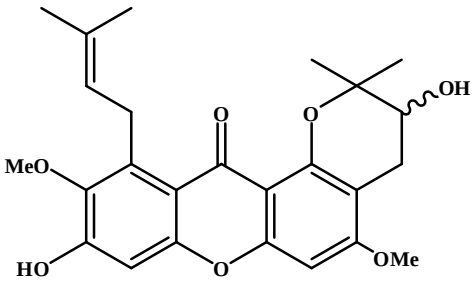
garcihombronone B, **d29**



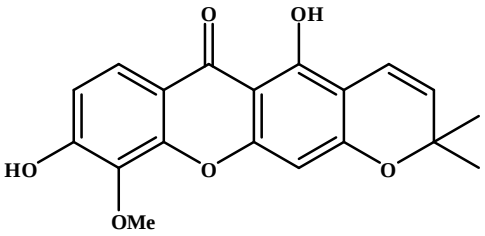
3-hydroxy-6-methoxy-5′-isopropyl-4′,5′-dihydrofuro[2′,3′:7,8]-6″,6″-dimethyl-4″,5″-dihydropyrano[2",3":1,2]xanthone, **d30**



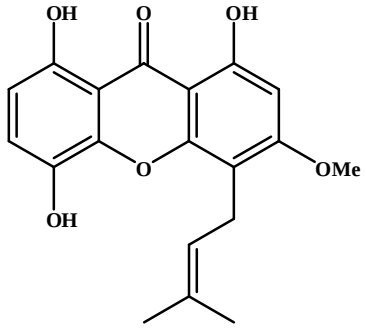
1,6-dihydroxy-7-methoxy-8-(3-methylbut-3-enyl)-6′,6′-dimethyl-4′,5′-dihydro pyrano[2′3′:3,2]xanthone, **d31**



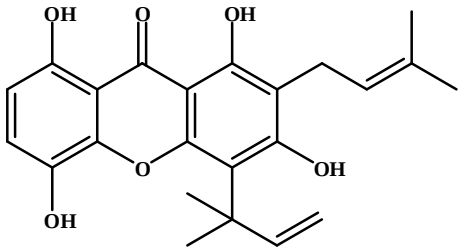
11-hydroxy-3-*O*-methyl-1-isomangostin, **d32**



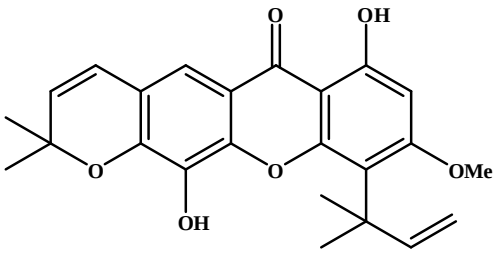
1,6-dihydroxy-5-methoxy-6, 6-dimethylpyrano [2',3':2,3]-xanthone, **d33**



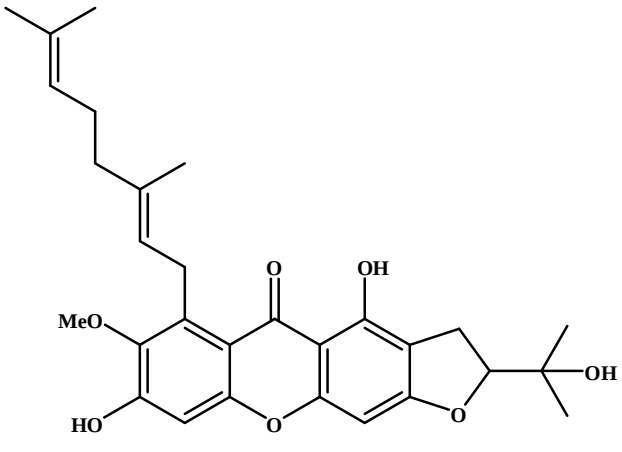
pedunxanthone A, **d34**



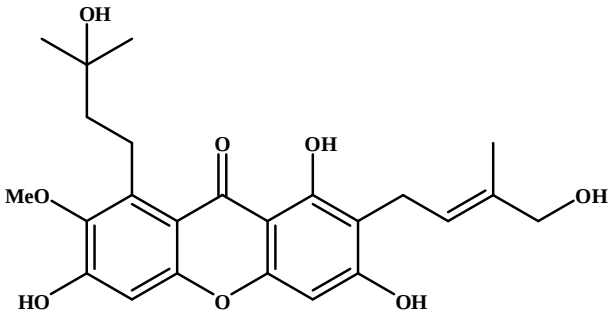
pedunxanthone B, **d35**



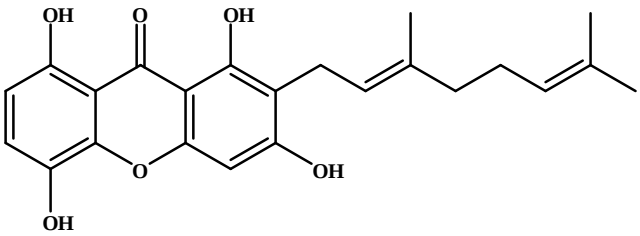
pedunxanthone C, **d36**



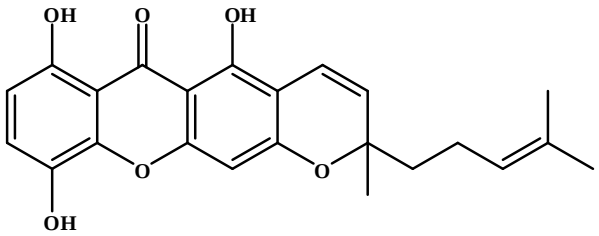
6-*O*-demethyloliverixanthone, **d37**



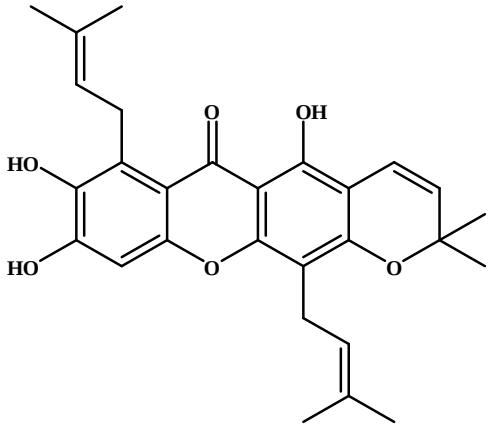
schomburgxanthone, **d38**



smeathxanthone A, **d39**

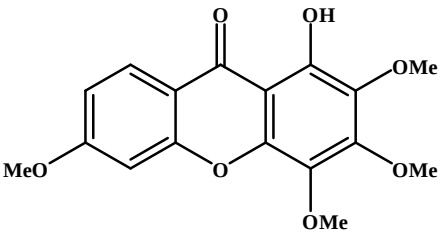


smeathxanthone B, **d40**

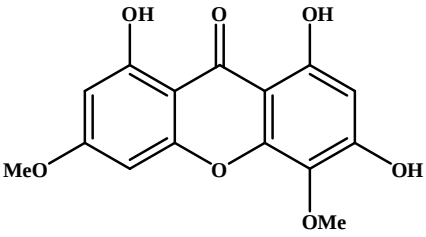


bannaxanthone I, **d41**

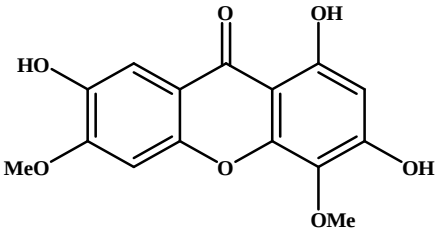
- **Pentaoxygenated xanthones**



dulcisxanthone C, **d42**



garcihombronone C, **d43**



garcihombronone D, **d44**

1.2.2 The biological activity of chemical composition in the plants (biflavoniods xanthones and triterpenoids)

Garcinia dulcis Kurz., (Guttiferae) is an Asian medicinal plants used in folk medicines. In Thailand, the stem bark of this plant has been used as an anti-inflammatory agent (มาโนชและเพ็ญนภา, 2540) and the fruit juice has been used in traditional medicine as an expectorant (วุฒิ, 2540). In Indonesia, the leaves and seeds have been used for the treatment of lymphatitis, parotitis and struma (Kasahara and Henmi, 1986).

Amentoflavone, morelloflavone, GB-1a, GB-1a, agathisflavone and GB-2a were isolated from *Rhus succedanea* and *Garcinia multiflora*. These compounds showed moderately activity against HIV-1 RT, with IC_{50} values of 119, 116, 236, 100 and 170 μM, respectively. Morelloflavone also showed significant antiviral activity against HIV-1 (strain LAV-1) in phytohemagglutinin stimulated primary human peripheral blood mononuclear cells at an EC_{50} value of 6.9 μM and a selectivity index value of approximately 10. (Lin, *et al*., 1997).

Endodesmiadiol, friedelin, canophyllol, canophyllal, cerin, morelloflavone, 8-deoxygartanin and 3-β-acetoxyoleanolic acid were isolated from the ethyl acetate extract of the stem bark of *Endodesmia calophylloides* (Guttiferae). These compounds were tested for antiplasmodial activity against the W2 strain of *Plasmodium falciparum*, which is resistant to chloroquine and other antimalarial drugs. They were found to exhibit antiplasmodial activity *in vitro* with IC_{50} values of 13.0, 7.2, 15.0, 18.2, 14.1, 23.6, 11.8, and 13.1 μM, respectively (Ngouamegne, *et al*., 2008).

Amentoflavone was isolated from the leaves of *Torreya nucifera*, which is traditionally used as a medicinal plant in Asia. These compounds showed most potent SARS-CoV3CL^{pro} inhibitory effect, with IC_{50} values of 8.3 μM (Ryu, *et al*., 2010).

Amentoflavone and 4- monomethoxy amentoflavone were isolated from the leaves of *Garcinia livingstonei*. These compounds had good activities (MIC 6 and 8 g/ml) against some nosocomial bacteria. (Kaikabo, *et al*., 2011).

Amentoflavone exerted potent cytotoxic effects against both MCF-7 and HeLa cells, with IC_{50} of 25 and 20 μM, respectively. It has been reported that amentoflavone has anti-inflammatory activity and pregulates hPPARγ in TNFα activated A549 cells. However, in the results, amentoflavone did not show noticeable cytotoxic activity against A549 cell line. Collectively, these observations suggest that amentoflavone is a potent agonist of hPPARγ with cytotoxic activities against human breast and cervical cancers (Lee, *et al*., 2012).

1.3 Objective

The objectives of this work were to investigate the chemical constituents from the leaves and stem bark of *Garcinia dulcis* and evaluate for their antibacterial activity.

CHAPTER 2

EXPERIMENTAL

2.1 Instruments and chemicals

Quick column chromatography (QCC) and column chromatography (CC) was performed by using silica gel 60 H (Merck) and silica gel 100 (70-230 Mesh ASTM, Merck), Sephadex^{TM} LH-20 (Amersham Biosciences, Sweden) and reversed-phase (RP), respectively. For thin-layer chromatography (TLC), aluminum sheets of silica gel 60 GF_{254} (20x20 cm, layer thickness 0.2 mm, Merck) were used for analytical purposes and the compounds were visualized under ultraviolet light. Solvent for extraction and chromatography were distilled at their boiling ranges prior to use. Melting points were recorded with a digital electrothermal melting point apparatus (Electrothermal 9100). Ultraviolet spectra were measured with a UV-160A spectrophotometer (SHIMADZU) and principle bands (λ_{max}) were recorded as wavelengths (nm) and log ε in methanol solution. Infrared spectra (IR) were obtained on a Perkin-Elmer 783 FTS165 FT-IR spectrophotometer and were recorded in wave number (cm^{-1}). ^{1}H and ^{13}C-nuclear magnetic resonance spectra were recorded with a FT-NMR Bruker Avance 300 MHz and 500 MHz spectrometer at Department of Chemistry, Faculty of Sicence, Prince of Songkla University. Spectra were recorded in acetone-d_6, $CDCl_3$ and DMSO–d_6 as δ value in ppm down field from TMS (internal standard δ 0.00). Low and high resolution mass spectra were recorded on a MAT 95 XL at Scientific Equipment Center, Prince of Songkla University.

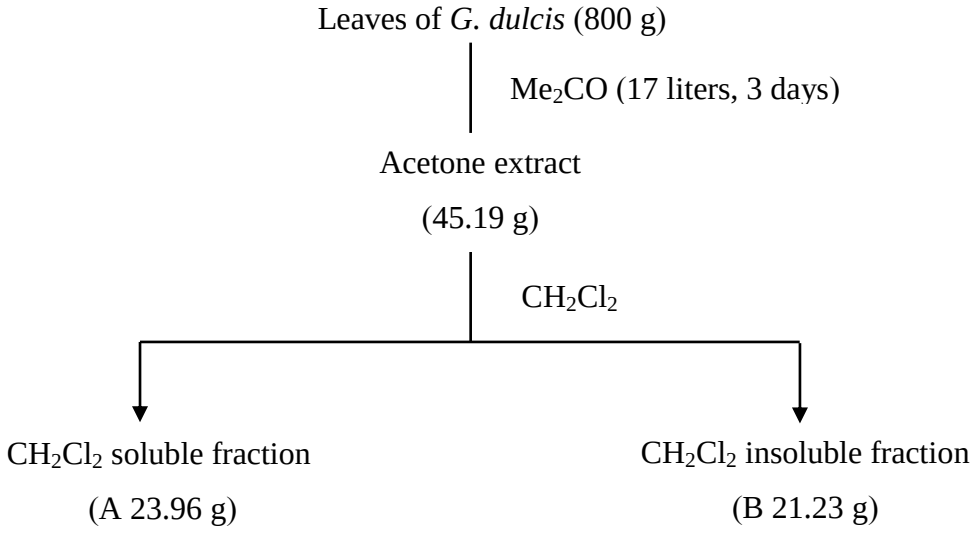
2.2 Plant material

The leaves and stem bark of *G. dulcis* was collected in October 2012 from Songkhla province in the southern part of Thailand. The voucher specimen (Coll. No. 02, Herbarium No. 0012652) has been deposited at Prince of Songkla University Herbarium, Biology Department, Faculty of Science, Prince of Songkla University, Thailand.

2.3 Chemical investigation of the leaves

2.3.1 Extraction and isolation

The leaves of *G. dulcis* (800 g) were chopped and immersed at room temperature in acetone (3 days) to give an acetone extract (45.19 g). The crude extract was dissolved in CH_2Cl_2 to give dichloromethane soluble (A 23.96 g) and insoluble fractions (B 21.23 g). The process of extraction was shown in **Scheme 1**.



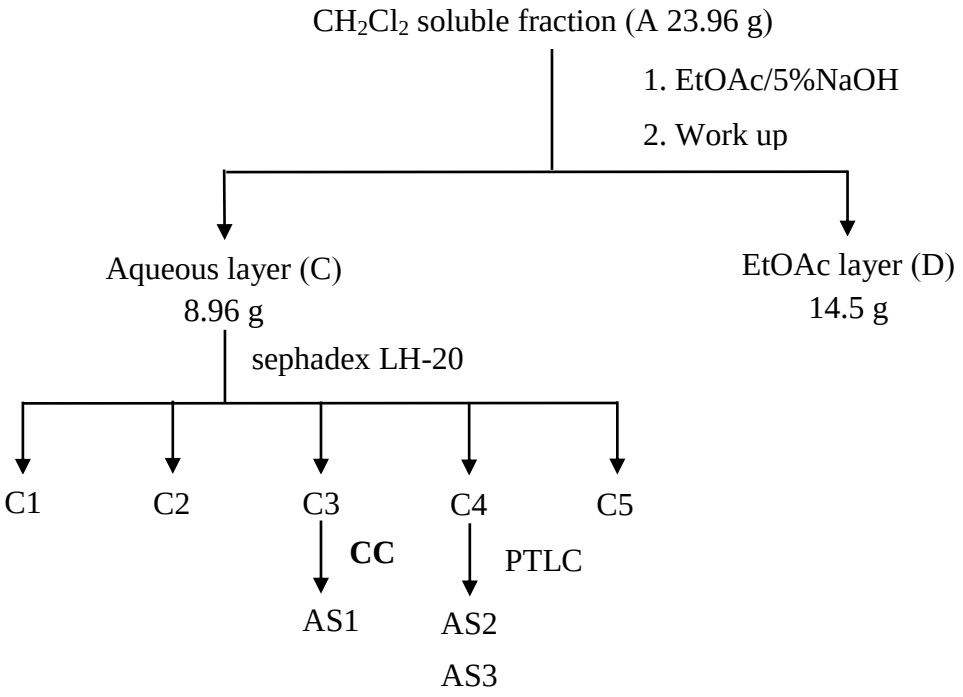
Scheme 1 Extraction of crude extracts from the leaves of *G. dulcis*

2.3.2 Purification of CH_2Cl_2 soluble fraction

The CH_2Cl_2 soluble fraction (**A**, 23.96 g), after removal of solvent was partitioned with EtOAc/5%NaOH to give, after work up, an aqueous layer (**C**, 8.96 g) and an EtOAc layer (**D**, 14.50 g). The aqueous layer **C** was subjected on sephadex LH-20 and eluted with 8:2 MeOH:CH_2Cl_2 to give fractions C1-C5 (**Table 2**). The selected fractions were further purified by CC and PTLC. Three pure compounds were obtained (**Scheme 2**).

Table 2 Physical characteristic and weight of fractions **C1-C5**

Fractions	Weight (g)	Appearance
C1	1.74	dark-green viscous liquid
C2	0.82	green viscous liquid
C3	1.30	green viscous liquid
C4	2.27	green viscous liquid
C5	2.85	brown viscous liquid



Scheme 2 Isolation of fractions **C1-C5** from the CH_2Cl_2 soluble fraction

Fractions C1 and C2

Chromatogram characteristics on normal phase TLC with 7:3 CH_2Cl_2: MeOH showed none of well-separated spots under UV-lamp. Further investigation was not carried out.

Fraction C3

Fraction C3 (208 mg) was chromatographed on CC using MeOH:CH_2Cl_2 (0.5:9.5) as eluent to give eleven fractions (E1-E11). Fraction E3 (208.3 mg) was chromatographed on CC using acetone:CH_2Cl_2:hexane (1.0:3.0:6.0) as an elutent to give **AS1** (1.3 mg).

Fraction C4

Fraction C4 (2.27 g) was chromatographed on CC using acetone:hexane (3:7) as an eluent to give twelve fractions (F1-F12). Fraction F6 (30.0 mg) was further purified by PTLC using MeOH:CH_2Cl_2 (2:8) as a mobile phase to give **AS2** (1.0 mg) and **AS3** (1.8 mg).

Fraction C5

Chromatogram characteristics on normal phase TLC with 7:3 CH_2Cl_2: MeOH showed one major UV-lamp. This fraction was combined with subfraction B2 of the dichloromethane insoluble extract.

AS1

Melting point: 193-194 ^{o}C

UV (MeOH) λ_{max} (nm) (log ε): 332 (1.98), 323 (2.00) and 203 (3.51)

FT-IR (neat) ν_{max} (cm^{-1}): 3382 (O-H stretching), 2943 (C-H stretching) and 1641 (C=C stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 6**

AS2

UV (MeOH) λ_{max} (nm) (log ε): 333 (3.23), 256 (3.69) and 202 (3.98)

FT-IR (neat) ν_{max} (cm^{-1}): 3218 (O-H stretching) and 1684 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 7**

AS3

UV (MeOH) λ_{max} (nm) (log ε): 337 (2.76), 326 (2.81), 289 (3.67), 256 (3.93) and 203 (4.35)

FT-IR (neat) ν_{max} (cm^{-1}): 3235 (O-H stretching) and 1690 (C=O stretching)

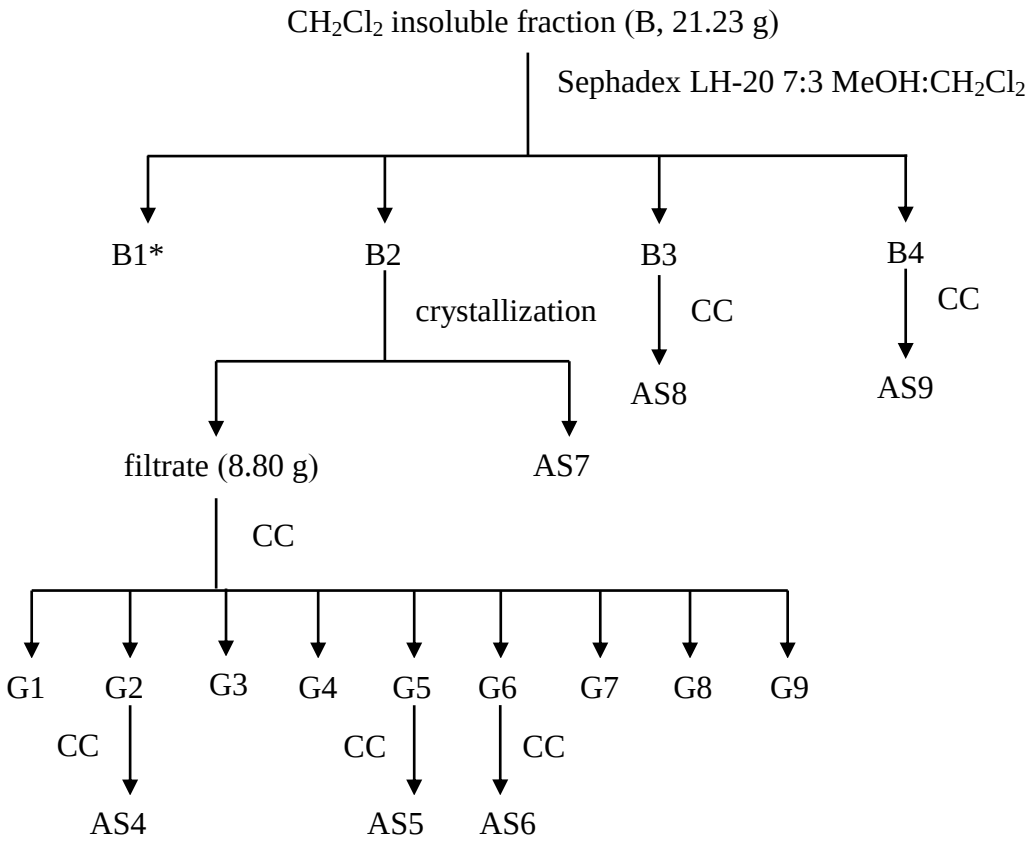
^{1}H NMR, ^{13}C NMR spectral data, see **Table 8**

2.3.3 Purification of CH_2Cl_2 insoluble fraction

The CH_2Cl_2 insoluble fraction (B, 21.23 g) was subjected to column chromatography using sephadex LH-20 as stationary phase and eluted with 7:3 MeOH:CH_2Cl_2. On the basis of their TLC characteristics, the fractions which contained the same major components were combined to give fractions B1-B4 (**Table 3**). The selected fractions were further purified by CC and crystallized. Six pure compounds were obtained (**Scheme 3**).

Table 3 Physical characteristic and weight of fractions **B1-B4**

Fractions	Weight (g)	Appearance
B1	7.61	green viscous liquid
B2	8.84	yellow solid mixed with brown liquid
B3	0.37	brown viscous liquid
B4	1.53	dark-brown viscous liquid



*No further investigation

Scheme 3 Isolation of fractions **B1-B4** from the CH_2Cl_2 insoluble fraction

Fraction B2

A yellow solid of **AS7** (40.0 mg) which formed in fraction B2 was filtered off, the filtrate (8.80g) was further purified by CC on silica gel and eluted with CH_2Cl_2:MeOH (7:3) to give nine fractions (G1–G9). Fraction G2 (34.0 mg) was purified by CC on silica gel and eluted with acetone:CH_2Cl_2:hexane (2.5:1.5:6.0) to give **AS4** (4.3 mg). Fraction G5 (738.3 mg) was purified by CC on silica gel and eluted with acetone:hexane (4:6) to give five fractions (H1-H5). Fraction H2 (362.4 mg) was purified by CC on silica gel and eluted with acetone:CH_2Cl_2:hexane (3:2:5) to give a yellow solid **AS5** (6.2 mg). Fraction G6 (730.5 mg) was purified by CC on silica gel and eluted with CH_2Cl_2:MeOH (9.7:0.3) to give a yellow powder **AS6** (5.5 mg).

Fraction B3

Fraction B3 (374.0 mg) was purified by CC on silica gel and eluted with MeOH:CH_2Cl_2 (1.8:8.2) to give twelve fractions (I1-I12). Fractions I7 (78.2 mg) was purified by CC silica gel and eluted with MeOH:CH_2Cl_2 (1.5:8.5) to give a yellow solid **AS8** (9.0 mg).

Fraction B4

Fraction B4 (1.53 g) was purified by CC on reversed-phase and eluted with MeOH:H_2O (2:8) to give fifteen fractions (J1-J15). Faction J14 (80.0 mg) was purified by CC on silica gel and eluted with MeOH:CH_2Cl_2 (7:3)to give **AS9** (1.2 mg).

AS4

Melting point: 233-234 ^oC

UV (MeOH) λ_{max} (nm) (log ε): 339 (4.42), 269 (4.47) and 203 (4.69)

FT-IR (neat) ν_{max} (cm^{-1}): 3421 (O-H stretching) and 1653 (C=O stretching)

^1H NMR, ^{13}C NMR spectral data, see **Table 9**

AS5

Melting point: 215-216 ^oC

UV (MeOH) λ_{max} (nm) (log ε): 291 (5.14) and 201 (5.54)

FT-IR (neat) ν_{max} (cm^{-1}): 3215 (O-H stretching) and 1635 (C=O stretching)

^1H NMR, ^{13}C NMR spectral data, see **Table 10**

AS6

Melting point: 236-238 ^oC

UV (MeOH) λ_{max} (nm) (log ε): 333 (4.05), 269 (4.09) and 202 (4.28)

FT-IR (neat) ν_{max} (cm^{-1}): 3402 (O-H stretching) and 1649 (C=O stretching)

^1H NMR, ^{13}C NMR spectral data, see **Table 11**

AS7

Melting point: 305-307 ^{o}C

UV (MeOH) λ_{max} (nm) (log ε): 344 (4.75) and 289 (4.93)

FT-IR (neat) ν_{max} (cm^{-1}): 3215 (O-H stretching) and 1641 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 12**

AS8

Melting point: 290-293 ^{o}C

UV (MeOH) λ_{max} (nm) (log ε): 348 (4.88), 289 (5.02) and 201 (5.41)

FT-IR (neat) ν_{max} (cm^{-1}): 3423 (O-H stretching), 1643 (C=O stretching), 1262 (S=O stretching) and 1042 (C-O-S stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 13**

AS9

Melting point: 247-250 ^{o}C

UV (MeOH) λ_{max} (nm) (log ε): 339 (3.17), 322 (3.21) and 292 (3.34)

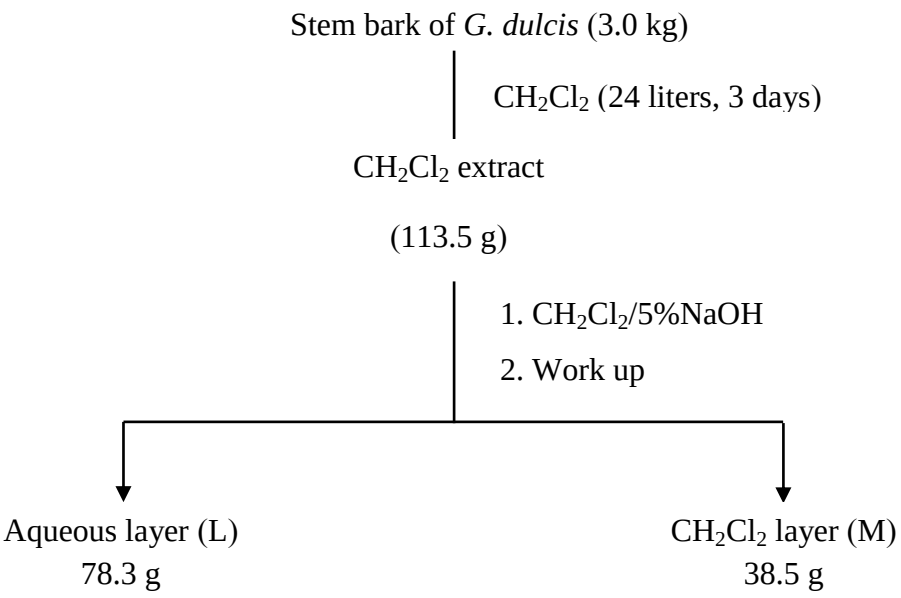
FT-IR (neat) ν_{max} (cm^{-1}): 3215 (O-H stretching) and 1622 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 14**

2.4 Chemical investigation of the stem bark

2.4.1 Extraction and isolation

The stem bark of *G. dulcis* (3.0 kg) was chopped and immersed at room temperature in CH_2Cl_2 (3 days) to give the CH_2Cl_2 extract (113.5 g). Partition of CH_2Cl_2 extract with CH_2Cl_2/5%NaOH gave aqueous layer after work up (**L**; 78.3 g) and CH_2Cl_2 layer (M; 38.5 g) (**Scheme 4)**. Fraction L was subjected on sephadex LH-20 and eluted with MeOH:CH_2Cl_2 (8:2) to give fractions L1-L3 (**Table 4**). The selected fractions were further purified by CC. Nine pure compounds were obtained (**Scheme 5)**.



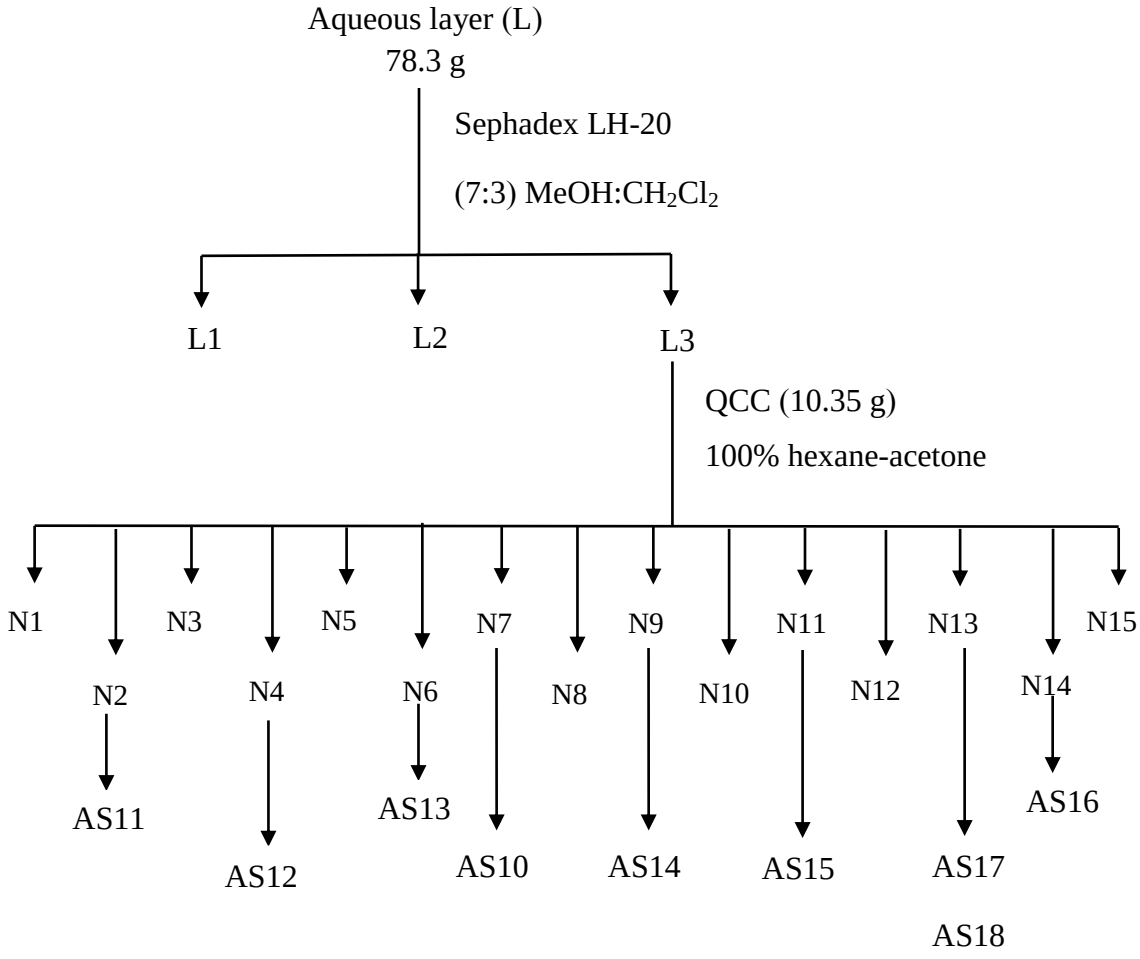
Scheme 4 Extraction of crude extracts from the stem bark of *G. dulcis*

2.4.2 Purification of aqueous layer (L) fraction

Aqueous layer L (78.3 g) was subjected on sephadex LH-20 and eluted with MeOH:CH_2Cl_2 (7:3) to give fractions (L1-L3). Fraction L3 (10.35 g) was separated by quick column chromatography over silica 60H using hexane, hexane-acetone and acetone as eluents. On the basis of their TLC characteristics, the fractions which contained the same major components were combined to give fifteen fractions (N1-N15). Fractions N2, N4, N6, N9, N11 and N15 were crystallized in hexane:acetone (7:3) to give yellow solids of **AS11**, **AS12, AS13, AS14, AS15** and **AS16** (9.6, 1.5, 6.0, 138.6, 43.5 and 11.9 mg), respectively. Fraction N7 was crystallized in hexane-acetone (7:3) to give a white solid of **AS10** (4.8 mg). Fraction N14 (118.0 mg) was purified by CC on silica gel and eluted with acetone:hexane (2:7) to give **AS17** (2.5 mg) and **AS18** (1.2 mg).

Table 4 Physical characteristic and weight of fractions **L1-L3**

Fractions	Weight (g)	Appearance
L1	16.43	brown viscous liquid
L2	36.02	yellow-brown viscous liquid
L3	10.35	yellow solid mixed with brown liquid



Scheme 5 Isolation of fractions **N1 – N15** from the aqueous layer **(L)**

Table 5 Physical characteristic and weight of fractions **N1-N15**

Fractions	Weight (g)	Appearance
N1	0.56	yellow gel
N2	0.15	yellow solid mixed yellow liquid
N3	0.66	yellow solid mixed yellow liquid
N4	0.10	yellow solid mixed yellow liquid
N5	0.22	yellow solid mixed yellow liquid
N6	0.10	yellow solid mixed yellow liquid
N7	0.33	white solid
N8	0.14	yellow solid mixed yellow liquid
N9	0.19	yellow solid mixed yellow liquid
N10	0.48	yellow solid mixed yellow liquid
N11	0.76	yellow solid mixed yellow liquid
N12	0.48	yellow solid mixed yellow liquid
N13	0.40	yellow solid mixed yellow liquid
N14	0.55	yellow solid mixed yellow liquid
N15	1.52	brown viscous liquid

AS10

Melting point : 280-282 ^{o}C

UV (MeOH) λ_{max} (nm) (log ε) : 313 (3.13), 269 (3.41), 244 (3.42) and 202 (4.64)

FT-IR (neat) ν_{max} (cm^{-1}): 3420 (O-H stretching), 1689 (C=O stretching) and 2939 (C-H stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 15**

AS11

Melting point: 203-205 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε): 382 (3.85), 322 (4.35), 267 (4.75) and 253 (4.79)

FT-IR (neat) ν_{max} (cm^{-1}): 3375 (O-H stretching) and 1645 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 16**

AS12

Melting point: 99-100 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε): 326 (3.90), 255 (4.33) and 205 (4.28)

FT-IR (neat) ν_{max} (cm^{-1}): 3361 (O-H stretching) and 1615 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 17**

AS13

Melting point: 194-196 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε) : 332 (4.01), 280 (4.40) and 256 (4.30)

FT-IR (neat) ν_{max} (cm^{-1}): 3420 (O-H stretching) and 1657 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 18**

AS14

Melting point: 188-189 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε): 318 (3.45), 265 (3.89), 250 (3.92), 239 (3.89) and 204 (391)

FT-IR (neat) ν_{max} (cm^{-1}): 3244 (O-H stretching) and 1640 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 19**

AS15

Melting point: 223-225 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε): 327 (3.15), 269 (3.62) and 247 (3.58)

FT-IR (neat) ν_{max} (cm^{-1}): 3422 (O-H stretching) and 1630 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 20**

AS16

Melting point: 240-243 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε): 329 (4.02), 280 (3.69) and 255 (4.30)

FT-IR (neat) ν_{max} (cm^{-1}): 3419 (O-H stretching) and 1640 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 21**

AS17

UV (EtOH) λ_{max} (nm) (log ε): 329 (4.53), 255 (4.82) and 208 (4.80)

FT-IR (neat) ν_{max} (cm^{-1}): 3525 (O-H stretching) and 1633 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 22**

AS18

Melting point: 102-105 ^{o}C

UV (EtOH) λ_{max} (nm) (log ε): 331 (4.05), 256 (4.41) and 203 (4.32)

FT-IR (neat) ν_{max} (cm^{-1}): 3229 (O-H stretching) and 1645 (C=O stretching)

^{1}H NMR, ^{13}C NMR spectral data, see **Table 23**

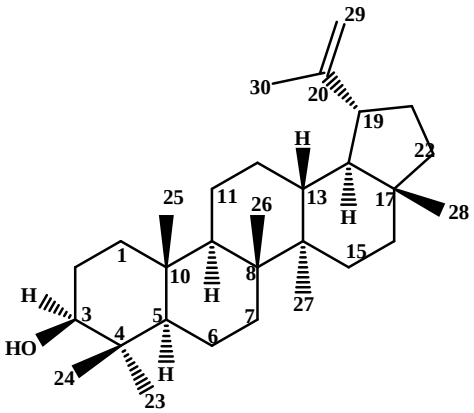
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Structural elucidation of compounds from the leaves and stem bark of *G. dulcis*

The crude acetone extract and dichloromethane extract from the leaves and stem bark of *G. dulcis* were subjected to repeated quick column, column chromatography over silica gel and Sephadex LH-20 to give eighteen compounds. Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data: ^{1}H, ^{13}C NMR, DEPT 135^{o}, DEPT 90^{o}, HMQC, HMBC, COSY and NOE. The physical properties and spectroscopic data were also compared with the reported values. Nine compounds were isolated from the leaves. They were identified as lupeol **(AS1)**, 4-hydroxy benzoic acid **(AS2)**, 4-hydroxy-3-methoxybenzoic acid **(AS3)**, 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxy-3-(3-methylbut-2-enyl)phenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-6-(3-methylbut-2-enyl)-4*H*-chromen-4-one **(AS4)** , GB-2a **(AS5)**, amentoflavone **(AS6)**, morelloflavone **(AS7)**, morelloflavone-7″-sulfate **(AS8)**, volkensiflavone **(AS9)**. Nine compounds were obtained from the stem bark. They were identified as oleanolic acid **(AS10)**, garciniaxanthone C **(AS11)**, garciniaxanthone A **(AS12)**, 1,4,8-trihydroxy-6-methoxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS13)**, 12b-hydroxy-des-D-garcigerrin A **(AS14)**, 1,2,5,6-tetrahydroxy-7-(3-methylbut-2-enyl)-3-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one **(AS15)**, 1,3,5,6-tetrahydroxy-2,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one**(AS16)**, garciniaxanthoneE **(AS17)**, 1,3,5,6-tetrahydroxy-4,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one **(AS18)**. **AS4**, **AS13**, **AS15**, **AS16** and **AS18** are new naturally occurrence compounds.

AS1: lupeol

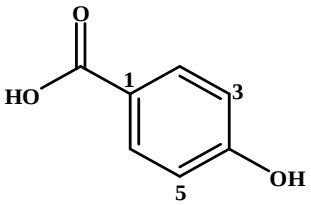


AS1 was a white solid, m.p. 193-194℃. The UV spectrum showed absorption bands at λ_{max} 203, 323 and 332 nm. The IR spectrum showed the absorption bands of O-H stretching at 3382, C-H stretching at 2943 and C=C stretching at 1641 cm^{-1}. The ^{1}H NMR spectrum (**Table 6**) showed resonances of seven methyl singlet signals at δ 0.76, δ 0.79, δ 0.83, δ 0.94, δ 0.97 and δ 1.03, along with one vinylic methyl at δ 1.68, two protons of an isopropenyl moiety at δ 4.68 (1H, *d*, 3.0, H-29a) and δ 4.57 (1H, *m*, H-29b) and a methine proton at δ 2.38 (1H, *m*, H-19) and an oxy-methine proton at δ 3.20 (1H, *dd*, 9.0, 3.0, H-3). These data are in agreement with those of lupeol (Reynolds *et al*., 1986). Thus **AS1** was assigned to be lupeol (Pakakrong, 2005).

Table 6 ^{1}H NMR spectrum data of **AS1** and **lipeol**

Position	**AS1; δ_H (mult., J_{Hz})**	**lupeol; δ_H (mult., J_{Hz})**
3	3.20 (*dd*, 9.0, 3.0)	3.18 (*dd*, 10.8, 5.1)
19	2.38 (*m*)	2.39 (*m*)
23	0.97 (*s*)	0.98 (*s*)
24	0.76 (*s*)	0.77 (*s*)
25	0.83 (*s*)	0.84 (*s*)
26	1.03 (*s*)	1.04 (*s*)
27	0.94 (*s*)	0.97 (*s*)
28	0.79 (*s*)	0.79 (*s*)
29a	4.68 (*d*, 3.0)	4.69 (*m*)
29b	4.57 (*m*)	4.56 (*m*)
30	1.68 (*s*)	1.69 (*s*)

AS2: 4-hydroxybenzoic acid

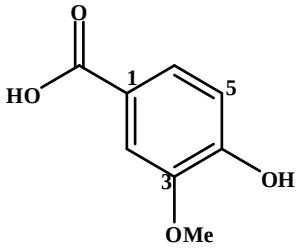


AS2 was obtained as a colorless gum. The UV spectrum showed absorption bands at λ_{max} 202, 256 and 333 nm. The IR spectrum exhibited absorption bands at 3218 and 1684 cm^{-1} for a hydroxyl group and a carbonyl group of a carboxylic acid, respectively. The ^{1}H NMR spectrum (**Table 7**) showed the resonances of doublet aromatic protons H-2/H-6 at δ 7.91 (J = 9.0 Hz) and doublet aromatic protons H-3/H-5 at δ 6.92 (J = 9.0 Hz) indicating 1,4-disubstituted benzene. These data were corresponded with those of 4-hydroxybenzoic acid (Choi *et al*., 2002). Therefore **AS2** was 4-hydroxybenzoic acid.

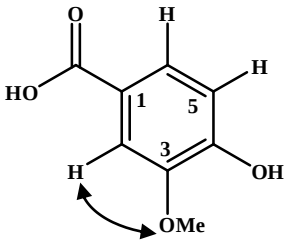
Table 7 ^{1}H NMR spectral data of **AS2** and **4-hydroxybenzoic acid**

Position	**AS2; δ_H (mult., J_{Hz})**	**4-hydroxybenzoic acid; δ_H (mult., J_{Hz})**
1	-	-
2,6	7.91 (*d*, 9.0)	7.93 (*d*, 8.7)
3,5	6.92 (*d*, 9.0)	6.84 (*d*, 8.7)
4	-	-
7	-	-

AS3: 4-hydroxy-3-methoxybenzoic acid



AS3 was obtained as a colorless gum. The UV spectrum showed absorption bands at λ_{max} 203, 256, 289, 326 and 337 nm. The IR spectrum exhibited absorption bands at 3235 and 1690 cm^{-1} for a hydroxyl group and a carbonyl group of carboxylic acid, respectively. The ^{1}H NMR spectrum (**Table 8**) showed the signals of doublet of doublet aromatic proton H-6 at δ 7.55 (J = 9.0, 1.8 Hz) and two signals of doublet aromatic protons H-2 and H-5 at δ 7.53 (J = 1.8 Hz) and δ 6.87 (*d*, J = 9.0 Hz) suggesting a 1,3,4-trisubstituted benzene ring and showed the resonance of a methoxyl group at δ 3.87. The assignment of the substituent was deduced from the NOE spectra. The enhancement of H-2 which was caused by irradiation 3-OMe at δ 3.87, in the NOE experiment supported that 3-OMe was adjacent to H-2. The spectral data of **AS3** corresponded to those of 4-hydroxy-3-methoxybenzoic acid (Chen *et al*., 2010).

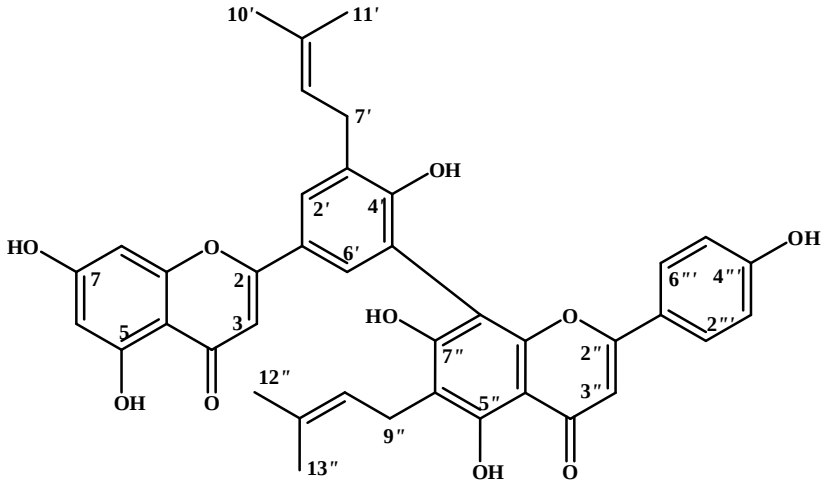


NOE of AS3

Table 8 ^{1}H NMR spectrum data of **AS3** and **4-hydroxy-3-methoxybenzoic acid**

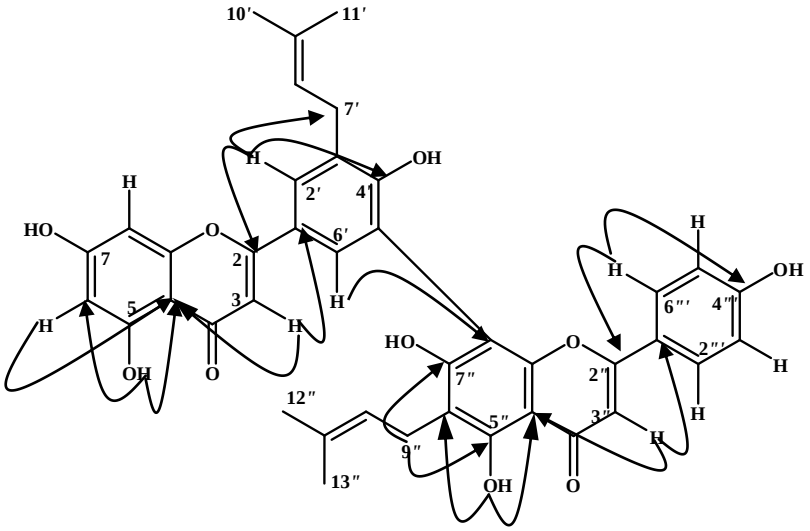
Position	**AS3; δ_H (mult., J_{Hz})**	**4-hydroxy-3-methoxybenzoic acid; δ_H (mult., J_{Hz})**
2	7.53 (*d*, 1.8)	7.54 (*d*, 2.2)
5	6.87 (*d*, 9.0)	6.90 (*d*, 8.3)
6	7.55 (*dd*, 9.0, 1.8)	7.58 (*dd*, 8.3, 2.2)
3-OMe	3.87 (*s*)	3.89 (*s*)

AS4: 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxy-3-(3-methylbut-2-enyl)phenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-6-(3-methylbut-2-enyl)-4*H*-chromen-4-one



AS4 was a pale yellow powder, m.p. 233-234 ^{o}C, EIMS at $[M]^{+}$ *m/z* 674.5 for $C_{40}H_{34}O_{10}$ (calcd 674.2). The UV spectrum showed absorption bands at λ_{max} 203, 269 and 339 nm. The IR spectrum showed the absorption bands of O-H stretching at 3421 and C=O stretching at 1653 cm^{-1}. The ^{1}H NMR spectrum (**Table 9**) suggested that it was a flavonylflavone which the methine olefinic protons H-3 and H-3″ resonated at δ 6.82 (*s*) and δ 6.77 (*s*). The resonances of a chelated hydroxyl protons 5-OH at δ 12.96, an olefenic methine proton H-3 at δ 6.82 (*s*), *meta* aromatic protons H-6 and H-8 at δ 6.16 and δ 6.43 (*d*, *J* = 1.8 Hz, each), *meta* aromatic protons H-2′ and H-6′ at δ 7.87 and δ 7.76 (*d*, *J* = 2.1 Hz, each) were assigned for the first unit. The HMBC correlation of 5-OH to C-4a (δ 103.5), C-6 (δ 99.3) and H-6 to C-4a confirmed the location of H-6. The HMBC correlation of H-2′/H-6′ to C-2 (δ 164.4) and H-3 to C-1′(δ 121.6) suggested the tetrasubstituted aromatic ring was at C-2. Protons H-6, H-8, 5-OH and H-3 all correlated to C-4a. The resonances of a chelated hydroxyl protons 5″-OH at δ 13.38 (*s*), olefinic proton H-3″ at 6.77 (*s*) and aromatic protons H-2‴/H-6‴ and H-3‴/ H-5‴ at δ 7.52 and 6.70 (AA′BB′ pattern, *J* = 8.7 Hz) were assigned for the second unit. The HMBC correlation of H-2‴/H-6‴ to C-2″ (δ 163.8) and H-3″ to C-1‴ (δ 121.9) suggested the disubstituted aromatic ring was at C-2″. In HMBC experiment, the correlations of 5″-OH and H-3″ to C-4a″ (δ 104.4)

and H-3″ to C-2″ confirmed the location of H-3″. Two sets of characteristic signals of prenyl group were displayed. According to COSY and HMBC correlations, the resonances at δ 3.30 (*m*, H-7′), δ 5.23 (*t*, *J* = 6.6 Hz, H-8′) and δ 1.74 (H-10′, H-11′) were assigned for 3′-prenyl group, whereas those the resonances at δ 3.30 (*m*, H-9″), at δ 5.42 (*t*, *J* = 7.2 Hz, H-10″) and at δ 1.63, 1.74 (*s*, H-12″ and H-13″) were assigned for 6″-prenyl group. According to HMBC correlations of H-7′ to C-2′ (δ 128.0) and H-9″ to C-5″ (δ 158.4) indicated that the 3′-prenyl group was at C-3′ and the 6″-prenyl group was at C-6″. The HMBC correlation of H-6′ to C-8″ allowed the two units of flavonoids connected via C-6 and C-8″. To fulfill the structure, the hydroxyl groups were placed at C-7, C-4′, C-7″ and C-4‴. The chemical shift of δ 164.5, δ 157.8, δ 160.0 and δ 161.4 were assigned at C-7, C-4′, C-7″ and C-4‴. The flavonoid units were corresponded to yinyanghuo D (Chen, *et al*., 1996) and 6-prenylapigenin (Lee, *et al*., 1998). Thus **AS4** was assigned to be 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxy-3-(3-methylbut-2-enyl)phenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-6-(3-methylbut-2-enyl)-4*H*-chromen-4-one.



