Chemical Constituents from the Root Bark and Leaves of *Artocarpus elasticus*

Prakit Chaithada

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Organic Chemistry

Prince of Songkla University

2010

Thesis Title Chemical Constituents from the Root Bark and Leaves of *Artocarpus elasticus*

Author Mr. Prakit Chaithada

Major Program Organic Chemistry

Major Advisor:

…..……...…….……

(Assoc. Prof. Dr. Wilawan Mahabusarakam)

Co-advisor:

…..……...…….……

(Dr. Suda Chakthong)

Examining Committee:

..……Chairperson

(Asst. Prof. Dr. Orasa Pancharoen)

..…….....……

(Assoc. Prof. Dr. Wilawan Mahabusarakam)

…..……...…….……

(Dr. Suda Chakthong)

…..……...…….……

(Assoc. Prof. Dr. Chatchanok Kalarai)

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.

…….……..…..

(Prof. Dr. Amornrat Phongdara)

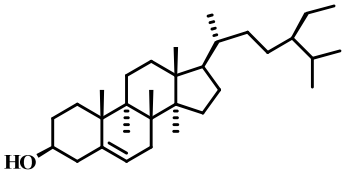
Dean of Graduate School

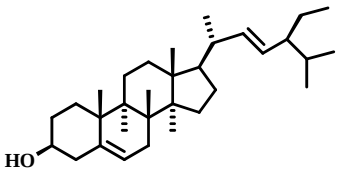
ชื่อวิทยานิพนธ์	องค์ประกอบทางเคมีจากเปลือกรากและใบกะออก (*Artocarpus elasticus*)
ผู้เขียน	นายประกิต ไชยธาดา
สาขาวิชา	เคมีอินทรีย์
ปีการศึกษา	2553

บทคัดย่อ

การศึกษาองค์ประกอบทางเคมีของเปลือกรากและใบกะออก (*Artocarpus elasticus*) แยกได้สารกลุ่ม prenylated dihydrochalcones ที่ยังไม่มีรายงานการวิจัย 5 สาร ได้แก่ 1-(2,4-dihydroxyphenyl)-3-(8-hydroxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-chromen-6-yl)propan-1-one **(PK13)**, 1-(2,4-dihydroxyphenyl)-3-(3,4-dihydroxy-2,5-bis(3-methylbut-2-enyl)phenyl) propan-1-one **(PK14)**, 1-(2,4-dihydroxyphenyl)-3-(7-((3,3-dimethyloxiran-2-yl)methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)propan-1-one **(PK15)**, 1-(2,4-dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7*b*-dihydro-1*aH*-oxireno[2,3-*c*]chromen-6-yl) propan-1-one **(PK17)** และ 1-(2,4-dihydroxyphenyl)-3-(7-hydroxy-6-(3-methylbut-2-enyl) benzofuran-5-yl)propan-1-one **(PK18)** นอกจากนี้ยังได้สารที่มีรายงานวิจัยแล้ว 13 สาร ได้แก่ สารผสมของ β-sitosterol และ stigmasterol **(PK1)**, (*E*)-4-(3',4'-dimethoxyphenyl)-3-butenyl acetate **(PK2)**, 5*a*,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-9-(3-methyl-2-buten-1-yl)-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one **(PK3)**, 4-hydroxybenzaldehyde **(PK4)**, 2,3,8-trihydroxy-11,11-dimethyl-13-(3-methyl-2-butenyl)-6-(2-methyl-1-propenyl)-6*H*, 7*H*,11*H*-bis[1]benzopyrano[4,3-*b*:6',7'-*e*]pyran-7-one **(PK5)**, (*E*)-4-(3',4'-dimethoxyphenyl)but-3-en-1-ol **(PK6)**, 2-(2,4-dihydroxyphenyl)-5-hydroxy-8,8-dimethyl-3-(3-methylbut-2-enyl)pyrano [3,2-*g*]chromen-4(8*H*)-one **(PK7)**, 5*a*,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-5*H*,7*H*, 11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one **(PK8)**, 6,7-dihydro-5,9,11,14-tetrahydroxy-3,3-dimethyl-6-(1-methylethenyl)-(-)-3*H*,8*H*-pyrano[3',2':4,5]benzo[1,2-*c*]xanthen-8-one **(PK9)**, 8,9-dihydro-6,10,11,13-tetrahydroxy-3,3-dimethyl-9-(1-methylethenyl)-3*H*,7*H*-benzo[*c*]pyrano [3,2-*h*]xanthen-7-one **(PK10)**, (*E*)-3-(4'-hydroxy-3'-methoxyphenyl)-2-propenoic acid **(PK11)**, 5-hydroxy-8,8-dimethyl-3-(3-methyl-2-butenyl)-2-(2,4,5-trihydroxyphenyl)-4*H*,8*H*-benzo[1,2-*b*: 3,4-*b'*]dipyran-4-one **(PK12)** และ (*S*)-2-(2,4-dihydroxyphenyl)-5-hydroxy-7-methoxychroman-

4-one **(PK16)** โครงสร้างของสารประกอบเหล่านี้วิเคราะห์โดยใช้ข้อมูลทางสเปกโทรสโกปี UV IR NMR MS และ เปรียบเทียบกับสารที่มีรายงานการวิจัยแล้ว





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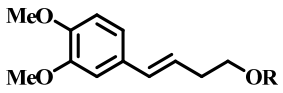

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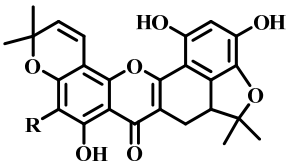
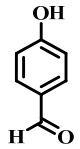
PK6 : R = H



PK3 : R = prenyl

PK8 : R = H



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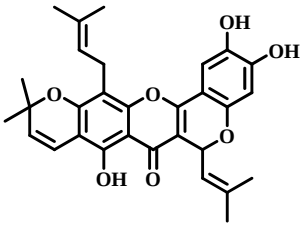

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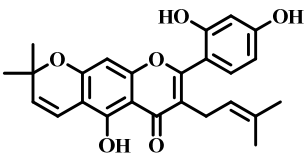

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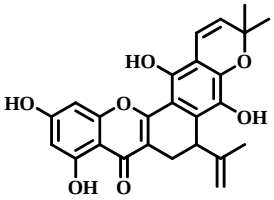

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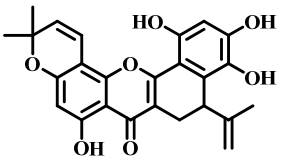

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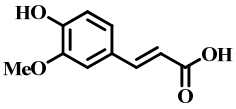

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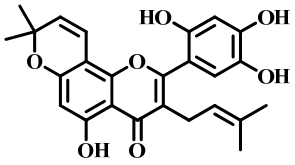

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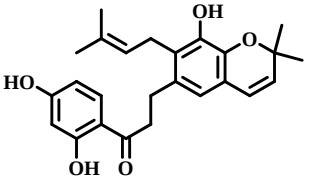

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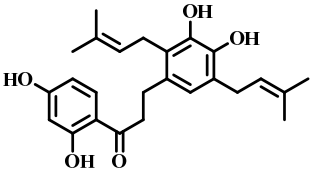

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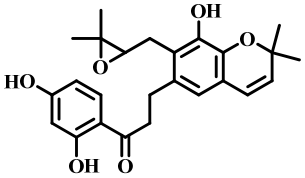

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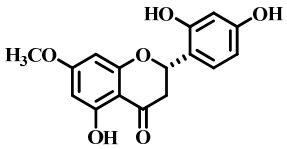

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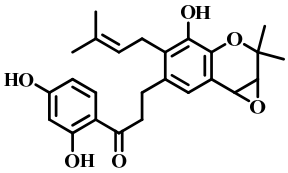

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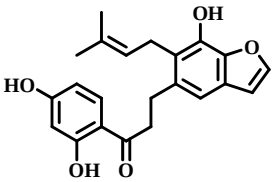


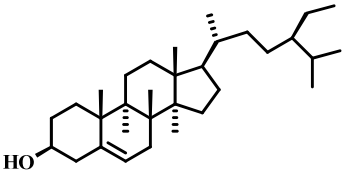
PK18

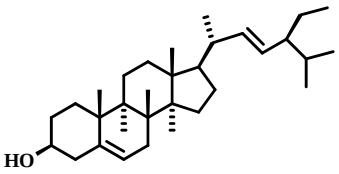
Thesis Title	Chemical Constituents from the Root Bark and Leaves of *Artocarpus elasticus*
Author	Mr. Prakit Chaithada
Major Program	Organic Chemistry
Acedemic Year	2010

ABSTRACT

Investigation of the chemical constituents from the root bark and leaves of *Artocarpus elasticus* yielded five new prenylated dihydrochalcones: 1-(2,4-dihydroxyphenyl)-3-(8-hydroxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-chromen-6-yl)propan-1-one **(PK13)**, 1-(2,4-dihydroxyphenyl)-3-(3,4-dihydroxy-2,5-bis(3-methylbut-2-enyl)phenyl)propan-1-one **(PK14)**, 1-(2,4-dihydroxyphenyl)-3-(7-((3,3-dimethyloxiran-2-yl)methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)propan-1-one **(PK15)**, 1-(2,4-dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7*b*-dihydro-1*aH*-oxireno[2,3-*c*]chromen-6-yl)propan-1-one **(PK17)** and 1-(2,4-dihydroxyphenyl)-3-(7-hydroxy-6-(3-methylbut-2-enyl)benzofuran-5-yl)propan-1-one **(PK18)**. Thirteen known compounds were also obtained: a mixture of *β*-sitosterol and stigmasterol **(PK1)**, (*E*)-4-(3',4'-dimethoxyphenyl)-3-butenyl acetate **(PK2)**, 5*a*,6-di hydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-9-(3-methyl-2-buten-1-yl)-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one **(PK3)**, 4-hydroxybenzaldehyde **(PK4)**, 2,3,8-trihydroxy-11,11-dimethyl-13-(3-methyl-2-butenyl)-6-(2-methyl-1-propenyl)-6*H*,7*H*,11*H*-bis[1]benzopyrano[4,3-*b*:6',7'-*e*]pyran-7-one **(PK5)**, (*E*)-4-(3',4'-dimethoxyphenyl)but-3-en-1-ol **(PK6)**, 2-(2,4-dihydroxyphenyl)-5-hydroxy-8,8-dimethyl-3-(3-methylbut-2-enyl)pyrano[3,2-*g*]chromen-4(8*H*)-one **(PK7)**, 5*a*,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano [3,2-*h*]xanthen-7-one **(PK8)**, 6,7-dihydro-5,9,11,14-tetrahydroxy-3,3-dimethyl-6-(1-methylethenyl)-(-)-3*H*,8*H*-pyrano[3',2':4,5]benzo[1,2-*c*]xanthen-8-one **(PK9)**, 8,9-dihydro-6,10,11,13-tetrahydroxy-3,3-dimethyl-9-(1-methylethenyl)-3*H*,7*H*-benzo[*c*] pyrano[3,2-*h*]xanthen-7-one **(PK10)**, (*E*)-3-(4'-hydroxy-3'-methoxyphenyl)-2-propenoic acid **(PK11)**, 5-hydroxy-8,8-dimethyl-3-(3-methyl-2-butenyl)-2-(2,4,5-trihydroxyphenyl)-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one **(PK12)** and (*S*)-2-(2,4-dihydroxyphenyl)-5-hydroxy-7-methoxychroman-4-one **(PK16)**. Their structures

were determined on the basis of UV, IR, NMR, MS and by comparison their spectroscopic data with those reported.