Major HMBC of AS4

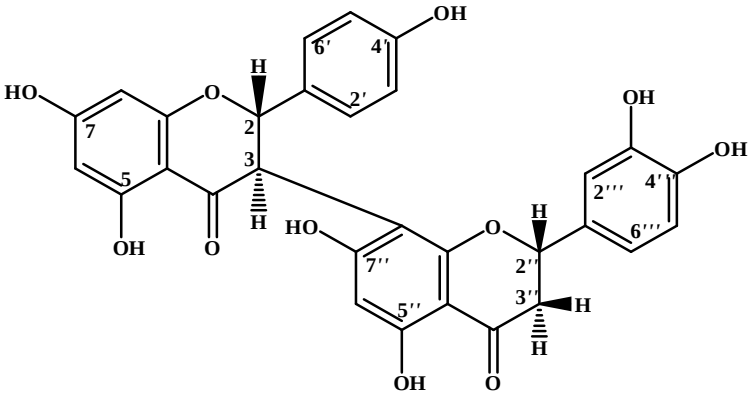
Table 9 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS4**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2	164.4 (C)	-	-
3	103.5 (CH)	6.82 (*s*)	C-4a, C-1′
4	182.1 (C=0)	-	-
4a	103.5 (C)	-	-
5	161.9 (C)	-	-
6	99.3 (CH)	6.16 (*d*, 1.8)	C-4a, C-5, C-7, C-8
7	164.5 (C)	-	-
8	94.5 (CH)	6.43 (*d*, 1.8)	C-4a, C-6, C-7, C-8a
8a	157.8 (C)	-	-
1′	121.6 (C)	-	-
2′	128.0 (CH)	7.87 (*d*, 2.1)	C-2, C-4′, C-6′, C-7′
3′	119.0 (C)	-	-
4′	157.8 (C)	-	-
5′	112.0 (C)	-	-
6′	129.8 (CH)	7.76 (*d*, 2.1)	C-2, C-2′, C-4′ , C-8″
7′	21.9 (CH_2)	3.30 (*m*)	C-5′, C-8′, C-9′
8′	122.4 (CH)	5.23 (*t*, 6.6)	C-10′, C-11′
9′	132.5 (C)	-	-
10′	18.2 (CH_3)	1.74 (*s*)	C-8′, C-9′, C-11′
11′	26.0 (CH_3)	1.74 (*s*)	C-8′, C-9′, C-10′
2″	163.8 (C)	-	-
3″	102.9 (CH)	6.77 (*s*)	C-4a″, C-1‴
4″	182.7 (C=O)	-	-
4a″	104.4 (C)	-	-
5″	158.4 (C)	-	-
6″	112.0 (C)	-	-
7″	160.0 (C)	-	-
8″	104.2 (C)	-	-
8a″	153.3 (C)	-	-

Table 9 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS4** (continued)

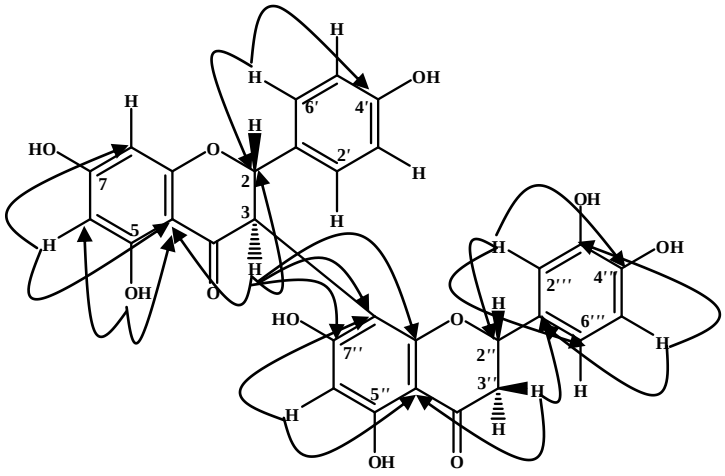
Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
9″	22.6 (CH_2)	3.30 (*m*)	C-5″, C-7″, C-10″, C-11″
10″	122.8 (CH)	5.42 (*t*, 7.2)	C-12″, C-13"
11″	131.1 (C)	-	-
12″	26.0 (CH_3)	1.63 (*s*)	C-9″, C-10″, C-13″
13″	18.3 (CH_3)	1.74 (*s*)	C-9″, C-10″, C-12″
1‴	121.9 (C)	-	-
2‴	128.6 (CH)	7.52 (*d*, 8.7)	C-2″, C-4‴, C-6‴
3‴	116.18 (CH)	6.70 (*d*, 8.7)	C-1‴, C-4‴, C-5‴
4‴	161.4 (C)	-	-
5‴	116.2 (CH)	6.70 (*d*, 8.7)	C-1‴, C-4‴, C-5‴
6‴	128.5 (CH)	7.52 (*d*, 8.7)	C-2″, C-4‴, C-6‴
5-OH	-	12.96 (*s*)	C-4a, C-5, C-6
5″-OH	-	13.38 (*s*)	C-4a″, C-5″, C-6″

AS5: (2*S*,2″*S*,3*R*)-2″-(3,4-dihydroxyphenyl)-2,3,2″,3″-tetrahydro-5,7,5″,7″-tetra hydroxy-2-(4-hydroxyphenyl)-[3,8″-Bi-4*H*-1-benzopyran]-4,4″-dione (GB-2a)



AS5 is a pale yellow solid, m.p. 215-216 ^{o}C. The ^{1}H and ^{13}C NMR spectrum in DMSO-d_6 displayed duplicated signals (in a ratio of 1:0.4), suggested the existence of two conformers at room temperature. The major reasons leading to the existence of such conformer being rotational restrictions about the interflavanone C-3, C-8″ bond. The major conformer (**Table 10**) showed the resonances of a chelated hydroxyl protons 5-OH at δ 12.19 (*s*), *meta* aromatic protons H-6 and H-8 at δ 5.90 and 5.79 (1H each, *br s*), *trans* methine protons H-2 and H-3 at δ 5.73 and 4.56 (1H each, *d*, *J* = 12.3 Hz) and aromatic protons H-2′/H-6′ and H-3′/H-5′ at δ 7.13 and 6.79 (2H each, *d*, *J* = 8.5 Hz). The HMBC correlation of H-6 to C-8 (δ 95.9), C-4a (δ 101.8) and 5-OH to C-6 (δ 96.5), C-4a suggested the aromatic proton H-6 was *ortho* to 5-OH. The HMBC correlation of H-2′/H-6′ to C-2 (δ 82.2) and H-2 to C-2′/C-6′ (δ 129.4) suggested the 1,4-disubstituted aromatic ring was connected to C-2. The ^{1}H NMR spectrum further showed a singlet of an aromatic proton H-6″ at δ 5.86 (*s*), an oxy-methine proton H-2″ at δ 5.43 (*br t*), non equivalent methylene protons H-3″ at δ 2.90, δ 2.60 (*m*) and ABX pattern aromatic protons H-2‴, H-5‴ and H-6‴ at δ 7.10 (*d*, *J* = 2.0 Hz), δ 6.64 (*d*, *J* = 8.5 Hz) and δ 6.73 (*dd*, *J* = 8.5, 2.0 Hz). Protons H-3″ and H-6″ correlated to C-4a″ (δ 102.1). The HMBC showed the correlations of H-2‴ to C-2″ (δ 79.0) and H-3″ to C-1‴ (δ 128.4) suggested the disubstituted benzene ring was connected to C-2″. This assigned structure was corresponded to a flavanone named eriodictyol (Schroder, G. *et al*., 2004) The HMBC correlation of H-3 to C-8a″ allowed the two units of flavonoids connected via C-3 and C-8″. To fulfill the structure, the hydroxyl groups were placed

at C-7, C-4′, C-7″, C-3‴ and C-4‴. The HMBC correlation of H-6, H-8 to carbon resonance at δ 166.9, H-2'/H-6′ to carbon resonance at δ 158.1, H-6″ to carbon resonance at δ 161.2, H-5‴ to carbon resonance at δ 145.7 and the correlation of H-2‴ to carbon resonance at δ 146.2 allowed C-7, C-4′, C-7″, C-3‴ and C-4‴ having chemical shift of δ 166.9, δ 158.1, δ 161.2, δ 145.7 and δ 146.2, respectively. The complete HMBC confirmed the structure of **AS5** as (2*S*,2″*S*,3*R*)-2″-(3,4-dihydroxyphenyl)-2,3,2″,3″-tetrahydro-5,7,5″,7″-tetrahydroxy-2-(4-hydroxyphenyl)-[3,8″-Bi-4*H*-1-benzopyran]-4,4″-dione or known as GB-2a (Ansari, *et al*., 1976).



Major HMBC of AS5

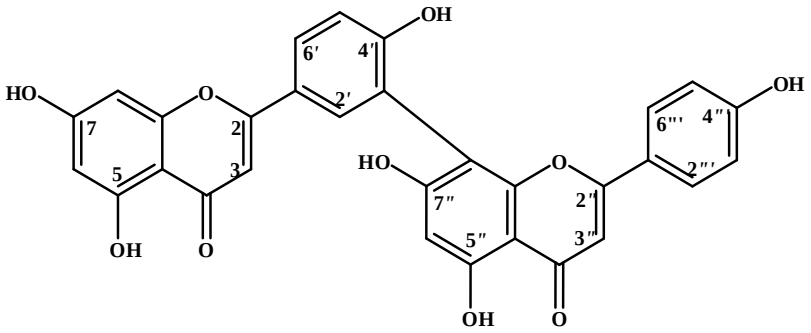
Table 10 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS5**

Position	δ_C (C-Type)	δ_H (multiplicity, J_{Hz})	HMBC
2	82.2 (CH)	5.73 (*d*, 2.3)	C-4, C-1′, C-2′, C-6′
3	47.8 (CH)	4.56 (*d*, 12.3)	C-2, C-4, C-7″, C-8″, C-8a″
4	197.1 (C=O)	-	-
4a	101.8 (C)	-	-
5	165.3 (C)	-	-
6	96.5 (CH)	5.90 (*br s*)	C-4a, C-5, C-7, C-8
7	166.9 (C)	-	-
8	95.9 (CH)	5.79 (*br s*)	C-6, C-4a, C-7, C-8a

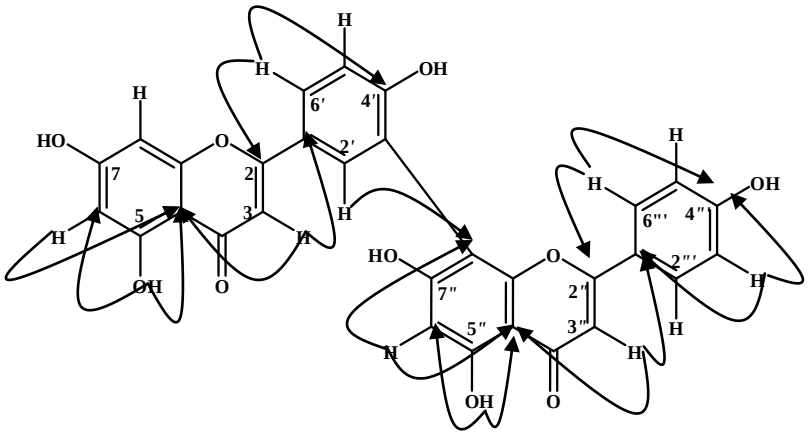
Table 10 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS5** (continued)

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
8a	163.3 (C)	-	-
1′	130.2 (C)	-	-
2′	129.4 (CH)	7.13 (*d*, 8.5)	C-2, C-6′, C-4′
3′	114.4 (CH)	6.79 (*d*, 8.5)	C-1′, C-2′, C-5′, C-4′
4′	158.1 (C)	-	-
5′	114.4 (CH)	6.79 (*d*, 8.5)	C-1′,C-3′, C-4′, C-6′
6′	129.4 (CH)	7.13 (*d*, 8.5)	C-2, C-2′, C-4′
2″	79.0 (CH)	5.43 (*br t*)	C-4″, C-1″, C-2‴’
3″	43.1 (CH_2)	2.90 (*m*)	C-2″, C-4″, C-1‴
		2.60 (*m*)	C-2″, C-4″, C-1‴
4″	196.6 (C=O)	-	-
4a″	102.1 (C)	-	-
5″	164.1 (C)	-	-
6″	95.5 (CH)	5.86 (*s*)	C-4a″, C-5″, C-7″, C-8″
7″	161.2 (C)	-	-
8″	101.8 (C)	-	-
8a″	162.5 (C)	-	-
1‴	128.4 (C)	-	-
2‴	129.0 (CH)	7.10 (*d*, 2.0)	C-2″, C-3‴, C-4‴, C-6‴
3‴	145.7 (C)	-	-
4‴	146.2 (C)	-	-
5‴	115.3 (CH)	6.64 (*d*, 8.5)	C-1‴, C-3‴, C-4‴
6‴	118.2 (CH)	6.73 (*dd*, 8.5, 2.0)	C-2″, C-1‴, C-2‴, C-4‴
5-OH	-	12.19 (*s*)	C-4a, C-5, C-6
4′-OH	-	9.61 (*s*)	C-4′, C-3′, C-5′
5″-OH	-	12.15 (*s*)	C-4a″, C-5″, C-6″
3‴-OH	-	9.20 (*s*)	C-3″, C-4″
4‴-OH	-	9.08 (*s*)	C-3″, C-4″, C-5″

AS6:8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxyphenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H*-chromen-4-one (amentoflavone)



AS6 is a yellow powder, m.p. 236-238 ^{o}C. The UV spectrum showed absorption bands at λ_{max} 333, 269 and 202 nm. The IR spectrum showed the absorption bands of O-H stretching at 3402 and C=O stretching at 1649 cm^{-1}. The ^{1}H NMR spectrum (**Table 11**) suggested that it was a flavonylflavone which the methine olefinic protons H-3 and H-3″ resonated at δ 6.39 (*s*). The resonances of chelated hydroxyl protons 5-OH at δ 12.67, meta aromatic protons H-6 and H-8 at δ 6.12 and 6.25 (*d*, *J* = 2.1 Hz), aromatic proton H-2′, H-5′ and H-6′ as an ABX pattern at δ 7.76 (*d*, *J* = 2.1 Hz), δ 7.05 (*d*, *J* = 8.7 Hz) and δ 7.67 (*dd*, *J* = 8.7, 2.1 Hz) were determined for the first unit. The HMBC correlation of 5-OH to C-4a (δ 109.2), C-6 (δ 104.2) and H-6 to C-4a confirmed the location of H-6. The HMBC correlation of H-3 to C-1′ (δ 126.9) and H-6′ to C-2 (δ 168.9) suggested the trisubstituted benzene ring was at C-2. The resonances of chelated hydroxyl proton 5″-OH at δ 12.86, aromatic proton H-6″ at δ 6.41 (*s*), aromatic proton H-2‴/H-6‴ and H-3‴/H-5‴ at δ 7.31 and δ 6.62 (*d*, *J* = 8.7 Hz each) were assigned for the second unit. The HMBC correlation of 5″-OH to C-6″ (δ 104.2), C-4a″ (δ 109.6), and H-6″ to C-4a″ confirmed the location of H-6″. The correlation of H-3″ to C-1‴ (δ 126.7) and H-2‴/H-6‴ to C-2″ (δ 168.9) suggested the *para*-disubstituted benzene ring was at C-2″. The HMBC correlation of H-2′ to C-8″ (δ 108.4) allowed the two units of flavonoids connected via C-6 and C-8″. Thus **AS6** was assigned to be 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxyphenyl)-5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H*-chromen-4-one or known as amentoflavone (Cao, *et al*., 1997).



Major HMBC of AS6

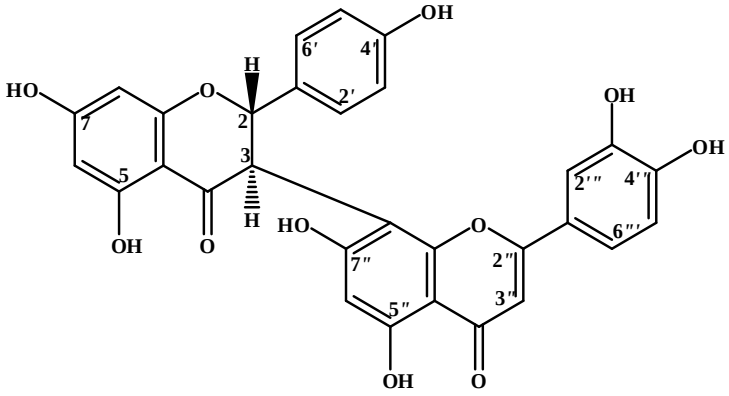
Table 11 ^{1}H, ^{13}C NMR and HMBC spectral data ($CDCl_3$+DMSO-d_6) of **AS6**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2	168.9 (C)	-	-
3	108.2 (CH)	6.39 (*s*)	C-4, C-4a, C-1′
4	188.9 (C=O)	-	-
4a	109.2 (C)	-	-
5	166.7 (C)	-	-
6	104.2 (CH)	6.12 (*d*, 2.1)	C-4a, C-5, C-7, C-8a
7	168.9 (C)	-	-
8	98.9 (CH)	6.25 (*d*, 2.1)	C-4a, C-6, C-7, C-8a
8a	162.6 (C)	-	-
1′	126.9 (C)	-	-
2′	136.1 (CH)	7.76 (*d*, 2.1)	C-2, C-4′, C-6′, C-8″
3′	124.8 (C)	-	-
4′	163.9 (C)	-	-
5′	120.9 (CH)	7.05 (*d*, 8.7)	C-1′ ,C-3′, C-4′
6′	132.3 (CH)	7.67 (*dd*, 8.7, 2.1)	C-2, C-2′, C-4′

Table 11 ^{1}H, ^{13}C NMR and HMBC spectral data ($CDCl_3$+DMSO-d_6) of **AS6** (continued)

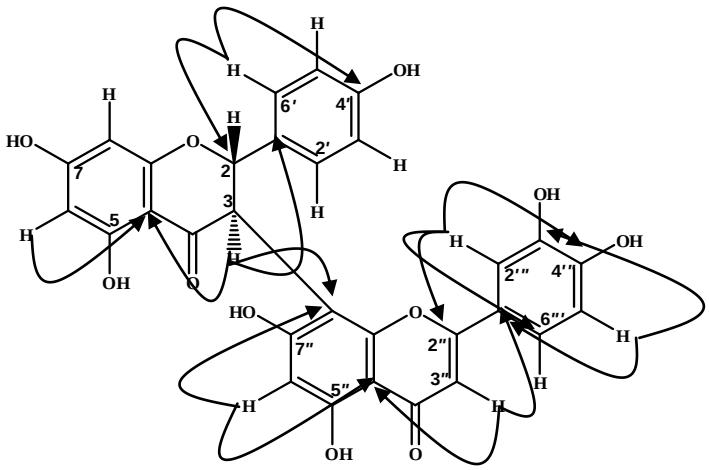
Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2″	168.9 (C)	-	-
3″	107.7 (CH)	6.39 (*s*)	C-2″, C-4″, C-4a″, C-1‴
4″	187.4 (C=O)	-	-
4a″	109.6 (C)	-	-
5″	166.3 (C)	-	-
6″	104.2 (CH)	6.41 (*s*)	C-4a″, C-5″, C-7″, C-8″
7″	166.2 (C)	-	-
8″	108.4 (C)	-	-
8a″	159.8 (C)	-	-
1‴	126.7 (C)	-	-
2‴	132.7 (CH)	7.31 (*d*, 8.7)	C-2″, C-4‴, C-6‴
3‴	121.6 (CH)	6.62 (*d*, 8.7)	C-1‴, C-4‴, C-5‴
4‴	165.8 (C)	-	-
5‴	121.6 (CH)	6.62 (*d*, 8.7)	C-1‴, C-3‴, C-4‴
6‴	132.7 (CH)	7.31 (*d*, 8.7)	C-2″, C-2‴, C-4‴
5-OH	-	12.67 (*s*)	C-4a, C-5, C-6
5″-OH	-	12.86 (*s*)	C-4a″, C-5″, C-6″

AS7: 5,7,4′,5″,7″,3″,4″-heptahydroxy-[3,8″]-flavonylflavanone (morelloflavone)



AS7 is a yellow solid, m.p. 305-307 °C. The ^{1}H and ^{13}C NMR spectrum in DMSO-d_6 displayed duplicated signals (in a ratio of 1:0.38), suggested the existence of two conformers at room temperature. The signals of major conformer (**Table 12**) were a singlet chelated hydroxyl protons 5-OH, 5″-OH at δ 12.30 and δ 13.10, two *meta* aromatic protons H-6, H-8 at δ 5.99 and δ 6.06, two doublets of *trans* methine protons H-2 and H-3 at (δ 5.73 and δ 4.92 J = 12.0 Hz) and AA′BB′ system of aromatic protons H-2′/H-6′ and H-3′/H-5′ at δ 7.17 and δ 6.41 (*d* each, J = 8.4 Hz). In HMBC experiment, protons H-6, H-8, 5-OH and H-3 all correlated to C-4a (δ 102.1). The chemical shift of δ 5.99 was assigned for H-6 due to HMBC correlation of 5-OH to C-6 (δ 95.8) and H-6 to C-5 (δ 164.3). The HMBC correlation of H-2′/H-6′ to C-2 (δ 81.4) and H-2 to C-2′/C-6′ (δ 128.7), suggested the 1,4-disubstituted aromatic ring was connected to C-2. This assigned structure was corresponded to a flavone named aromadendrine (Lee, I.-K. *et al*., 1995). The ^{1}H NMR spectrum further showed singlet of aromatic protons H-6″ at δ 6.24, singlet olefinic proton H-3″ at δ 6.60 and a 1,3,4-trisubstituted benzene (δ 7.45, *d*, J = 2.4 Hz, H-2‴; δ 6.92, *d*, J = 8.4 Hz, H-5‴; δ 7.27, *dd*, J = 8.4, 2.4 Hz, H-6‴). Protons H-3″ and H-6″ correlated to C-4a″ (δ 103.6). The HMBC showed the correlation of H-2‴, H-6‴ to C-2″ (δ 164.1) and H-3″ to C-1‴ (δ 121.5) suggested the 1,3,4-trisubstituted benzene was connected to C-2″. The HMBC correlation of H-3 to C-8a″ allowed the two units of flavonoids connected via C-3 and C-8″. To fulfill the structure, the hydroxyl groups were placed at C-7, C-4′, C-7″, C-3‴ and C-4‴. The HMBC correlation of H-6, H-8 to carbon resonance at δ 167.0, H-2′/H-6′ to carbon resonance at δ 157.8, H-6″ to carbon resonance at δ 162.1, H-2‴, H-5‴ to carbon resonance at

δ 161.0 and the correlation of H-2‴, H-6‴ to carbon resonance at δ 150.1 allowed C-7, C-4′, C-7″, C-4‴ and C-4‴ having chemical shift of δ 167.0, δ 157.8, δ 162.1, δ 161.0 and δ 150.1, respectively. The complete HMBC confirmed the structure of **AS7** as 5,7,4′,5″,7″,3″,4″-heptahydroxyl-[3,8″]-flavonylflavanone or known as morelloflavone (Li *et al*., 2002)



Major HMBC of AS7

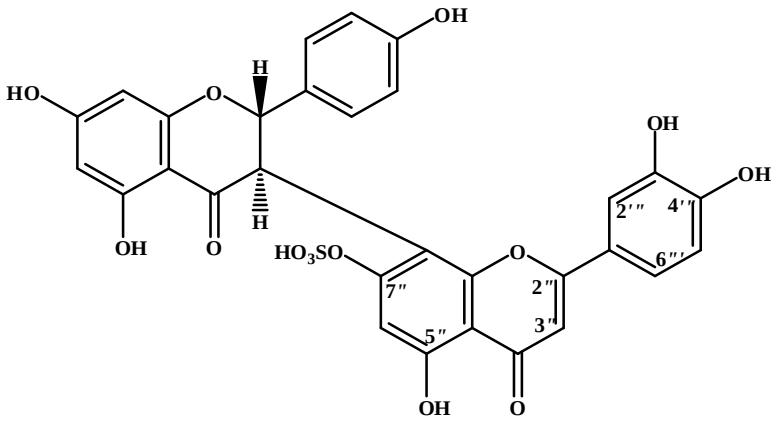
Table 12 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS7**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2	81.4 (CH)	5.73 (*d*, 12.0)	C-4, C-1′
3	49.1 (CH)	4.92 (*d*, 12.0)	C-2, C-4, C-4a, C-1′, C-8″
4	196.7 (C=O)	-	-
4a	102.1 (C)	-	-
5	164.3 (C)	-	-
6	95.8 (CH)	5.99 (*s*)	C-4a, C-5, C-7, C-8
7	167.0 (C)	-	-
8	96.7 (CH)	6.06 (*s*)	C-4a, C-7
8a	163.3 (C)	-	-
1′	128.6 (C)	-	-
2′	128.7 (CH)	7.17 (*d*, 8.4)	C-2, C-4′, C-5′, C-4′
3′	114.9 (CH)	6.41 (*d*, 8.4)	C-2′, C-4′, C-5′

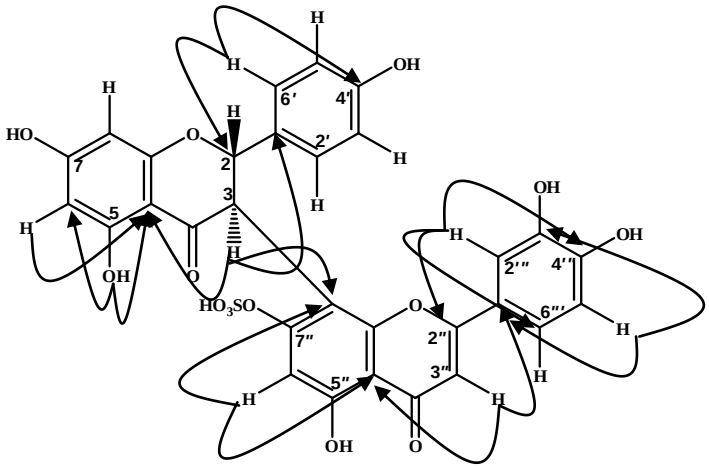
Table 12 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS7** (continued)

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
4′	157.8 (C)	-	-
5′	114.9 (CH)	6.41 (*d*, 8.4)	C-3′, C-4′, C-6′
6′	128.7 (CH)	7.17 (*d*, 8.4)	C-2, C-2′, C-4′, C-5′
2″	164.1 (C)	-	-
3″	102.7 (CH)	6.60 (*s*)	C-4″, C-4a″, C-1‴
4″	182.1 (C=O)	-	-
4a″	103.6 (C)	-	-
5″	163.9 (C)	-	-
6″	99.1 (CH)	6.24 (*s*)	C-5″, C-4a″, C-7″, C-8″
7″	162.1 (C)	-	-
8″	101.0 (C)	-	-
8a″	155.7 (C)	-	-
1‴	121.5 (C)	-	-
2‴	113.7 (CH)	7.45 (*d*, 2.4)	C-2″, C-4‴, C-6‴
3‴	161.0 (C)	-	-
4‴	150.1 (C)	-	-
5‴	116.6 (CH)	6.92 (*d*, 8.4)	C-1‴, C-4‴
6‴	119.8 (CH)	7.27 (*dd*, 8.4, 2.4)	C-2″, C-1‴, C-2‴, C-4‴
5-OH	-	12.30 (s)	C-4a, C-5, C-6
5″-OH	-	13.10 (s)	-

AS8: (2*S*,3*R*)-2'-(3,4-dihydroxyphenyl)-5,5',7-trihydroxy-2-(4-hydroxyphenyl)-4,4'-dioxo-3,8'-bichroman-7'-yl hydrogen sulfate (morelloflavone-7″-sulfate)



AS8 was a yellow solid, m.p. 290-293℃. The UV spectrum showed absorption bands at λ_{max} 201, 289 and 348 nm. The IR spectrum showed the absorption bands of O-H stretching at 3423, C=O stretching at 1643, S=O stretching at 1262 and C-O-S stretching at 1042 cm^{-1}.The ^{1}H, ^{13}C NMR, COSY and HMBC spectrum (**Table 13**) of **AS8** was much similar to **AS7**. The ^{1}H NMR spectrum showed the resonances of *trans* methine protons H-2 and, H-3 (δ 5.81 and 4.83, J = 12.0 Hz), methine olefinic protons H-3″ (δ 6.60, *s*), chelated hydroxyl protons 5-OH (δ 12.19) and 5″-OH (δ 12.95), *meta* aromatic protons H-6 (δ 5.92) and H-8 (δ 5.94), *para*-disubstituted benzene H-2′/H-6′ (δ 7.18) and H-3′/H-5′ (δ 6.31), aromatic proton H-6″ (δ 7.05) as for **AS7**. The protons resonances of **AS8** were almost identical to those of **AS7**, except for the H-6″ (δ 7.05) of **AS8** appearance at much lower field than that of **AS7** (δ 6.24). According to the IR spectrum that showed S=O stretching at 1262 and C-O-S stretching at 1042 cm^{-1} and the chemical shift of C-7″ (δ 158.1) allowed to assigned $-OSO_3H$ at C-7. The structure of **AS8** was supported by HMBC correlation. In HMBC spectrum, the flavonyl moiety displayed the correlations of 5-OH to C-6 (δ 96.6), C-4a (δ 101.9); H-6 to C-4a, C-7 (δ 166.9), C-8 (δ 95.6); H-8 to C-4a, C-7; H-2′/H-6′ to C-2 (δ 81.4) and H-3 to C-8″ (δ 104.6). Moreover, in HMBC spectrum, the flavanone moiety displayed the correlations of 5″-OH to C-6″ (δ 102.8), C-4a″ (δ 105.5); H-6″ to C-4a″ C-8″; H-2‴ /H-6‴ to C-2″. Thus **AS8** was assigned to be morelloflavone-7″-sulfate (Li, *et al*., 2002).



Major HMBC of AS8

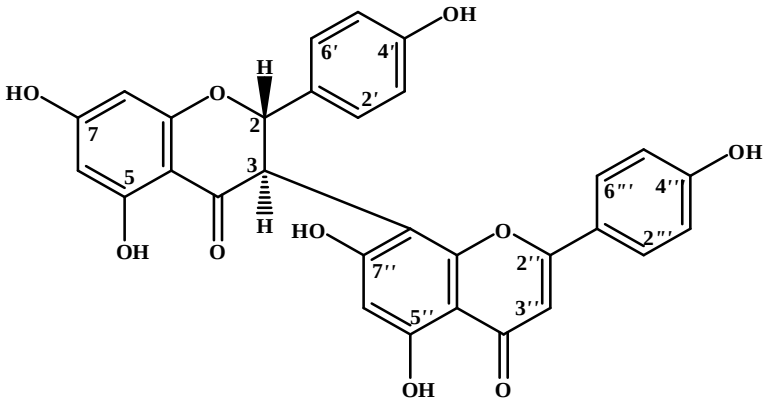
Table 13 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS8**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2	81.4 (CH)	5.81 (*d*, 12.0)	C-4, C-1′
3	49.0 (CH)	4.83 (*d*, 12.0)	C-4, C-2, C-1', C-7″, C-8″, C-8a″
4	195.8 (C=O)	-	-
4a	101.9 (C)	-	-
5	164.3 (C)	-	-
6	96.6 (CH)	5.92 (*d*, 2.1)	C-4a, C-5, C-7, C-8
7	166.9 (C)	-	-
8	95.6 (CH)	5.94 (*d*, 2.1)	C-4a, C-6, C-7, C-8a
8a	163.3 (C)	-	-
1′	128.9 (C)	-	-
2′	129.0 (CH)	7.18 (*d*, 8.4)	C-2, C-4′, C-6′
3′	114.6 (CH)	6.31 (*d*, 8.4)	C-1′, C-4′, C-5′
4′	157.5 (C)	-	-
5′	114.6 (CH)	6.31 (*d*, 8.4)	
6′	129.0 (CH)	7.18 (*d*, 8.4)	C-2, C-2′, C-4′
2″	164.4 (C)	-	-
3″	102.9 (CH)	6.60 (*s*)	C-2″, C-4″, C-4a″, C-1‴
4″	182.4 (C=O)	-	-
4a″	105.5 (C)	-	-

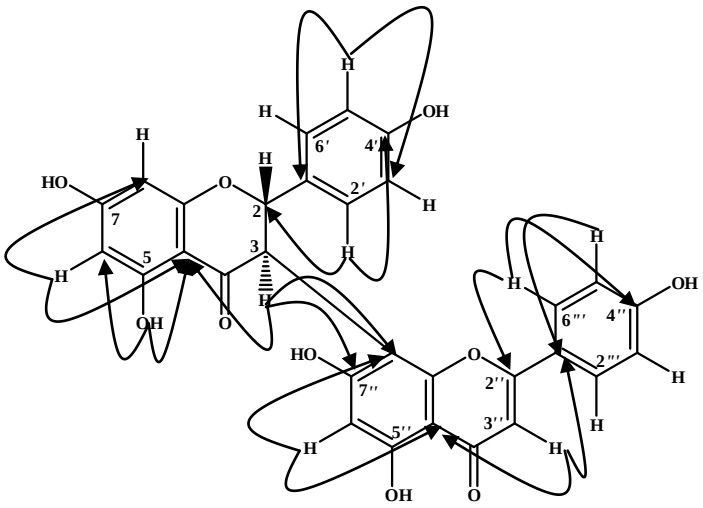
Table 13 ^{1}H, ^{13}C NMR and HMBC spectral data (DMSO-d_6) of **AS8** (continued)

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
5″	160.2 (C)	-	-
6″	102.8 (CH)	7.05 (*s*)	C-4a″, C-5″, C-7″, C-8″
7″	158.1 (C)	-	-
8″	104.6 (C)	-	-
8a″	154.8 (C)	-	-
1‴	121.4 (C)	-	-
2‴	113.8 (CH)	7.39 (*br s*)	C-2″, C-3‴, C-4‴, C-6‴
3‴	146.1 (C)	-	-
4‴	150.4 (C)	-	-
5‴	116.6 (CH)	6.88 (*d*, 8.1)	C-1‴, C-3‴, C-4‴
6‴	119.9 (CH)	7.40 (*d*, 8.1)	C-1‴, C-2‴, C-4‴
5-OH	-	12.19 (*s*)	C-4a, C-5, C-6
5″-OH	-	12.95 (*s*)	-

AS9: (2*S*,3*R*)-2,3-dihydro-5,5′,7,7'-tetrahydroxy-2,2'-bis(4-hydroxyphenyl)- [3,8″-Bi- 4*H*-1-benzopyran] -4,4″-dione (volkensiflavone)



AS9 is a yellow solid, m.p. 247-250 °C. The ^{1}H and ^{13}C NMR spectrum in $CDCl_3$+DMSO-d_6 displayed duplicated signals (in a ratio of 1:0.67), suggesting the existence of two conformers at room temperature. The ^{1}H and ^{13}C NMR was similar to those of **AS7**. The ^{1}H NMR spectrum (**Table 14**) suggested that it was a flavonylflavanone which the *trans* methine protons H-2, H-3 resonated at δ 5.75 and 4.65 (J = 12.0 Hz) and the methine olefinic protons H-3″ resonated at δ 6.23 (*s*). The ^{1}H NMR spectrum showed the resonances of chelated hydroxyl protons 5-OH (δ 12.20), *meta* aromatic protons H-6 (δ 5.95) and H-8 (δ 5.97), two *para*-disubstituted benzene H-2′/H-6′ (δ 6.99), H-3′/H-5′ (δ 6.41) and H-2‴/H-6‴ (δ 7.45), H-3‴/ H-5‴ (δ 6.86). The spectrum pattern of **AS9** was similar to that of **AS7**, except for the presence of 1,4-disubstituted benzene instead of 1,3,4-trisubstituted benzene. In HMBC spectrum, the flavonyl moiety displayed the correlations of 5-OH to C-6 (δ 95.8), C-4a (δ 102.3); H-6 to C-4a, C-7 (δ 167.2), C-8 (δ 96.8); H-8 to C-4a, C-7; H-2′/H-6′ to C-2 (δ 82.0) and H-3 to C-8″ (δ 101.2). In HMBC spectrum, the flavanone moiety displayed the correlations of H-3″ to C-4a″ (δ 104.2), C-1‴ (δ 122.5); H-6″ to C-4a″, C-8″; H-2‴ /H-6‴ to C-2″ (δ 164.3). The HMBC correlation of **AS9** showed the same pattern as that of **AS7**. **AS9** then was assigned as (2*S*,3*R*)-2,3-dihydro-5,5′,7,7'-tetrahydroxy-2,2'-bis(4-hydroxyphenyl)-[3,8″-Bi-4*H*-1-benzopyran]-4,4″-dione which was known as volkensiflavone (Ansari, *et al*., 1976).



Major HMBC of AS9

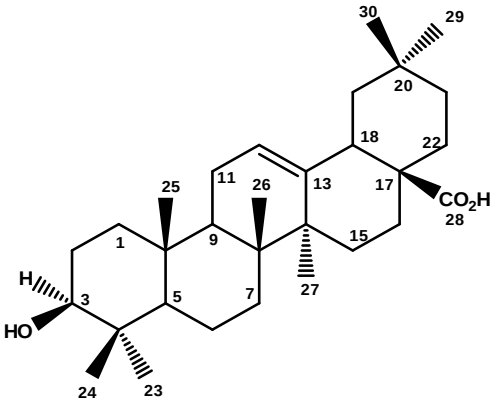
Table 14 ^{1}H, ^{13}C NMR and HMBC spectral data ($CDCl_3$+DMSO-d_6) of **AS9**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2	82.0 (CH)	5.75 (*d*, 12.0)	C-1′, C-2′, 6′
3	48.7(CH)	4.65 (*d*, 12.0)	C-4, C-7″, C-8″
4	196.5 (C=O)	-	-
4a	102.3 (C)	-	-
5	164.4 (C)	-	-
6	95.8 (CH)	5.95 (*s*)	C-4a, C-5, C-7, C-8
7	167.2 (C)	-	-
8	96.8 (CH)	5.97 (*s*)	C-6, C-7, C-4a
8a	163.5 (C)	-	-
1′	128.8 (C)	-	-
2′	128.7 (CH)	6.99 (*d*, 8.4)	C-2, C-1′, C-4′, C-6′
3′	115.3 (CH)	6.41 (*d*, 8.4)	C-1′, C-5′, C-4′
4′	157.0 (C)	-	-
5′	115.3 (CH)	6.41 (*d*, 8.4)	C-1′, C-3′, C-4′

Table 14 ^{1}H, ^{13}C NMR and HMBC spectral data ($CDCl_3$+DMSO-d_6) of **AS9** (continued)

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
6′	128.7 (CH)	6.99 (*d*, 8.4)	C-2, C-1′, C-2′, C-4′
2″	164.3 (C)	-	-
3″	103.4 (CH)	6.23 (*s*)	C-2″, C-4a″, C-5″, C-1‴
4″	182.2 (C=O)	-	-
4a″	104.2 (C)	-	-
5″	161.0 (C)	-	-
6″	99.0 (CH)	6.25 (*s*)	C-4a″, C-5″, C-7″, C-8″
7″	161.6 (C)	-	-
8″	101.2 (C)	-	-
8a″	156.0 (C)	-	-
1‴	122.5 (C)	-	-
2‴	128.8 (CH)	7.45 (*d*, 8.7)	C-2″, C-4‴, C-6‴
3‴	116.5 (CH)	6.86 (*d*, 8.7)	C-1‴, C-5‴, C-4‴
4‴	161.0 (C)	-	-
5‴	116.5 (CH)	6.86 (*d*, 8.7)	C-1‴, C-3‴, C-4‴
6‴	128.7 (CH)	7.45 (*d*, 8.7)	C-2″, C-2‴, C-4‴
5-OH	-	12.20 (*s*)	C-4a, C-5, C-6
5″-OH	-	12.20 (*s*)	-

AS10: oleanolic acid

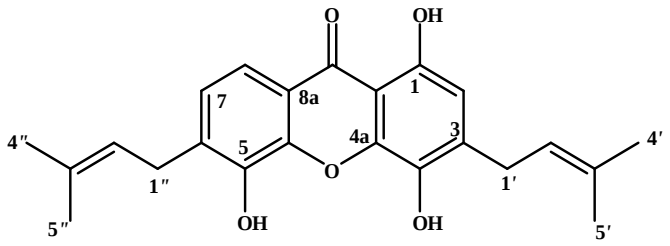


AS10 was a white solid, m.p. 280-282 ^{o}C. The UV spectrum showed absorption bands at λ_{max} 313, 269, 244 and 202 nm. The IR spectrum showed the absorption bands of O-H stretching at 3420, C=O stretching at 1689 and C-H stretching at 2939 cm^{-1}. The ^{1}H NMR spectrum (**Table 15**) showed the resonances of seven methyl singlet signals at δ 0.75, δ 0.77, δ 0.90, δ 0.91, δ 0.93, δ 0.99, δ 1.13, an olefinic proton at δ 5.28 (*t*, 3.0, H-12), a methine proton at δ 2.83 (*dd*, 13.8, 4.2, H-18) and an oxy-methine proton at δ 3.23 (*dd*, 12.0, 6.0, H-3). These data were identical to those of oleanolic acid. Thus **AS10** was assigned to be oleanolic acid (Pakakrong, 2005)

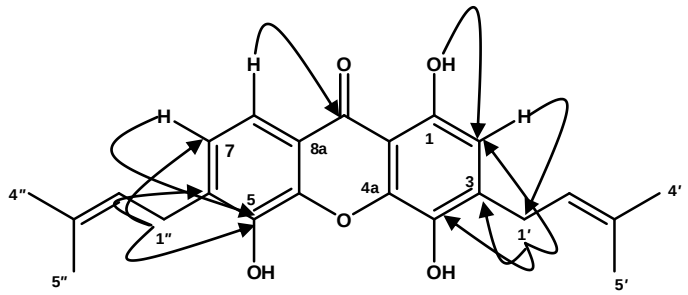
Table 15 ^{1}H NMR spectral data ($CDCl_3$) of **AS10** and **oleanolic acid**

Position	**AS10; δ_H (mult., J_{Hz})**	**oleanolic acid; δ_H (mult., J_{Hz})**
3	3.23 (*dd*, 12.0, 6.0)	3.22 (*dd*, 10.8, 4.5)
12	5.28 (*t*, 3.0)	5.28 (*t*, 3.3)
18	2.83 (*dd*, 13.8, 4.2)	2.82 (*dd*, 14.4, 3.9)
23	0.99 (*s*)	0.99 (*s*)
24	0.75 (*s*)	0.76 (*s*)
25	0.93 (*s*)	0.93 (*s*)
26	0.77 (*s*)	0.78 (*s*)
27	1.13 (*s*)	1.13 (*s*)
29	0.90 (*s*)	0.90 (*s*)
30	0.91 (*s*)	0.91 (*s*)

AS11: 1,4,5-trihydroxy-3,6-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one (garciniaxanthone C)



AS11 was a yellow solid, m.p. 203-205 ^{o}C. The UV spectrum showed absorption bands at λ_{max} 253, 267, 322 and 382 nm. The IR spectrum showed the absorption bands of O-H stretching at 3375 and C=O stretching at 1645 cm^{-1}. The ^{1}H NMR spectrum (**Table 16**) showed a singlet of a chelated hydroxyl proton 1-OH at δ 11.94 and a singlet of aromatic proton H-2 at δ 6.54. The location of H-2 was supported by the HMBC correlation of 1-OH to C-2 (δ 109.8). A prenyl group was indicated from the resonances of methylene protons H-1′ at δ 3.42 (*d*, *J* = 7.2 Hz), methine olefinic proton H-2′ at δ 5.34 (*br t*, *J* = 7.2 Hz) and two allylic methyl groups H-4′ at δ 1.75 and H-5′ at δ 1.73. The HMBC correlation of H-1′ to C-2, C-3 (δ 135.0), C-4 (δ 138.0) and H-2 to C-1′ (δ 29.0) suggested that the prenyl group was *ortho* to H-2. The doublet resonance, with *J* = 8.1 Hz, of *ortho* aromatic protons H-7 and H-8 were shown at δ 7.17 and δ 7.60. The low field chemical shift of δ 7.60 was assigned for H-8 due to the resonance effect of the carbonyl group and was also comfirmed by HMBC correlations of H-8 to C-9 (δ 182.9). The presence of the second prenyl group was indicated from resonances of H-1″ at δ 3.47 (*d*, *J* = 7.2 Hz), H-2″ at δ 5.34 (*br t*, *J* = 7.2 Hz), H-4″ at δ 1.75 and H-5″ at δ 1.73. The HMBC correlation of H-1″ to C-5 (δ 143.0), C-6 (δ 135.7), C-7 (δ 125.0) suggested that the prenyl group was at C-6. Finally the hydoxy groups 4-OH and 5-OH were placed at C-4 and C-5 to fulfill the structure. Since H-2 and H-1′ showed correlation to the oxy carbon that resonated at δ 138.0, H-7 and H-1″ showed correlation to the oxy carbon that resonated at δ 143.0, the carbon resonances at δ 138.0 and δ 143.0 then were assigned for C-4 and C-5, respectively. The ^{13}C NMR data and HMBC correlation corresponded to the assigned structure. Thus **AS11** was assigned to be 1,4,5-trihydroxy-3,6-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one. It was known as garciniaxanthone C (Minami, *et al*., 1994).