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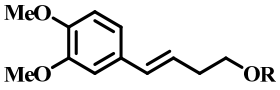
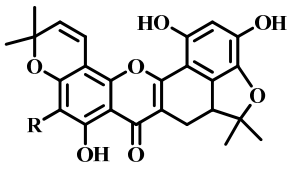


PK2 : R = CH_3CO

PK6 : R = H



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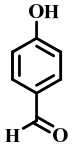
PK8 : R = H



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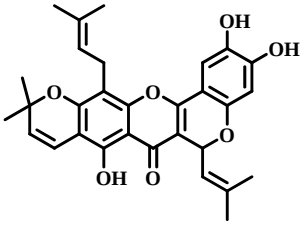

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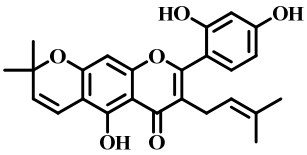

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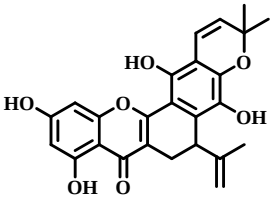

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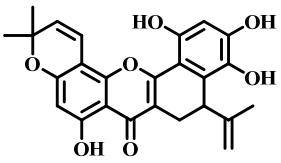

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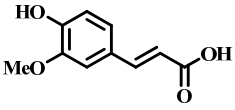

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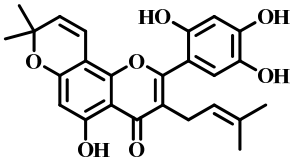

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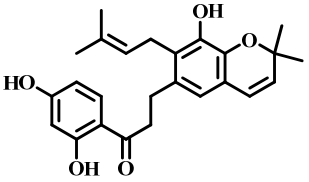

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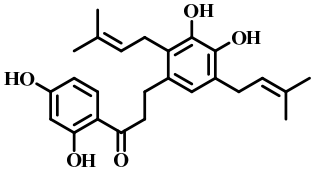

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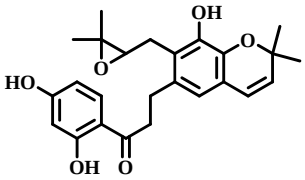

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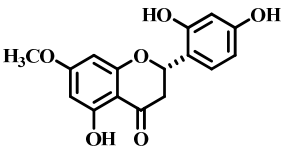

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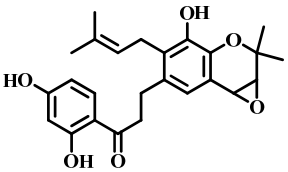

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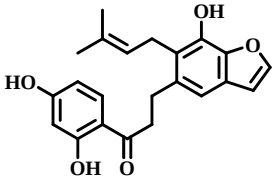

PK18

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Finally, none of this would have been possible without love and encouragement of my family and colleagues. I thank them for their understanding during all of the times when I could not be with them and their steady love that supports me.

Prakit Chaithada

THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The purpose of this research is to investigate the chemical constituents from the root bark and leaves of *Artocarpus elasticus*. It is a part of the basic research on the utilization of Thai medicinal plants. This research will contribute significantly to scientific basis of traditional medicine. Seven prenylated flavones, five prenylated dihydrochalcones, two phenylbutenoids, a phenylpropanoids, a benzaldehyde derivatives, a flavanones and a mixture of triterpenoids were isolated from this plant. Some of the compounds showed strong antibacterial activity. Moreover, some compounds of these have been reported to show cytotoxicity, anti-inflammatory and antioxidation activities. So further study on the biological activity of the isolated compounds should be performed which can lead to active compounds. Therefore Thai plant can be utilized as a natural resource of potential drugs.

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LIST OF ILLUSTRATIONS

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LIST OF ABBREVIATIONS AND SYMBOLS

s	=	singlet
d	=	doublet
t	=	triplet
m	=	multiplet
dd	=	doublet of doublet
dt	=	doublet of triplet
mt	=	multiplet of triplet
qd	=	quartet of doublet
td	=	triplet of doublet
ddd	=	doublet of doublet of doublet
br	=	broad
br s	=	broad singlet
br d	=	broad doublet
g	=	gram
kg	=	kilogram
mg	=	milligram
%	=	percent
nm	=	nanometer
m.p.	=	melting point
cm^{-1}	=	reciprocal centimeter (wave number)
δ	=	chemical shift relative to TMS
J	=	coupling constant
λ_{max}	=	maximum wavelength
ν	=	absorption frequencies
ε	=	molar extinction coefficient
$^{\circ}C$	=	degree of celcius
MHz	=	Megahertz
ppm	=	part per million
IR	=	Infrared

LIST OF ABBREVIATIONS AND SYMBOLS (continued)