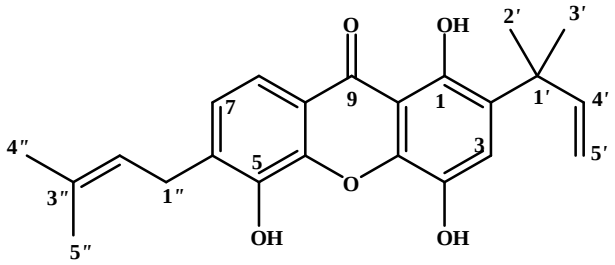


Major HMBC of AS11

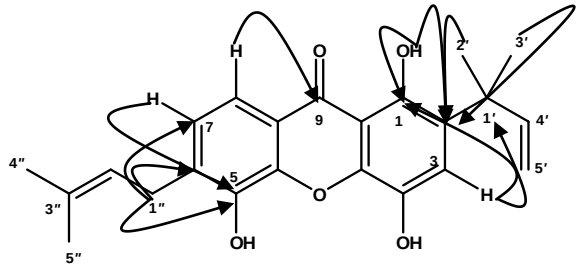
Table 16 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS11**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	153.0 (C)	-	-
2	109.8 (CH)	6.54 (*s*)	C-1, C-3, C-4, C-9a, C-1′
3	135.0 (C)	-	-
4	138.0 (C)	-	-
4a	141.2 (C)	-	-
4b	144.1 (C)	-	-
5	143.0 (C)	-	-
6	135.7 (C)	-	-
7	125.0 (CH)	7.17 (*d*, 8.1)	C-5, C-8a, C-1″
8	115.2 (CH)	7.60 (*d*, 8.1)	C-4b, C-6, C-9
8a	119.0 (C)	-	-
9	182.9 (C)	-	-
9a	106.0 (C)	-	-
1′	29.0 (CH_2)	3.42 (*d*, 7.2)	C-2, C-3, C-4, C-2′, C-3′
2′	122.0 (CH)	5.34 (*br t*, 7.2)	-
3′	132.2 (C)	-	-
4′	17.0 (CH_3)	1.75 (*s*)	C-2′, C-3′, C-5′
5′	25.0 (CH_3)	1.73 (*s*)	C-2′, C-3′, C-4′
1″	28.2 (CH_2)	3.47 (*d*, 7.2)	C-5, C-6, C-7, C-2″, C-3″
2"	121.3 (CH)	5.34 (*br t*, 7.2)	-
3"	132.9 (C)	-	-
4″	17.0 (CH_3)	1.75 (*s*)	C-2″, C-3″, C-5″
5″	25.0 (CH_3)	1.73 (*s*)	C-2″, C-3″, C-4″
1-OH	-	11.94 (*s*)	C-1, C-2, C-9a

AS12: 1,4,5-trihydroxy-6-(3-methylbut-2-enyl)-2-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one (garciniaxanthone A)



AS12 was a yellow solid, m.p. 99-100 ^{o}C. The UV spectrum showed absorption bands at λ_{max} 205, 255 and 326 nm. The IR spectrum showed the absorption bands of O-H stretching at 3361 and C=O stretching at 1615 cm^{-1}. The ^{1}H NMR spectrum (**Table 17**) showed signals of a hydrogen-bonded hydroxyl proton 1-OH (δ 12.96), *ortho* aromatic protons H-7 and H-8 (δ 7.24 and δ 7.66, J = 8.1 Hz) and C-6 prenyl group (δ 5.34, *t*, J = 7.2 Hz, H-2″; δ 3.51, *d*, J = 7.2 Hz, H-1″; δ 1.76, *s*, H-4″; δ 1.73, *s*, H-5″) as for **AS11**. The location of a prenyl group at C-6 was supported by HMBC correlation of H-1″ to C-5 (δ 143.0), C-6 (δ 135.2), C-7 (δ 125.0). Proton H-8 was supported by HMBC correlation of H-8 to C-9 (δ 182.9). Proton H-3 which was shown at δ 7.32 was placed *meta* to 1-OH due to HMBC correlations of H-3 and 1-OH to C-1 (δ 152.5). The presence of 1,1-dimethylallyl group was assigned from two singlets of *gem*-dimethyl protons (H-2′, H-3′) at δ 1.53 (3H each, *s*), two doublet of doublet of terminal olefinic protons (H-5′*E*, H-5′*Z*) at δ 5.03 (J = 17.7, 1.2 Hz), δ 5.00 (J = 10.8,1.2 Hz) and a doublet of doublet of a methine proton (H-4′) at δ 6.32 (J = 17.7, 10.8 Hz). This side chain was placed at C-2 according to HMBC correlation of H-2′/H-3′, 1-OH to C-2 (δ 128.6) and H-3 to C-1′ (δ 40.1). Finally the hydoxy groups 4-OH and 5-OH were placed at C-4 and C-5 to fulfill the structure. Since H-7 and H-1″ showed correlation to the oxy carbon that resonated at δ 143.0, this chemical shift then was assigned for C-5. Consequently the chemical shift at δ 136.0 was assigned for C-4. The ^{13}C NMR data and HMBC correlation corresponded to the assigned structure. Thus **AS12** was assigned as 1,4,5-trihydroxy-6-(3-methylbut-2-enyl)-2-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one or known as garciniaxanthone A (Minami, *et al*., 1994).

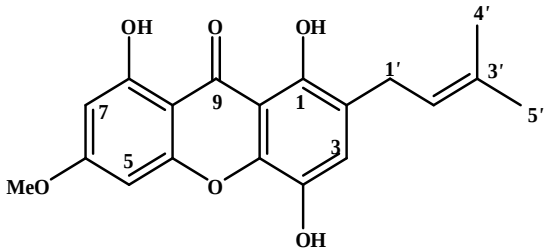


Major HMBC of AS12

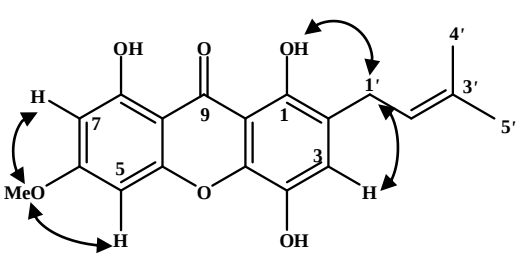
Table 17 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS12**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	152.5 (C)	-	-
2	128.6 (C)	-	-
3	122.2 (CH)	7.32 (*s*)	C-1, C-4a, C-1′
4	136.0 (C)	-	-
4a	141.2 (C)	-	-
4b	144.1 (C)	-	-
5	143.0 (C)	-	-
6	135.2 (C)	-	-
7	125.0 (CH)	7.24 (*d*, 8.1)	C-5, C-8a, C-1"
8	115.2 (CH)	7.66 (*d*, 8.1)	C-5a, C-6, C-9
8a	118.9 (C)	-	-
9	182.9 (C)	-	-
9a	108.2 (C)	-	-
1′	40.1 (C)	-	-
2′	26.0 (CH_3)	1.53 (s)	C-2, C-1′, C-3′, C-4′
3′	26.0 (CH_3)	1.53 (s)	C-2, C-1′, C-2′, C-4′
4′	145.0 (CH)	6.32 (*dd*, 17.7, 10.8)	C-1′, C-2′, C-3′
5'(E)	110.1 (CH_2)	5.03 (*dd*, 17.7, 1.2)	C-1′, C-4′
5'(Z)	110.1 (CH_2)	5.00 (*dd*, 10.8, 1.2)	C-1′, C-4′
1″	28.2 (CH_2)	3.51 (*d*, 7.2)	C-5, C-6, C-7, C-2″, C-3″
2″	121.3 (CH)	5.34 (*t*, 7.2)	-
3″	133.0 (C)	-	-
4″	17.0 (CH_3)	1.76 (*s*)	C-2″, C-3″, C-5″
5″	25.0 (CH_3)	1.73 (*s*)	C-2″, C-3″, C-4″
1-OH	-	12.96 (*s*)	C-1, C-2, C-9a

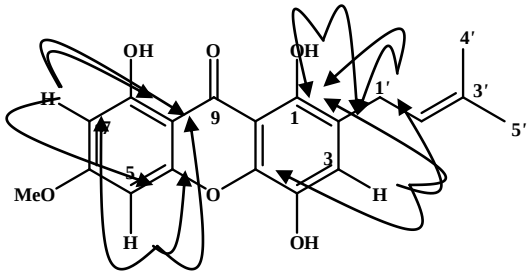
AS13:1,4,8-trihydroxy-6-methoxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one



AS13 was a yellow solid, m.p. 194-196 ^{o}C, with the molecular formula $C_{19}H_{18}O_6$. The UV spectrum showed absorption bands at λ_{max} 256, 280 and 332 nm. The IR spectrum showed the absorption bands of O-H stretching at 3420 and C=O stretching at 1657 cm^{-1}. The ^{1}H NMR spectrum (**Table 18**) showed signals of chelated hydroxyl protons 1-OH at δ 11.43 and 8-OH at δ 12.00, a methoxyl proton 6-OMe at δ 3.95, an isolated aromatic proton H-3 at δ 7.19 and *meta* aromatic protons H-5 and H-7 at δ 6.51 and δ 6.33 (*d, J* = 1.8 Hz). The presence of a prenyl group was indicated from the resonances of a methine olefinic proton H-2′ at δ 5.32 (*br t, J* = 7.2 Hz), a methylene proton H-1′ at δ 3.32 (*d, J* = 7.2 Hz) and two allylic methyl groups H-4′ and H-5′ at δ 1.74. The HMBC correlations of 1-OH and H-1′ to C-1 (δ 150.2), C-2 (δ 122.7) suggested that the prenyl group was *ortho* to the chelated hydroxyl group (1-OH). The aromatic proton H-3 was confirmed by HMBC correlation of H-3 to C-1 (δ 150.2), C-1′ (δ 26.5) and C-4a (δ 143.0). The HMBC correlations of H-5 to C-4b (δ 157.9), C-7 (δ 97.2), C-8a (δ 103.5) and H-7 to C-5 (δ 92.7), C-8 (δ 163.0), C-8a (δ 103.5) confirmed the location of aromatic proton H-5 and H-7. The methoxyl group 6-OMe was indicated *ortho* to aromatic protons H-5 and H-7 due to HMBC correlation of H-5, H-7 and 6-OMe to C-6 (δ 167.7). The assignments of 6-OMe and prenyl group were also confirmed by NOE experiment. Irradiation at the resonance of 6-OMe (δ 3.95) enhanced the resonances of H-5 (δ 6.51) and H-7 (δ 6.33). Irradiation at the resonance of H-1′ (δ 3.32) enhanced the resonances of 1-OH (δ 11.43) and H-3 (δ 7.19). To fulfill the structure, the hydroxyl group 4-OH was placed at C-4. Since H-3 showed correlation to the oxy carbon that resonated at δ 136.6, the chemical shift of δ 136.6 then was assigned for C-4. The ^{13}C NMR data and HMBC correlations corresponded to the assigned structure. Thus **AS13** was assigned to be 1,4,8-trihydroxy-6-methoxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one. It is a new xanthone derivative and is an isomer of afzeliixanthone A (Waffo, *et al*., 2006).



NOE of AS13

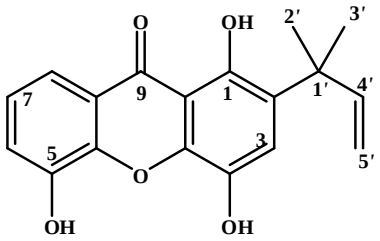


Major HMBC of AS13

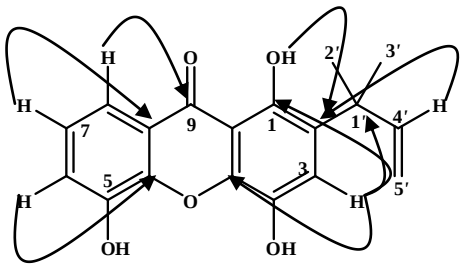
Table 18 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS13**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	150.2 (C)	-	-
2	122.7 (C)	-	-
3	124.3 (CH)	7.19 (*s*)	C-1, C-4, C-4a, C-1′
4	136.6 (C)	-	-
4a	143.0 (C)	-	-
4b	157.9 (C)	-	-
5	92.7 (CH)	6.51 (*d*, 1.8)	C-4b, C-6, C-7, C-8a
6	167.7 (C)	-	-
7	97.2 (CH)	6.33 (*d*, 1.8)	C-5, C-6, C-8, C-8a
8	163.0 (C)	-	-
8a	103.5 (C)	-	-
9	185.1 (C)	-	-
9a	107.4 (C)	-	-
1′	26.5 (CH_2)	3.32 (*d*, 7.2)	C-1, C-2, C-3, C-2″
2′	121.9 (CH)	5.32 (*br t*, 7.2)	-
3′	132.6 (C)	-	-
4′	16.9 (CH_3)	1.74 (*s*)	C-2′, C-3′
5'	24.9 (CH_3)	1.74 (*s*)	C-2′, C-3′
6-OMe	55.7 (OCH_3)	3.95 (*s*)	C-6
1-OH	-	11.43 (*s*)	C-1, C-2, C-9a
8-OH	-	12.00 (*br s*)	-

AS14: 1,4,5-trihydroxy-2-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one
(12b-hydroxy-des-*D*-garcigerrin A)



AS14 was a yellow solid, m.p. 188-189 ^{o}C. The UV spectrum showed absorption bands at λ_{max} 204, 239, 250, 265 and 318 nm. The IR spectrum showed the absorption bands of O-H stretching at 3244 and C=O stretching at 1640 cm^{-1}. The ^{1}H NMR spectrum (**Table 19**) showed signals of a chelated hydroxyl proton 1-OH (δ 12.68), an aromatic proton H-3 (δ 7.32) and a 1,1-dimethylallyl group [H-2′, H-3′ at δ 1.54 (*s*), H-5′*Z* at δ 5.00 (*dd*, *J* = 10.2,1.2 Hz), H-5′*E* at δ 5.05 (*br s*), H-4′ at δ 6.29 (*dd*, *J* = 18.0, 10.2 Hz)]. The location of 1,1-dimethylallyl group at C-2 and H-3 were supported by HMBC correlations of 1-OH and H-4′ to C-2 (δ 123.9) and H-3 to C-1 (δ 147.5), C-4a (δ 136.1) and C-1′ (δ 35.6). The resonances of H-6, H-7 and H-8 were shown as ABM system at δ 7.21 (*d*, *J* = 7.5 Hz), δ 7.24 (*t*, *J* = 7.5 Hz) and δ 7.71 (*dd*, *J* = 7.5, 2.1 Hz), respectively. The most deshielded resonance was assigned for H-8 according to an anisotropic effect of the carbonyl group. The assignments of H-6, H-7 and H-8 were supported by ^{3}J coupling of H-6 to C-4b (δ 139.3), H-7 to C-8a (δ 116.2) and H-8 to C-9 (δ 178.2) on the HMBC experiment. To fulfill the structure, 4-OH and 5-OH were assigned. Thus **AS14** was identified to be 1,4,5-trihydroxy-2-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one or known as 12b-hydroxy-des-*D*-garcigerrin A (Sordat-Diserens, *et al*., 1991).

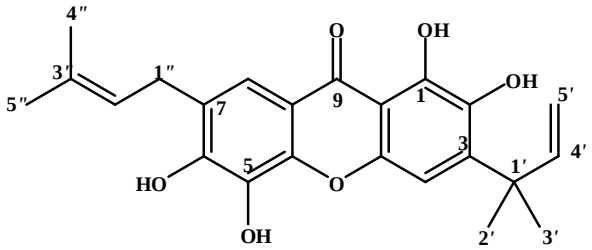


Major HMBC of AS14

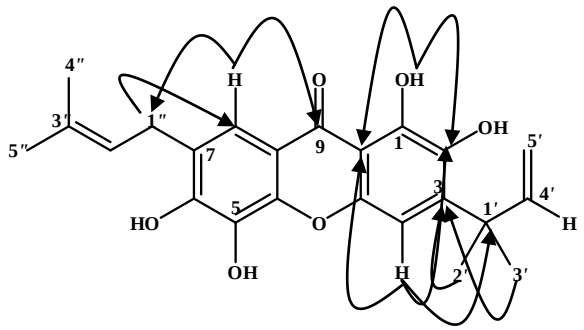
Table 19 ^{1}H, ^{13}C NMR and HMBC spectral data ($CDCl_3$+DMSO-d_6) of **AS14**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	147.5 (C)	-	-
2	123.9 (C)	-	-
3	117.3 (CH)	7.32 (*s*)	C-1, C-4, C-4a, C-1′
4	131.2 (C)	-	-
4a	136.1 (C)	-	-
4b	139.3 (C)	-	-
5	141.2 (C)	-	-
6	115.8 (CH)	7.21 (*d*, 7.5)	C-4b, C-5, C-8
7	119.2 (CH)	7.24 (*t*, 7.5)	C-5, C-8a
8	111.0 (CH)	7.71 (*dd*, 7.5,2.1)	C-4b, C-6, C-9
8a	116.2 (C)	-	-
9	178.2 (C)	-	-
9a	103.6 (C)	-	-
1′	35.6 (C)	-	-
2′, 3′	22.0 (CH_3)	1.54 (*s*)	C-2, C-4′
4′	142.5 (CH)	6.29 (*dd*, 18.0, 10.2)	C-2, C-1′, C-2′, C-3′
5′(E)	105.7 (CH_2)	5.05 (*s*)	C-1′, C-4′
5′(Z)	105.7 (CH_2)	5.00 (*dd*, 10.2, 1.2)	C-1′, C-4′
1-OH	-	12.68 (*s*)	C-1, C-2, C-9a

AS15: 1,2,5,6-tetrahydroxy-7-(3-methylbut-2-enyl)-3-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one



AS15 was a yellow solid, m.p. 223-225 ^{o}C, with the molecular formula $C_{23}H_{24}O_6$. The UV spectrum showed absorption bands at λ_{max} 247, 269 and 327 nm. The IR spectrum showed the absorption bands of O-H stretching at 3422 and C=O stretching at 1630 cm^{-1}. The ^{1}H NMR spectrum (**Table 20**) showed signals of a chelated hydroxyl proton (δ 13.06, 1-OH), a 1,1-dimethylallyl unit [H-2′/H-3′, δ 1.61; H-5′*Z*, δ 5.04 (*d*, *J* = 10.5 Hz); H-5′*E*, δ 5.16 (*d*, *J* = 17.7 Hz); H-4′, δ 6.42 (*dd*, *J* = 17.7, 10.5 Hz)] and a prenyl group [H-1″, δ 3.45 (*d*, *J* = 7.2 Hz); H-2″, 5.39 (*t*, *J* = 7.2 Hz); H-4″, 1.75 (*s*) and H-5″, 1.73 (*s*)]. The singlet aromatic proton H-4 which resonated at δ 7.32 was placed *para* to the chelated hydroxyl group (1-OH) since both H-4 and 1-OH showed ^{3}J HMBC correlation to C-2 (δ 139.1) and C-9a (δ 109.7). While the singlet aromatic proton H-8 which resonated at δ 7.57 was placed *peri* to carbonyl carbon due to H-8 correlated to carbonyl carbon (C-9, δ 182.2). The HMBC correlations of H-2′/H-3′ to C-3 (δ 126.4) and H-4 to C-1′ (δ 40.1) suggested the 1,1-dimethylallyl unit *ortho* to the aromatic H-4. The correlation of H-8 to C-1″ (δ 28.0) and H-1″ to C-8 (δ 116.2) indicated the prenyl group *ortho* to H-8. To fulfill the structure, three of hydroxyl group were assigned at C-2, C-5 and C-6. The HMBC correlations of 1-OH to the carbon resonance at δ 139.1 and H-8 to the carbon resonance at δ 151.0 allowed oxy carbons C-2 and C-6 having chemical shifts of δ 139.1 and δ 151.0, respectively. The remaining oxy carbon resonance at δ 131.5 then was assigned for C-5. Thus **AS15** was assigned to be 1,2,5,6-tetrahydroxy-7-(3-methylbut-2-enyl)-3-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one. It is a new xanthone derivative and is an isomer of subelliptenone B (Iinuma, M. *et al*. 1993).

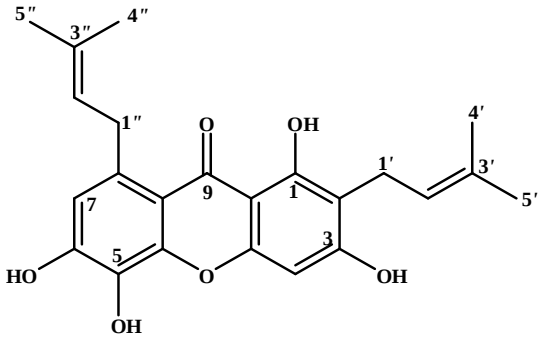


Major HMBC of AS15

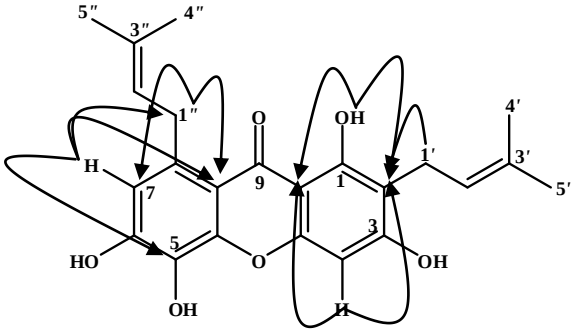
Table 20 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS15**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	146.3 (C)	-	-
2	139.1 (C)	-	-
3	126.4 (C)	-	-
4	121.6 (CH)	7.32 (*s*)	C-2, C-3, C-4a, C-9a, C-1′
4a	146.0 (C)	-	-
4b	146.3 (C)	-	-
5	131.5 (C)	-	-
6	151.0 (C)	-	-
7	127.0 (CH)	-	-
8	116.2 (CH)	7.57 (*s*)	C-4b, C-6, C-9, C-1″
8a	112.6 (C)	-	-
9	182.2 (C)	-	-
9a	109.7 (C)	-	-
1′	40.1 (C)	-	-
2′	26.9 (CH_3)	1.61 (s)	C-3, C-1′, C-3′, C-4′
3′	26.9 (CH_3)	1.61 (s)	C-3, C-1′, C-2′, C-4′
4′	148.5 (CH)	6.42 (*dd*, 17.7, 10.5)	C-3, C-1′, C-2′, C-3′
5′(*E*)	108.8 (CH_2)	5.16 (*d*, 17.7)	C-1′, C-4′
5′(*Z*)	108.8 (CH_2)	5.04 (*d*, 10.5)	C-1′, C-4′
1″	28.0 (CH_2)	3.45 (*d*, 7.2)	C-6, C-7, C-8, C-2″, C-3″
2″	121.5 (CH)	5.39 (*t*, 7.2)	C-4″, C-5″
3"	133.0 (C)	-	-
4″	25.0 (CH_3)	1.75 (*s*)	C-2″, C-3″, C-5″
5"	17.0 (CH_3)	1.73 (*s*)	C-2″, C-3″, C-4″
1-OH	-	13.06 (*s*)	C-1, C-2, C-9a

AS16: 1,3,5,6-tetrahydroxy-2,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one



AS16 was a yellow solid, m.p 240-243 ^{o}C, with the molecular formula $C_{23}H_{24}O_6$. The UV spectrum showed absorption bands at λ_{max} 255, 280 and 329 nm. The IR spectrum showed the absorption bands of O-H stretching at 3419 and C=O stretching at 1640 cm^{-1}. The ^{1}H NMR spectrum (**Table 21**) exhibited signals of a chelated hydroxyl proton 1-OH at δ 13.82 and two isolated aromatic protons at δ 6.48 (H-4) and 6.77 (H-7). Two sets of two prenyl groups were displayed at δ 5.28 (H-2′, *t*, 7.2), 5.39 (H-2″, *t*, *J* = 7.2), 3.35 (H-1′, *d*, *J* = 7.2), 3.97 (H-1″, *d*, *J* = 7.2), 1.78 (H-4′, *s*), 1.65 (H-5′, *s*), 1.74 (H-4″, *s*) and 1.72 (H-5″, *s*). Proton H-4, 1-OH and H-2′ of 2-prenyl group showed ^{3}J HMBC correlations to C-2 (δ 110.2) indicating that H-4 was *para* to 1-OH, whereas a prenyl side chain was *ortho* to 1-OH. The 8-prenyl side chain was placed *peri* to the carbonyl group and *ortho* to H-7 due to the correlations of H-1″ to C-8a (δ 111.3), C-7 (δ 113.8) and H-7 correlated to C-8a, C-1″ (δ 32.8). The molecular formula of $C_{23}H_{24}O_6$ allowed to complete the structure with hydroxyl groups at C-3, C-5 and C-6. The HMBC correlations of H-4 to the carbon resonance at δ 162.1 suggested that this chemical shift belonged to the oxy carbon C-3. The HMBC correlations of H-7 to carbon resonances at δ 130.5 and δ 150.1 suggested oxycarbons C-5 and C-6 having chemical shifts of δ 130.5 and δ 150.1, respectively. The oxy carbon C-5 was resonated effected by two *ortho* hydroxyl group, the higher field chemical shift (δ 130.5) then was confirmed for C-5. **AS16** then was proposed as 1,3,5,6-tetrahydroxy-2,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one. It is a new xanthone derivative and is an isomer of γ-mangostin (Mahabusarakam, *et al*., 1987).

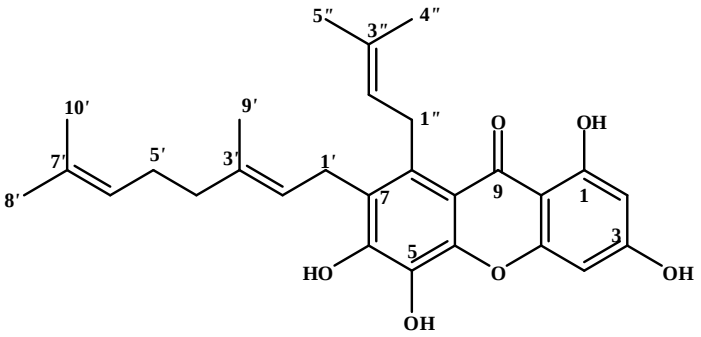


Major HMBC of AS16

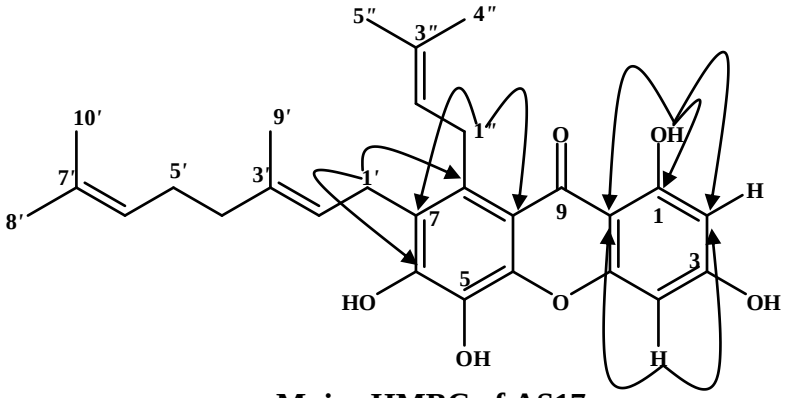
Table 21 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS16**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	161.0 (C)	-	-
2	110.2 (C)	-	-
3	162.1 (C)	-	-
4	92.5 (CH)	6.48 (*s*)	C-2, C-3, C-4a, C-9, C-9a
4a	158.7 (C)	-	-
4b	135.7 (C)	-	-
5	130.5 (C)	-	-
6	150.1 (C)	-	-
7	113.8 (CH)	6.77 (*s*)	C-5, C-6, C-8a, C-1″
8	135.7 (C)	-	-
8a	111.3 (C)	-	-
9	181.5 (C)	-	-
9a	102.6 (C)	-	-
1′	21.1 (CH_2)	3.35 (*d*, 7.2)	C-1, C-2, C-3, C-2′, C-3′
2′	122.6 (CH)	5.28 (*t*, 7.2)	-
3′	130.5 (C)	-	-
4′	17.11 (CH_3)	1.78 (*s*)	C-2′, C-3′, C-5′
5′	24.9 (CH_3)	1.65 (*s*)	C-2′, C-3′, C-4′
1″	32.8 (CH_2)	3.97 (*d*, 7.2)	C-7, C-8, C-8a, C-2″, C-3″
2"	123.5 (CH)	5.39 (*t*, 7.2)	-
3"	131.6 (C)	-	-
4″	16.9 (CH_3)	1.74 (*s*)	C-2″, C-3″, C-5″
5"	25.0 (CH_3)	1.72 (*s*)	C-2″, C-3″, C-4″
1-OH	-	13.82 (*s*)	C-1, C-2, C-9a

AS17: (*E*)-2-(3,7-dimethylocta-2,6-dienyl)-3,4,6,8-tetrahydroxy-1-(3-methylbut-2-enyl)-9*H*-xanthen-9-one (garciniaxanthone E)



AS17 was an orange gummy oil. The UV spectrum showed absorption bands at λ_{max} 208, 255 and 329 nm. The IR spectrum showed the absorption bands of O-H stretching at 3525 and C=O stretching at 1633 cm^{-1}. The ^{1}H NMR spectrum (**Table 22**) showed signals of one singlet chelated hydroxyl group (1-OH) at δ 13.61 and two doublets of *meta* aromatic protons (H-2, H-4) at δ 6.18 and 6.35 (J = 1.8 Hz). The assignment of H-2 and H-4 were supported by HMBC correlation of 1-OH to C-2 (δ 97.8), C-9a (δ 103.0); H-2 to C-9a, C-4 (δ 92.9) and H-4 to C-2, C-9a. The signals of a prenyl side chain were displayed; an olefinic proton H-2″ at δ 5.08 (*br t, J* = 6.0 Hz), benzylic methylene protons H-1″ at δ 4.10 (*d, J* = 6.0 Hz), methyl groups H-4″, H-5″ at δ 1.78 (*s*) and 1.66 (*s*). Due to the low field chemical shift of methylene protons H-1″ (δ 4.10), the prenyl group then was placed nearby the carbonyl group. The remaining signals including a doublet of methylene protons H-1′ at δ 3.47 (J = 6.0 Hz), broad triplets of olefinic protons H-2′, H-6′ at δ 5.08, multiplets of methylene protons H-4′, H-5′ at δ 2.00, δ 2.05 and three singlet signals of methyl groups H-8′, H-9′, H-10′ at δ 1.56, δ 1.78 and δ 1.61, respectively, corresponded to a geranyl group. The geranyl side chain was located at C-7 *ortho* to phenyl group according to the cross peak of H-2′ and H-1″ to C-7 (δ 126.0) in HMBC correlation. Three hydroxyl groups were substituted at C-3 (δ 164.4), C-5 (δ 130.8) and C-6 (δ 149.2) to fulfill structure. The HMBC data that H-2, H-4 correlated to the resonance at δ 164.4, while H-1′ correlated to the resonance at δ 149.2, suggested C3 and C6 have chemical shifts of δ 164.4 and δ 149.2, respectively. Thus **AS17** was assigned to be (*E*)-2-(3,7-dimethylocta-2,6-dienyl)-3,4,6,8-tetrahydroxy-1-(3-methylbut-2-enyl)-9*H*-xanthen-9-one or known as garciniaxanthone E (Minami, *et al*., 1996).



Major HMBC of AS17

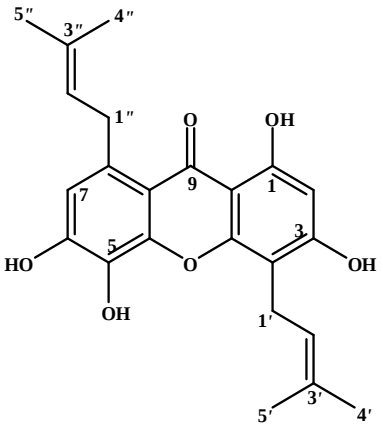
Table 22 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS17**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	164.2 (C)	-	-
2	97.8 (CH)	6.18 (*d*, 1.8)	C-3, C-4, C-9a
3	164.4 (C)	-	-
4	92.92 (CH)	6.35 (*d*, 1.8)	C-2, C-3, C-4a, C-9a
4a	156.7 (C)	-	-
4b	145.5 (C)	-	-
5	130.8 (C)	-	-
6	149.2 (C)	-	-
7	126.0 (CH)	-	-
8	134.1 (C)	-	-
8a	111.0 (C)	-	-
9	182.5 (C)	-	-
9a	103.0 (C)	-	-
1′	24.2 (CH_2)	3.47 (*d*, 6.0)	C-6, C-7, C-8, C-2′, C-3′
2′	123.0 (CH)	5.08 (*br t*, 6.0)	-
3′	134.8 (C)	-	-
4′	39.5 (CH_2)	2.00 (*m*)	C-2′, C-3′, C-5′, C-6′, C-9′
5′	26.4 (CH_2)	2.05 (*m*)	C-3′, C-4′, C-6′, C-7′
6′	124.2 (CH)	5.08 (*br t*, 6.0)	-

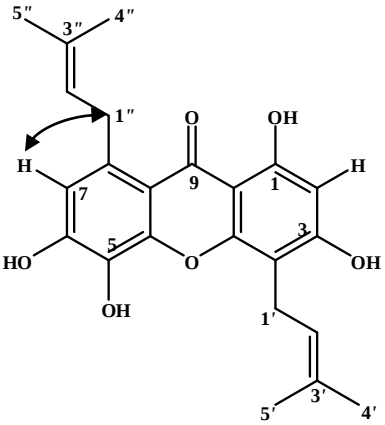
Table 22 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS17** (Continued)

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
7′	130.0 (C)	-	-
8′	16.8 (CH_3)	1.56 (*s*)	C-6′, C-7′, C-10′
9′	15.6 (CH_3)	1.78 (*s*)	C-2′, C-3′, C-4′
10′	25.0 (CH_3)	1.61 (*s*)	C-6′, C-7′, C-8′
1″	24.9 (CH_2)	4.10 (*d*, 6.0)	C-7, C-8, C-8a, C-2″, C-3″
2"	124.6 (CH)	5.08 (*br t*, 6.0)	-
3"	127.7 (C)	-	-
4″	17.4 (CH_3)	1.78 (*s*)	C-2″, C-3″, C-5″
5"	24.9 (CH_3)	1.66 (*s*)	C-2″, C-3″, C-4″
1-OH	-	13.61 (*s*)	C-1, C-2, C-9a

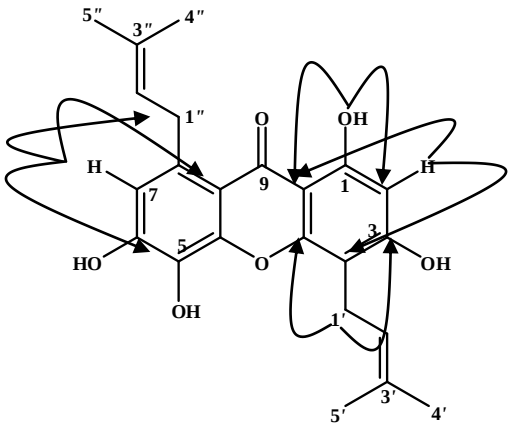
AS18: 1,3,5,6-tetrahydroxy-4,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one



AS18 was a yellow solid, m.p. 102-105 ^{o}C, with the molecular formula $C_{23}H_{24}O_6$. The UV spectrum showed absorption bands at λ_{max} 203, 256 and 331 nm. The IR spectrum showed the absorption band of O-H stretching at 3229 and C=O stretching at 1645 cm^{-1}. The ^{1}H NMR spectrum (**Table 23**) showed the resonances of a chelated hydroxyl proton (1-OH, δ 13.49), two isolated aromatic protons (H-2,δ 6.29 and H-7, 6.80), two of prenyl groups at δ 5.38 (H-2', br *t*, 7.2), 5.38 (H-2″, *br t*, 7.2), 3.57 (H-1′, *d*, 7.5), 4.00 (H-1″, *d*, 7.5), 1.83 (H-4′, *s*), 1.64 (H-5', s) and δ 1.72 (H-4″ and H-5 ″, *s*) as for **AS16** with a little change of the chemical shifts of one aromatic proton (δ 6.48, H-4 of **AS16**; δ 6.29, H-2 of **AS18**). The HMBC and NOE experiments indicated that a prenyl group and an aromatic proton (δ 6.29) were at C-8 and C-2 as for its isomer, **AS16**. The aromatic proton that resonated at δ 6.29 was assigned for H-2 due to the HMBC correlation of H-2 to C-9a (δ 102.0) and its carbon (C-2) correlated to 1-OH. Furthermore, the correlations of H-2 and H-1′ to C-4 (δ 106.0) revealed that the prenyl group was at C-4. The molecular formula of $C_{23}H_{24}O_6$ together with the carbon chemical shifts of δ 162.5, δ 130.7 and δ 150.8 allowed to assigns hydroxyl groups at C-3, C-5 and C-6. The HMBC correlations of H-1′ to carbon resonance at δ 162.5, and H-7 to carbon resonance at δ 130.7 and δ 150.8 allowed C-3, C-5 and C-6 having chemical shift of δ 162.5, 130.7 and δ 150.8, respectively. Thus **AS18** was assigned to be 1,3,5,6-tetrahydroxy-4,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one. It is a new xanthone derivative and is an isomer of cudratricusxanthone B (Zou, *et al*. 2004).



NOE of AS18



Major HMBC of AS18

Table 23 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS18**

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
1	161.0 (C)	-	-
2	97.8 (CH)	6.29 (*s*)	C-4, C-9a
3	162.5 (C)	-	-
4	106.0 (C)	-	-
4a	154.2 (C)	-	-
4b	135.7 (C)	-	-
5	130.7 (C)	-	-
6	150.8 (C)	-	-
7	113.8 (CH)	6.80 (*s*)	C-5, C-6, C-8a, C-1″
8	135.8 (C)	-	-
8a	111.5 (C)	-	-
9	181.5 (C)	-	-
9a	102.0 (C)	-	-
1′	21.1 (CH_2)	3.57 (*d*, 7.5)	C-3, C-4, C-5, C-2′, C-3′
2′	123.0 (CH)	5.38 (*br t*, 7.2)	-
3′	130.7 (C)	-	-
4′	17.00 (CH_3)	1.83(*s*)	C-2′, C-3′, C-5′
5′	25.0 (CH_3)	1.64(*s*)	C-2′, C-3′, C-4′
1″	32.8 (CH_2)	4.00 (*d*, 7.5)	C-7, C-8, C-8a, C-2″, C-3″

Table 23 ^{1}H, ^{13}C NMR and HMBC spectral data (Acetone-d_6) of **AS18** (continued)

Position	**δ_C (C-Type)**	**δ_H (multiplicity, J_{Hz})**	**HMBC**
2"	123.7 (CH)	5.38 (*t*, 7.2)	-
3"	131.9 (C)	-	-
4″	17.0 (CH_3)	1.72 (*s*)	C-2″, C-3″, C-5″
5"	25.0 (CH_3)	1.72 (*s*)	C-2″, C-3″, C-4″
1-OH	-	13.49 (*s*)	C-1, C-2, C-9a

3.2 Antibacterial activity of the isolated compounds from the leaves and stem bark of *G. dulcis*

The acetone extract and dichloromethane extract from the leaves and stem bark of *G. dulcis* were tested for antibacterial activity on *Staphylococus aureus* ATCC25923 and methicillin-resistant strain MRSA. It was found that the extract from the leaves had no effect on these microorganisms up to a dose of 200 μg/mL, the extract from the stem bark showed activity with MIC 16-32 μg/mL.

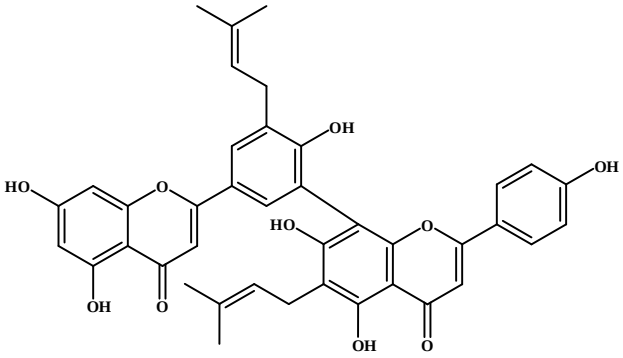
Some of the pure compounds obtained from the leaves and stem bark extract were evaluated for their antibacterial activity against *S. aureus* ATCC25923 and MRSA. Compounds **AS5**, **AS7** and **AS16** were more active than the crude extract (MIC 64-128 μg/mL). Among the active compound **AS14** showed the strongest inhibitory activity with a MIC value of 2 μg/mL against *S. aureus* and 1 μg/mL against MRSA, however it was less active than vancomycin, the standard antibiotic (MIC 0.5 μg/mL). **AS4**, **AS6**, **AS11** and **AS13** showed no activity against four bacterial strains tested at 200 μg/mL. Compounds **AS1, AS2, AS3, AS8, AS9, AS10, AS12, AS15, AS17** and **AS18** were not tested due to insufficient amount.

CONCLUSION

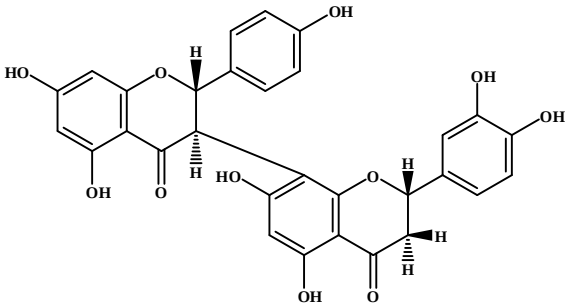
With the aim of studying of the chemical constituents of the leaves and stem bark of *G. dulcis*, we found that the leaves were a source of biflavonoids (**AS4**, **AS5**, **AS6**, **AS7**, **AS8**, **AS9**), whereas the stem bark were a source of xanthones (**AS11**, **AS12**, **AS13**, **AS14**, **AS15**, **AS16**, **AS17**, **AS18**). Apart from biflavonoids and xanthones, triterpenoids (**AS1**, **AS10**) and benzene derivatives (**AS2**, **AS3**) were also isolated.

AS14 was the most active compound against *S. aureus* ATCC25923 and methicillin-resistant *S. aureus* (MIC 1 and 2 μg/mL). **AS5**, **AS7** and **AS16** showed significant activity against *S. aureus* ATCC25923 (MIC 64-128 μg/mL) and methicillin-resistant *S. aureus*, (64-128 μg/mL). They could not inhibit the growth of *E. coli* ATCC25922, *P. aeruginosa* ATCC27853 at 200 μg/mL. **AS4**, **AS6**, **AS11** and **AS13** showed no activity against four bacterial strains tested at 200 μg/mL. Compounds **AS1**, **AS2**, **AS3**, **AS8**, **AS9**, **AS10**, **AS12**, **AS15**, **AS17** and **AS18** were not tested.