UV	=	Ultraviolet-Visible
NMR	=	Nuclear Magnetic Resonance
2D NMR	=	Two Dimentional Nuclear Magnetic Resonance
COSY	=	Correlated Spectroscopy
DEPT	=	Distortionless Enhancement by Polarization Transfer
HMBC	=	Heteronuclear Multiple Bond Correlation
HMQC	=	Heteronuclear Multiple Quantum Coherence
CC	=	column chromatography
TMS	=	tetramethylsilane
Acetone-d_6	=	deuteroacetone
DMSO-d_6	=	deuterodimethylsulphoxide
$CDCl_3$	=	deuterochloroform
MeOH	=	methanol
CH_2Cl_2	=	dichloromethane
TLC	=	thin layer chromatography
MIC	=	Minimum Inhibition Concentration

CHAPTER 1
INTRODUCTION

1.1 Introduction

A natural product is a chemical compound produced by a living organism found in nature. It usually has a pharmacological or biological activity for use in pharmaceutical drug discovery and drug design. All plants produce chemical compounds as part of their normal metabolic activities. Herbalism is a traditional medicinal or folk medicine practice based on the use of plants and plant extracts. Herbal plant is abundantly found in Thailand, so the research of the chemical constituents in Thai herbal plant is necessary.

The *Artocarpus* genus belongs to the mulberry family, Moraceae. It is a large evergreen tree consisting of 60 species approximately. Most species of *Artocarpus* are widespread in Southeast Asia; a few cultivated species are more widely distributed, especially *A. altilis* and *A. heterophyllus*. Economically the genus is of appreciable importance as a source of edible fruits, such as *A. heterophyllus* (Jack-fruit), *A. champeden* (Chempedak), and *A. altilis* (Breadfruit). Recently, there have been increasing reports of prenylated flavonoids. In spite of the structural diversity of them, they have been isolated from a rather limited number of plant families especially the Leguminosae, Moraceae and Asteraceae. They were most frequently found in roots and bark, but also occur in the aerial parts, buds and seeds. Prenylflavonoids isolated from *A. communis* and *A. elasticus* revealed significant cytotoxic effect against human cancer cell lines (Cidade *et al*., 2001). The root bark and the heartwood have been described as containing chemical compounds with antioxidant properties. Wei and co-workers (Wei *et al*., 2005) indicated that artocarpanone from the roots of *A. heterophyllus* significantly inhibits the LPS-induced NO production and iNOS protein expression in RAW 264.7 cells which the large amount of NO produced in response to lipopolysaccharide (LPS) plays an important role in inflammatory conditions (Stoclet *et al*., 1998). The antifungal and antimicrobial effect of flavonoids is mainly attributed to presence of phenolic

compounds which have high affinity for proteins and act as inhibitors of microbial enzymes. Many of the isoprenylated flavonoids also showed potent cytotoxic activity against various cell lines, including murine leukemia P388, KB, mouse L-1210 and colon 38, inhibition of arachidonate 5-lipoxygenase, antiplatelet activity, and antibacterial activity against cariogenic bacteria (Nomura *et al*., 1998). There are several activities in *Artocarpus* genus. In Thailand, fourteen species of *Artocarpus*: *A. altilis* สาเก, *A. alitssimus* ไสน, *A. chaplasha* หาดส้าน, *A. dadah* หาดรุม, *A. elasticus* กะออก, *A. gomezianus* หาดหนุน, *A. heterophyllus* ขนุน, *A. integer* จำปาดะ, *A. kemando* ขนุนป่า, *A. lacucha* มะหาด, *A. lanceifolius* ขนุนป่า, *A. nitidus* มะหาดข่อย, *A. rigidus* spp. *asperulus* ขนุนปาน, *A. rigidus* spp. *rigidus* ขนุนป่า are widely distributed (Smitinand, T. 2544).

1.2 Review of Literatures

1.2.1 The Chemical Constituents of *Artocarpus* genus

The chemical constituents which were isolated from *Artocarpus* genus before 2008 were summarized in the thesis of Aeesoh Yanya (2009). The additional constituents of this genus from 2008 to 2010 were summarized in **Table 1** (Based on SciFinder Scholar database). Several of compounds have been reported in the *Artocarpus* genus, such as 2-arylbenzofuran, flavonoids, stibenoids, triterpenes *etc*.

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

Compounds	Structure	Bibliography
1. *A. altilis*		
fruits		
artocarpesin	**1**	Amarasinghe
artoindonesianin F	**2**	*et al*., 2008
3β-acetoxyolean-12-en-11-one	**3**	
cycloartenyl acetate	**4**	
isoartocarpesin	**5**	

Table 1 (continued)

Compounds	Structure	Bibliography
(3-methyl-2-butenyl)-(*E*)-2,3',4,5'-stilbenetetrol	**6**	
moracin M	**7**	
norartocarpanone	**8**	
norartocarpetin	**9**	
oxyresveratrol	**10**	
sitosterol	**11**	
sitosterol *β*-D-glucopyranoside	**12**	
2. *A. communis*		
leaves		
5'-geranyl-2',4',4-trihydroxychalcone	**13**	Fang *et al*.,
isolespeol	**14**	2008
lespeol	**15**	
3,4,2',4'-tetrahydroxy-3'-geranyldihydro-chalcone	**16**	
xanthoangelol	**17**	
cortex of roots		
artochamin B	**18**	Lin *et al*.,
artochamin D	**19**	2009
artocommunol CC	**20**	
artoflavone A	**21**	
artomunoisoxanthone	**22**	
cyclogeracommunin	**23**	
dihydroartomunoxanthone	**24**	
3. *A. elasticus*		
non specified		
artelastoheterol	**25**	Lin *et al*.,
artonol A	**26**	2009
cycloartelastoxanthone	**27**	
cycloartobiloxanthone	**28**	

Table 1 (continued)

Compounds	Structure	Bibliography
wood		
artocarpin	**29**	Musthapa
artoindonesianin E1	**30**	*et al*., 2009
cycloartocarpin	**31**	
cudraflavones A	**32**	
cudraflavones C	**33**	
4. *A. heterophyllus*		
twigs		
artocarpesin	**1**	Zheng *et al*.,
artocarpin	**29**	2009
artoheterophyllin A	**34**	
artoheterophyllin B	**35**	
artoheterophyllin C	**36**	
artoheterophyllin D	**37**	
artonin A	**38**	
artonin J	**39**	
p-counmaric acid	**40**	
cudraflavones B	**41**	
cycloheterophyllin	**42**	
dihydrophaseic acid 4'-*O*-*β*-D-glucopyranoside	**43**	
2-(2,4-dihydroxy-6-methoxyphenyl)-5-hydroxy-7-methoxy-6-(3-methyl-l-buten-l-yl)-3-(3-methyl-2-buten-l-yl)-4*H*-1-benzopyran-4-one	**44**	
(*E*)-5-(6-hydroxybenzofuran-2-yl)-4-(3-methylbut-l-enyl)benzene-1,3-diol	**45**	
6-prenyl- 4',5,7-trihydroxyflavone	**46**	
4-hydroxybenzoic acid	**47**	
licoflavone C	**48**	

Table 1 (continued)

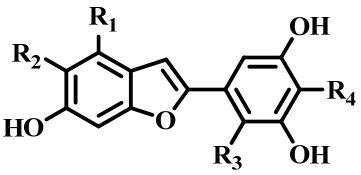
Compounds	Structure	Bibliography
moracin M	**7**	
norartocarpetin	**9**	
vanillic acid	**49**	
pulps		
cis-antheraxanthin	**50**	de Faria
all-*trans*-*α*-carotene	**51**	*et al*., 2009
9-*cis*-*β*-carotene	**52**	
13-*cis*-*β*-carotene	**53**	
15-*cis*-*β*-carotene	**54**	
all-*trans*-*β*-carotene	**55**	
all-*trans*-*α*-cryptoxanthin	**56**	
all-*trans*-*β*-cryptoxanthin	**57**	
all-*trans*-lutein	**58**	
cis-luteoxanthin	**59**	
all-*trans*-luteoxanthin	**60**	
all-*trans*-neochrome	**61**	
9-*cis*-neoxanthin	**62**	
all-*trans*-neoxanthin	**63**	
9-*cis*-violaxanthin	**64**	
all-*trans*-zeaxanthin	**65**	
cis-zeinoxanthin	**66**	
all-*trans*-zeinoxanthin	**67**	
fruits		
artocarpesin	**1**	Fang *et al*.,
norartocarpetin	**9**	2008
oxyresveratrol	**10**	

Table 1 (continued)

Compounds	Structure	Bibliography
5. *A. lowii*		
leaves		
2',4-dihydroxy-3',4'-(2,2-dimethylchromene) chalcone	**68**	Jamil *et al*., 2008
2',4'-dihydroxy-4-methoxy-3'-prenyldihydro chalcone	**69**	
2',4',4-trihydroxy-3'-prenylchalcone	**70**	
6. *A. nobilis*		
root bark		
artobiloxanthone	**71**	Jayasinghe *et al*., 2008
artonin E	**72**	
artonin E 2'-methylether	**73**	
artonin V 2'-methylether	**74**	
cycloartobiloxanthone	**28**	
dihydroisoartonin E 2'-methylether	**75**	
isoartonin E 2'-methylether	**76**	
7. *A. tonkinensis*		
leaves		
alphitonin-4-O-β-D-glucopyranoside	**77**	Dang *et al*., 2009
artonkin-4'-O-β-D-glucopyranoside	**78**	
kaempherol-3-O-β-D-glucopyranoside	**79**	
maesopsin-4-O-β-D-glucopyranoside	**80**	

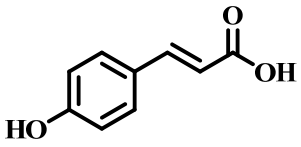
Structures of compounds from *Artocarpus* genus

a. 2-arylbenzofurans

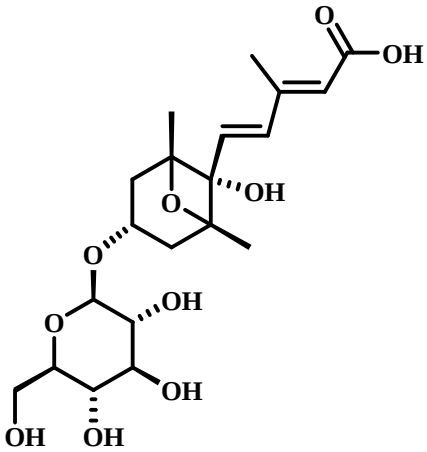


R_1	R_2	R_3	R_4	
H	H	H	H	**7 :** moracin M
	OMe		H	**34 :** artoheterophyllin A
H	H	H		**45 :** (*E*)-5-(6-hydroxybenzofuran-2-yl)-4-(3-methylbut-l-enyl)benzene-1,3-diol