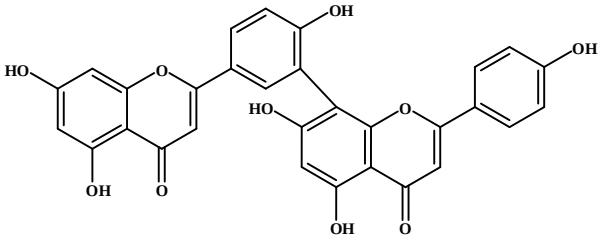
Biflvonoids



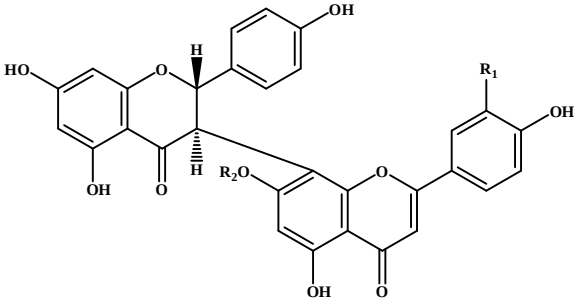
AS4 ; 8-(5-(5,7-dihydroxy-4-oxo-4*H*-chromen-2-yl)-2-hydroxy-3-(3-methylbut-2-enyl)phenyl)-5,7-dihydroxy-2-(4-hydroxy phenyl)-6-(3-methylbut-2-enyl)-4*H*-chromen-4-one



AS5 ; GB-2a

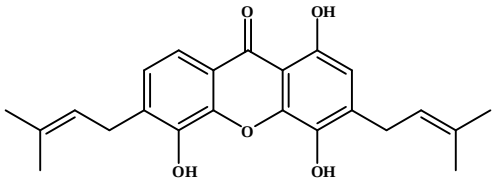


AS6 ; amentoflavone

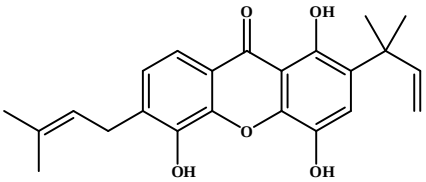


AS7 : R_1 = OH, R_2 = H ; morelloflavone
AS8 : R_1 = OH, R_2 = SO_3H ; morelloflavone-7"-sulfate
AS9 : R_1, R_2 = H ; volkensiflavone

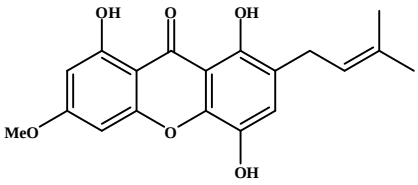
Xanthones



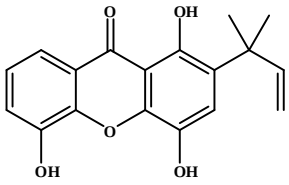
AS11 ; garciniaxanthone C



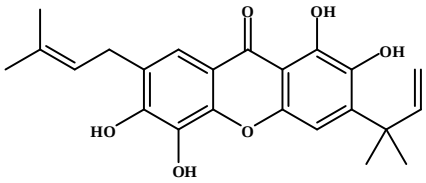
AS12 ; garciniaxanthoneA



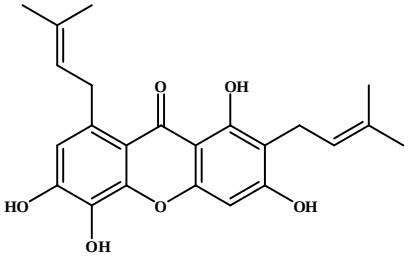
AS13 ; 1,4,8-trihydroxy-6-methoxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one



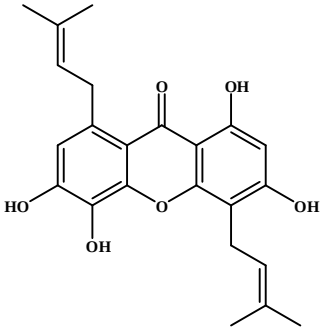
AS14 ; 12b-hydroxy-des-D-garcigerrin A



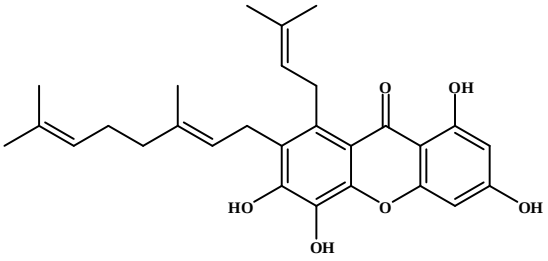
AS15 ; 1,2,5,6-tetrahydroxy-7-(3-methylbut-2-enyl) -3-(2-methylbut-3-en-2-yl)-9*H*-xanthen-9-one



AS16 ; 1,3,5,6-tetrahydroxy-2,8-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one

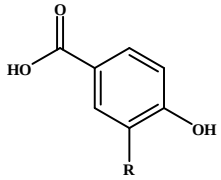


AS18 ; 1,3,5,6-tetrahydroxy-4,8-bis(3-methyl but-2-enyl)-9*H*-xanthen-9-one

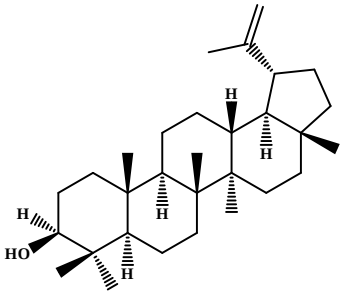


AS17 ; garciniaxanthone E

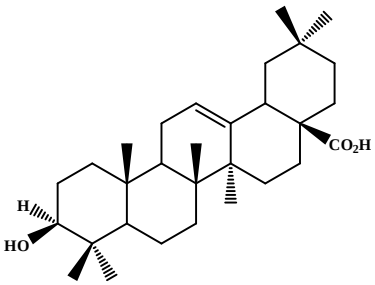
Benzene derivatives and triterpenoids



AS2 : R = H ; 4-hydroxy benzoic acid
AS3 : R = OMe ; 4-hydroxy-3-methoxybenzoic acid



AS1 ; lupeol



AS10 ; oleanolic acid

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APPENDIX

- **^{1}H-NMR and ^{13}C-NMR spectra of AS1-AS18**

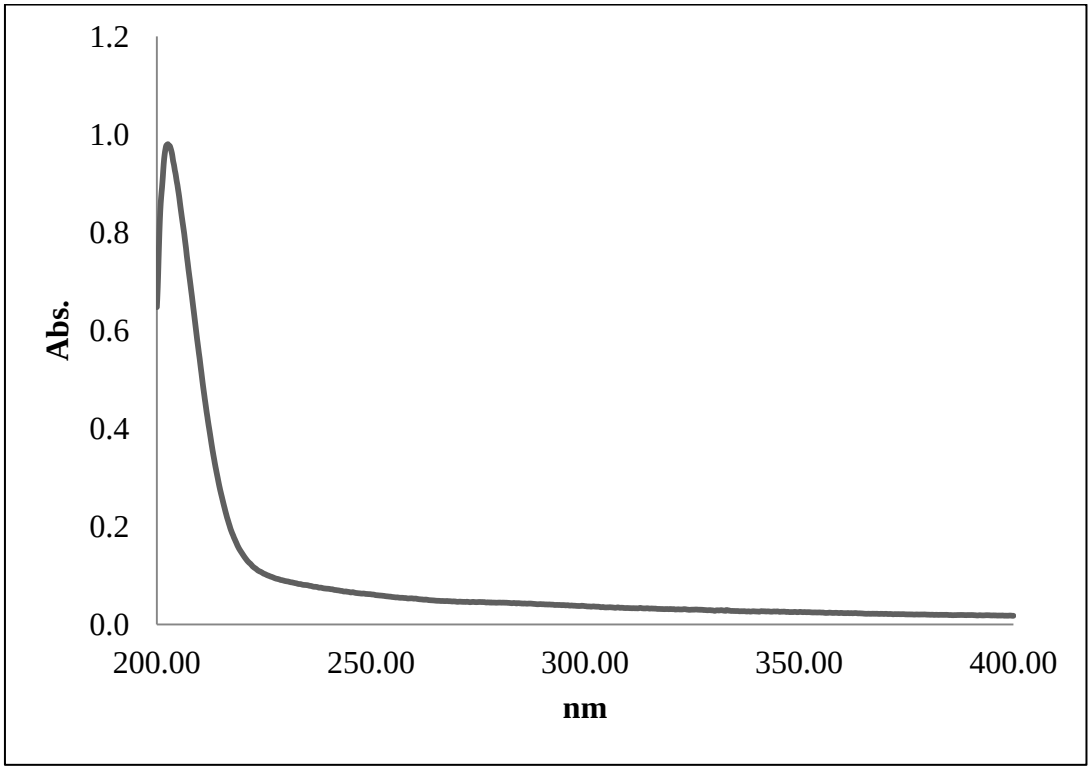

Figure 2 UV (MeOH) spectrum of **AS1**

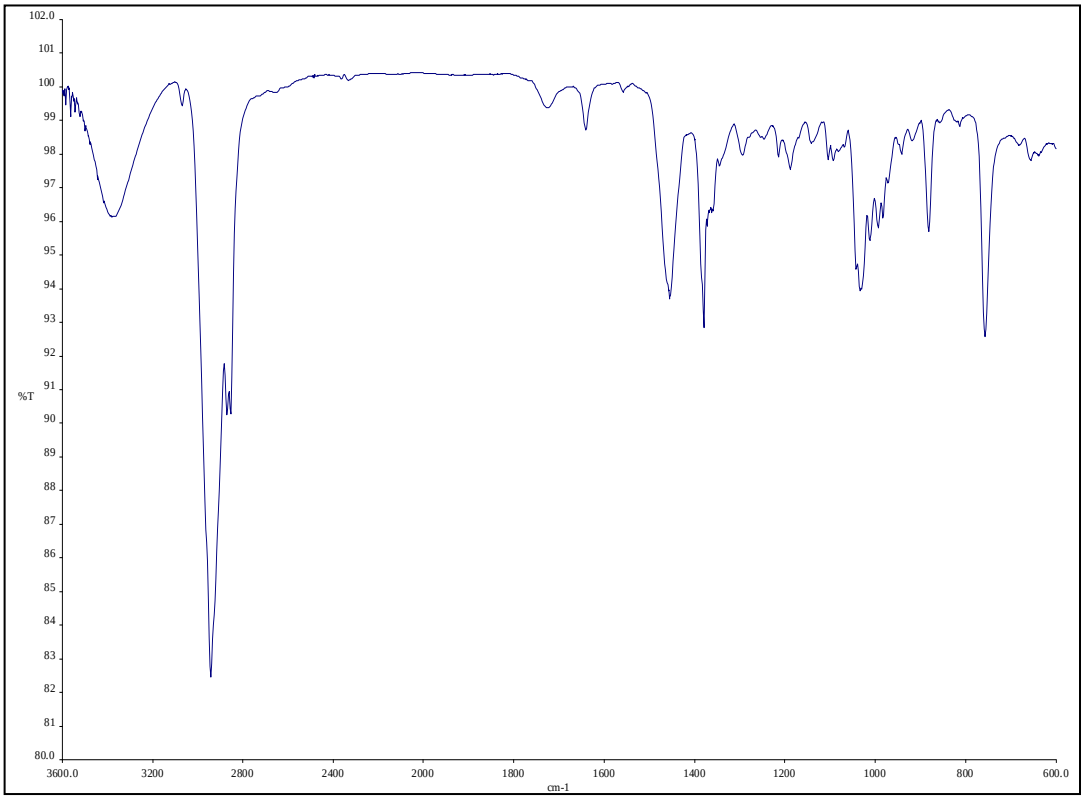

Figure 3 IR (neat) spectrum of **AS1**

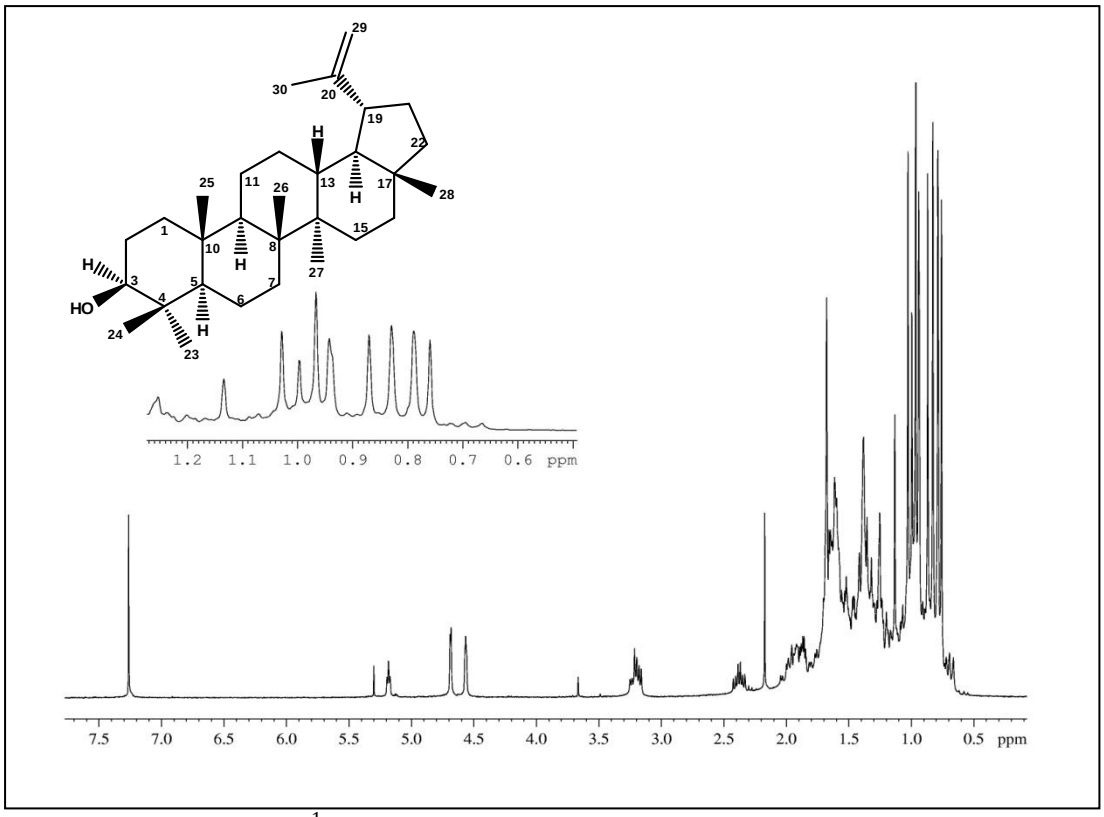

Figure 4 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of **AS1**

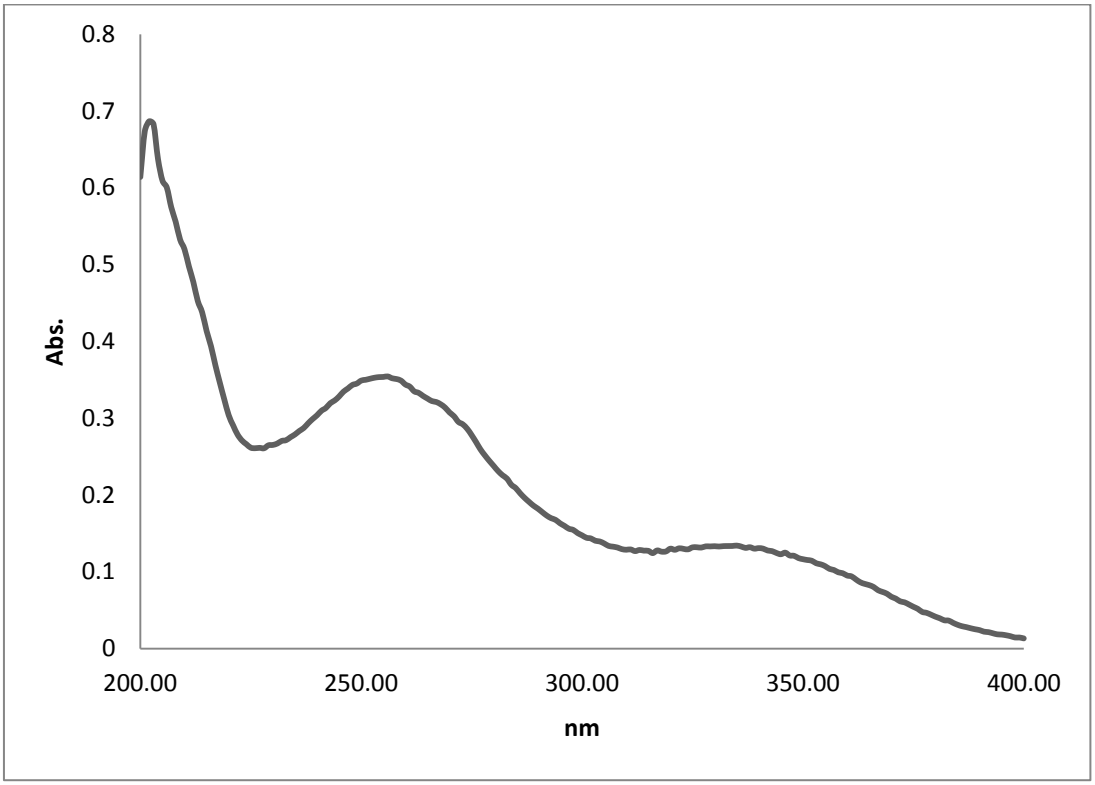

Figure 5 UV (MeOH) spectrum of **AS2**

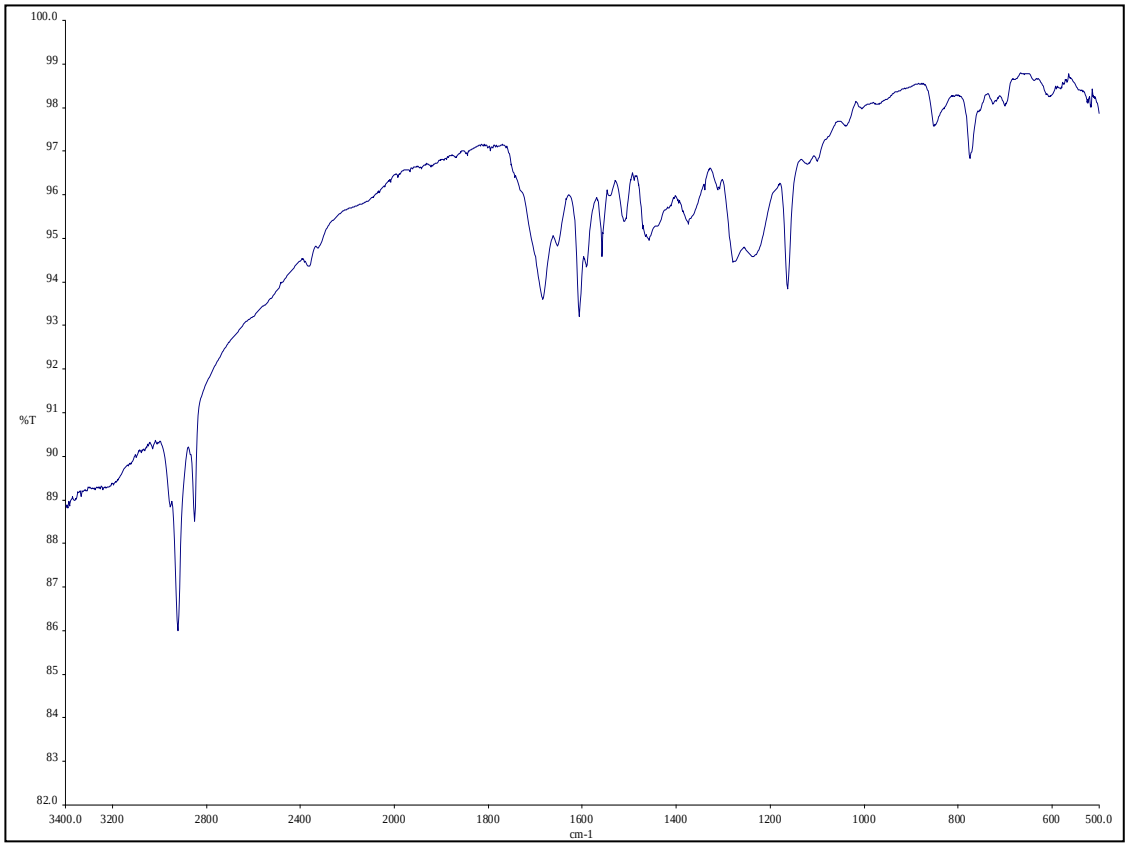

Figure 6 IR (neat) spectrum of **AS2**

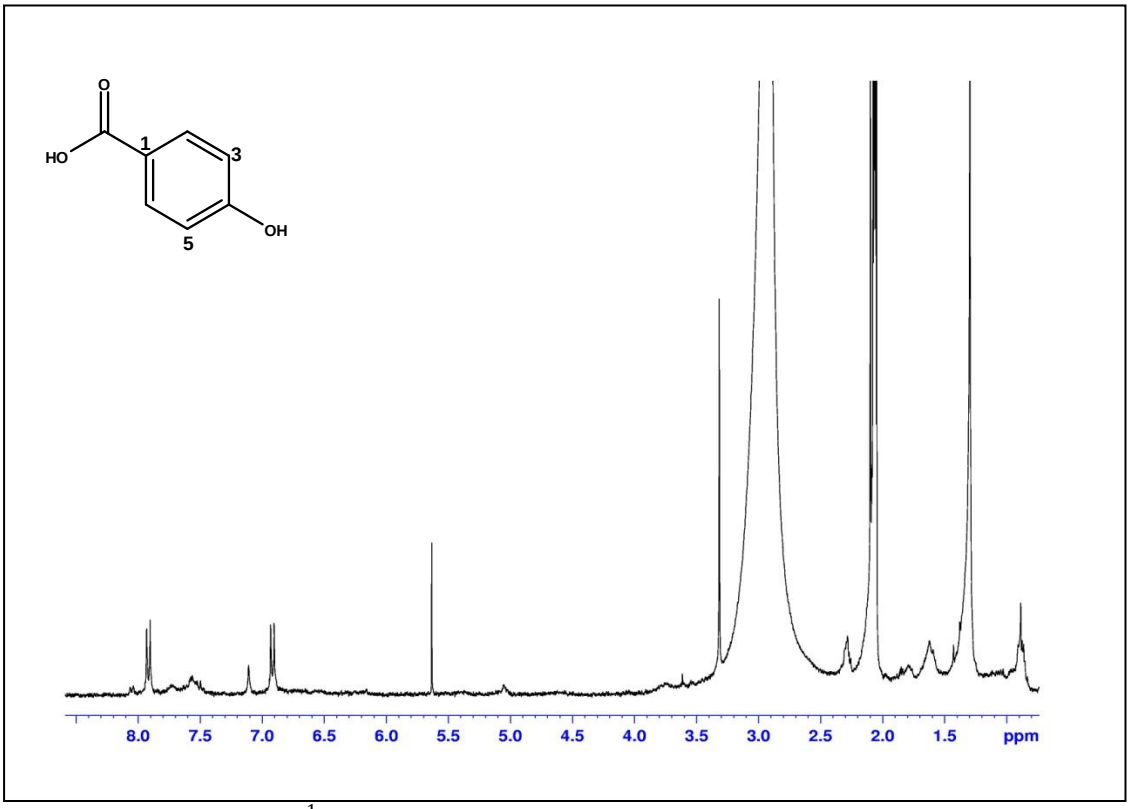

Figure 7 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of **AS2**

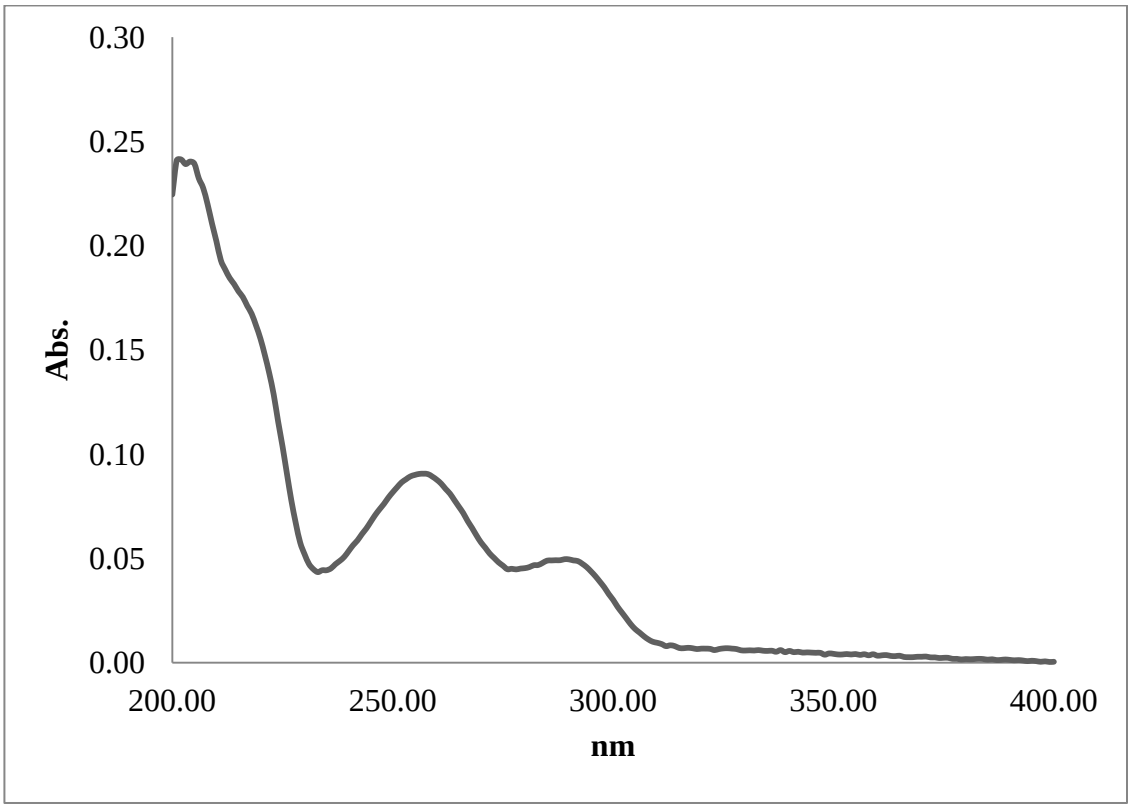

Figure 8 UV (MeOH) spectrum of **AS3**

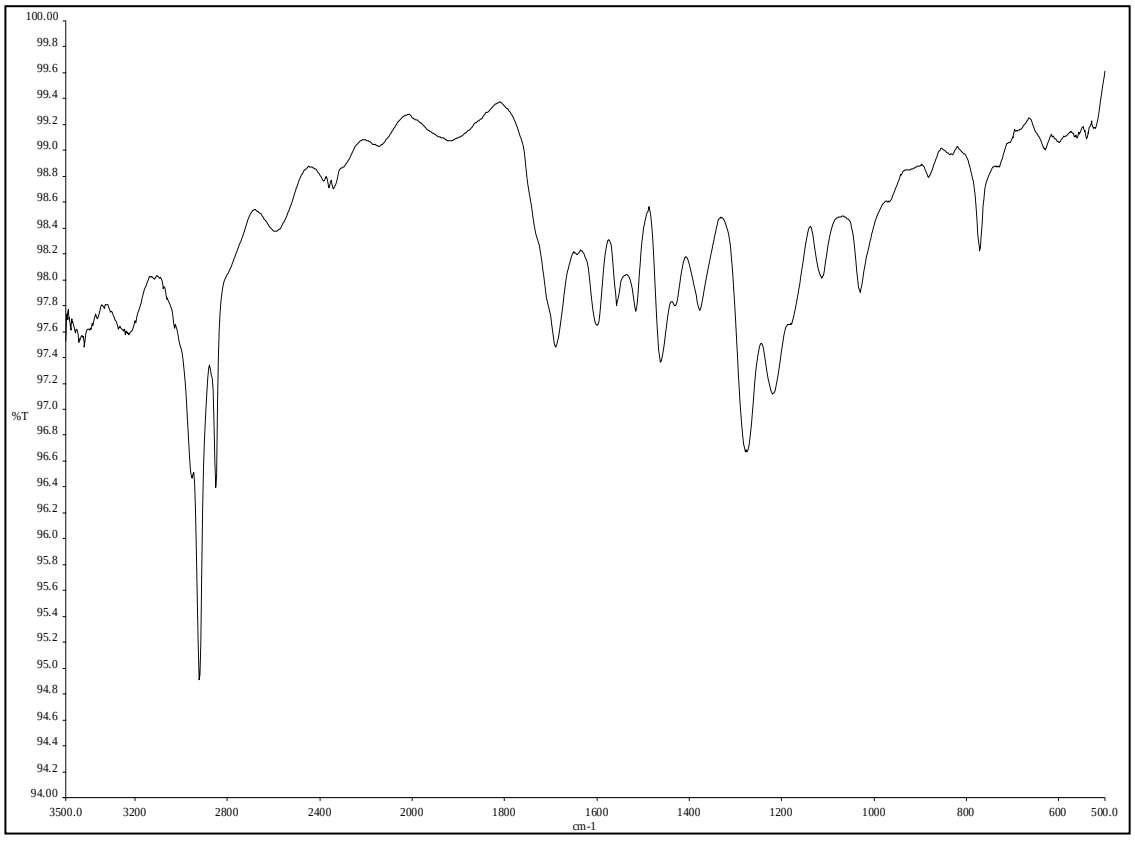

Figure 9 IR (neat) spectrum of **AS3**

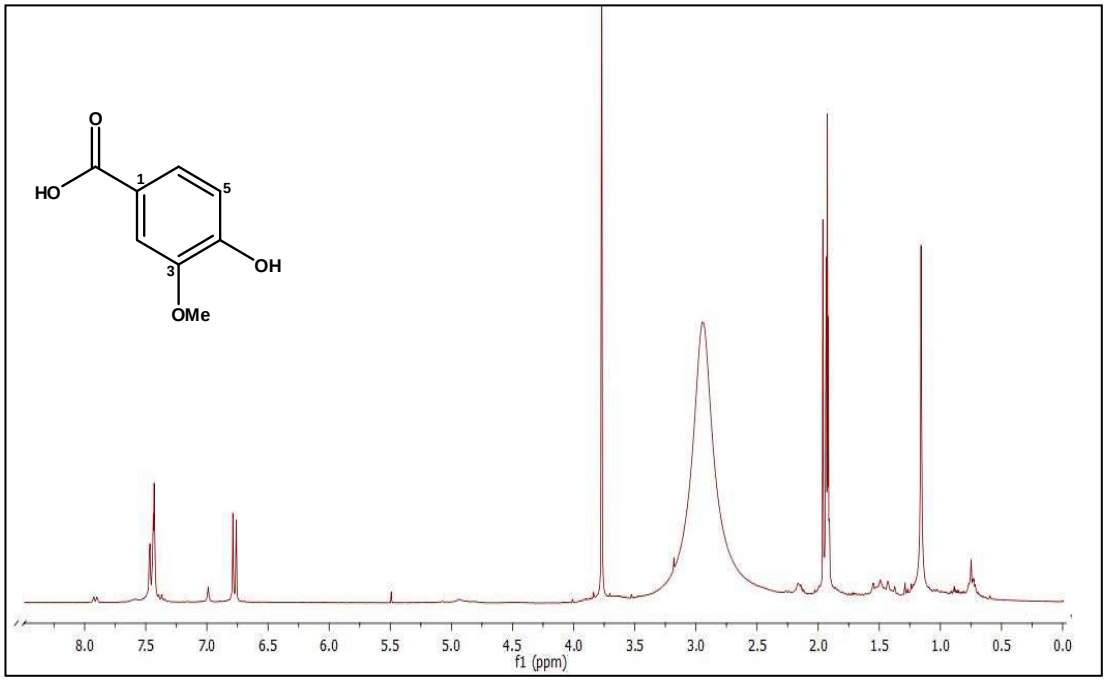

Figure 10 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD) spectrum of **AS3**