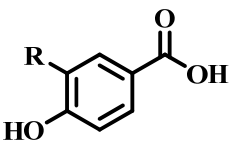
b. carboxylic acid



40 : *p*-counmaric acid

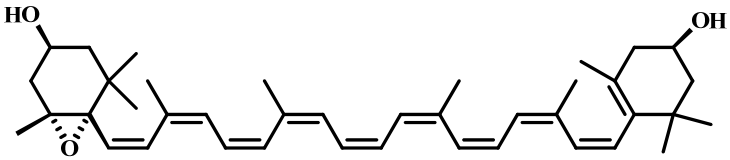


43 : dihydrophaseic acid 4'-*O*-*β*-D-glucopyranoside

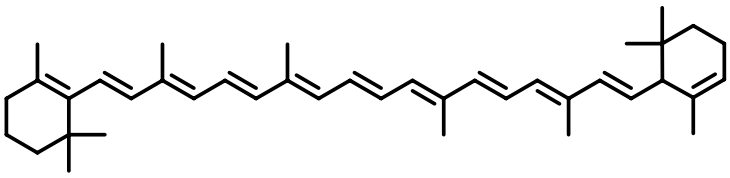


	R	
47 :	H	4-hydroxybenzoic acid
49 :	OMe	vanillic acid

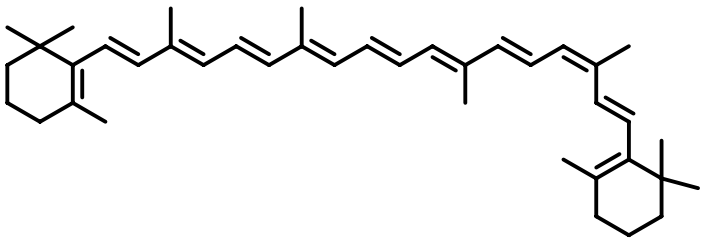
c. carotenoid



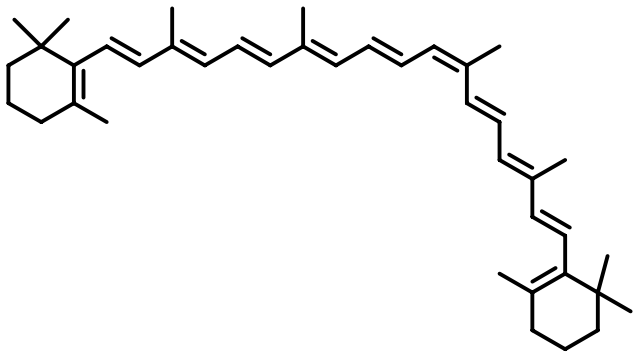
50 : *cis*-antheraxanthin



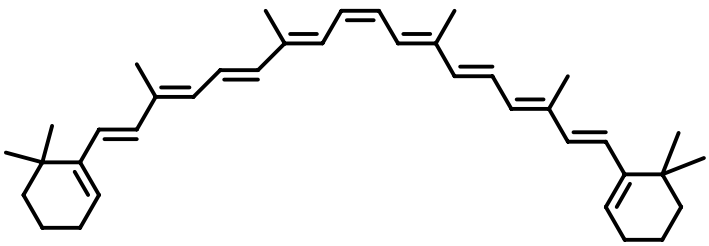
51 : all-*trans*-α-carotene



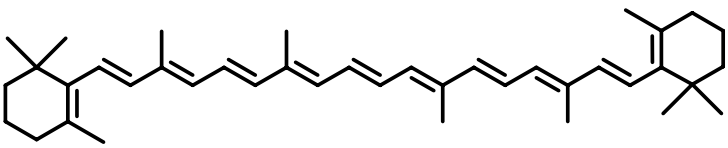
52 : 9-*cis*-β-carotene



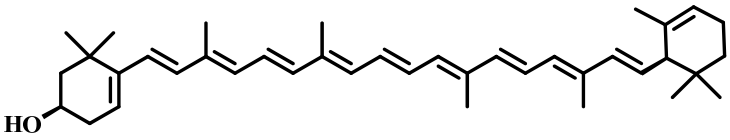
53 : 13-*cis*-β-carotene



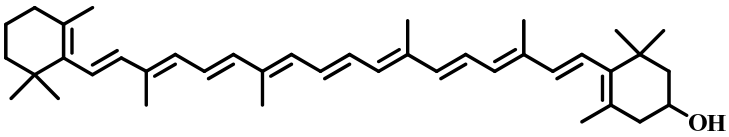
54 : 15-*cis*-β-carotene



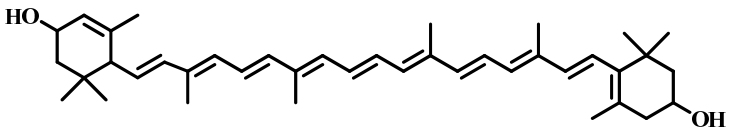
55 : all-*trans*-β-carotene



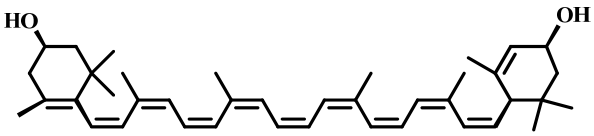
56 : all-*trans*-α-cryptoxanthin



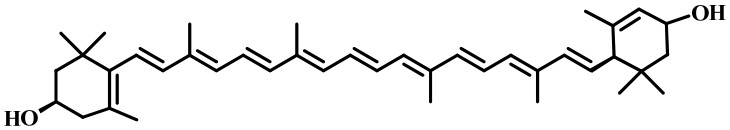
57 : all-*trans*-β-cryptoxanthin



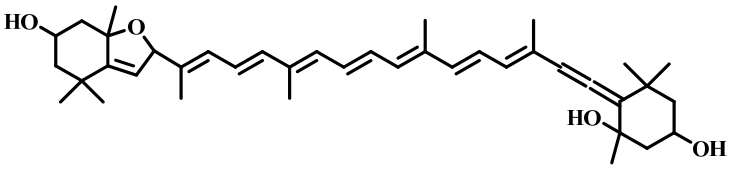
58 : all-*trans*-lutein



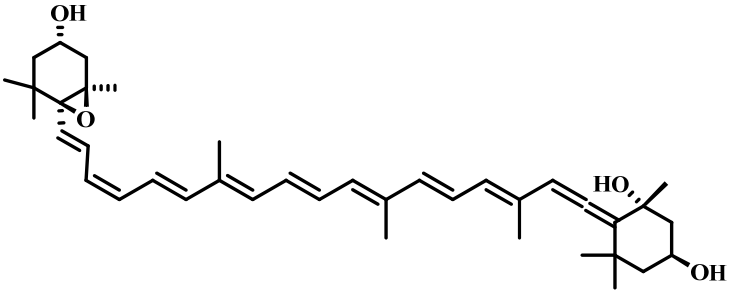
59 : *cis*-luteoxanthin



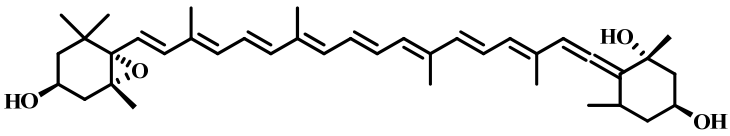
60 : all-*trans*-luteoxanthin



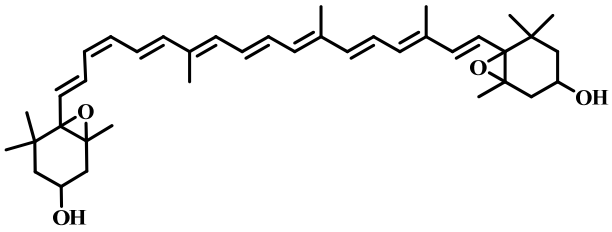
61 : all-*trans*-neochrome



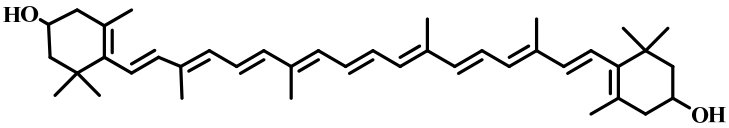
62 : 9-*cis*-neoxanthin



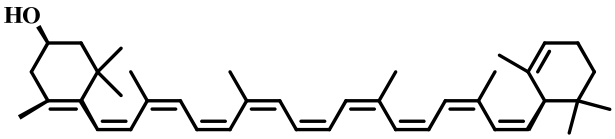
63 : all-*trans*-neoxanthin



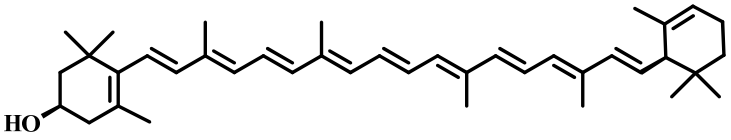
64 : 9-*cis*-violaxanthin



65 : all-*trans*-zeaxanthin

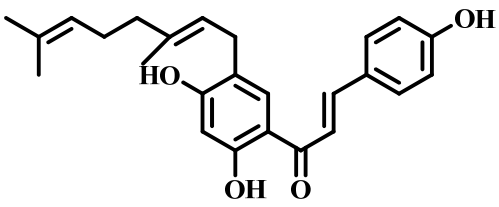


66 : *cis*-zeinoxanthin

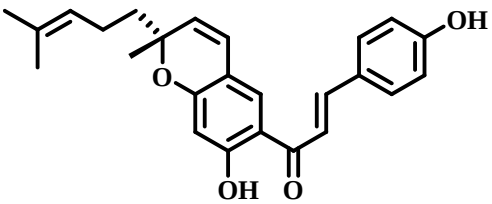


67 : all-*trans*-zeinoxanthin

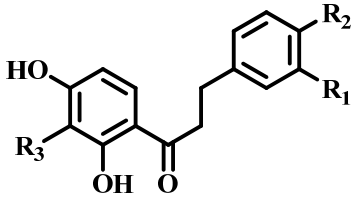
d. chalcones

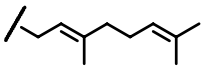
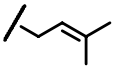


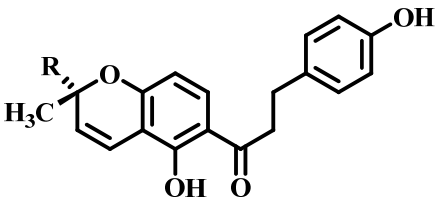
13 : 5'-geranyl-2',4',4-trihydroxychalcone

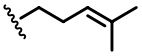


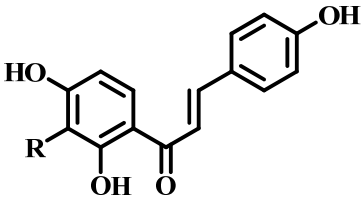
14 : isolespeol

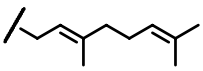
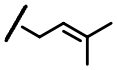


	R_1	R_2	R_3	
16 :	OH	OH		3,4,2',4'-tetrahydroxy-3'-geranyldihydrochalcone
69 :	H	OMe		2',4'-dihydroxy-4-methoxy-3'-prenyldihydrochalcone