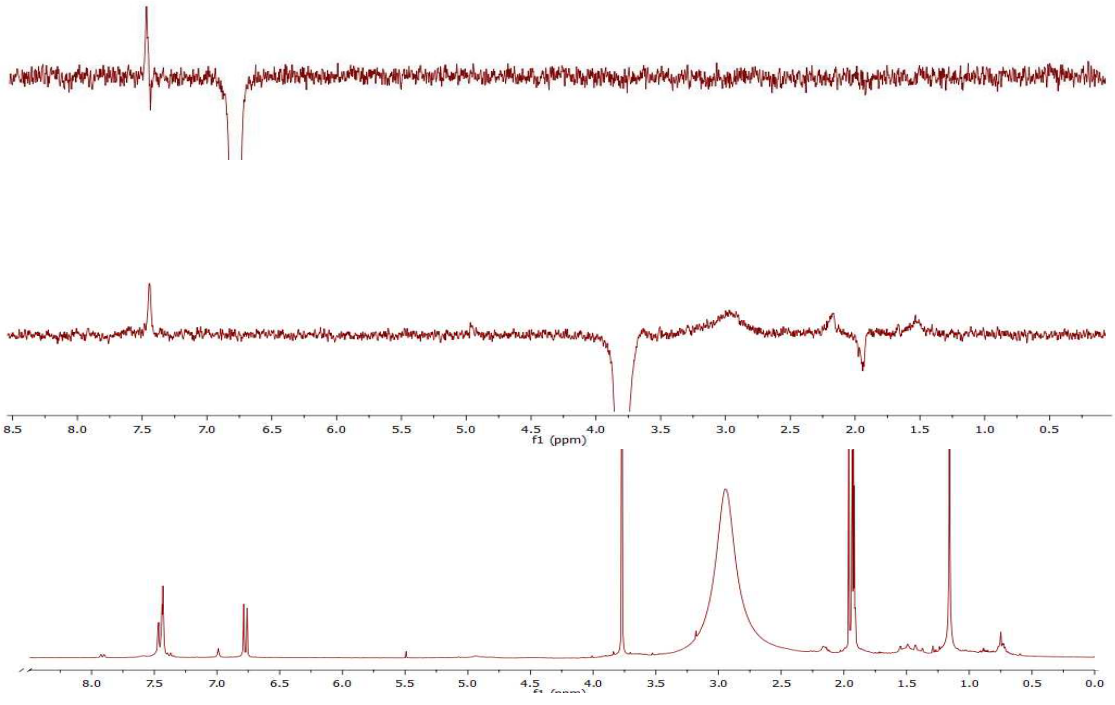

Figure 11 NOE (300 MHz) (Acetone-d_6) spectrum of **AS3**

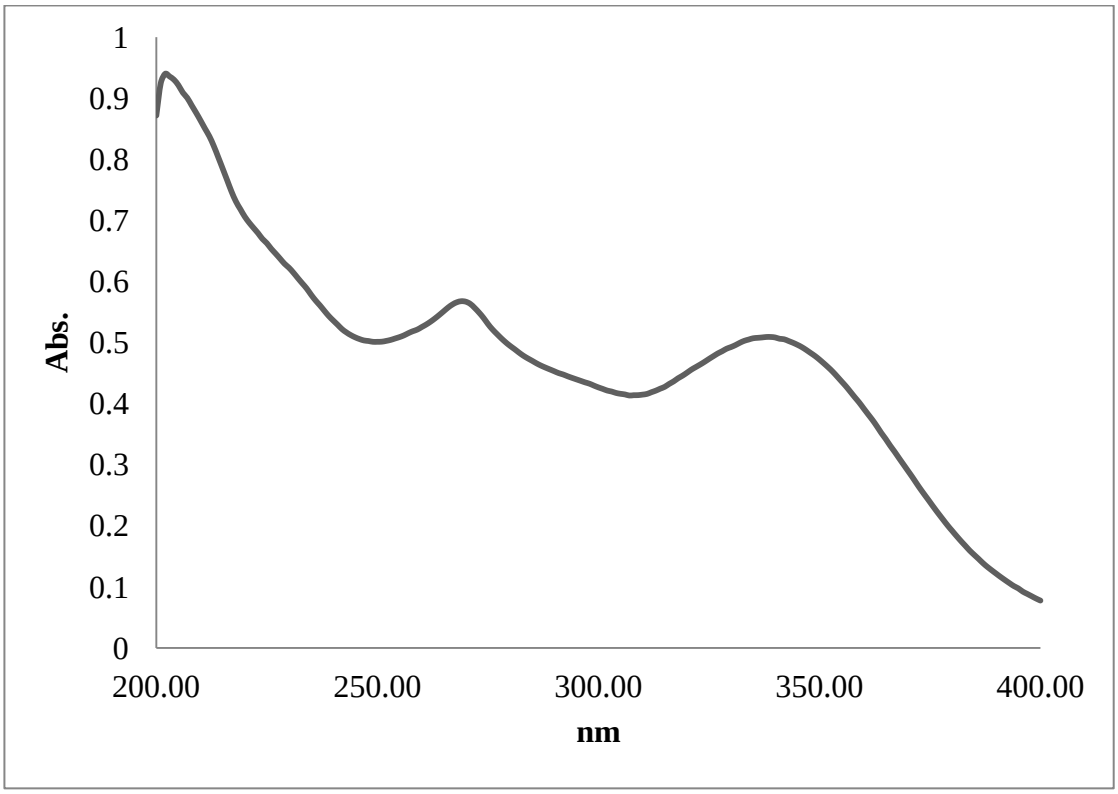

Figure 12 UV (MeOH) spectrum of **AS4**

Figure 13 IR (neat) spectrum of **AS4**

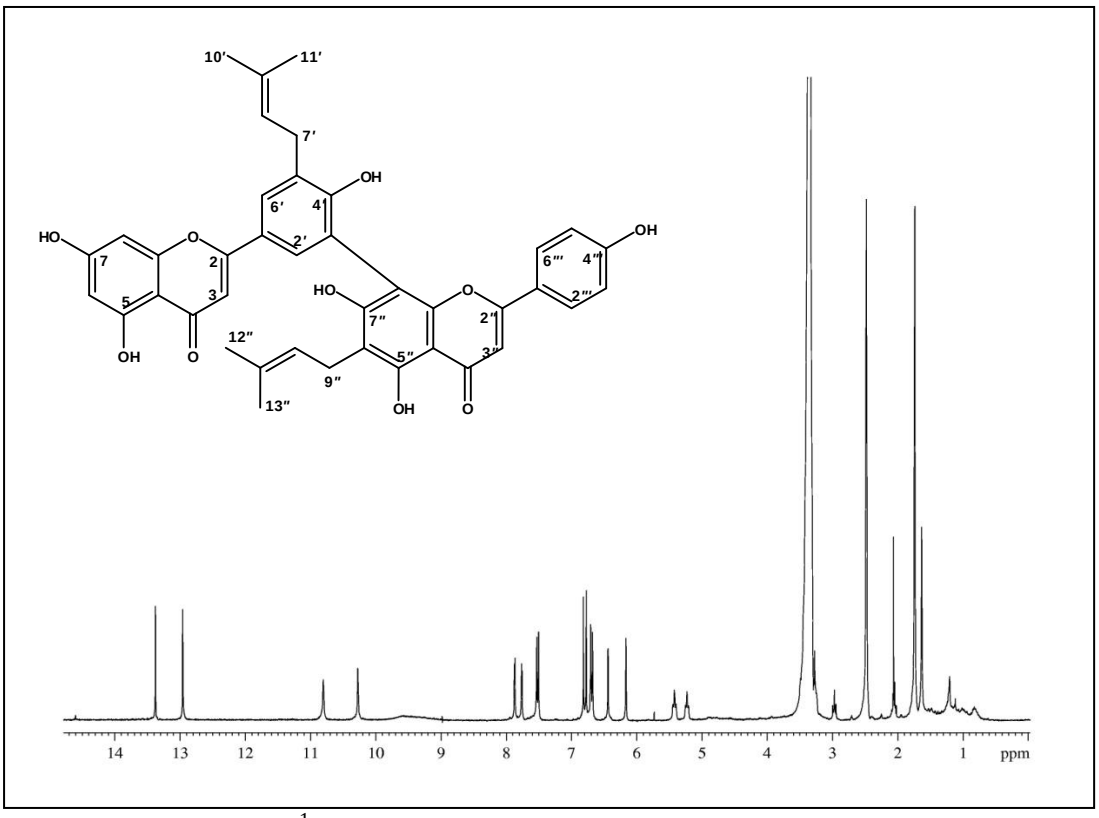

Figure 14 ^{1}H NMR (300 MHz) (DMSO-d_6) spectrum of **AS4**

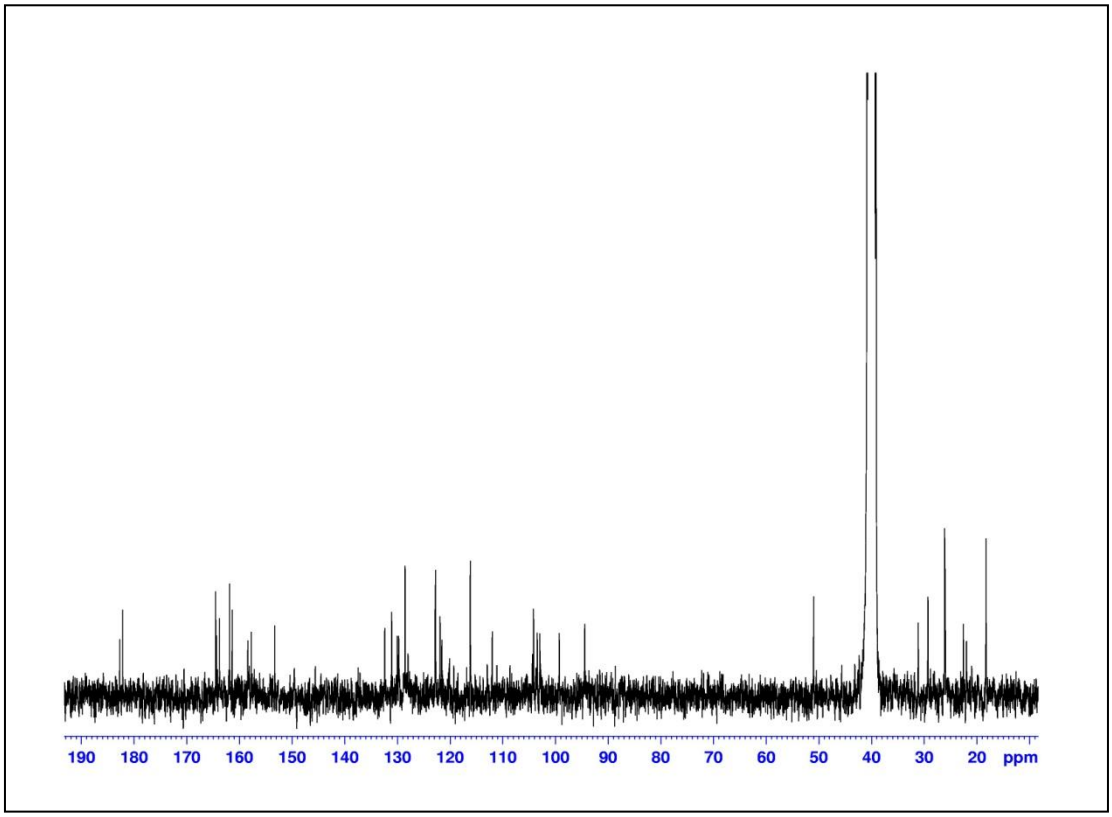

Figure 15 ^{13} C NMR (75 MHz) (DMSO-d_6) spectrum of **AS4**

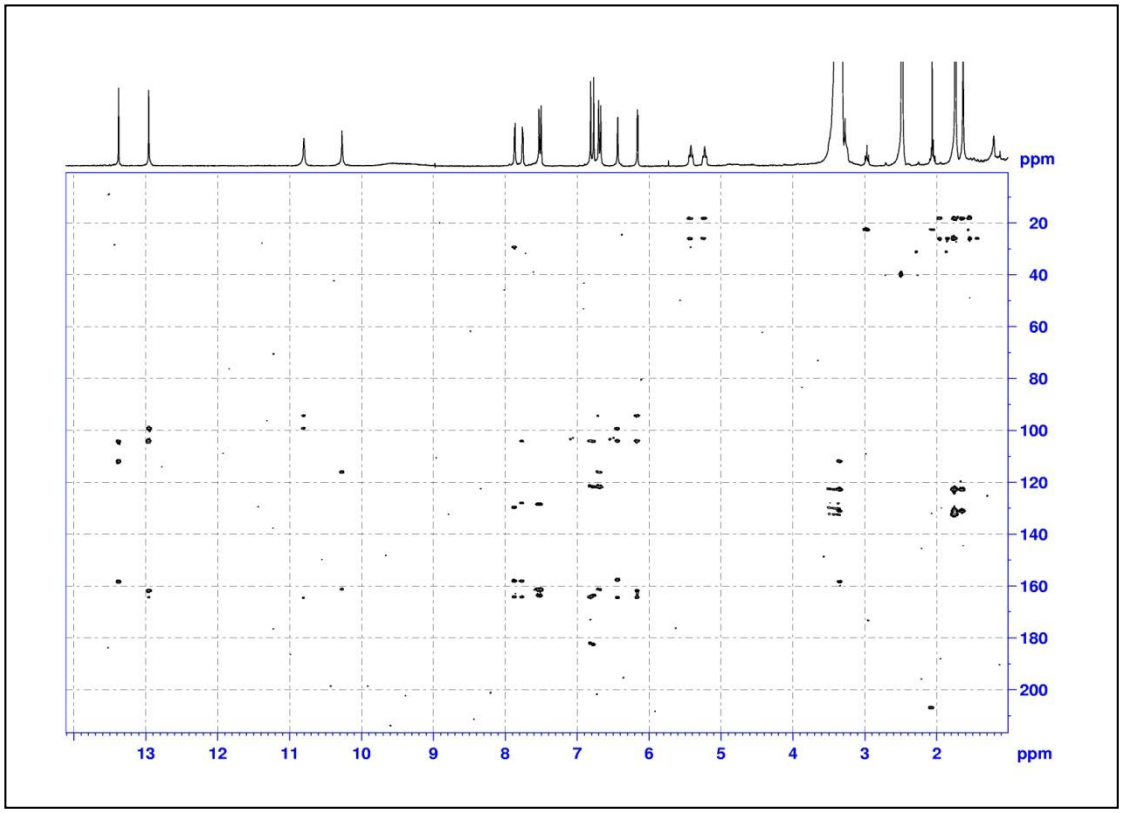

Figure 16 2D HMBC (DMSO-d_6) spectrum of **AS4**

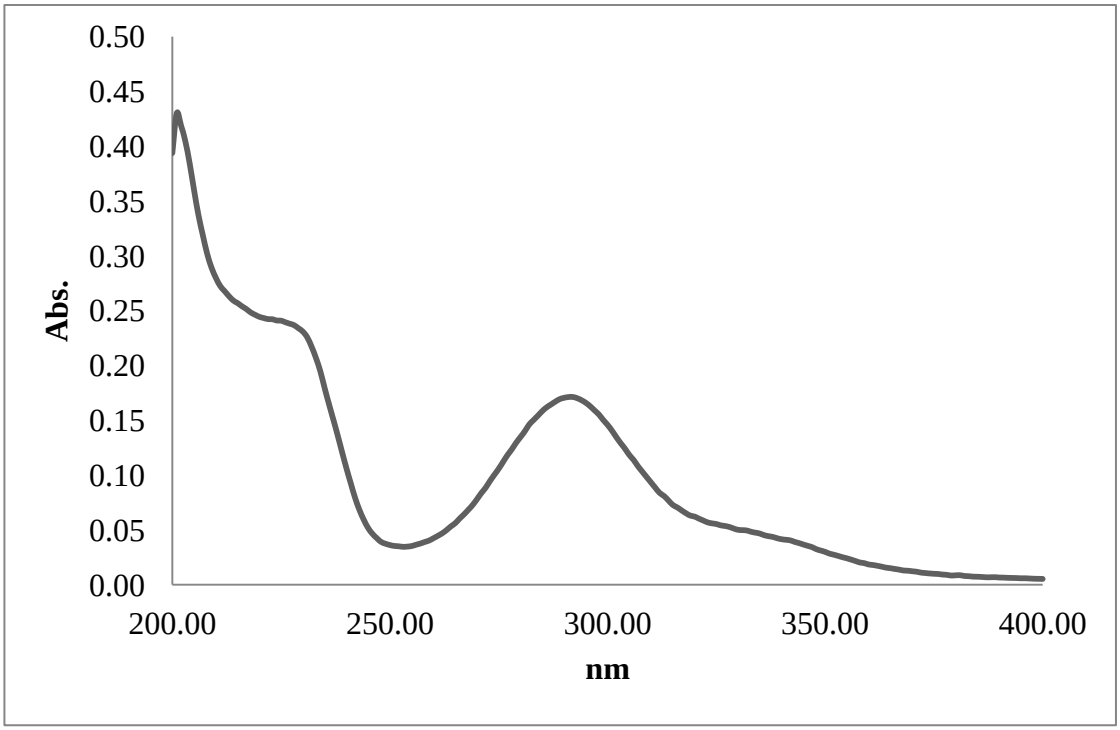

Figure 17 UV (MeOH) spectrum of **AS5**

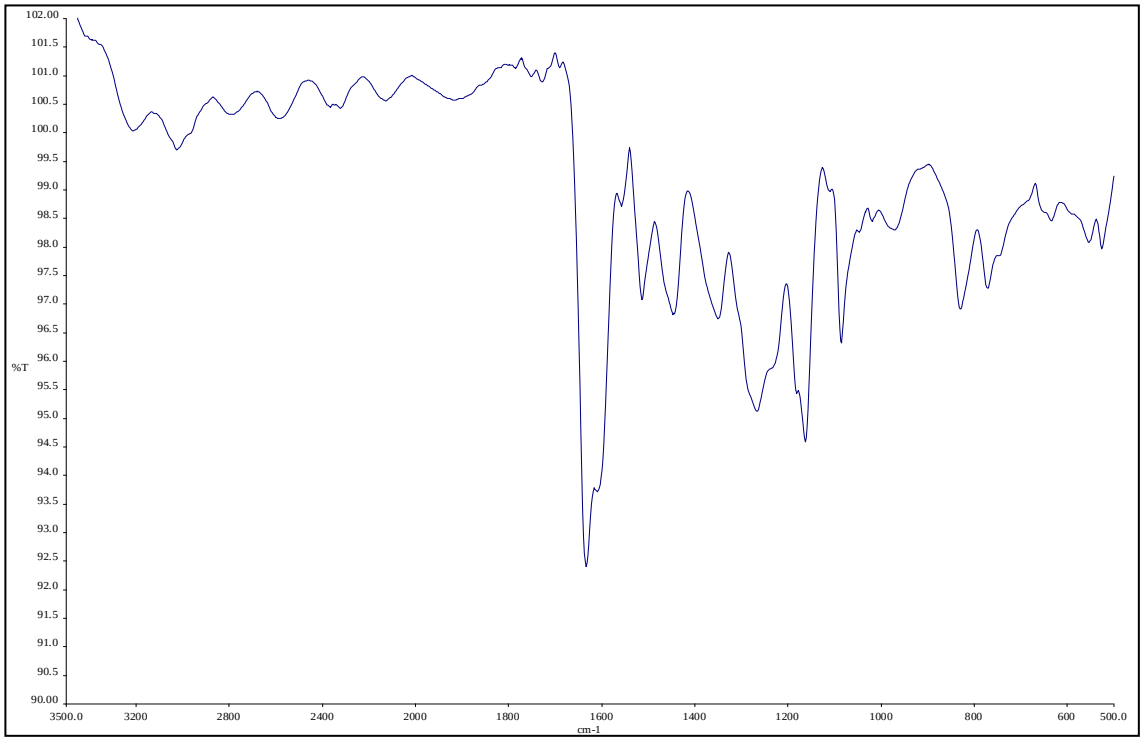

Figure 18 IR (neat) spectrum of **AS5**

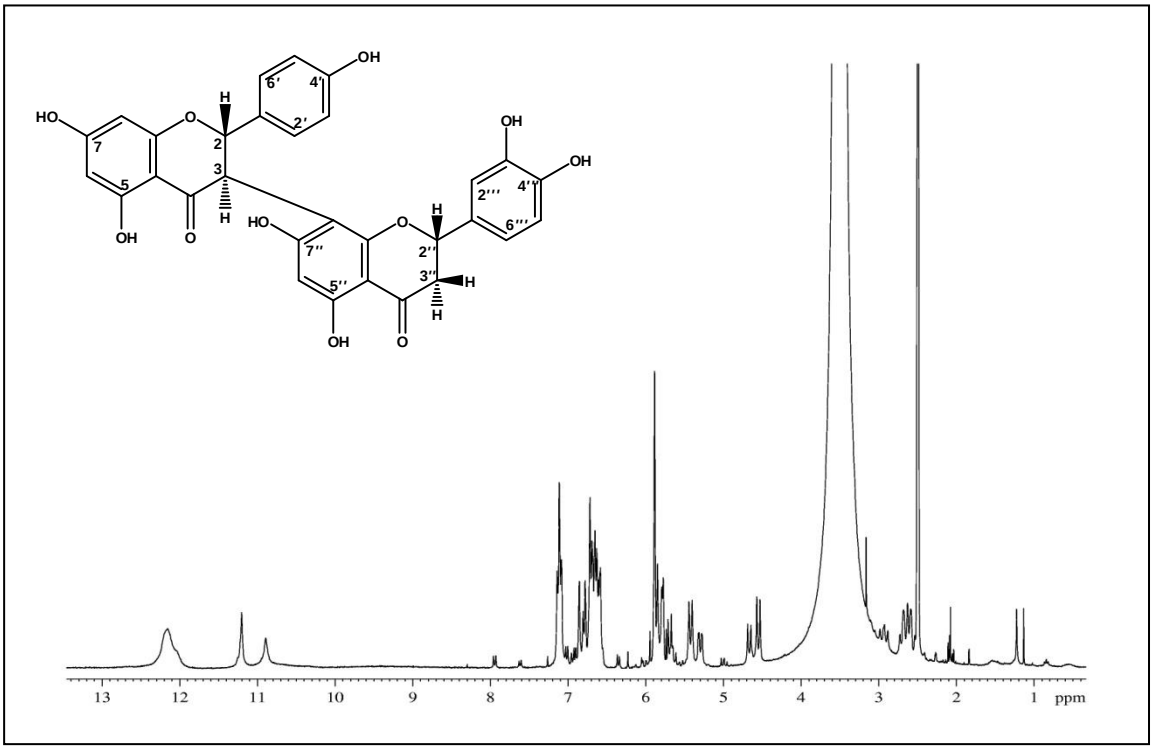

Figure 19 ^{1}H NMR (300 MHz) (DMSO-d_6) spectrum of **AS5**

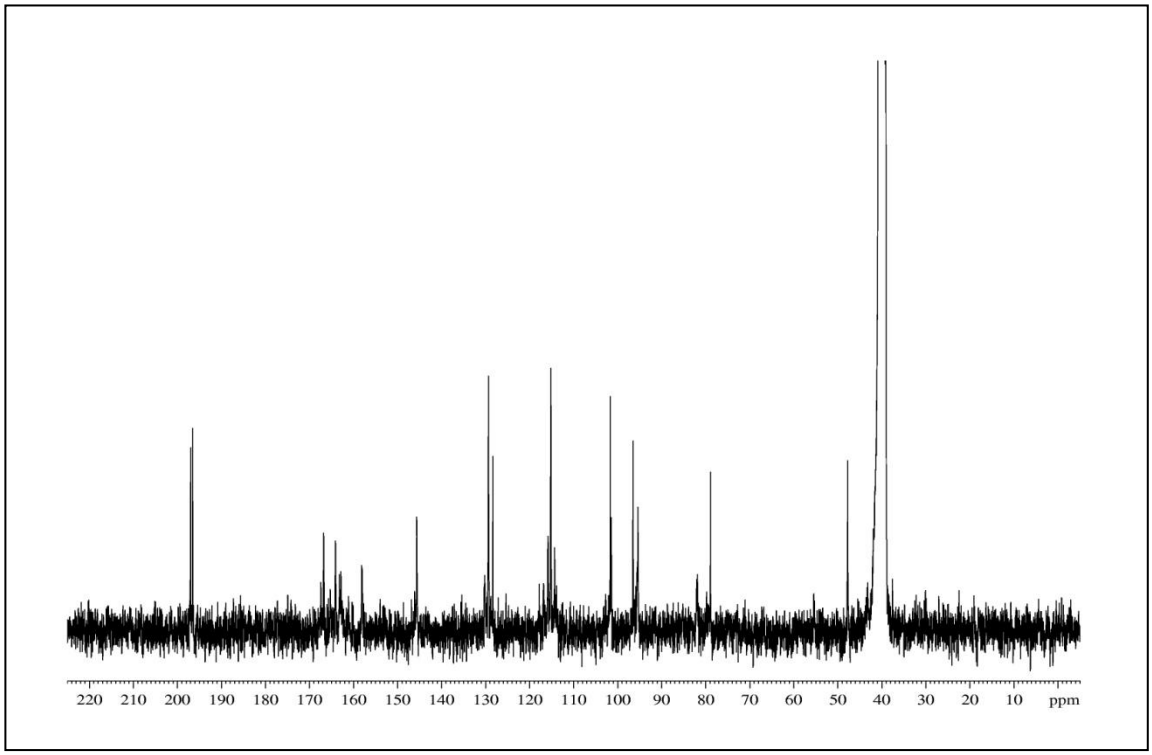

Figure 20 ^{13}C NMR (75 MHz) (DMSO-d_6) spectrum of **AS5**

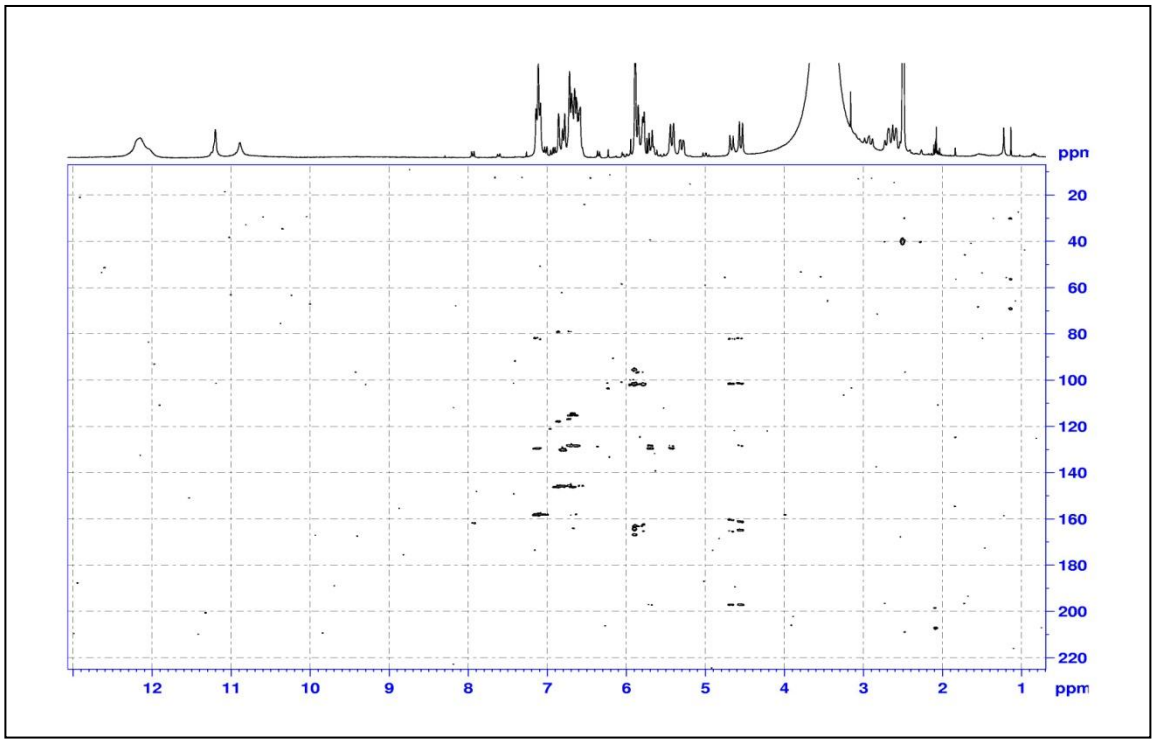

Figure 21 2D HMBC (DMSO-d_6) spectrum of **AS5**

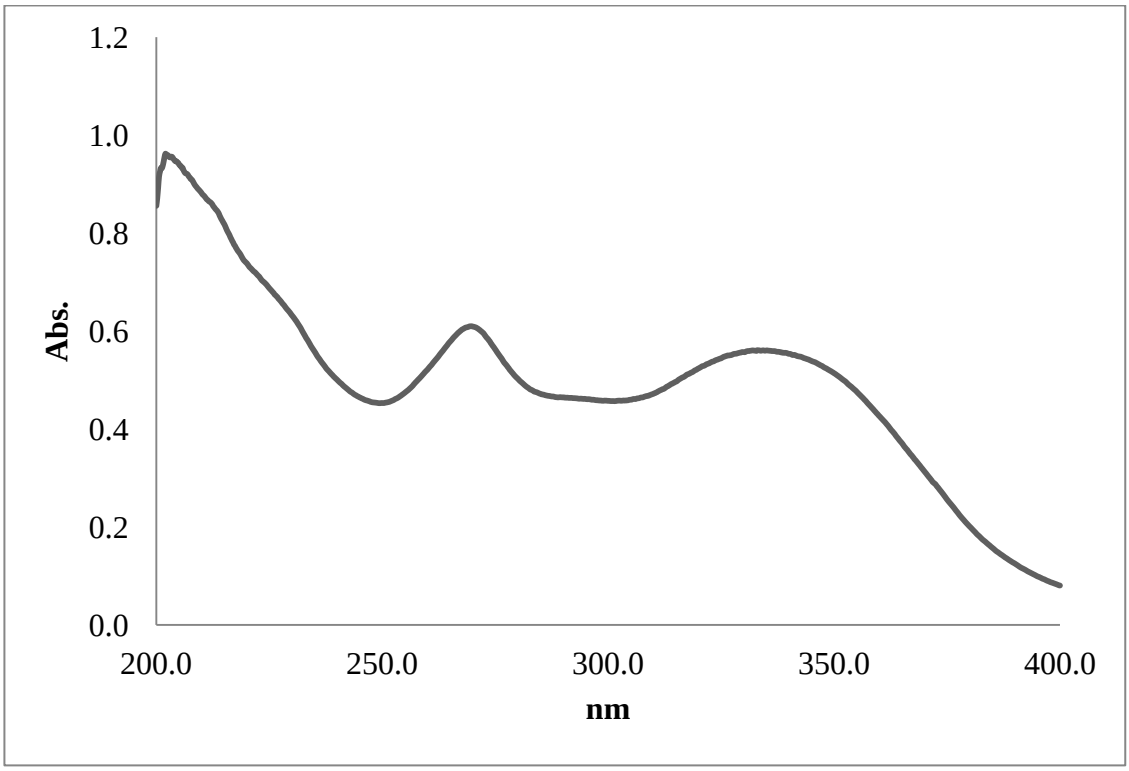

Figure 22 UV (MeOH) spectrum of **AS6**

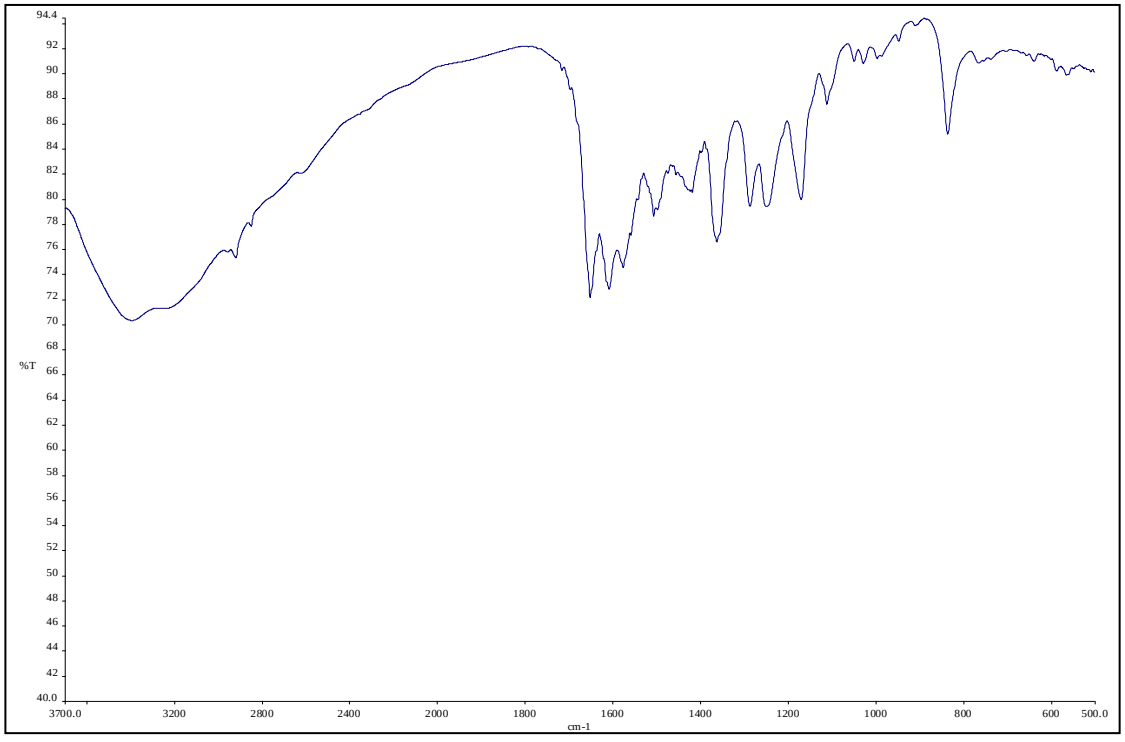

Figure 23 IR (neat) spectrum of **AS6**

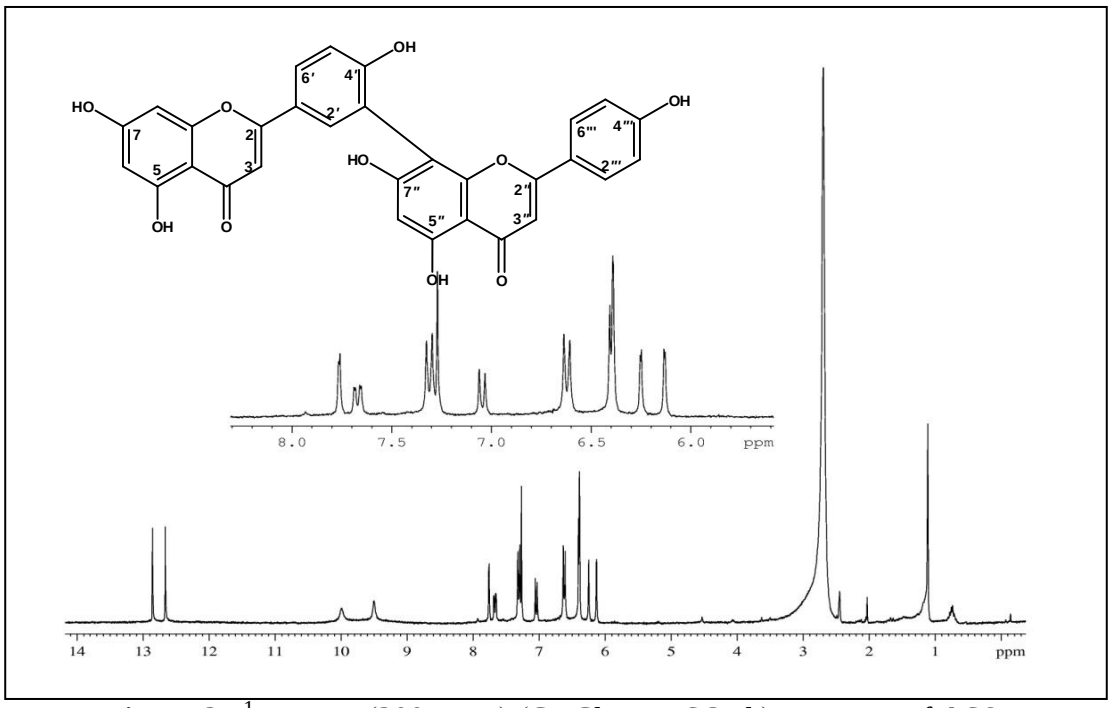

Figure 24 ^{1}H NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS6**

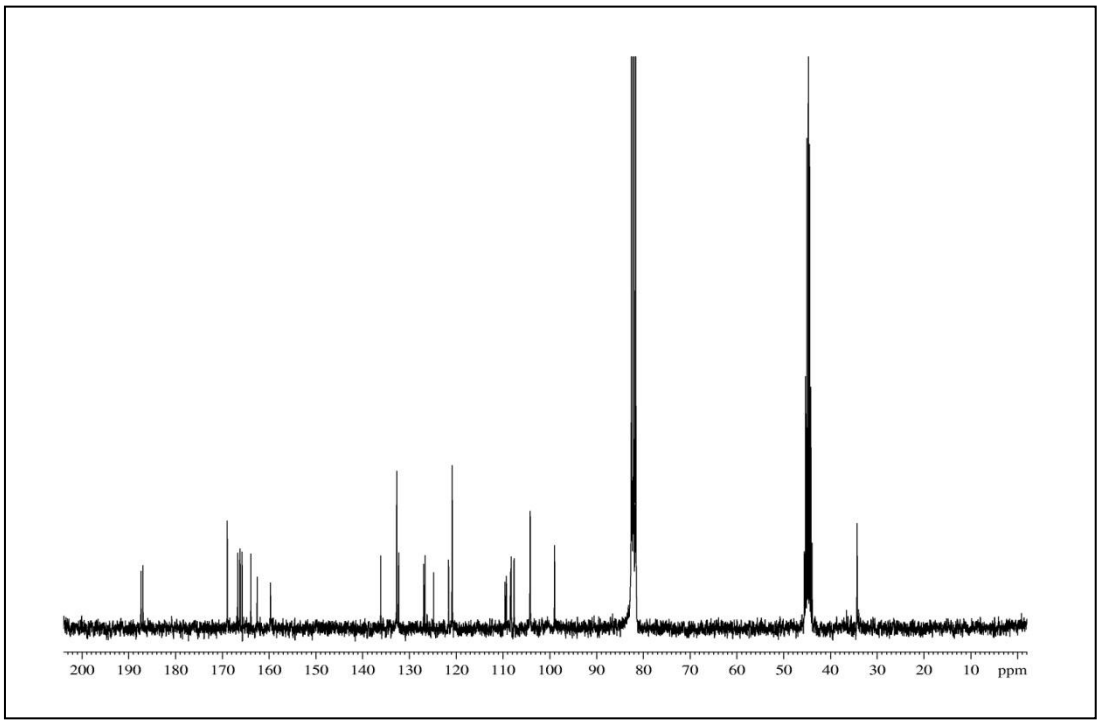

Figure 25 ^{13}C NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS6**

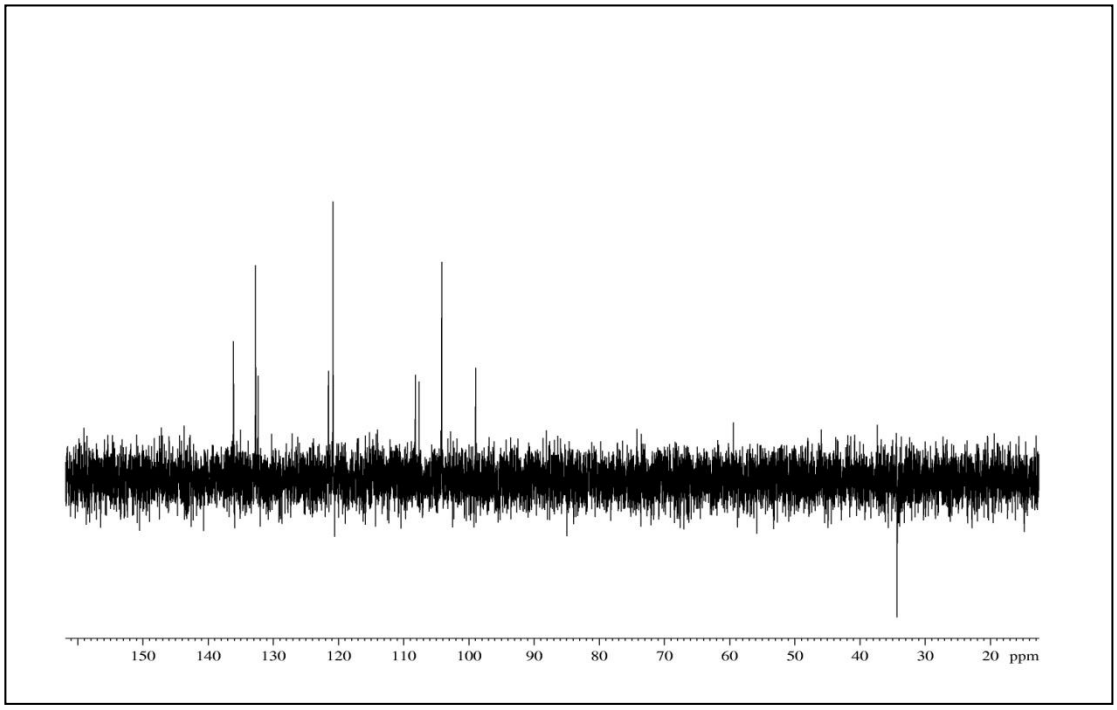

Figure 26 DEPT 135° ($CDCl_3$+DMSO-d_6) spectrum of **AS6**

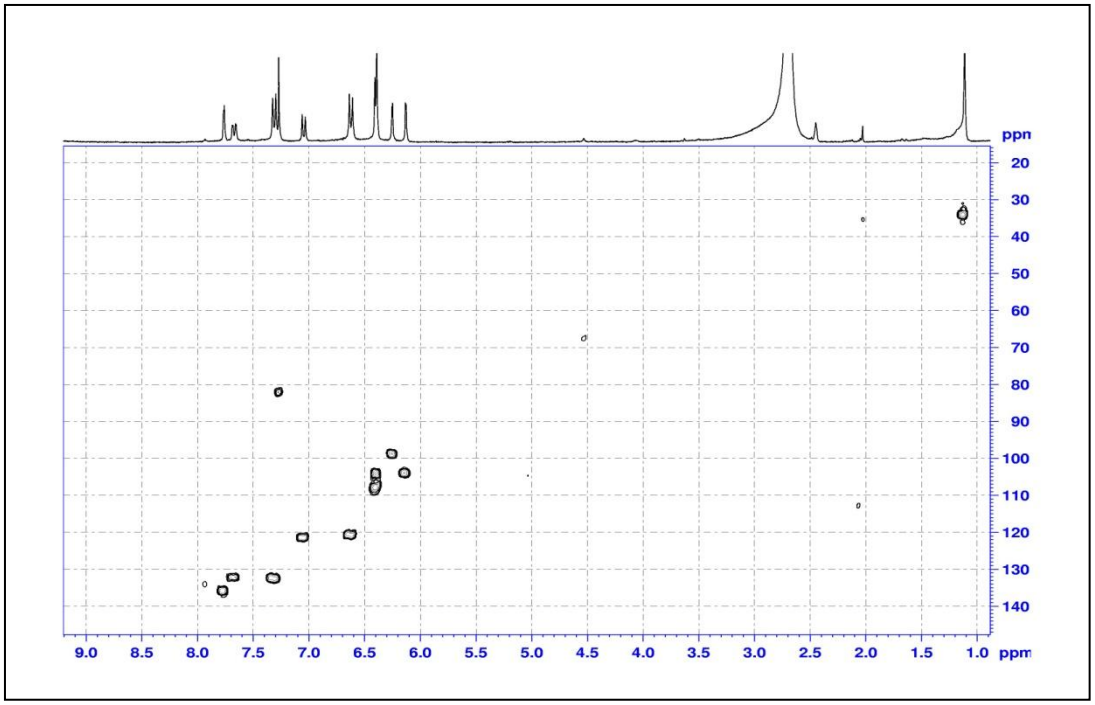

Figure 27 2D HMQC ($CDCl_3$+DMSO-d_6) spectrum of **AS6**

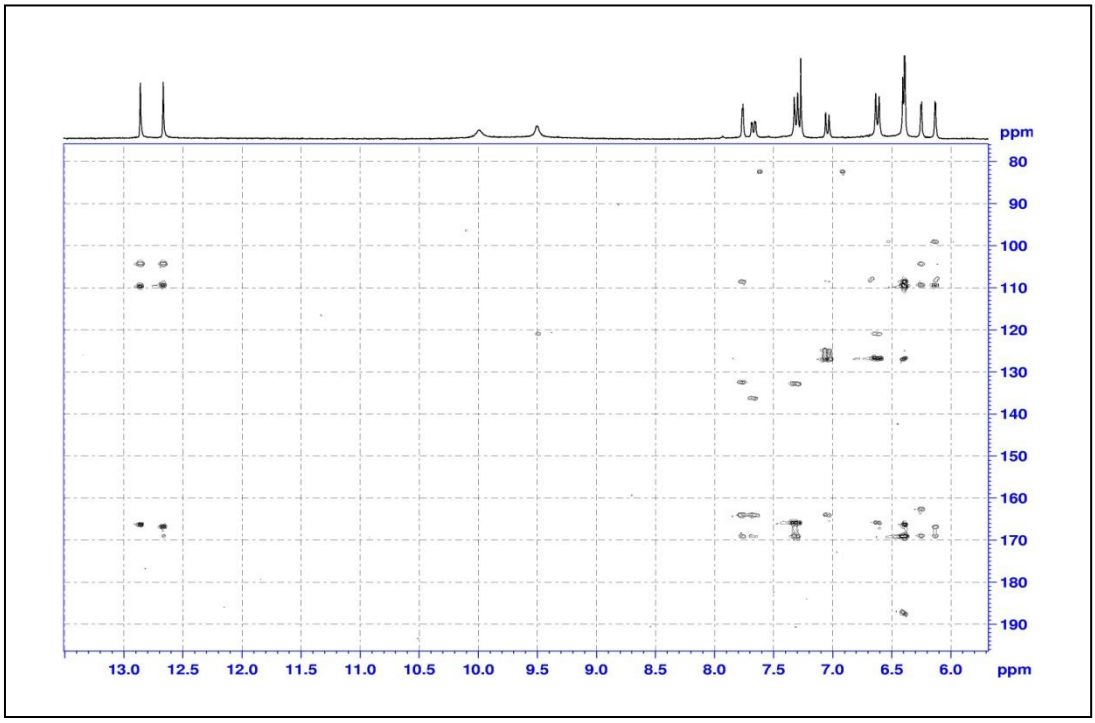

Figure 28 2D HMBC ($CDCl_3$+DMSO-d_6) spectrum of **AS6**

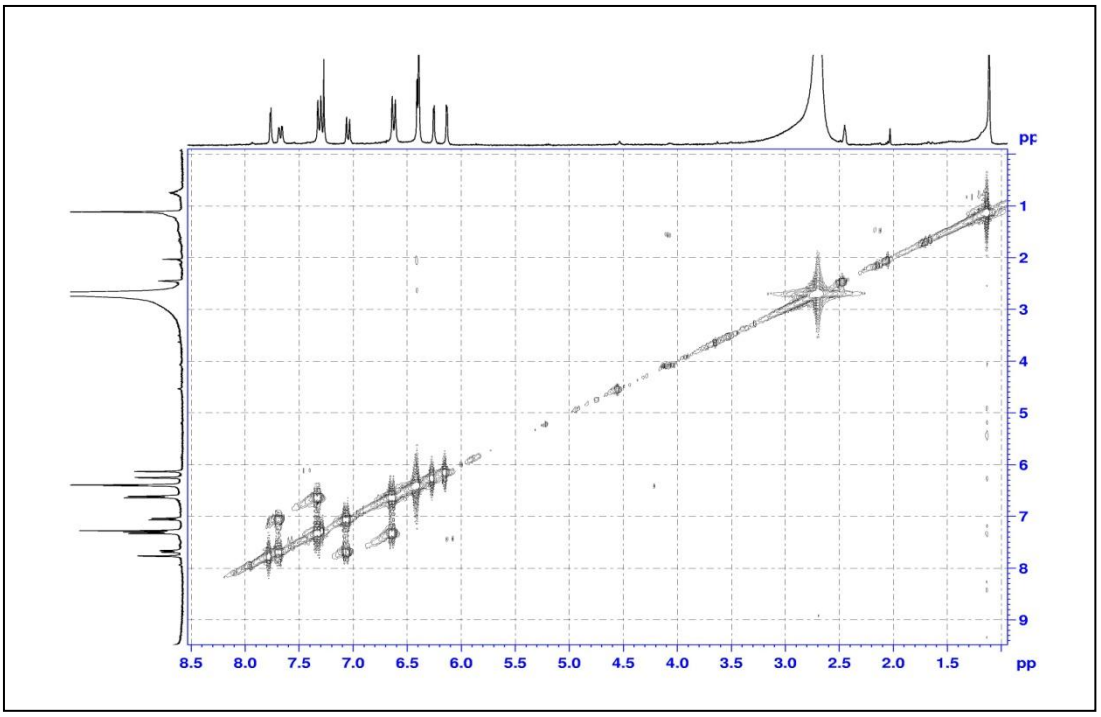

Figure 29 2D COSY ($CDCl_3$+DMSO-d_6) spectrum of **AS6**

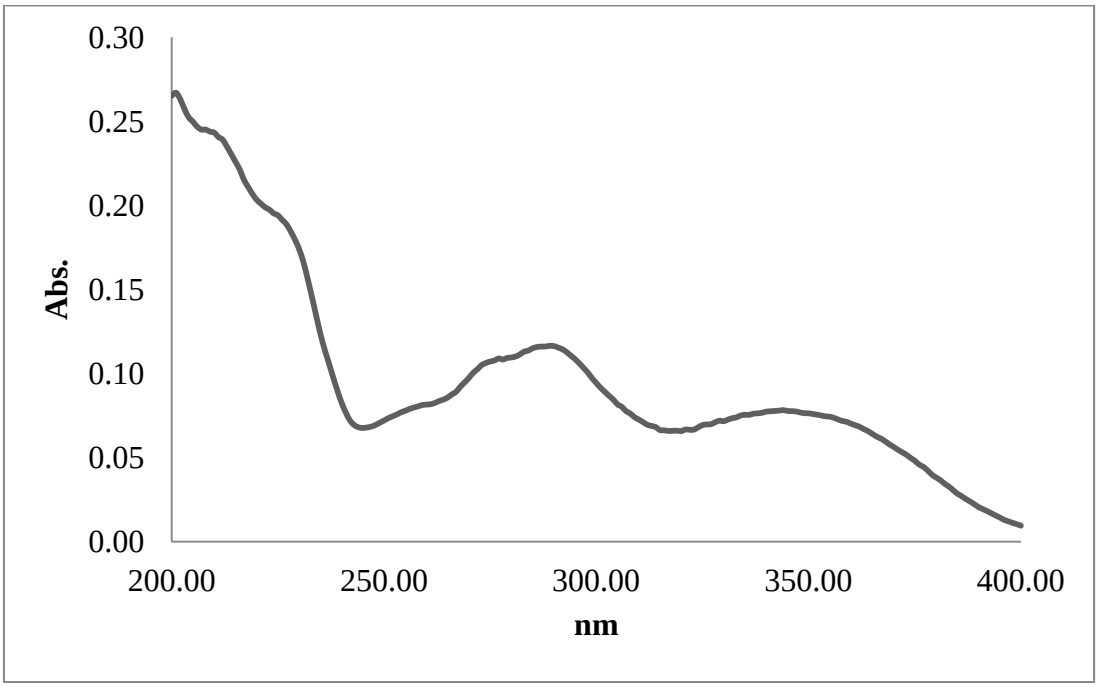

Figure 30 UV (MeOH) spectrum of **AS7**

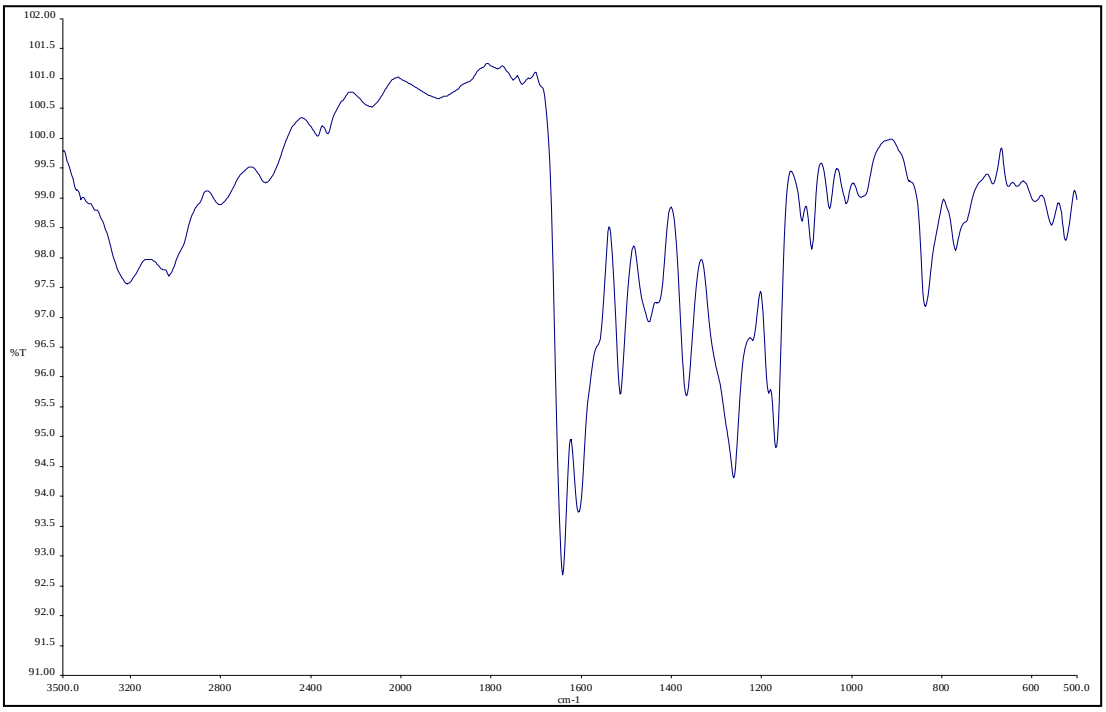

Figure 31 IR (neat) spectrum of **AS7**

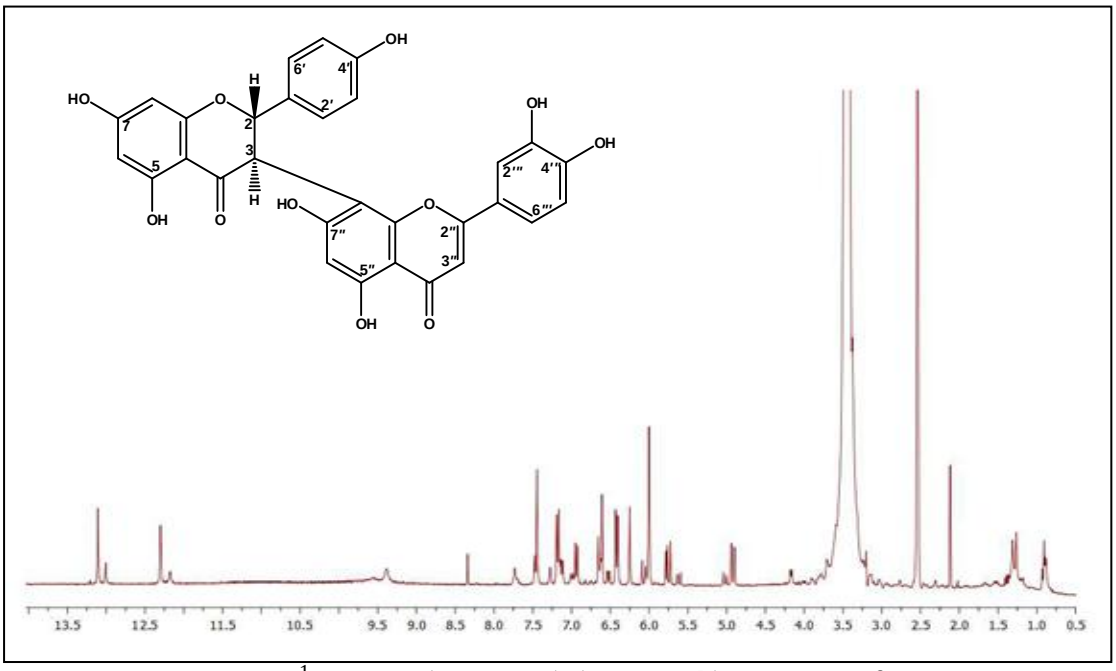

Figure 32 ^{1}H NMR (300 MHz) (DMSO-d_6) spectrum of **AS7**

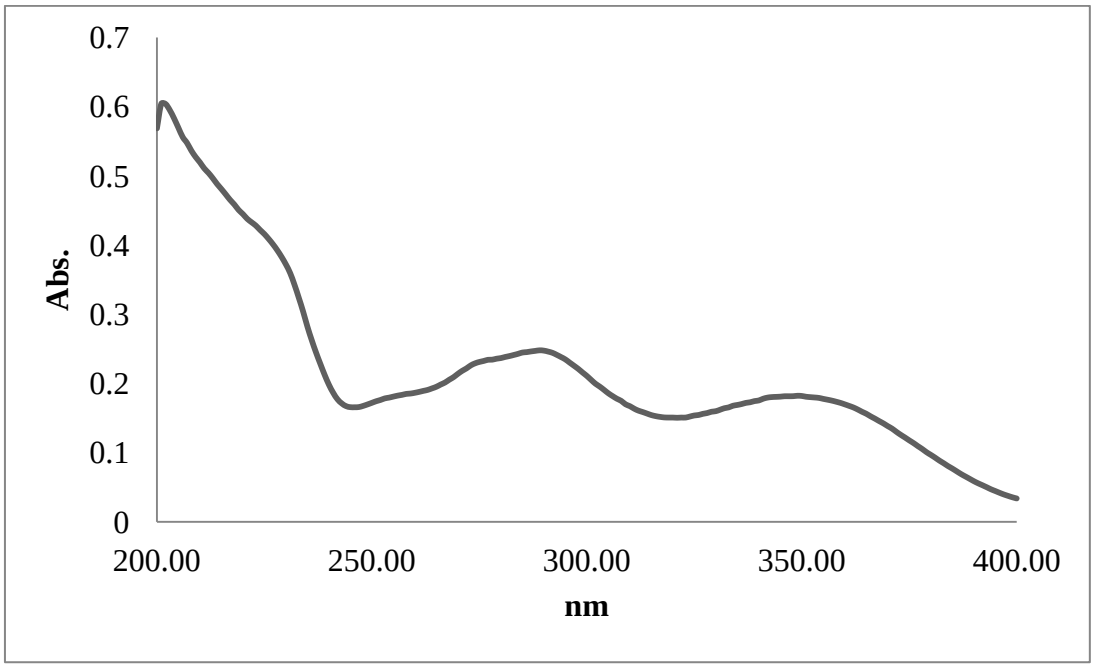

Figure 33 UV (MeOH) spectrum of **AS8**

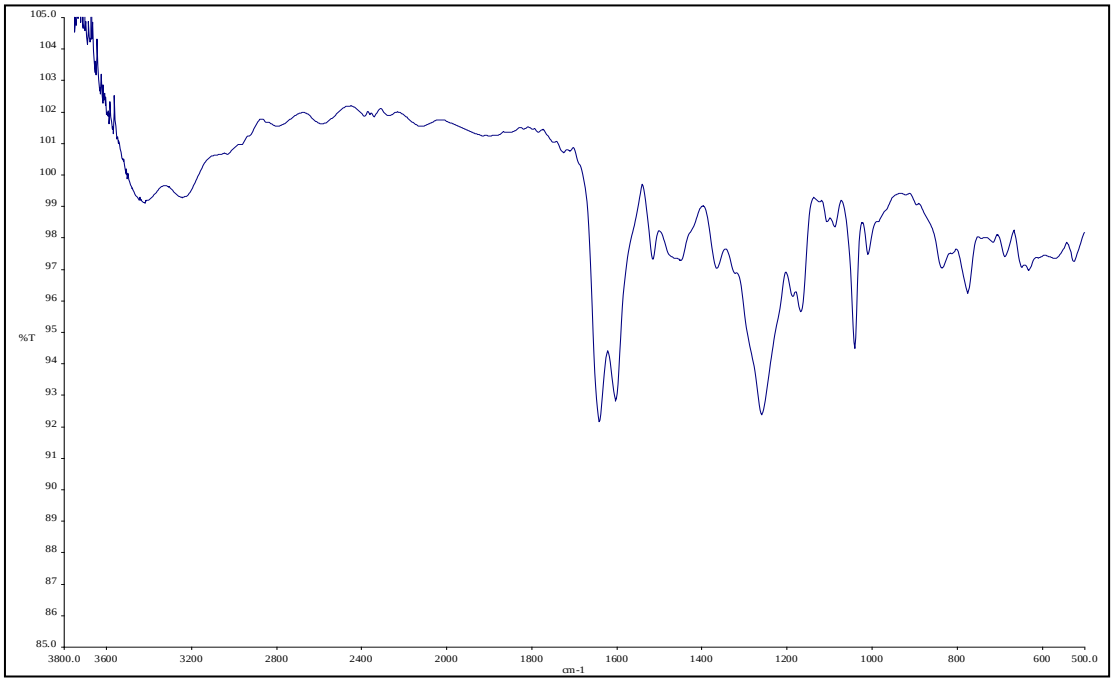

Figure 34 IR (neat) spectrum of **AS8**

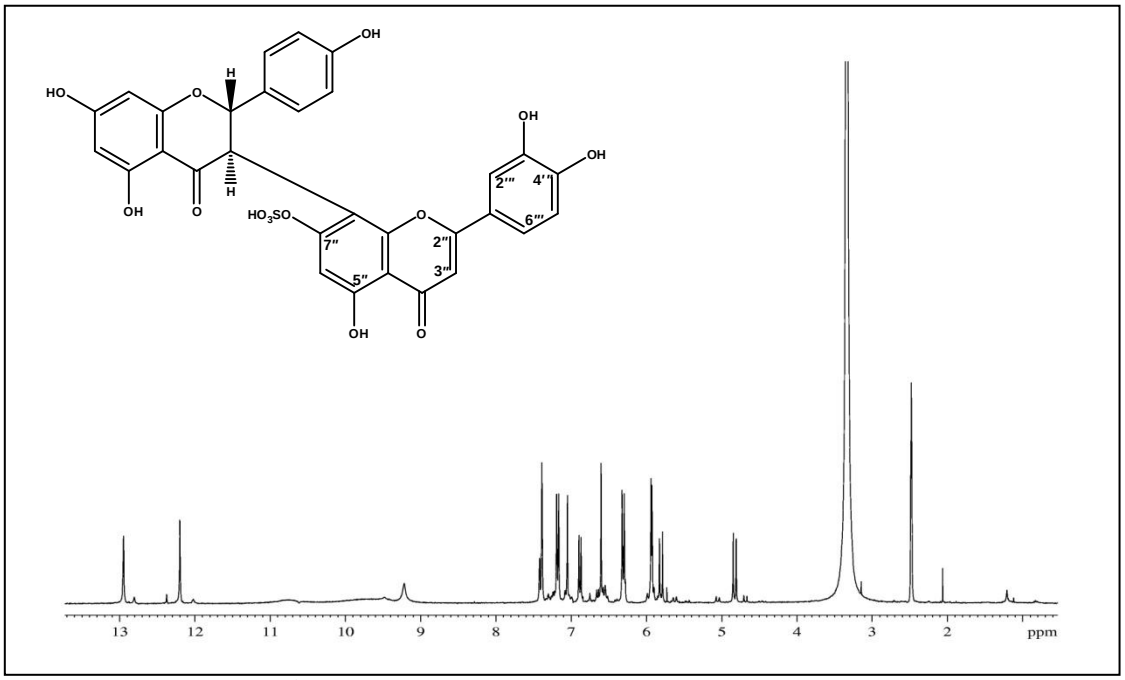

Figure 35 ^{1}H NMR (300 MHz) (DMSO-d_6) spectrum of **AS8**

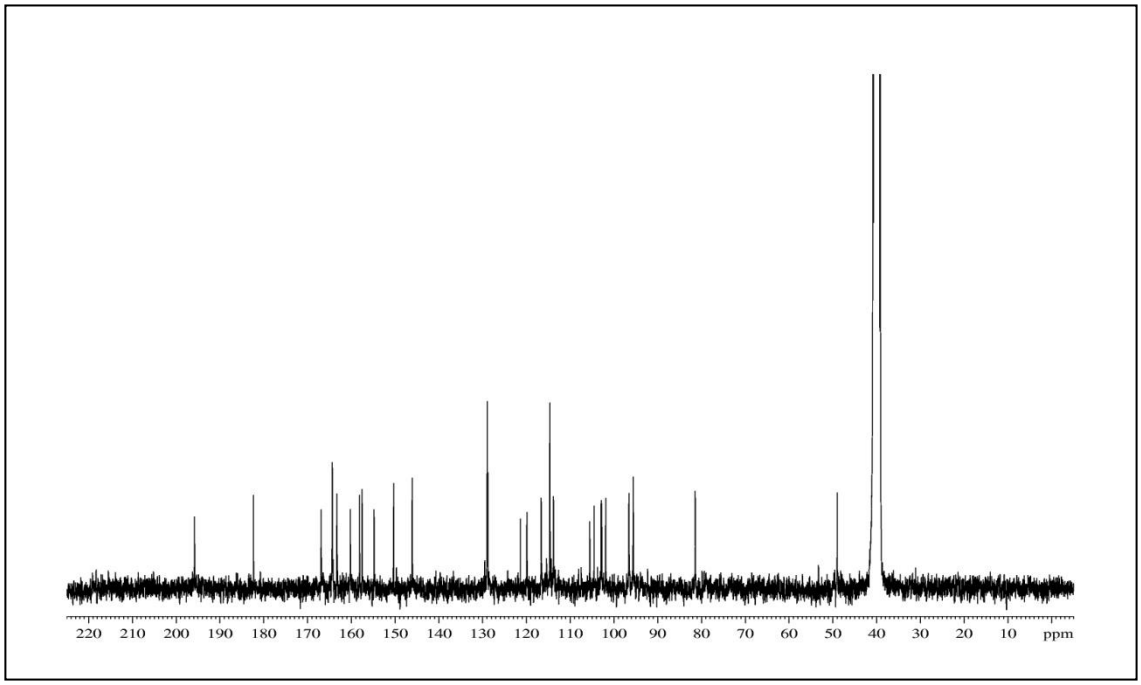

Figure 36 ^{13}C NMR (75 MHz) (DMSO-d_6) spectrum of **AS8**

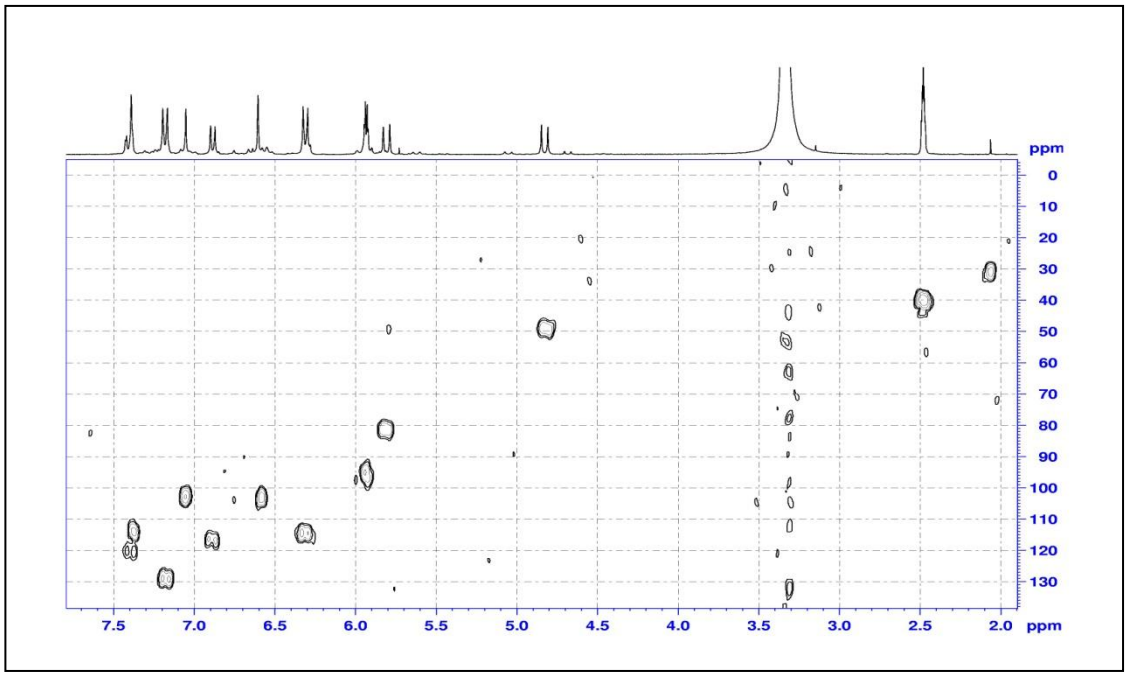

Figure 37 2D HMQC (DMSO-d_6) spectrum of **AS8**

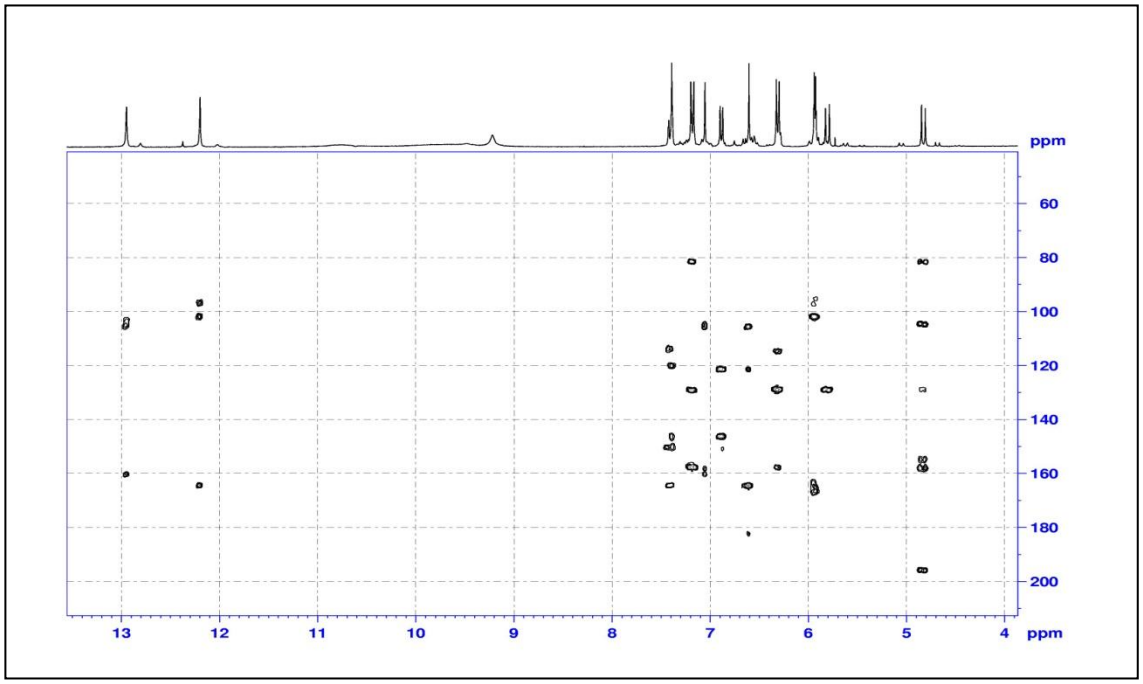

Figure 38 2D HMBC (DMSO-d_6) spectrum of **AS8**

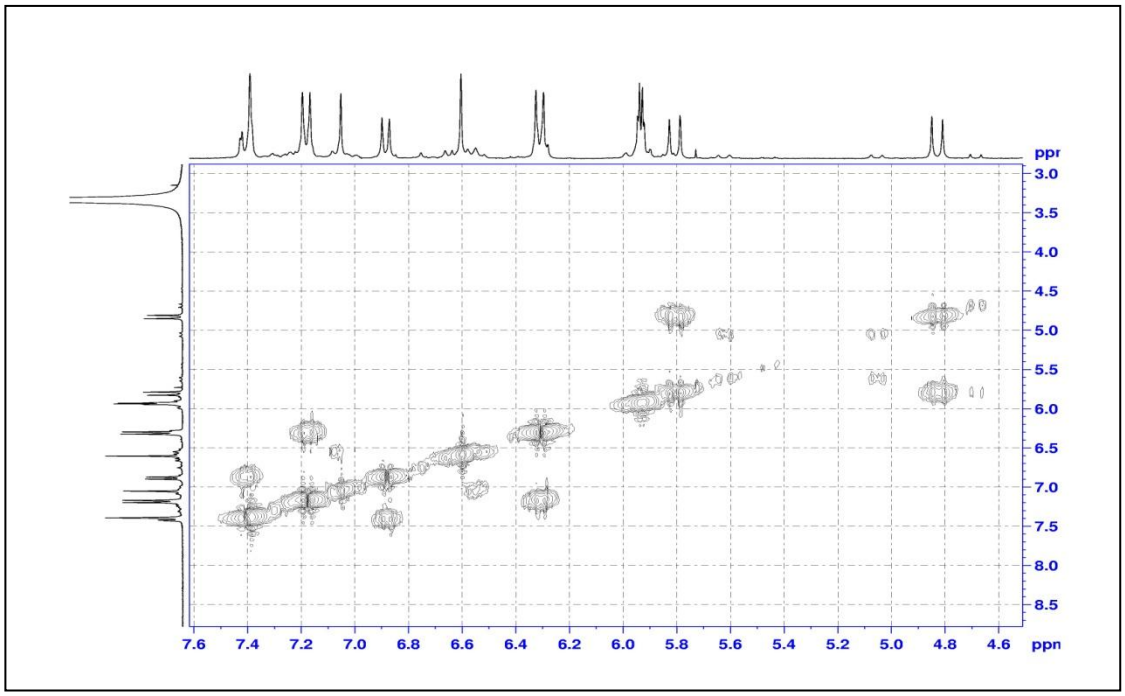

Figure 39 2D COSY (DMSO-d_6) spectrum of **AS8**

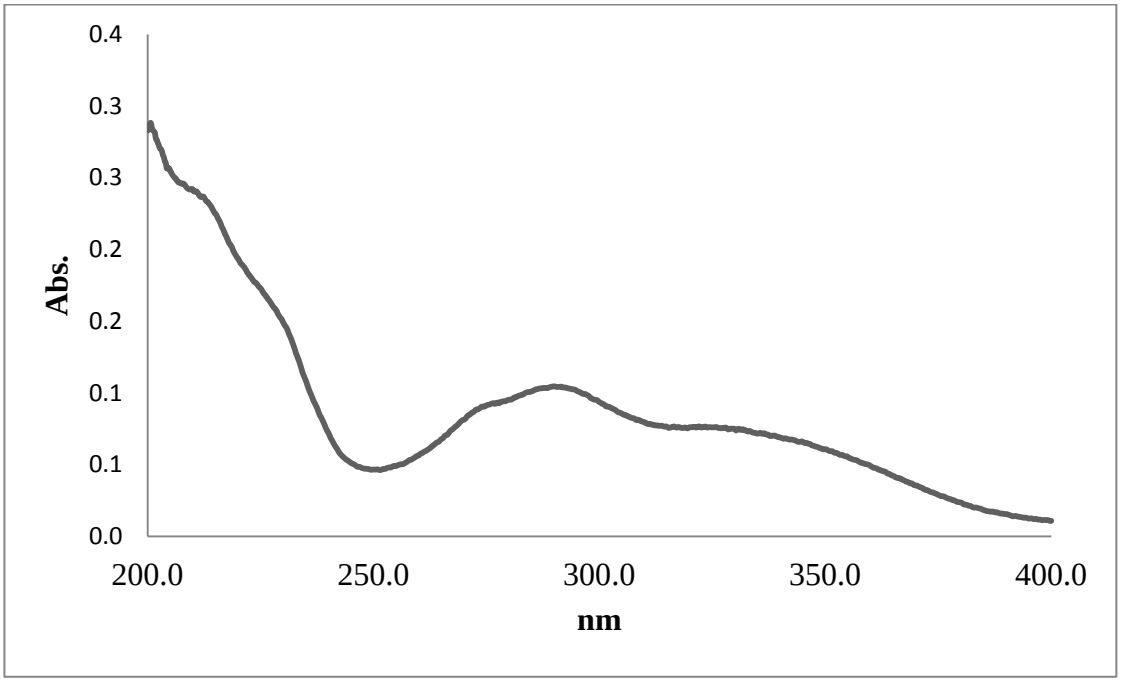

Figure 40 UV (MeOH) spectrum of **AS9**

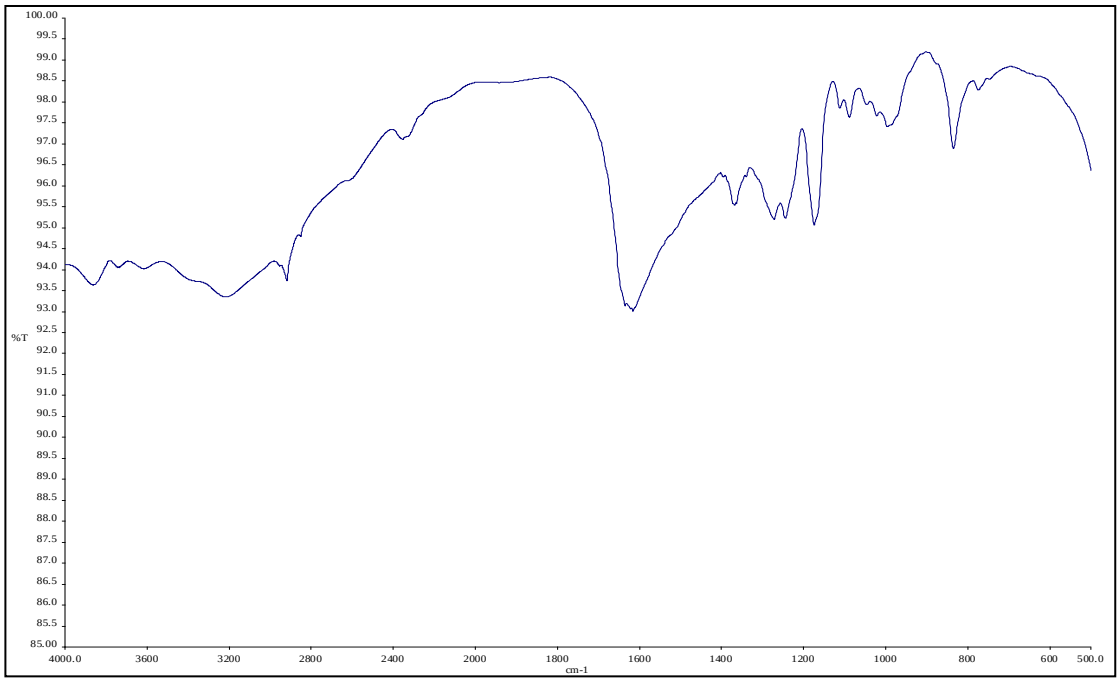

Figure 41 IR (neat) spectrum of **AS9**

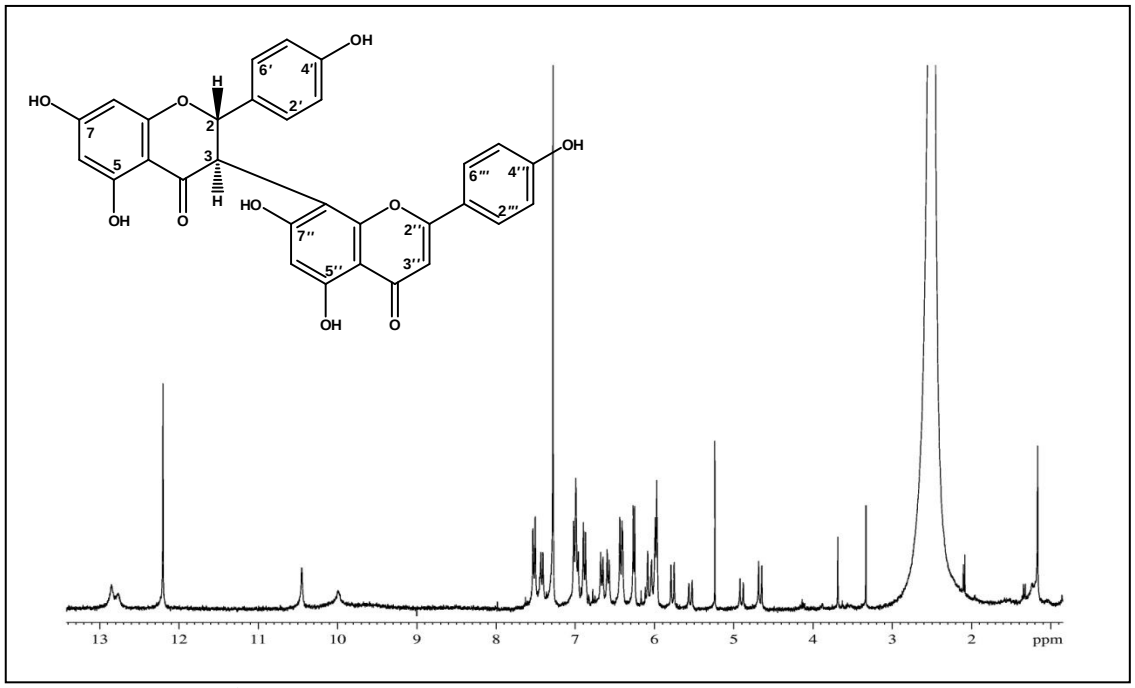

Figure 42 ^{1}H NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS9**

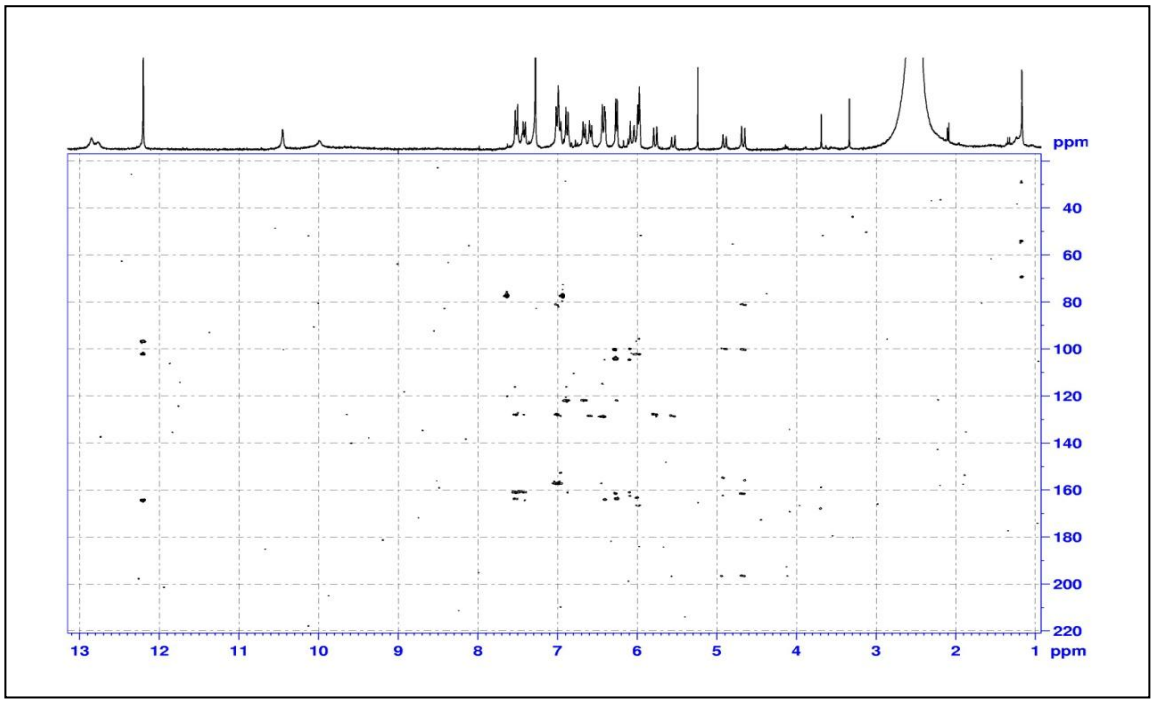

Figure 43 2D HMBC ($CDCl_3$+DMSO-d_6) spectrum of **AS9**

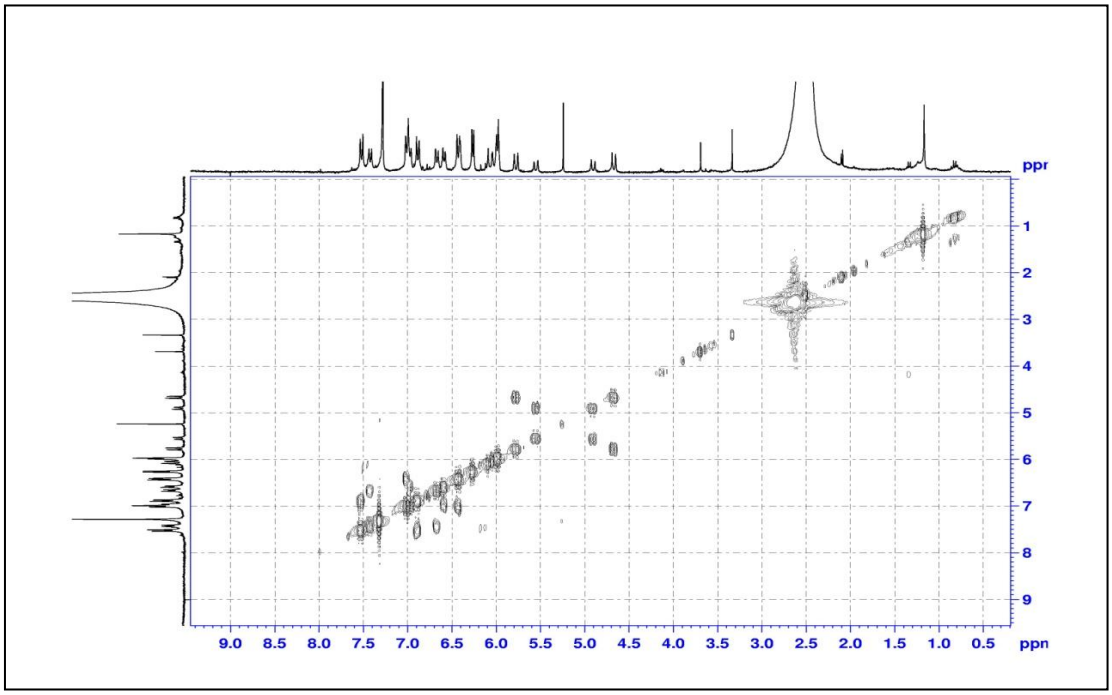

Figure 44 2D COSY ($CDCl_3$+DMSO-d_6) spectrum of **AS9**

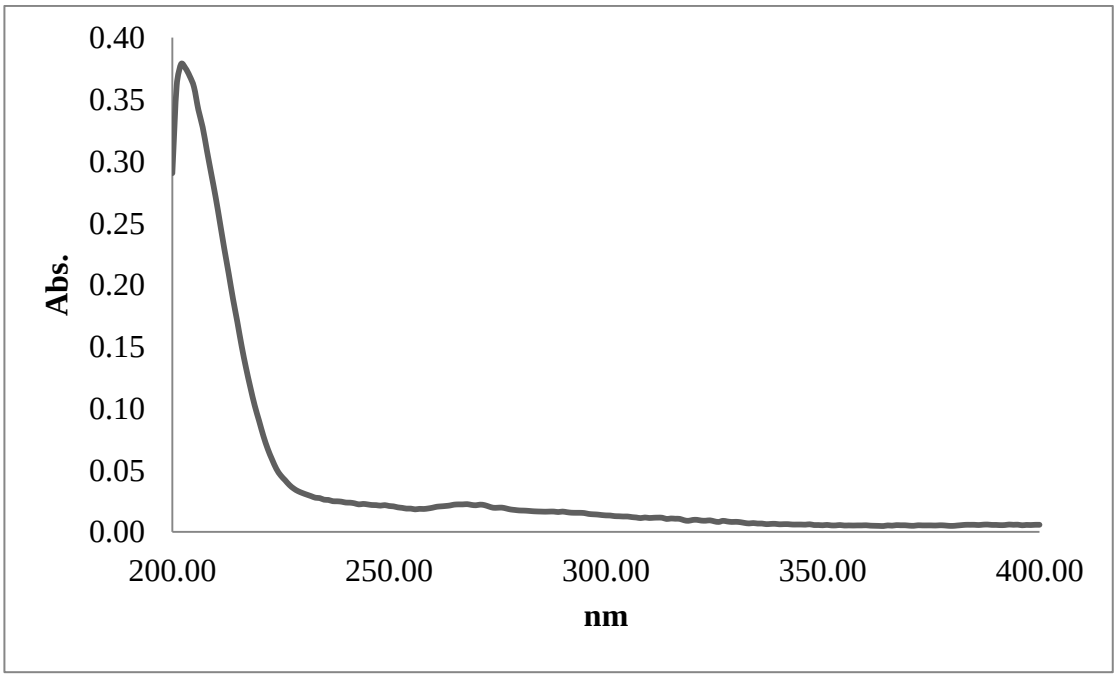

Figure 45 UV (MeOH) spectrum of **AS10**

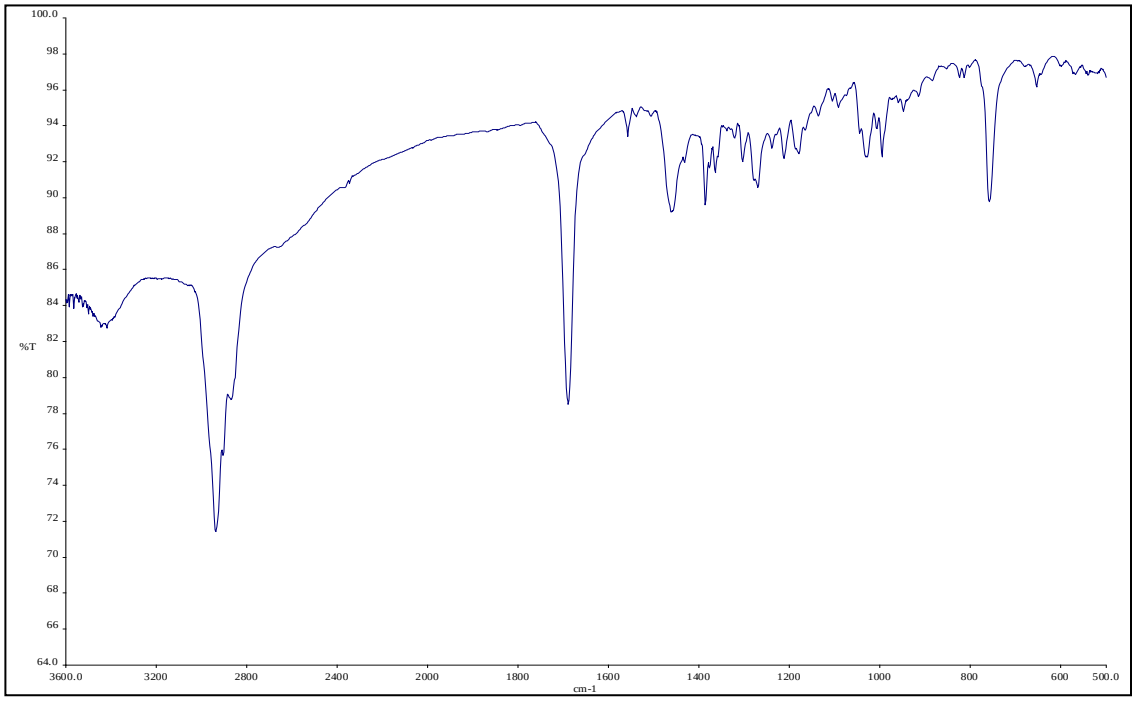

Figure 46 IR (neat) spectrum of **AS10**

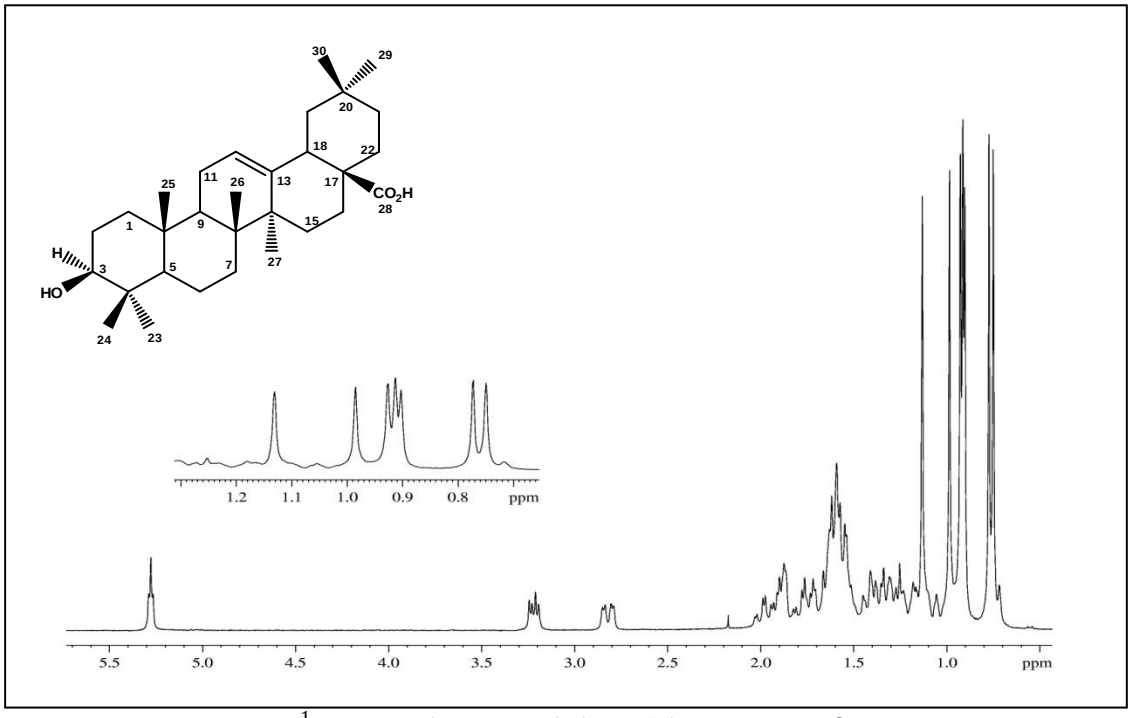

Figure 47 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of **AS10**

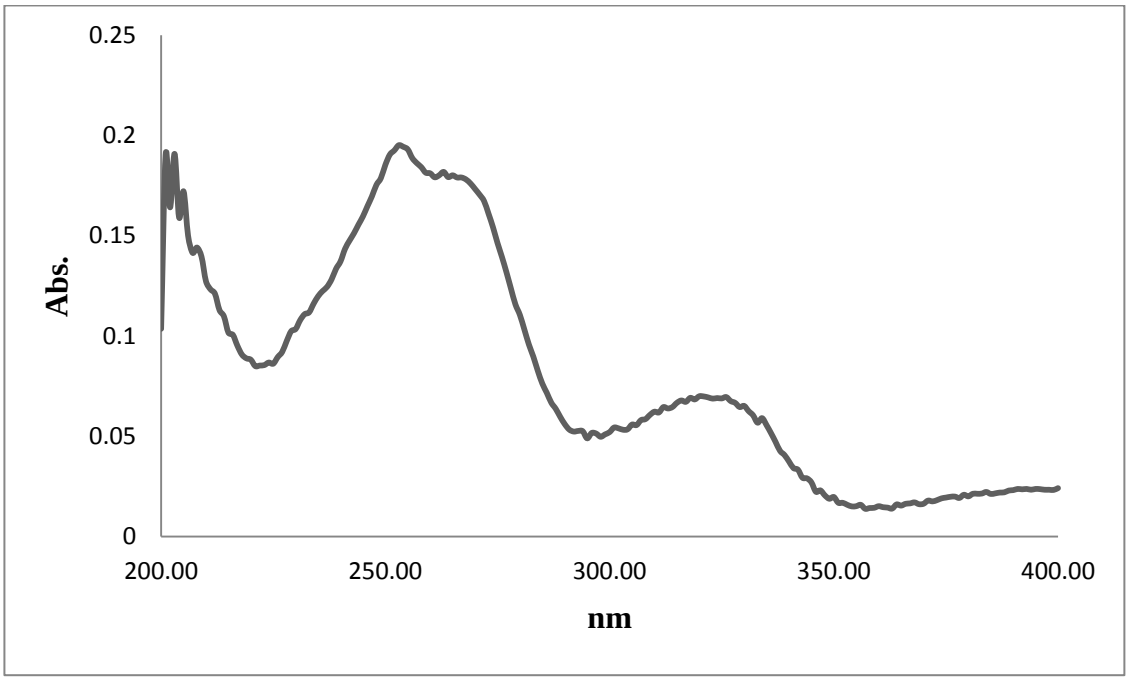

Figure 48 UV (EtOH) spectrum of **AS11**

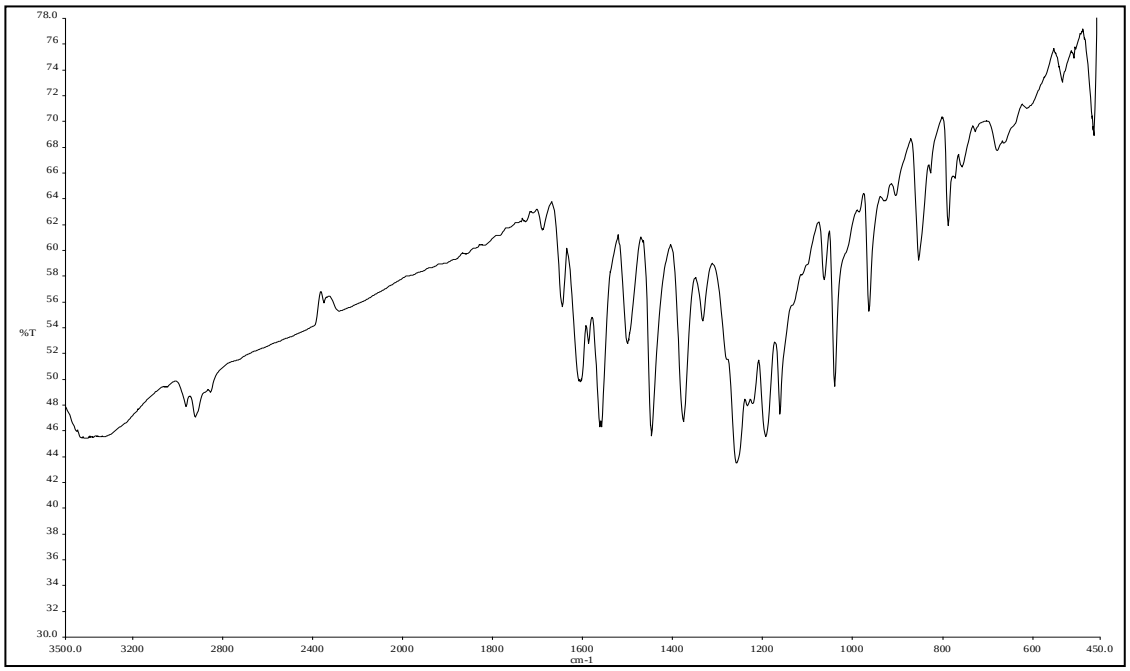

Figure 49 IR (neat) spectrum of **AS11**

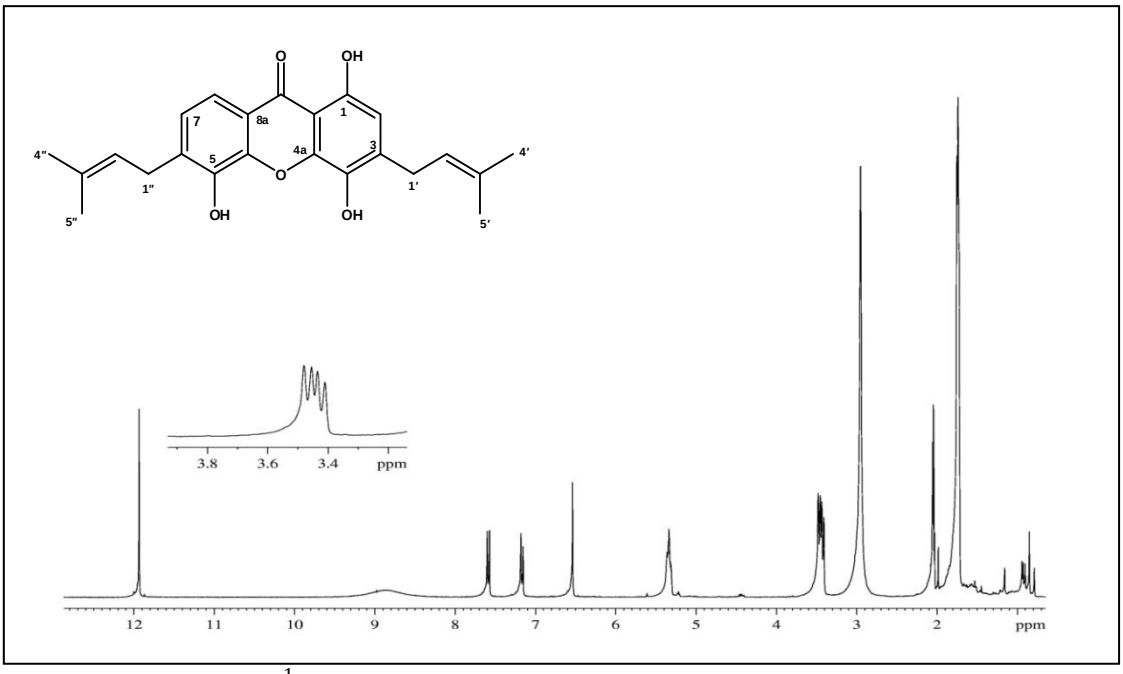

Figure 50 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS11**

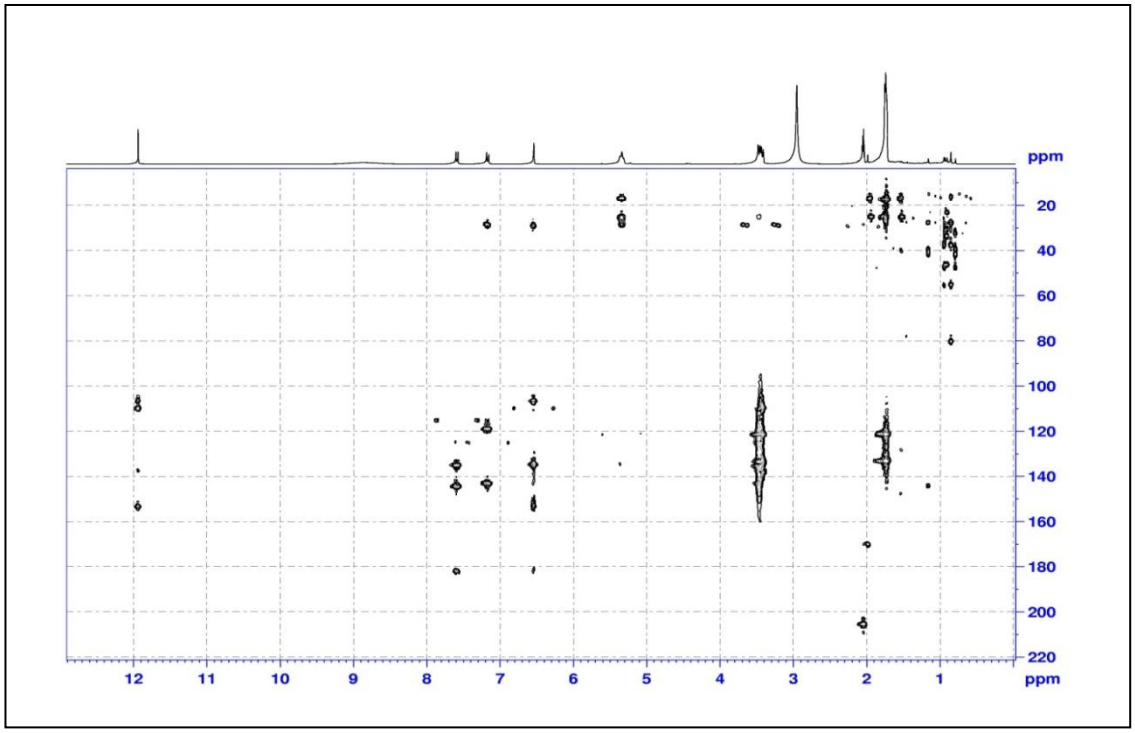

Figure 51 2D HMBC (Acetone-d_6) spectrum of **AS11**

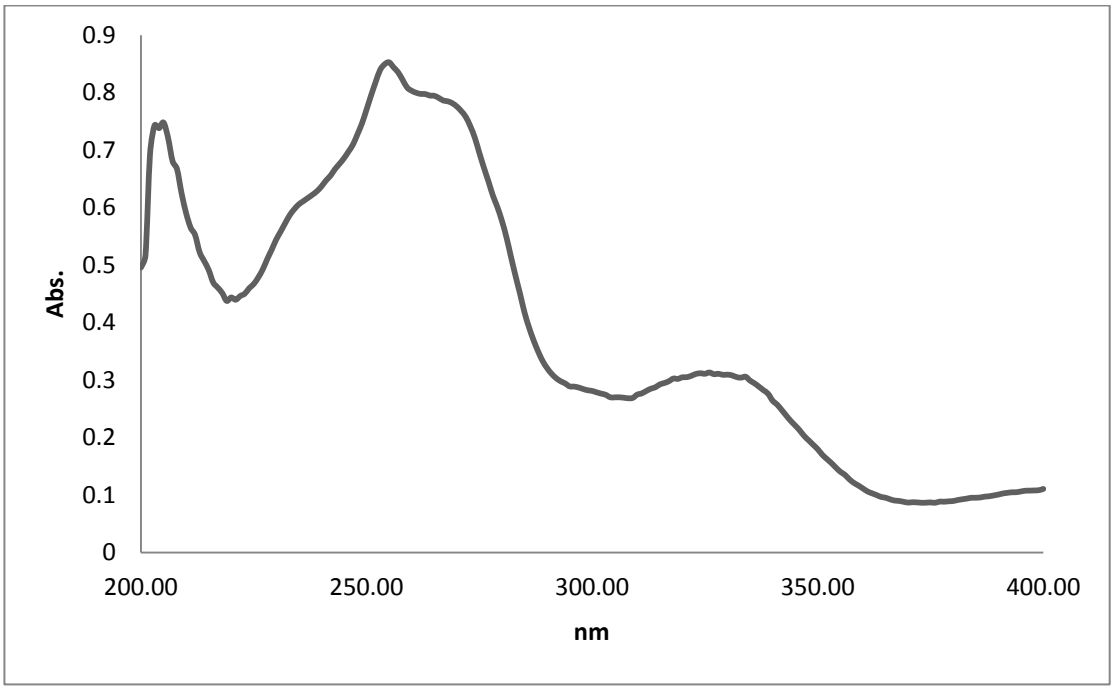

Figure 52 UV (EtOH) spectrum of **AS12**

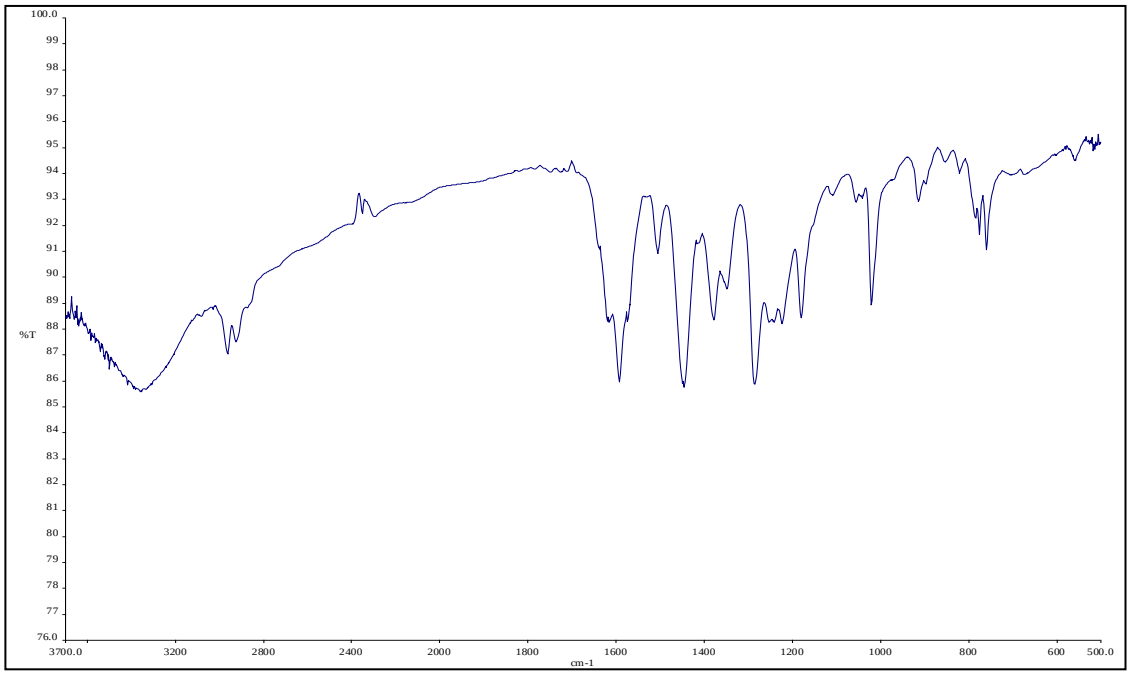

Figure 53 IR (neat) spectrum of **AS12**

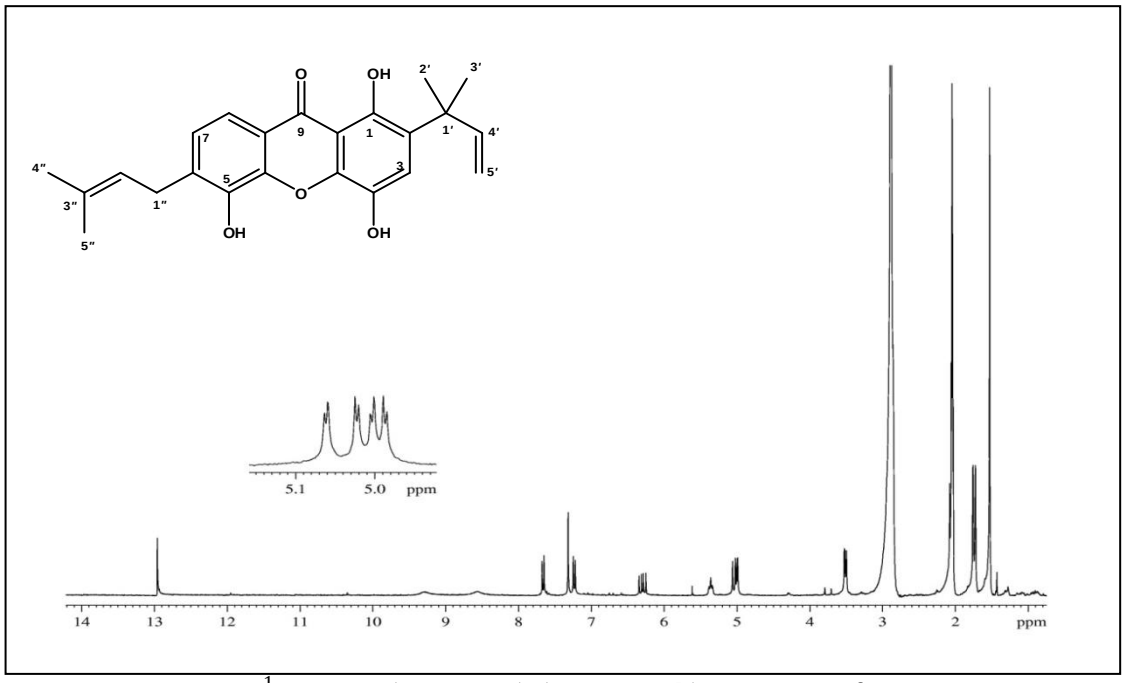

Figure 54 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS12**

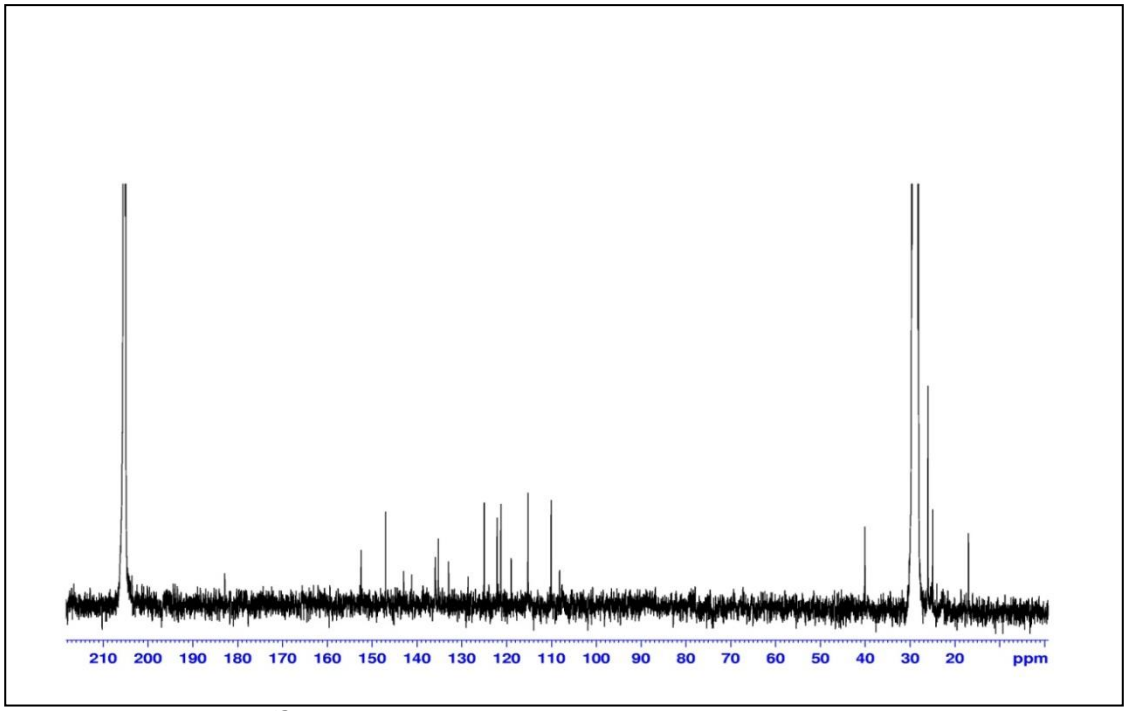

Figure 55 ^{13}C NMR (75 MHz) (Acetone-d_6) spectrum of **AS12**

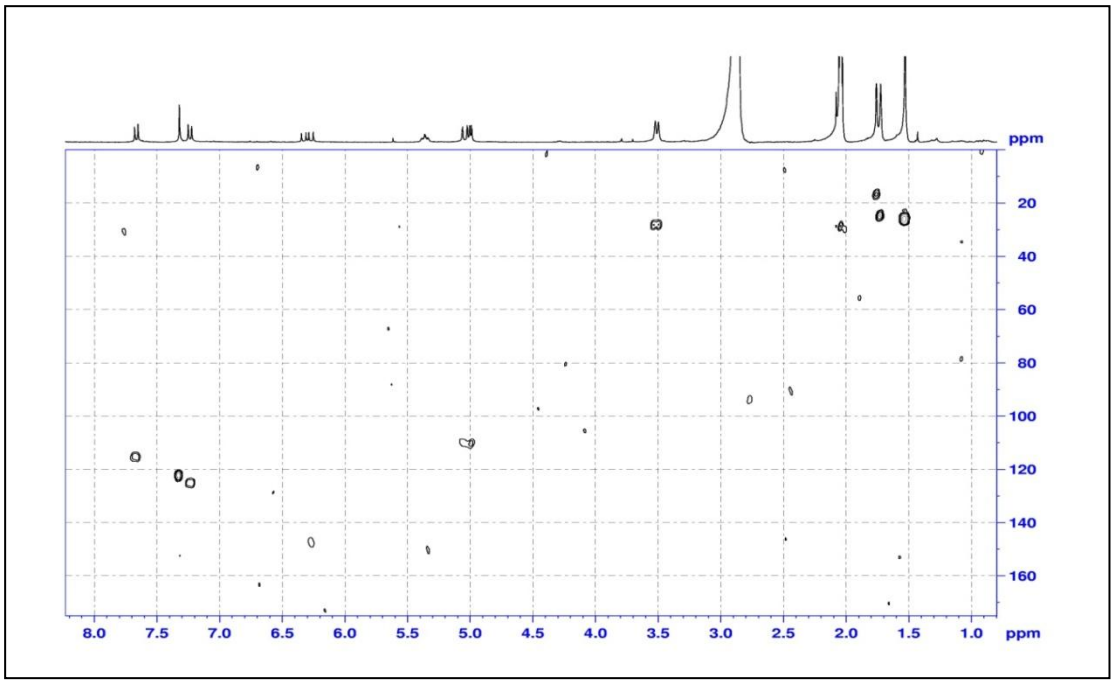

Figure 56 2D HMQC (300 MHz) (Acetone-d_6) spectrum of **AS12**

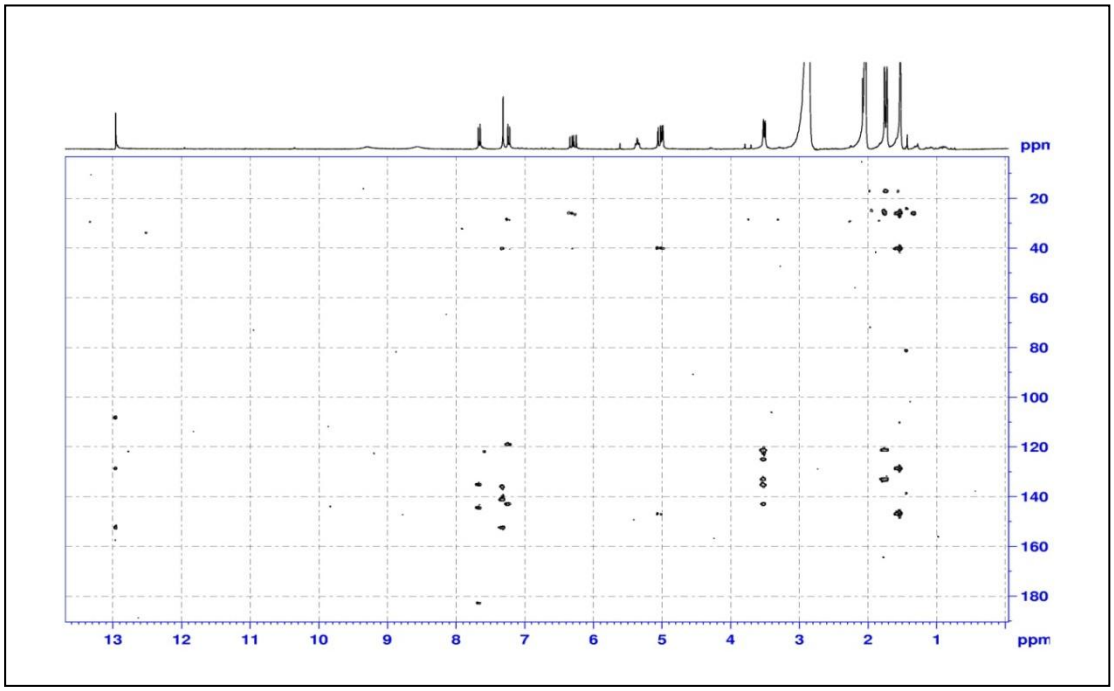

Figure 57 2D HMBC (Acetone-d_6) spectrum of **AS12**

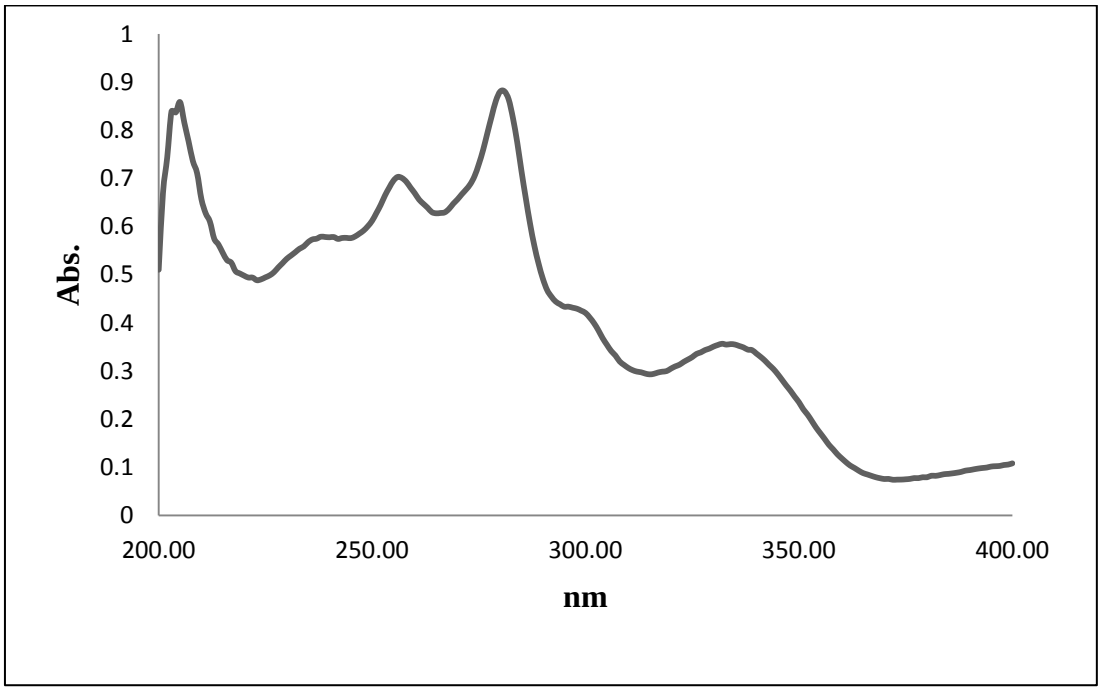

Figure 58 UV (EtOH) spectrum of **AS13**

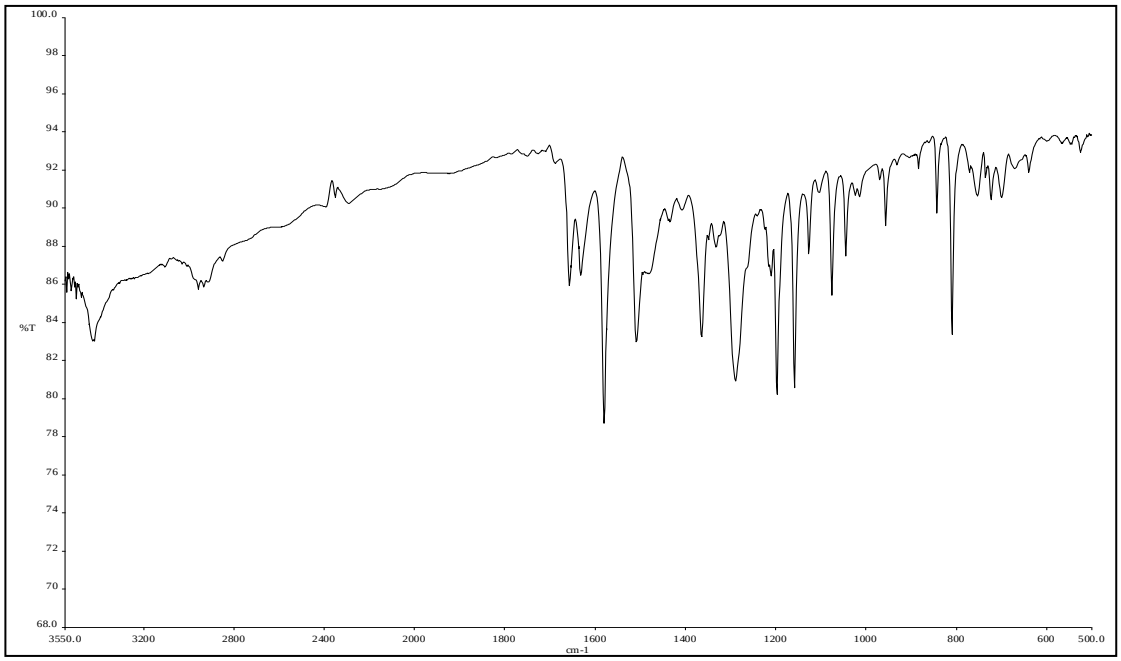

Figure 59 IR (neat) spectrum of **AS13**

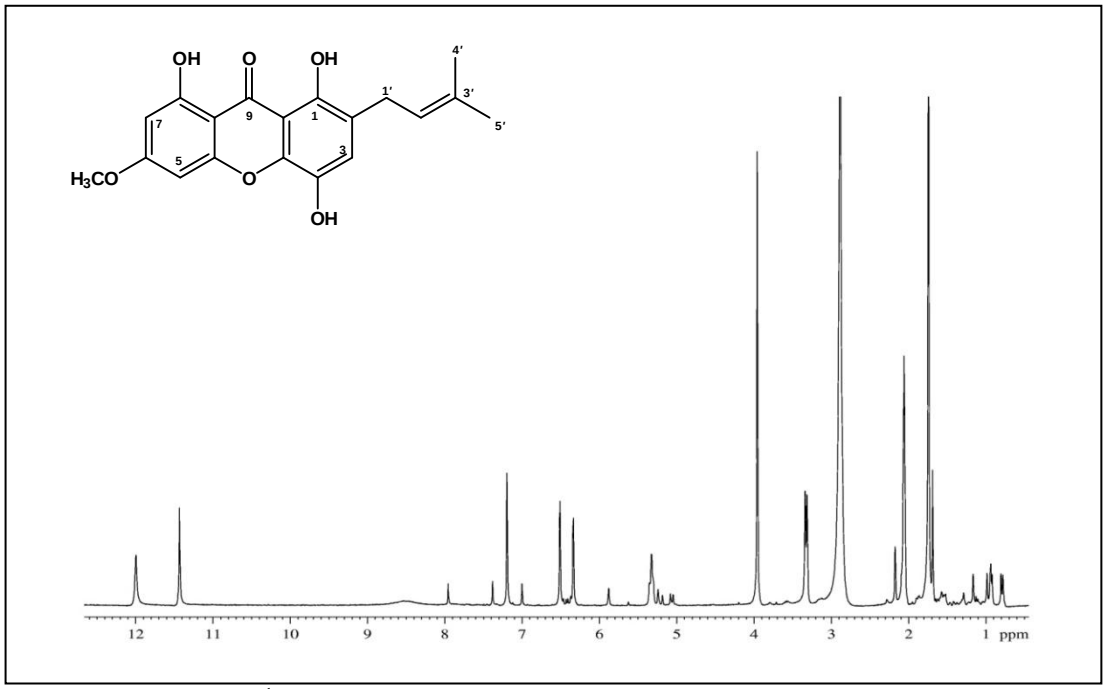

Figure 60 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS13**

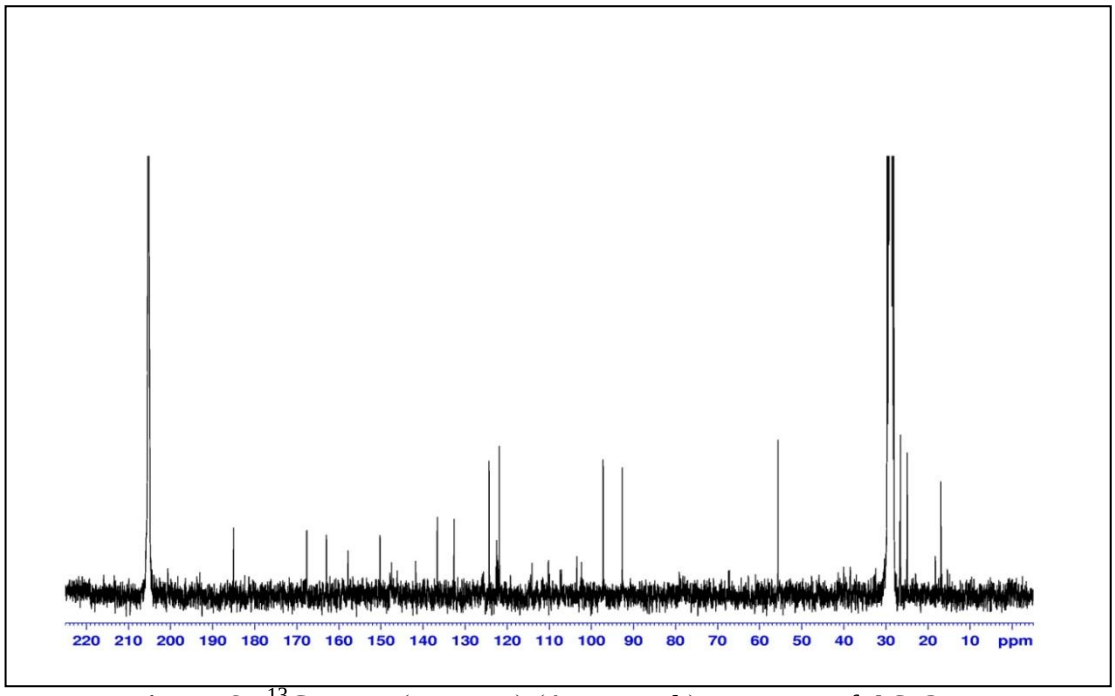

Figure 61 ^{13}C NMR (75 MHz) (Acetone-d_6) spectrum of **AS13**

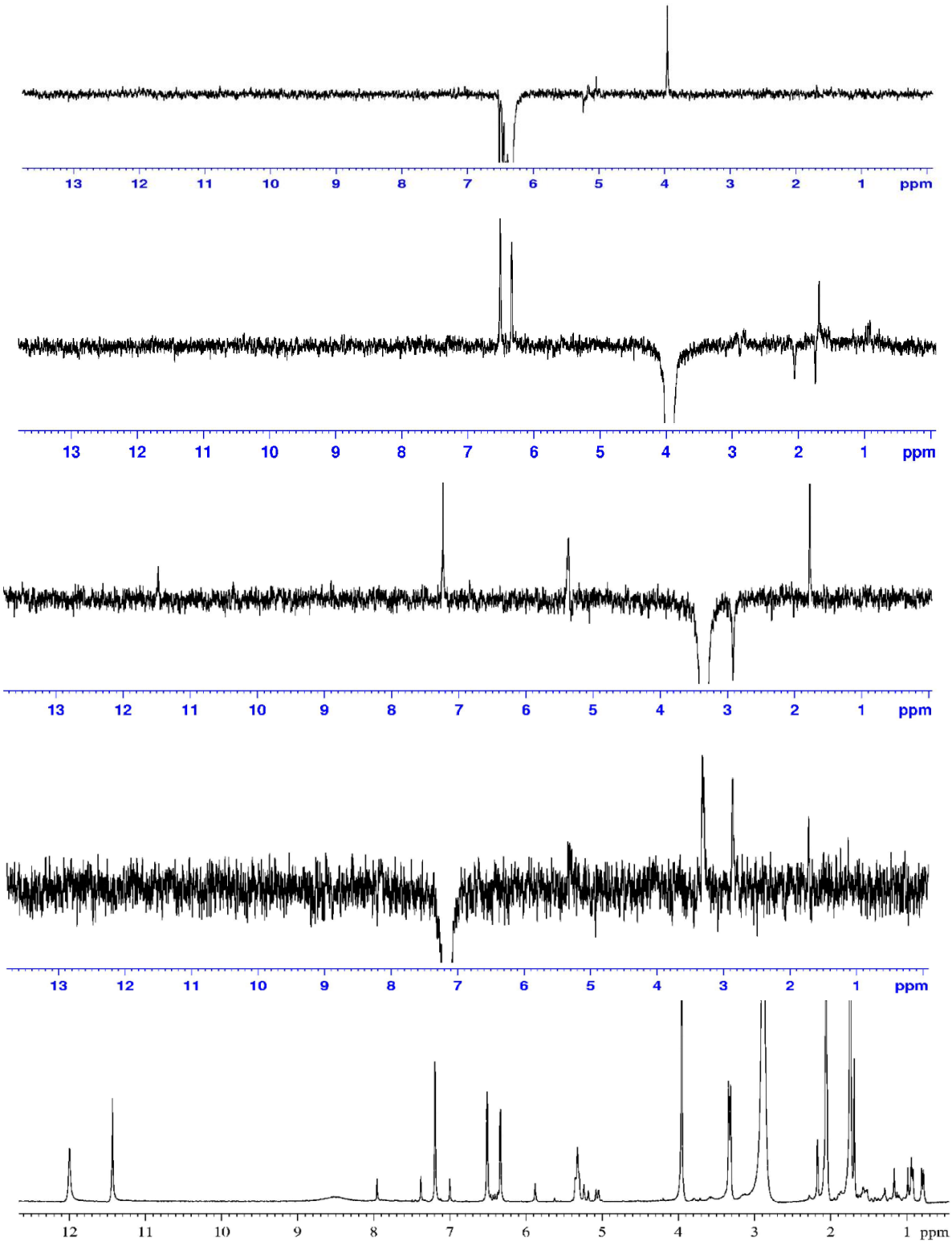

Figure 62 NOE (300 MHz) (Acetone-d_6) spectrum of **AS13**

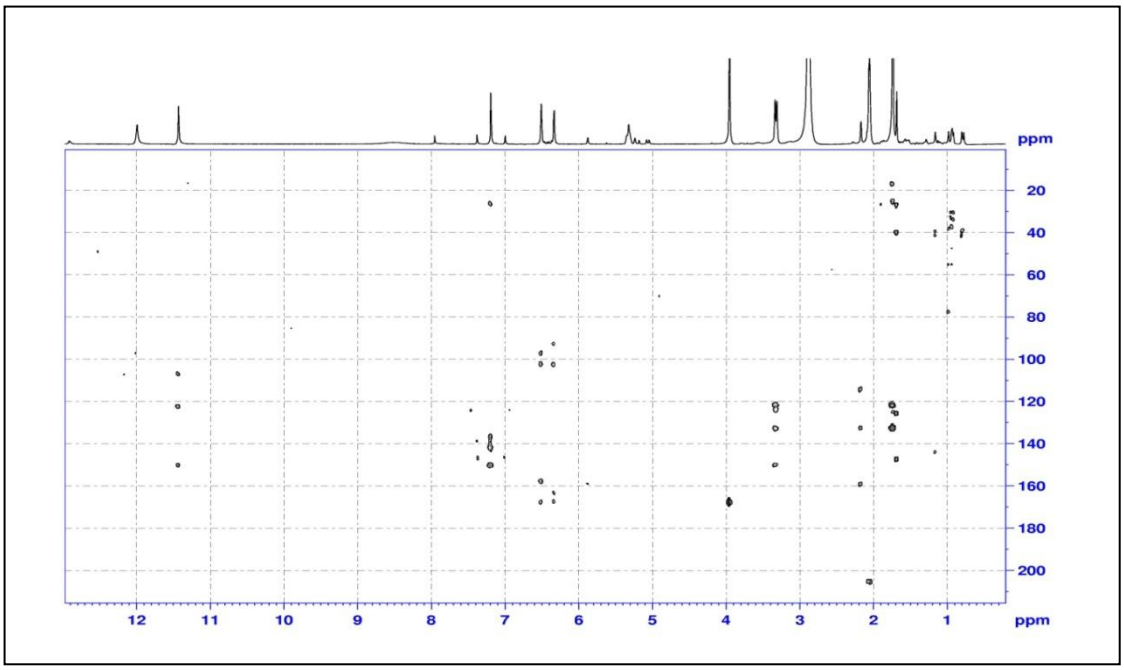

Figure 63 2D HMBC (300 MHz) (Acetone-d_6) spectrum of **AS13**

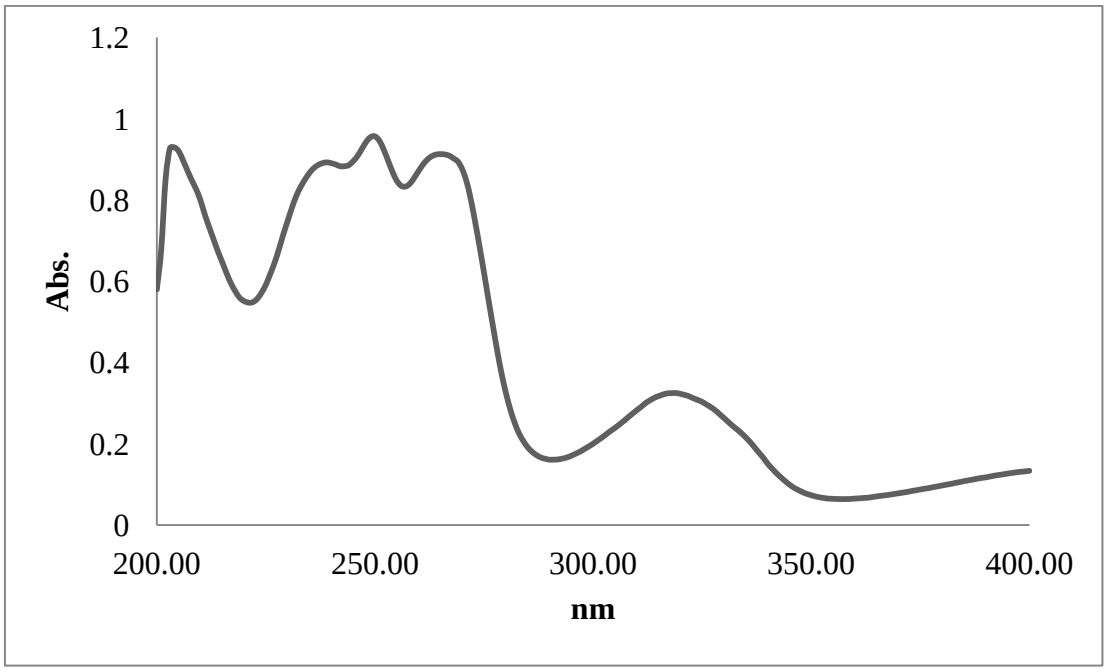

Figure 64 UV (EtOH) spectrum of **AS14**

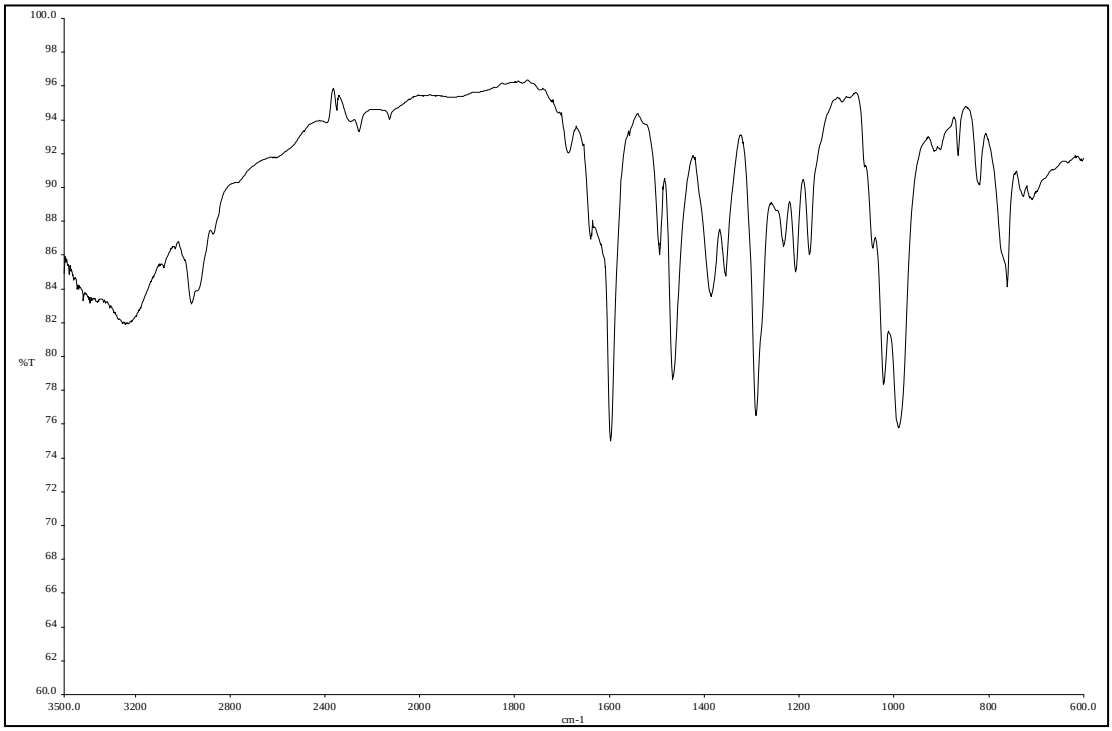

Figure 65 IR (neat) spectrum of **AS14**

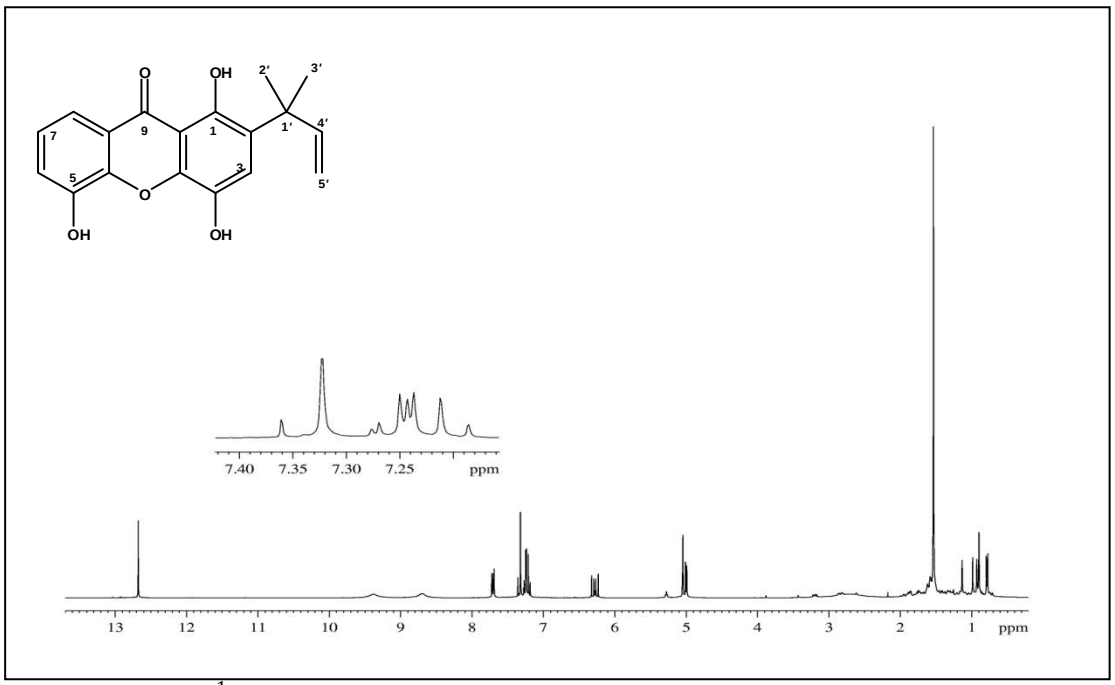

Figure 66 ^{1}H NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS14**

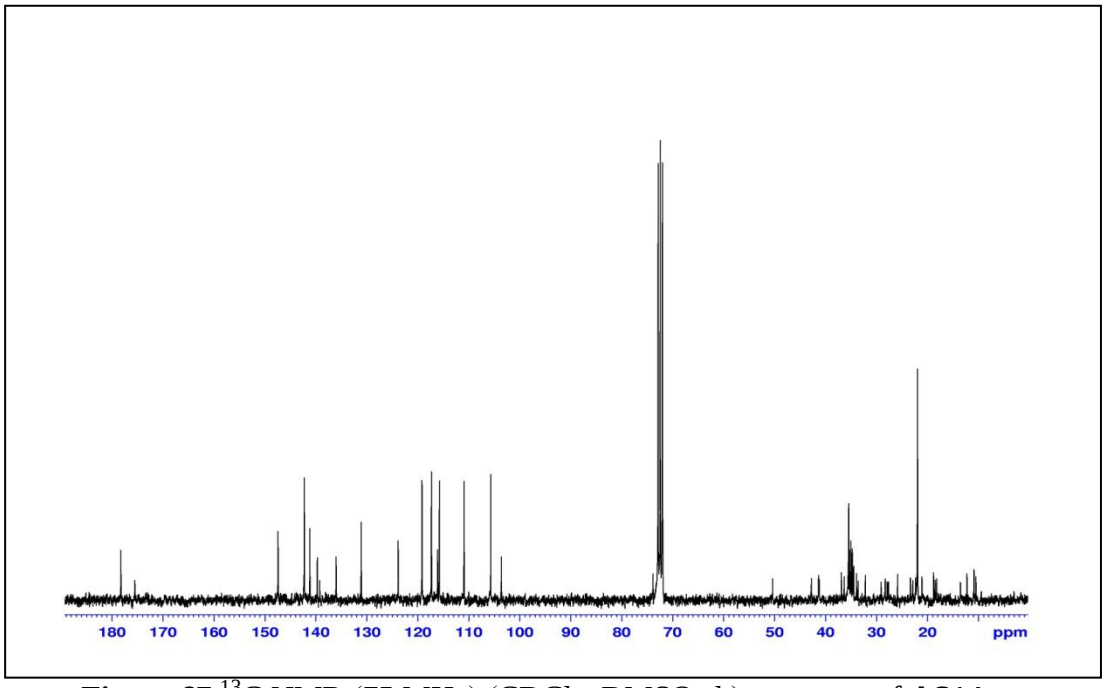

Figure 67 ^{13}C NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS14**

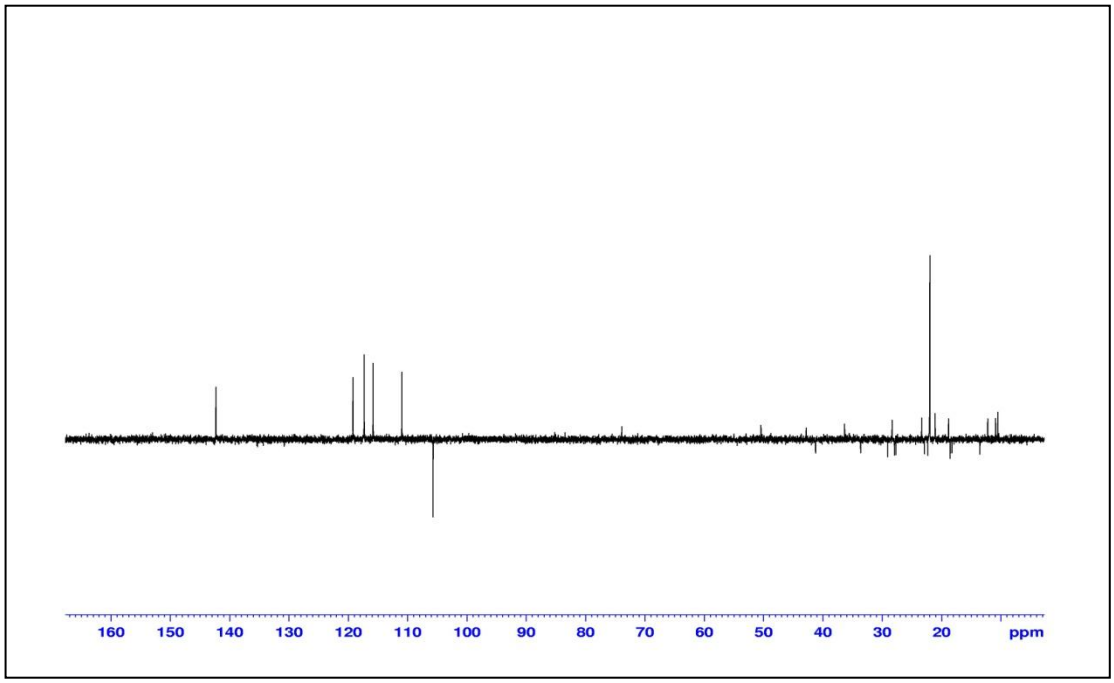

Figure 68 DEPT 135˚($CDCl_3$+DMSO-d_6) spectrum of **AS14**

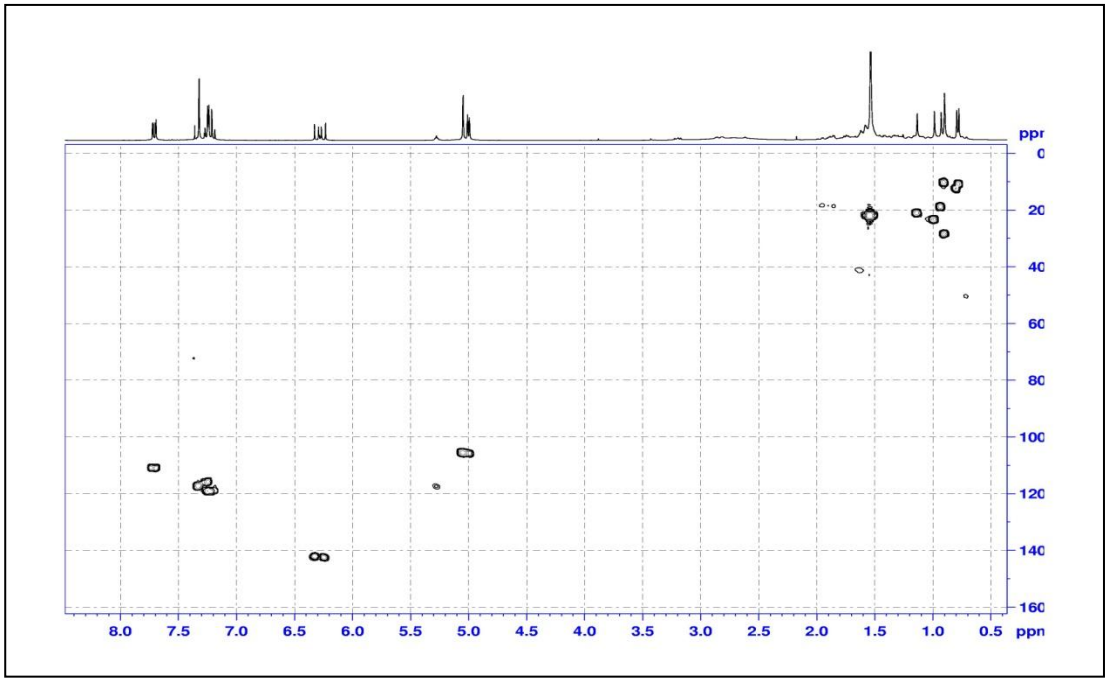

Figure 69 2D HMQC (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS14**

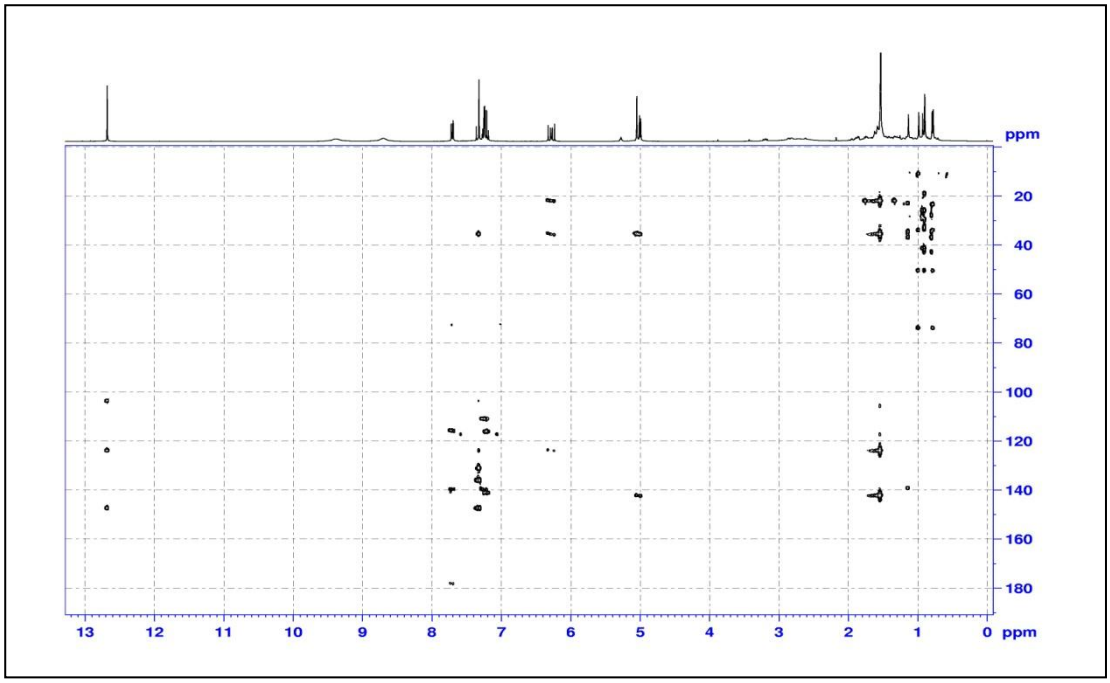

Figure 70 2D HMBC (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **AS14**

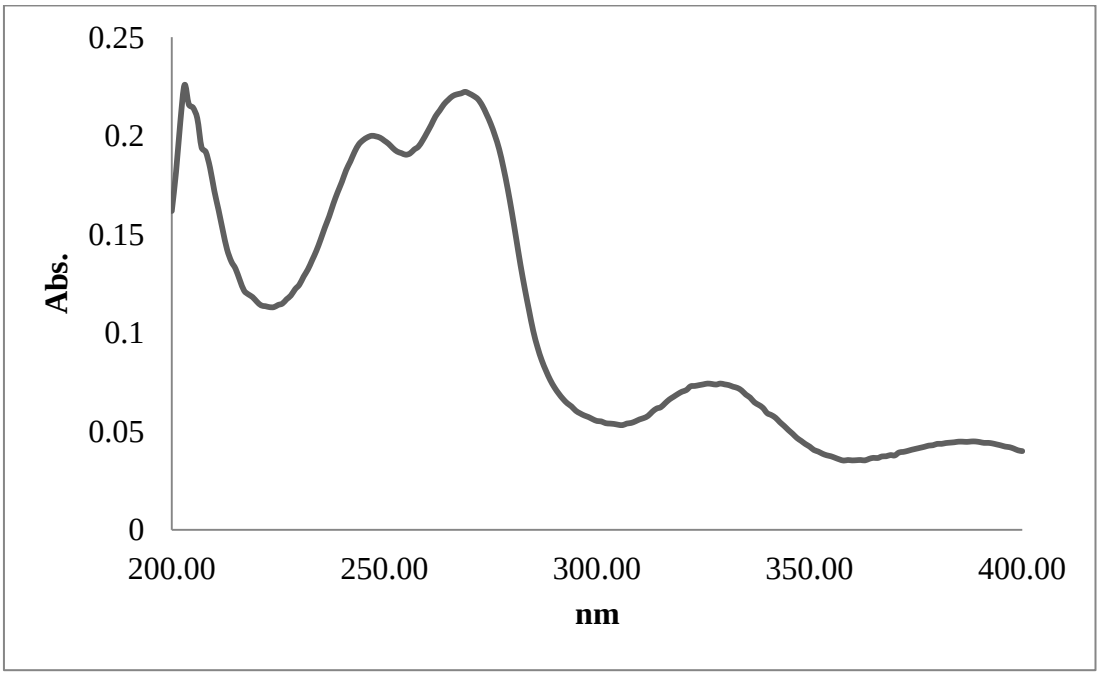

Figure 71 UV (EtOH) spectrum of **AS15**

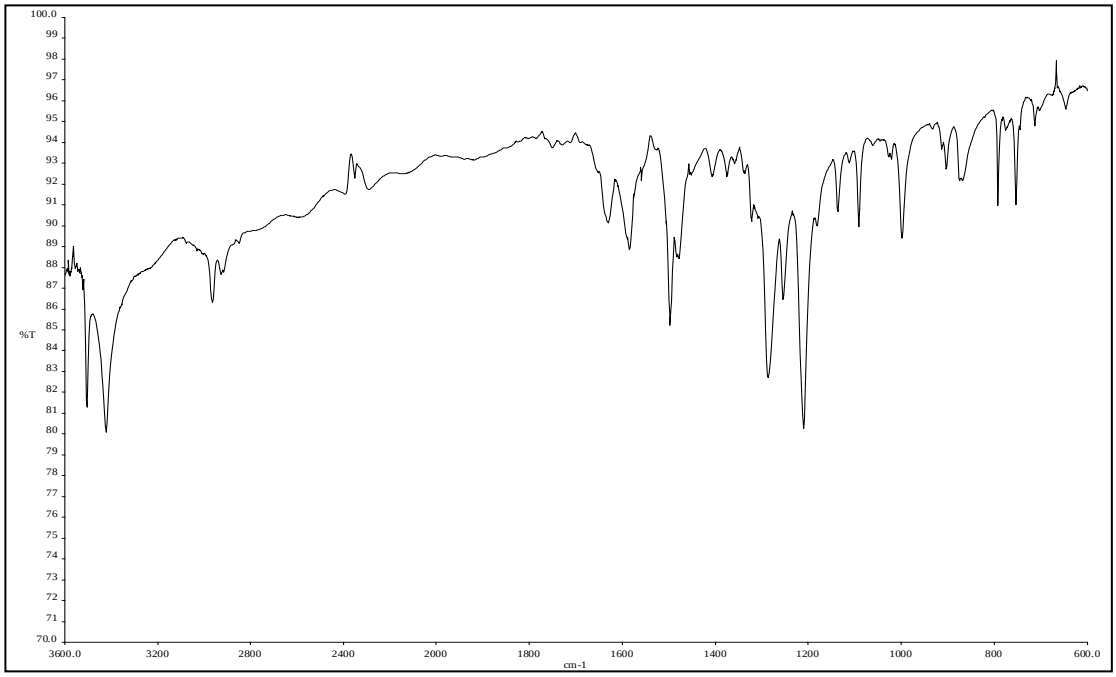

Figure 72 IR (neat) spectrum of **AS15**

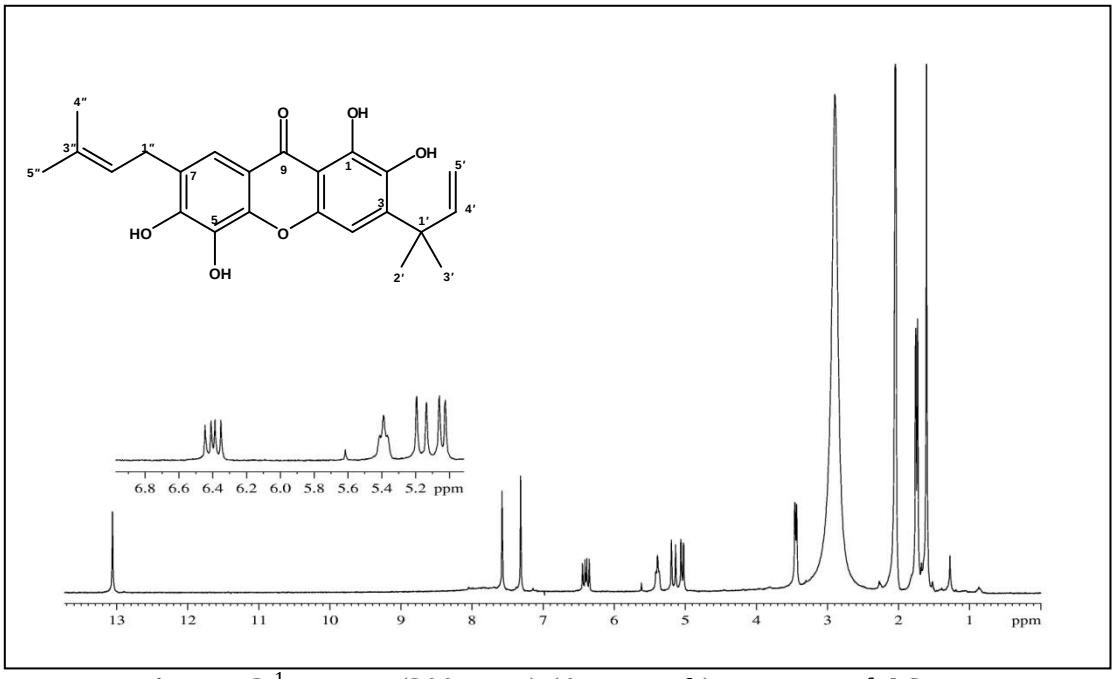

Figure 73 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS15**

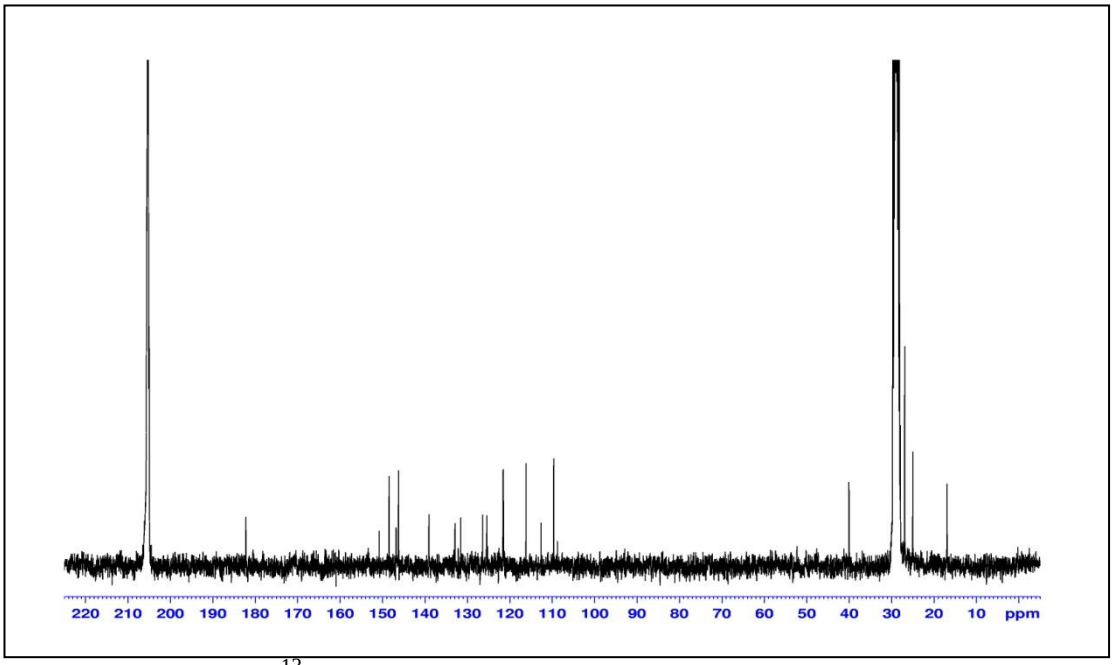

Figure 74 ^{13}C NMR (75 MHz) (Acetone-d_6) spectrum of **AS15**

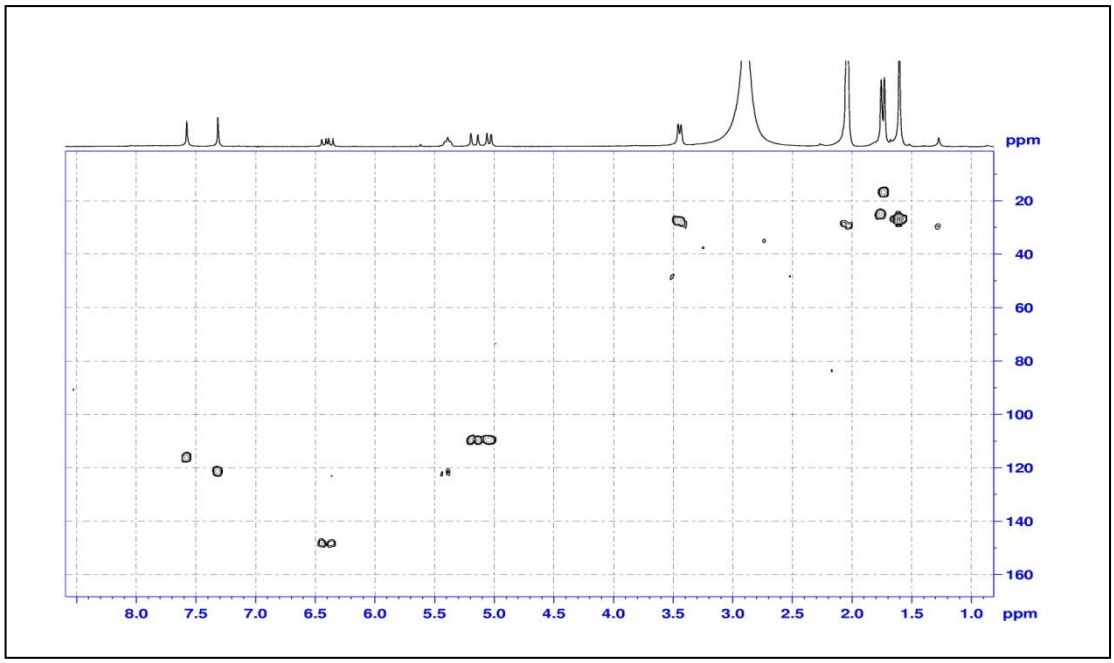

Figure 75 2D HMQC (300 MHz) (Acetone-d_6) spectrum of **AS15**

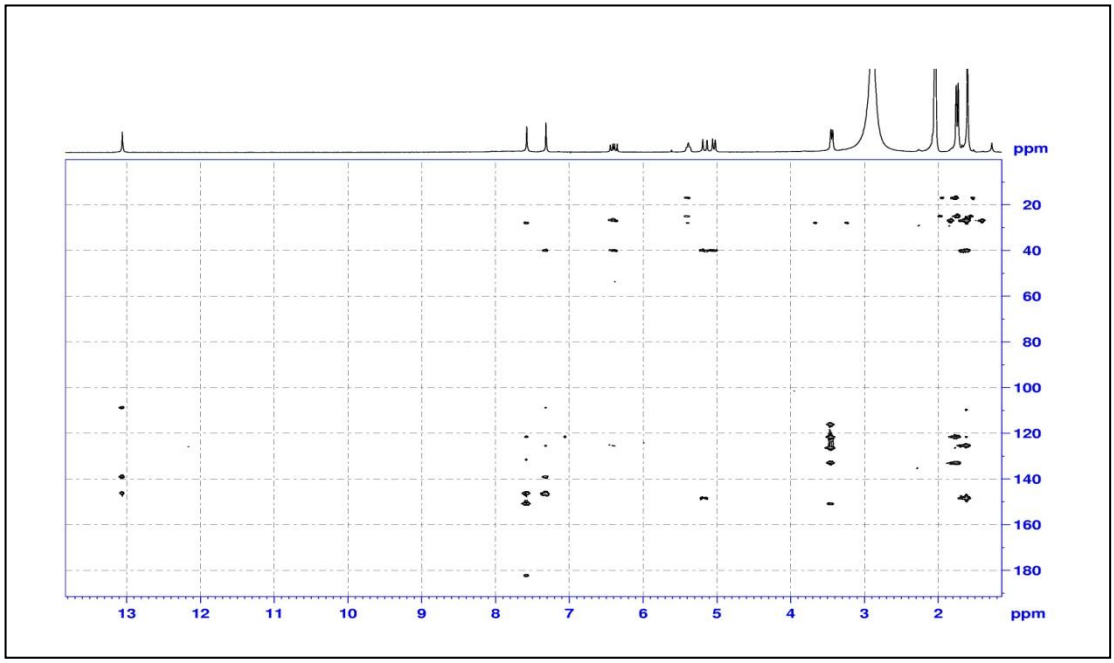

Figure 76 2D HMBC (300 MHz) (Acetone-d_6) spectrum of **AS15**

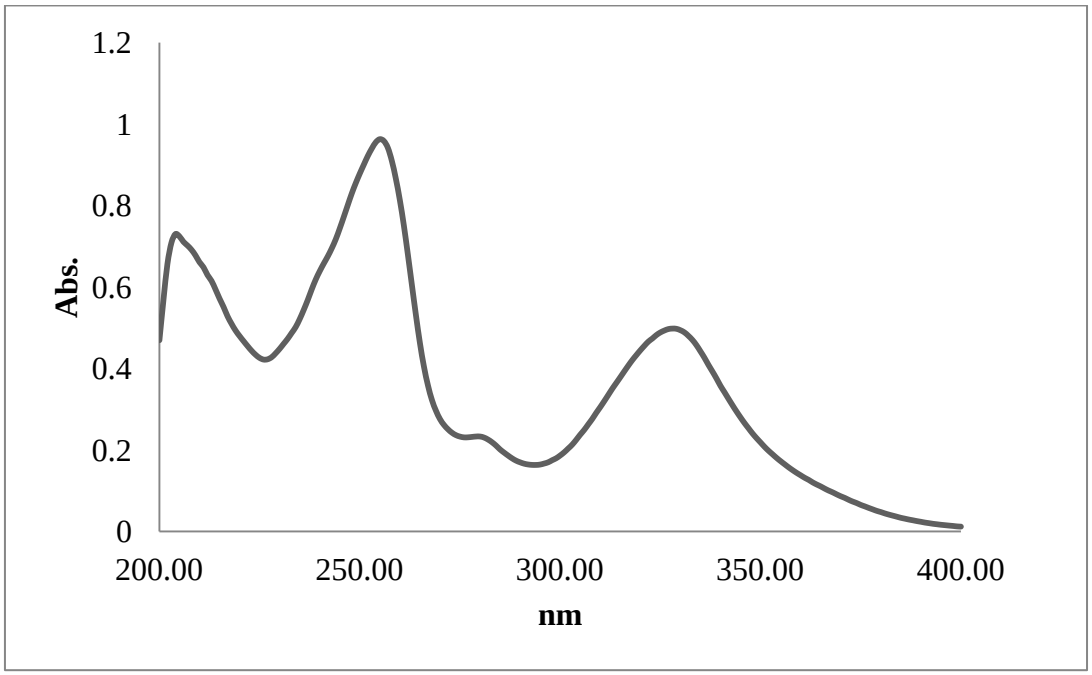

Figure 77 UV (EtOH) spectrum of **AS16**

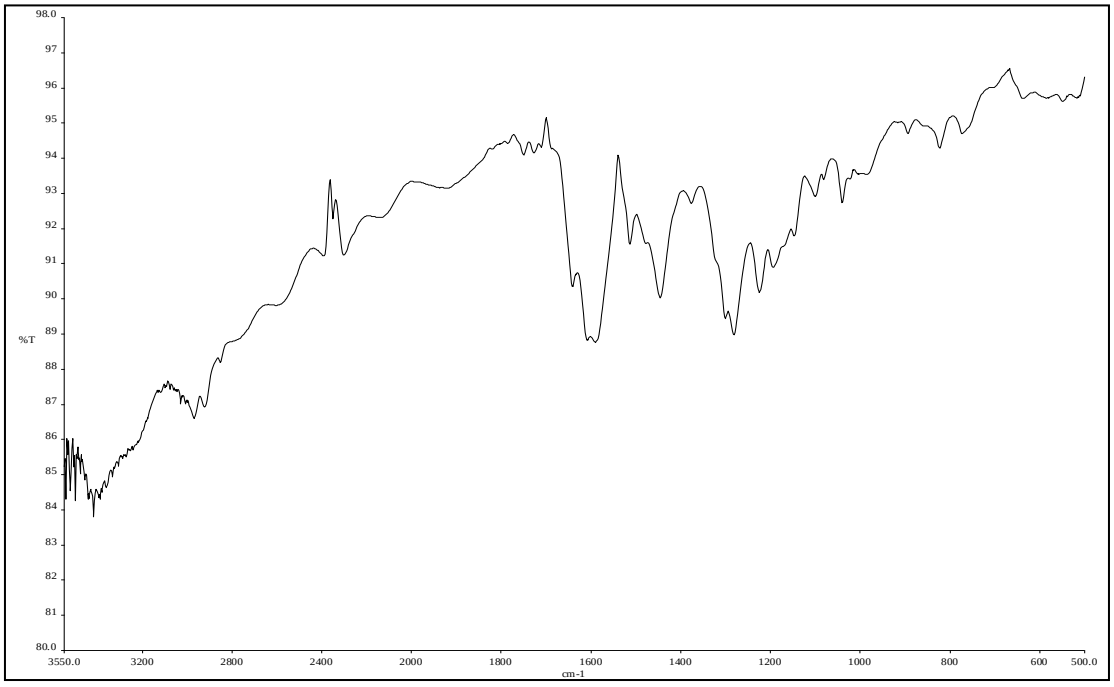

Figure 78 IR (neat) spectrum of **AS16**

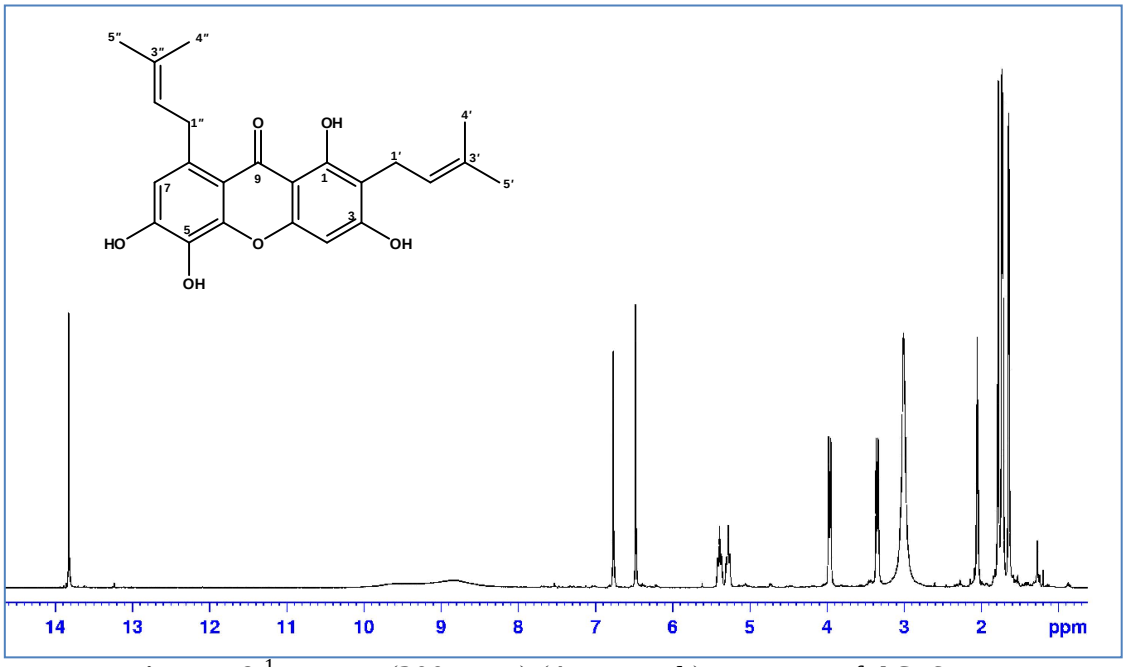

Figure 79 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS16**

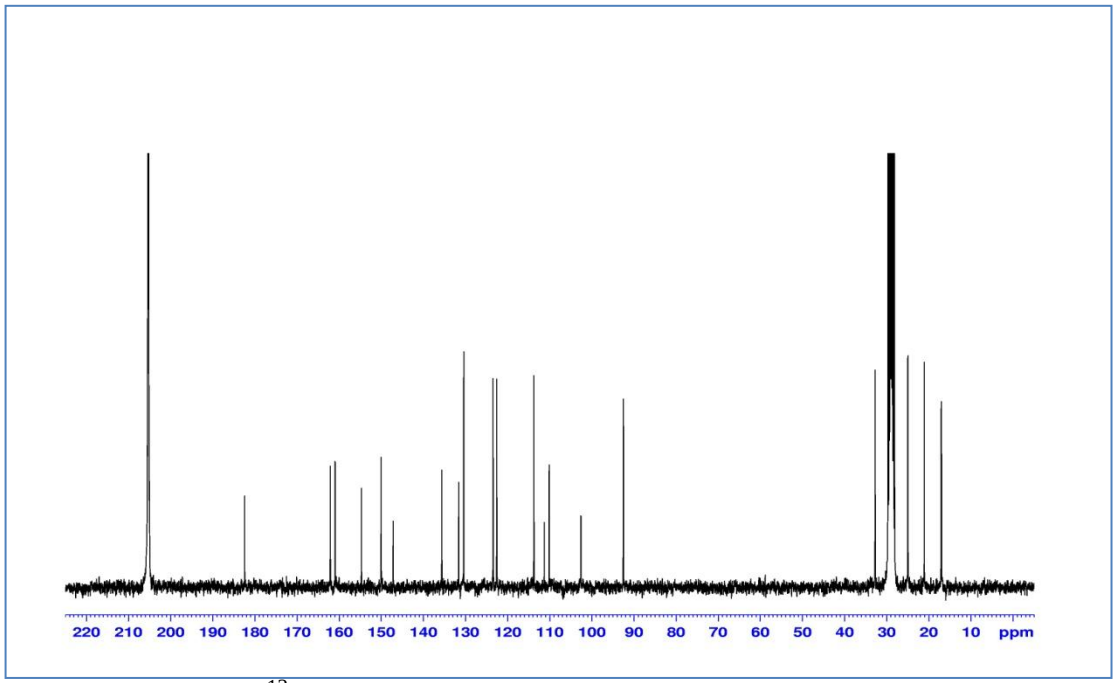

Figure 80 ^{13}C NMR (75 MHz) (Acetone-d_6) spectrum of **AS16**

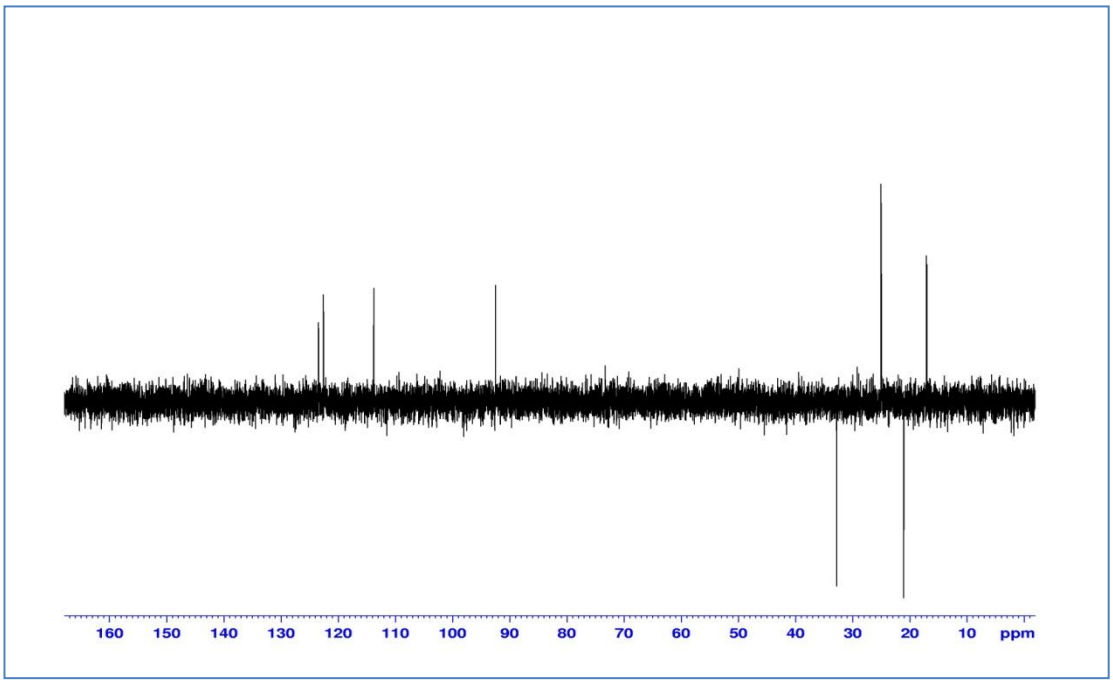

Figure 81 DEPT 135˚(Acetone-d_6) spectrum of **AS16**

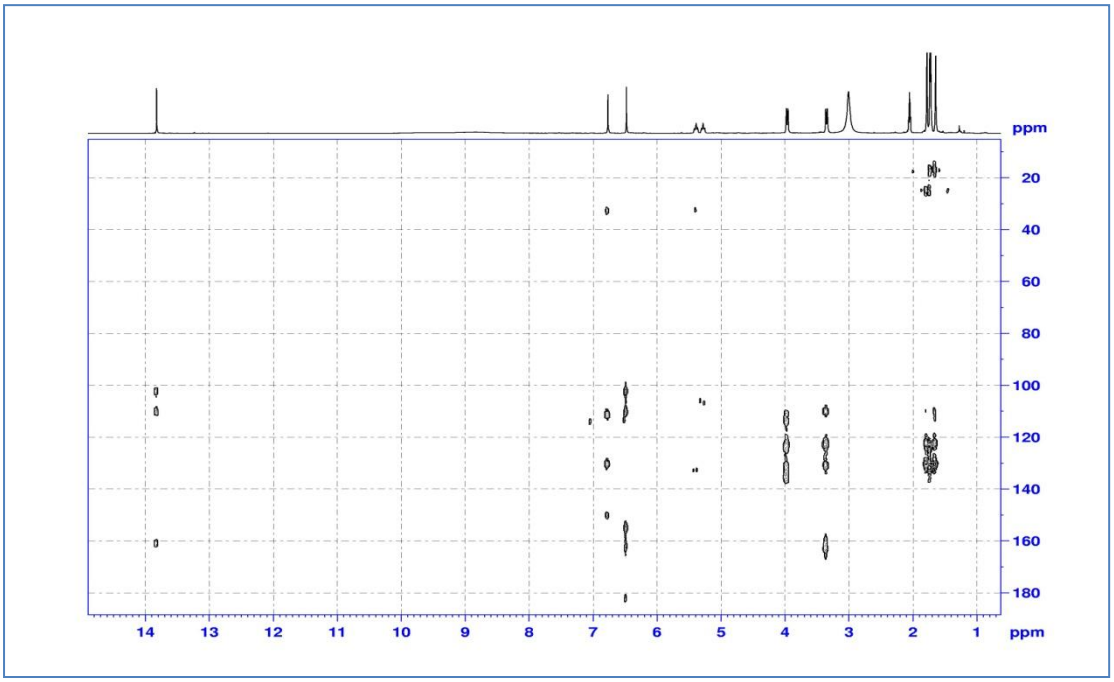

Figure 82 2D HMBC (300 MHz) (Acetone-d_6) spectrum of **AS16**

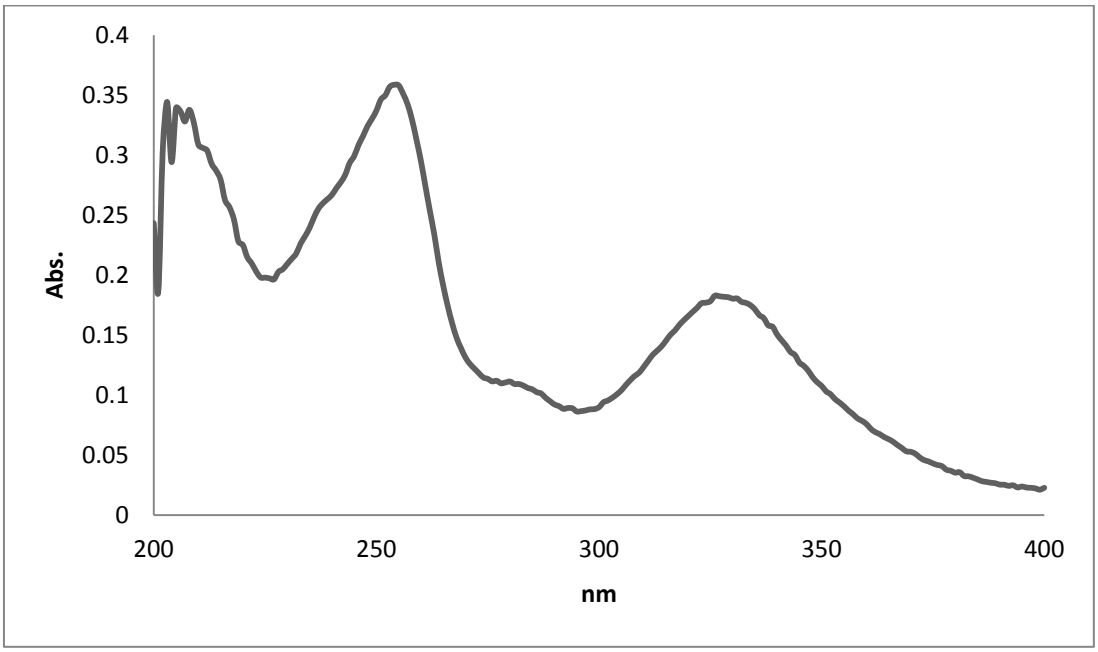

Figure 83 UV (EtOH) spectrum of **AS17**

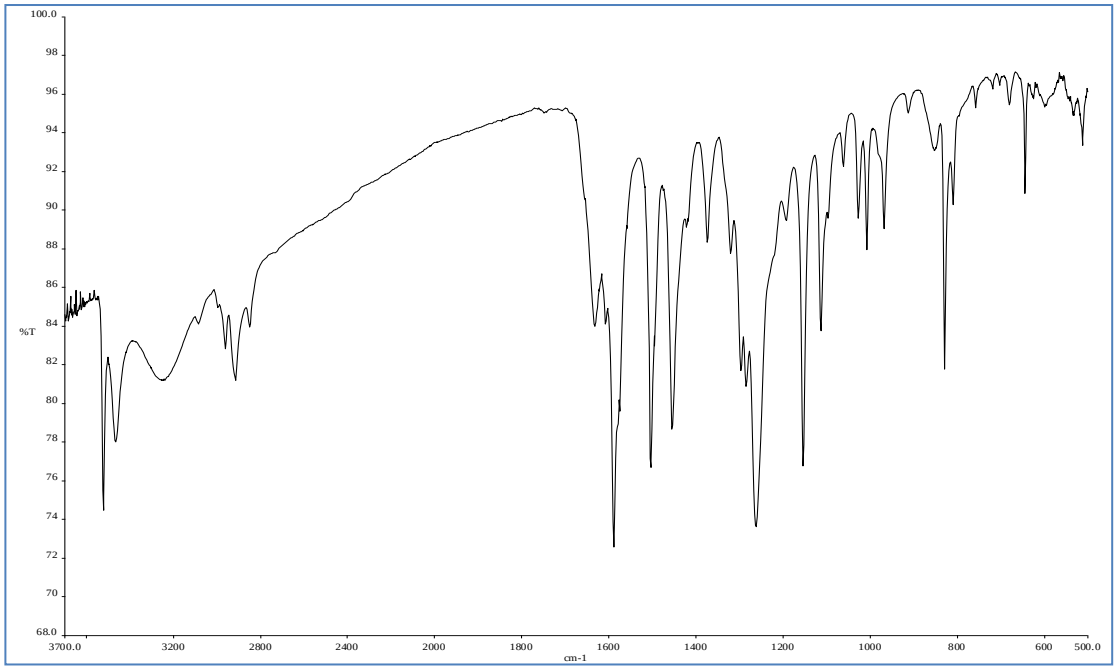

Figure 84 IR (neat) spectrum of **AS17**

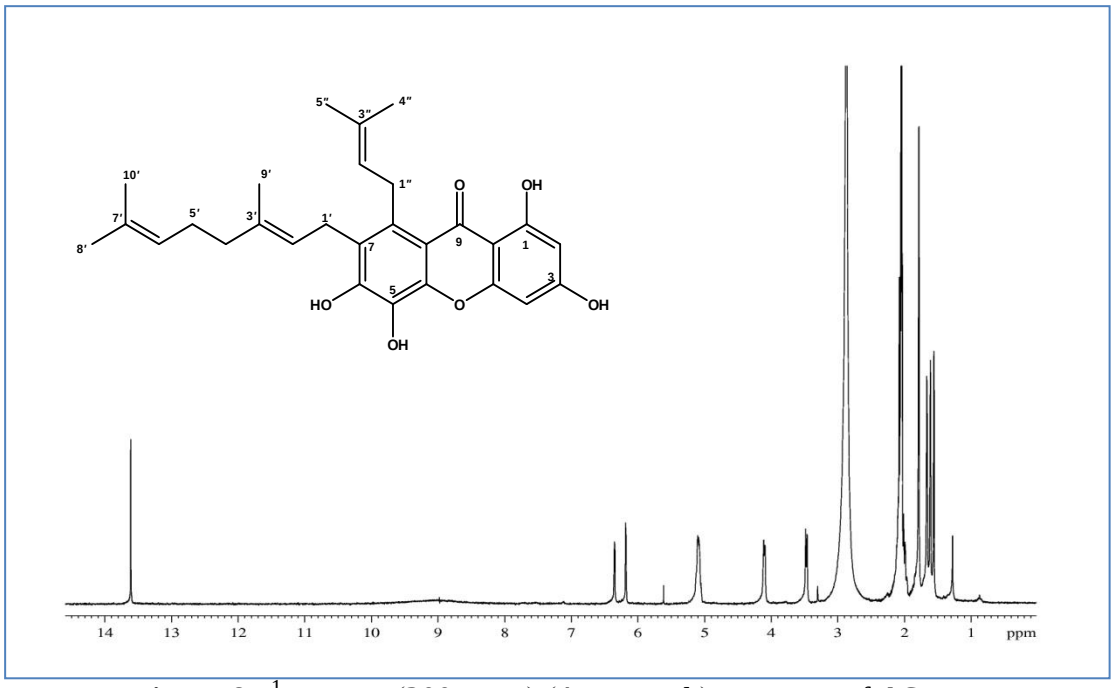

Figure 85 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS17**

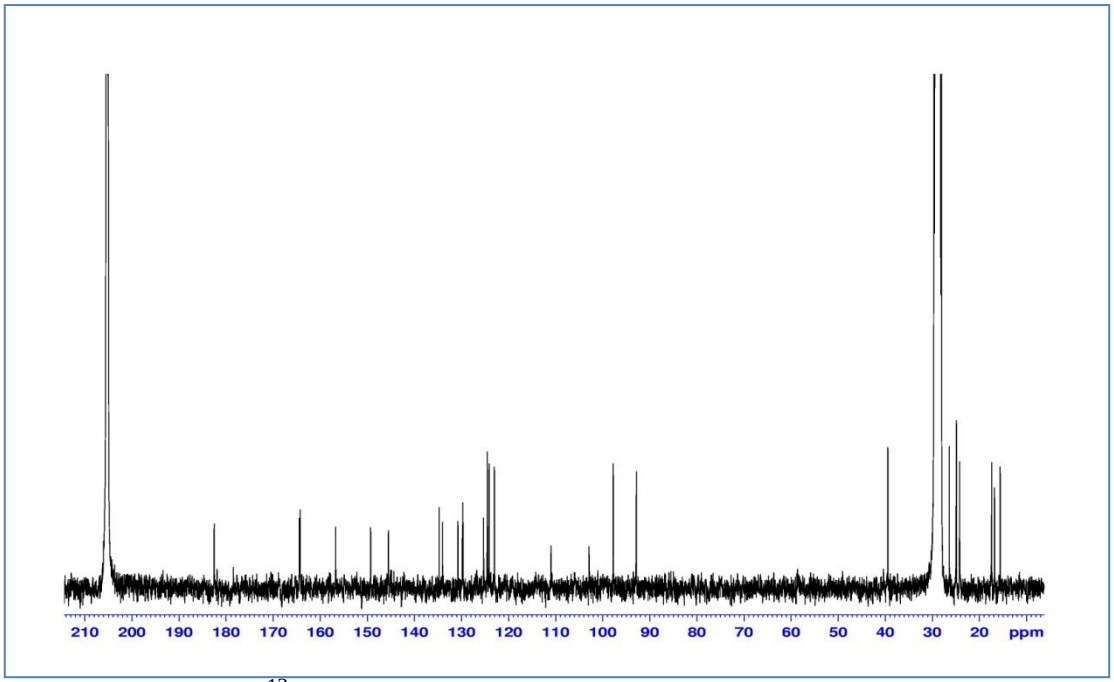

Figure 86 ^{13}C NMR (75 MHz) (Acetone-d_6) spectrum of **AS17**

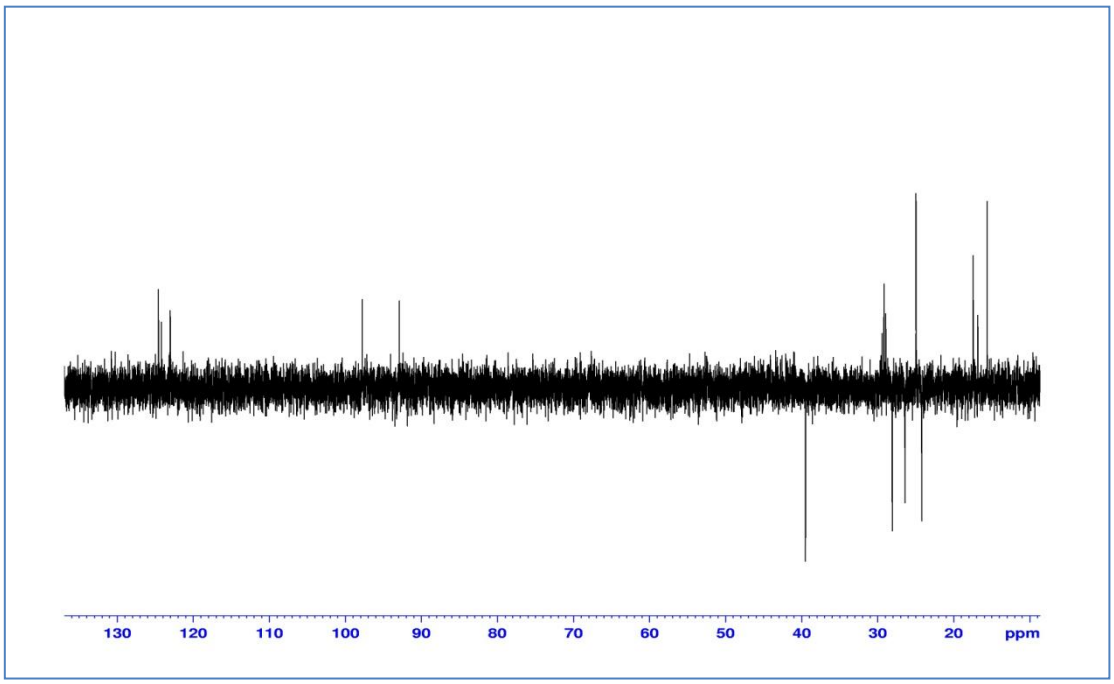

Figure 87 DEPT 135˚(Acetone-d_6) spectrum of **AS17**

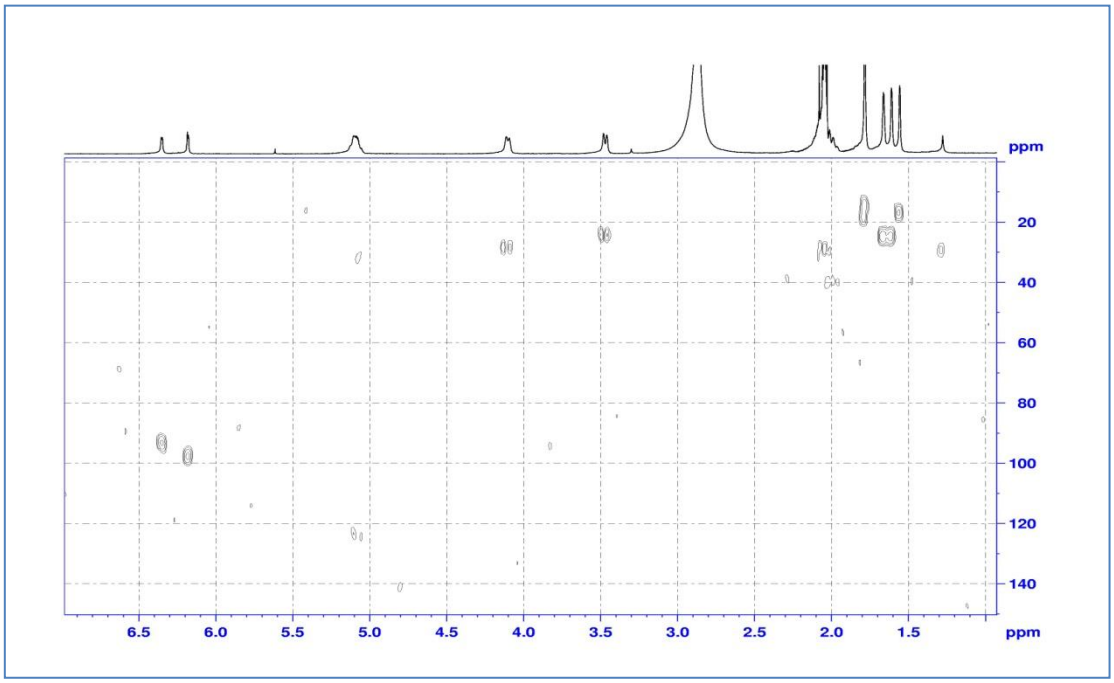

Figure 88 2D HMQC (300 MHz) (Acetone-d_6) spectrum of **AS17**

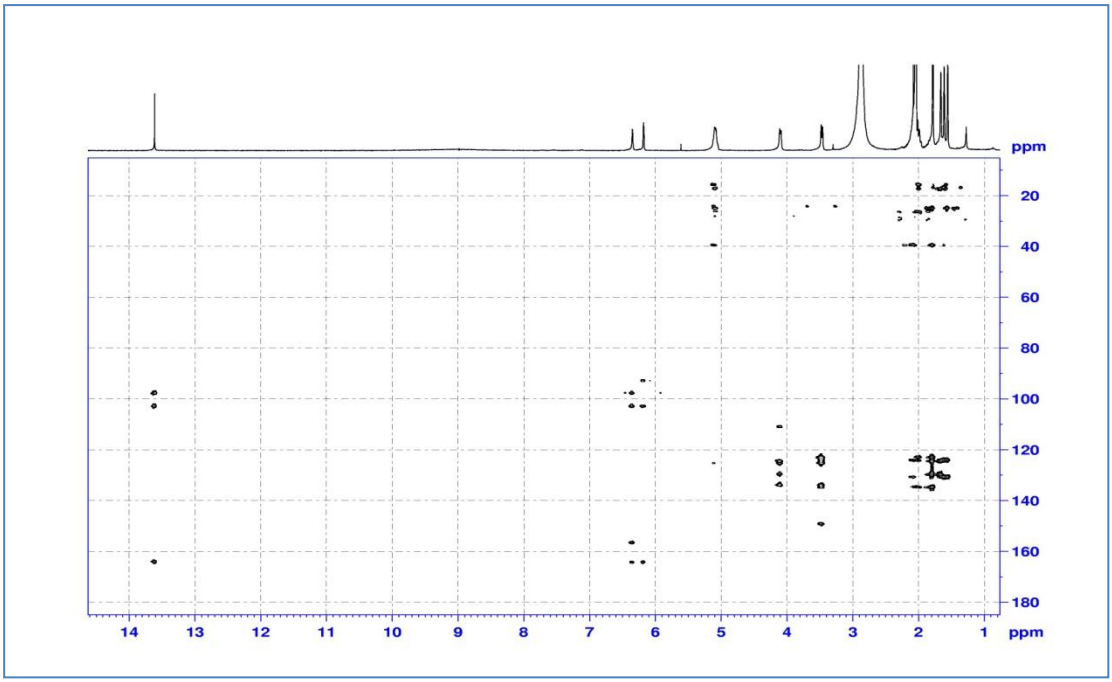

Figure 89 2D HMBC (300 MHz) (Acetone-d_6) spectrum of **AS17**

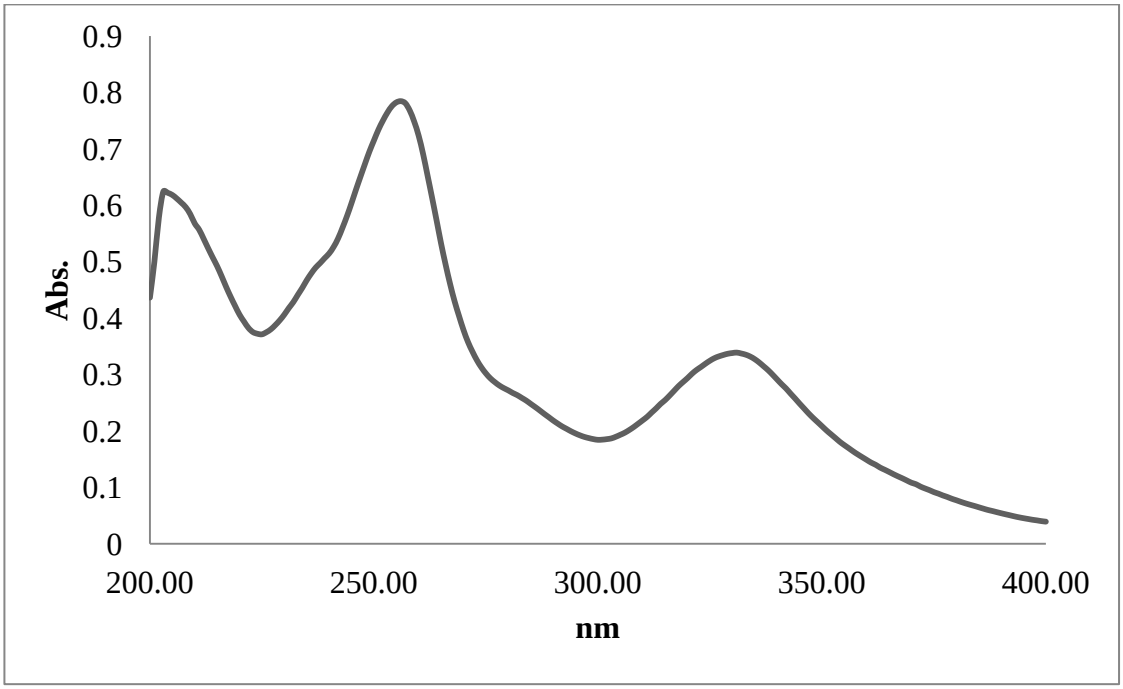

Figure 90 UV (EtOH) spectrum of **AS18**

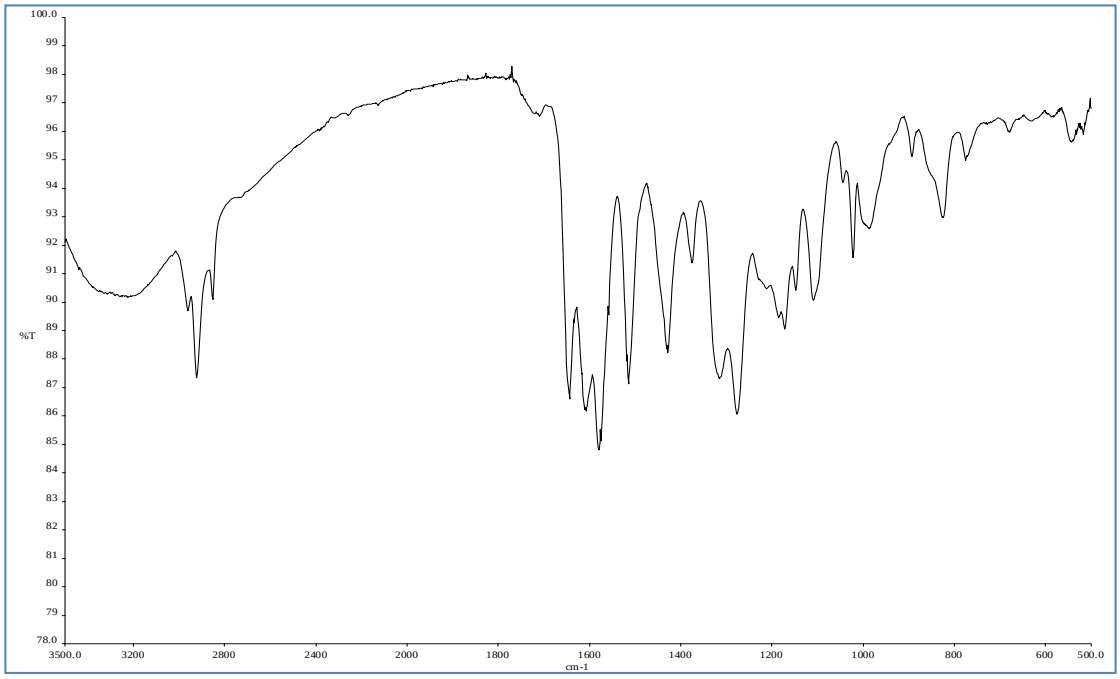

Figure 91 IR (neat) spectrum of **AS18**

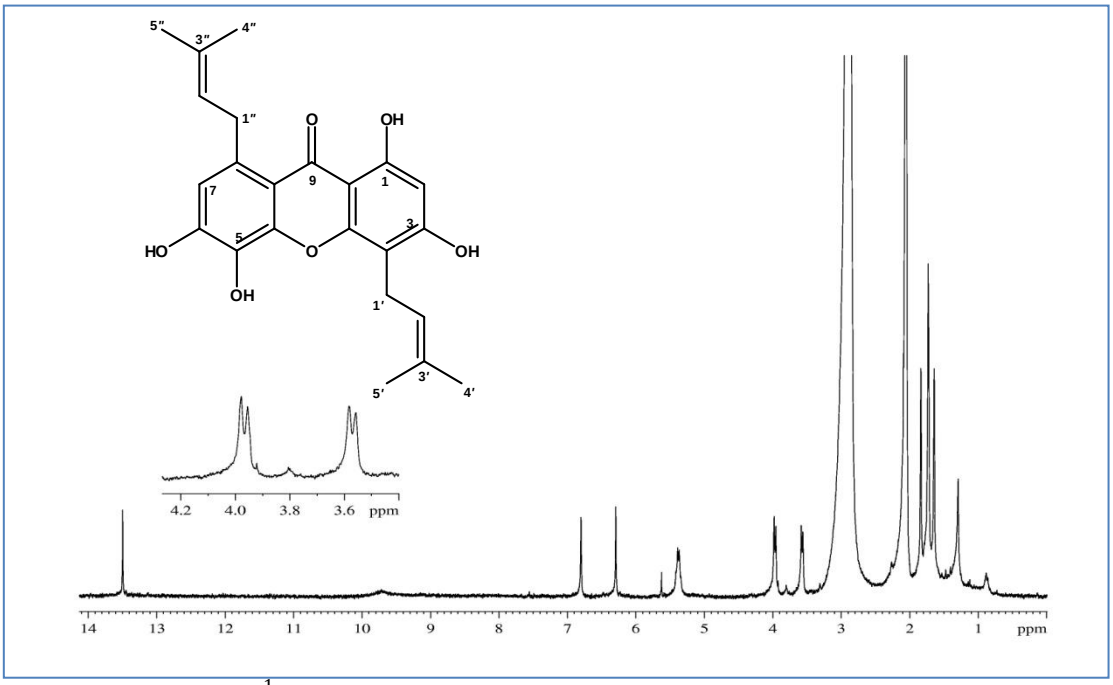

Figure 92 ^{1}H NMR (300 MHz) (Acetone-d_6) spectrum of **AS18**

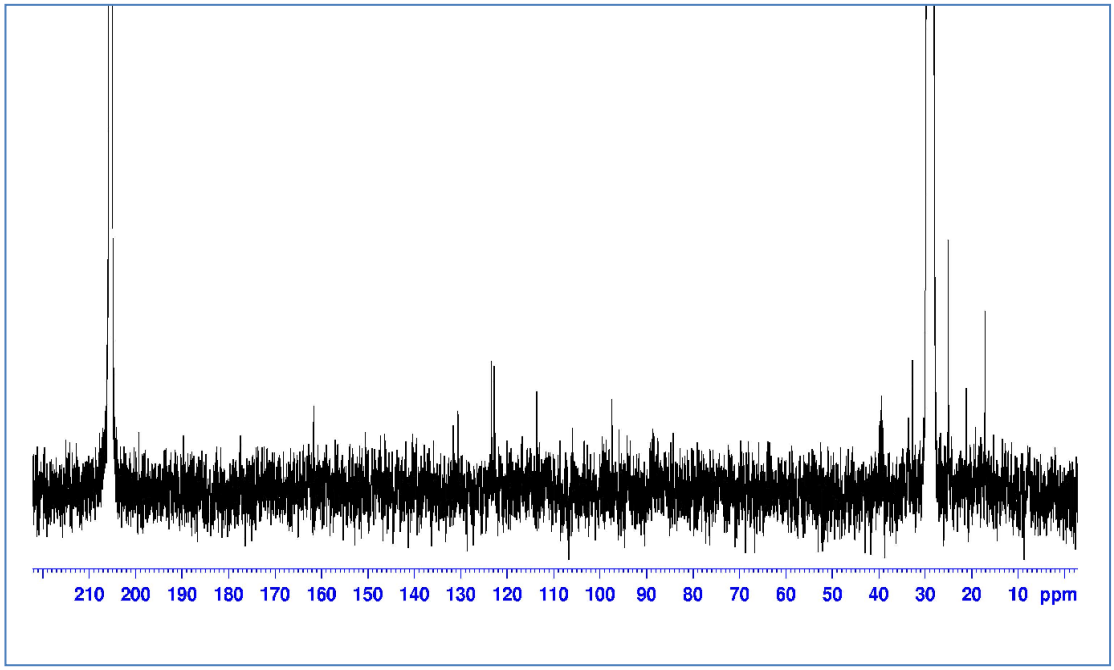

Figure 93 ^{13}C NMR (75 MHz) (Acetone-d_6) spectrum of **AS18**

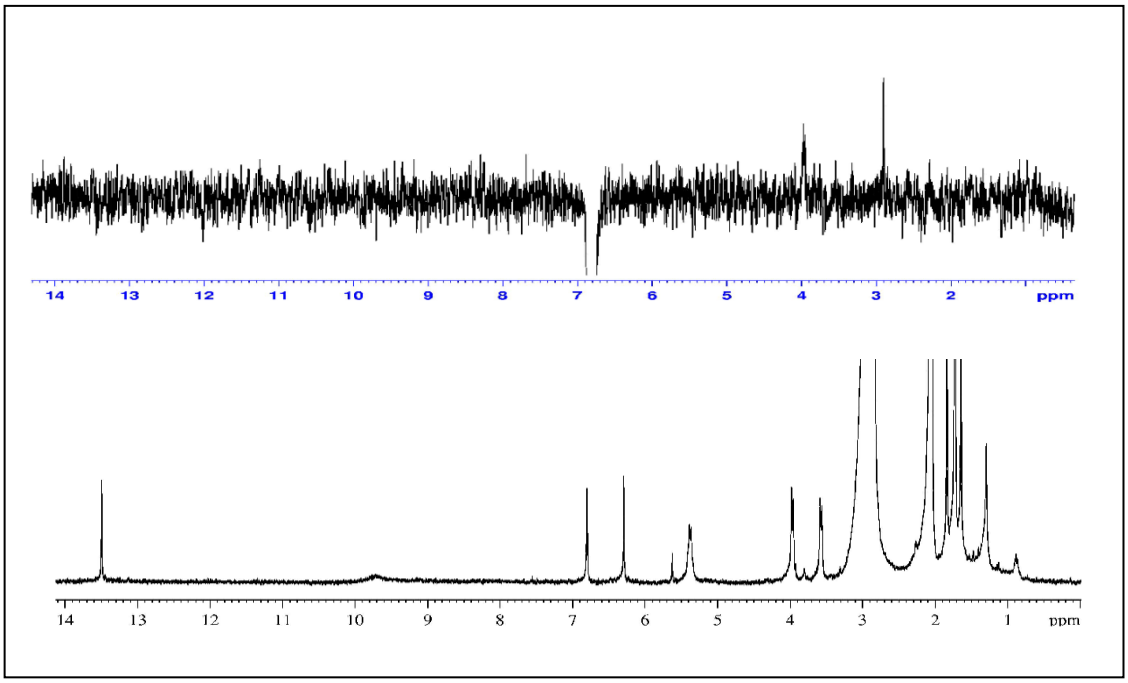

Figure 94 NOE (300 MHz) (Acetone-d_6) spectrum of **AS18**

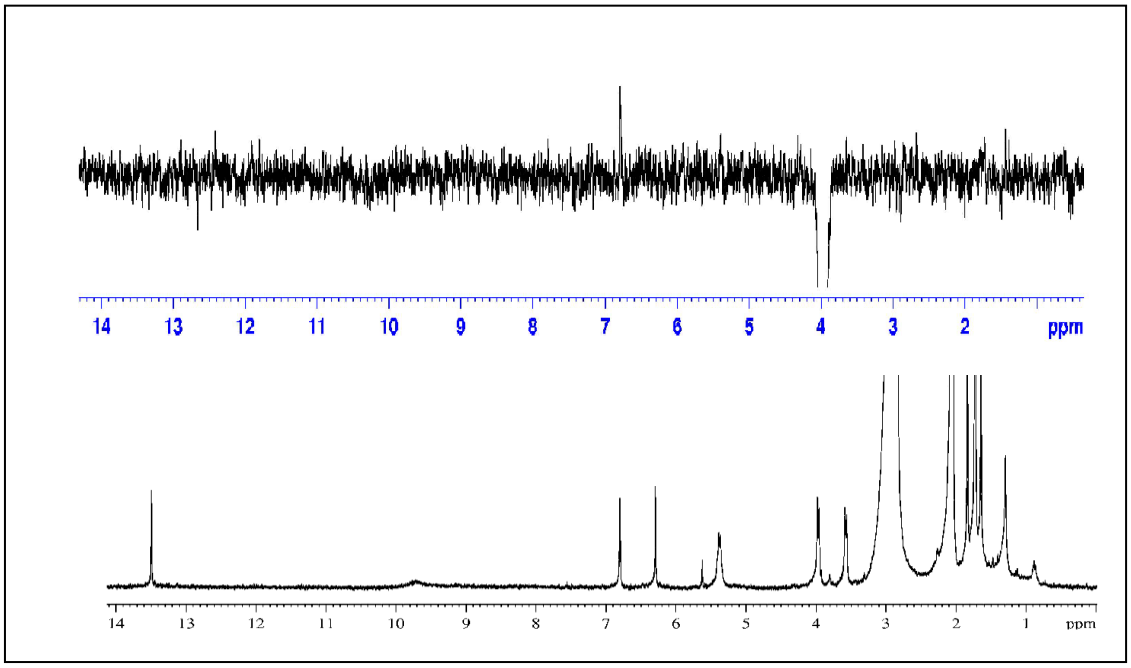

Figure 95 NOE (300 MHz) (Acetone-d_6) spectrum of **AS18**

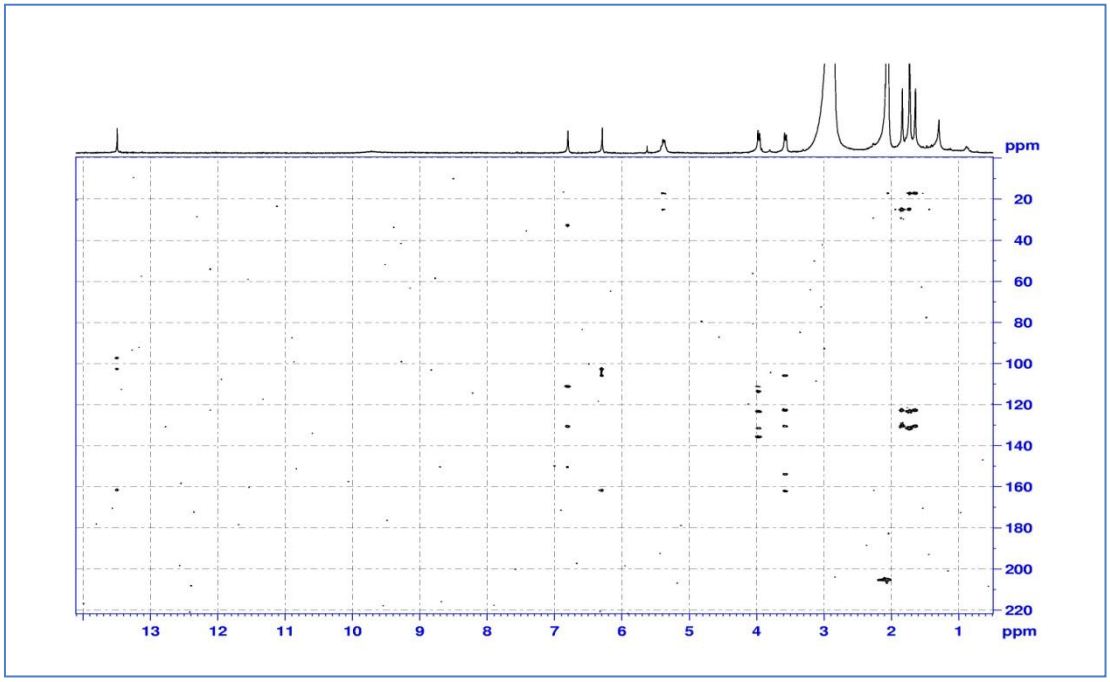

Figure 96 2D HMBC (300 MHz) (Acetone-d_6) spectrum of **AS18**

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Scholarship Awards during Enrolment

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2. Graduate School, Prince of Songkla University
3. Teacher Assistant for undergraduate-level, Faculty of Science, Prince of Songkla University

List of Publication and Proceeding

Arun Saelee, Wilawan Mahabusarakam. "Biflavonoids from the Leaves of *Garcinia dulcis*". Pure and Applied Chemistry International Conference 2013, The Tide Resort, Chon Buri, Thailand, 23-25 January 2013. (Poster presentation)

Arun Saelee, Wilawan Mahabusarakam. "Phenolic Compounds from the Leaves of *Garcinia dulcis*". The 5th International Conference on Natural Products for Health and Beauty (NATPRO 5. Moevenpick Resort & Spa Karon Beach Phuket, Thailand, May 6-8, 2014. (poster presentation)