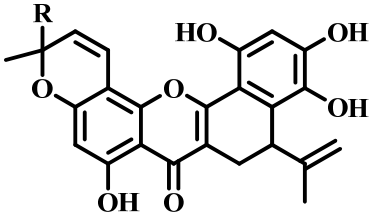


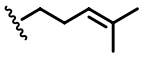
	R	
15 :		lespeol
68 :	CH_3	2',4-dihydroxy-3',4'-(2,2-dimethylchromene)chalcone

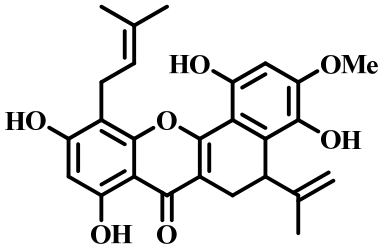


	R	
17 :		xanthoangelol
70 :		2',4',4-trihydroxy-3'-prenylchalcone

e. dihydrobenzoxanthones

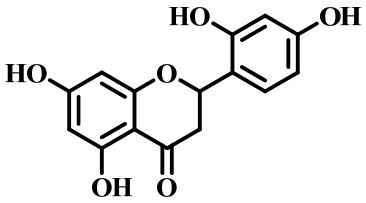


	R	
22 :		artomunoisoxanthone
71 :	CH_3	artobiloxanthone



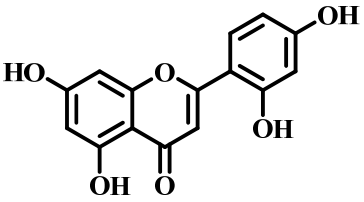
24 : dihydroartomunoxanthone

f. flavanones



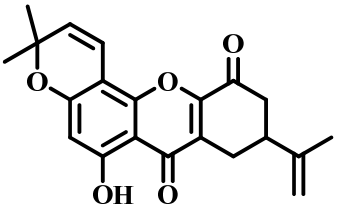
8 : norartocarpanone

g. flavones



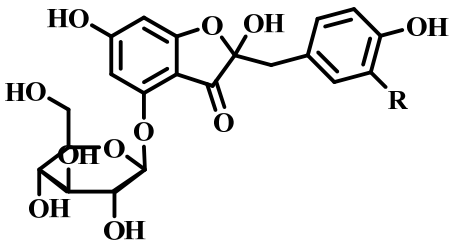
9 : norartocarpetin

h. flavonoid-derived xanthones



26 : artonol A

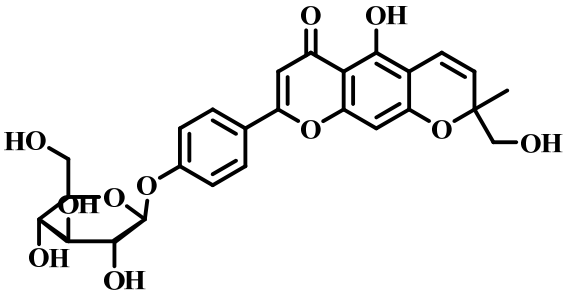
i. flavonoid glycosides



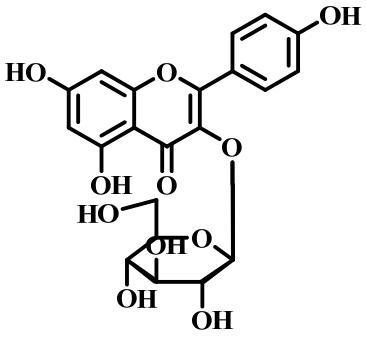
R

77 : OH alphitonin-4-O-β-D-glucopyranoside

80 : H maesopsin-4-O-β-D-glucopyranoside

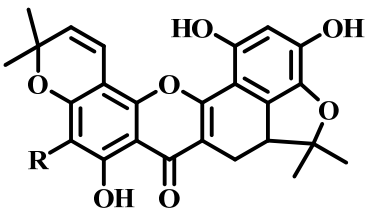


78 : artonkin-4'-O-β-D-glucopyranoside

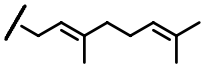


79 : kaempherol-3-O-β-D-glucopyranoside

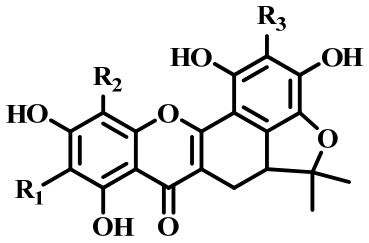
j. furanodihydrobenzoxanthones

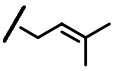
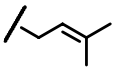
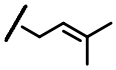


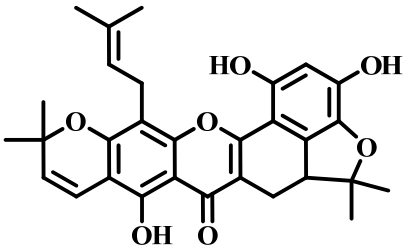
R

27 :  cycloartelastoxanthone

28 : H cycloartobiloxanthone

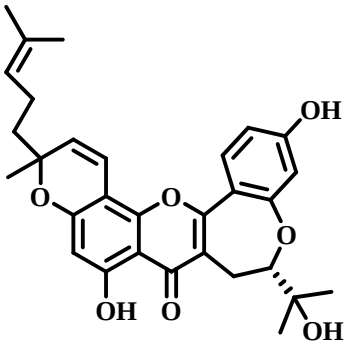


	R_1	R_2	R_3	
36 :			H	artoheterophyllin C
39 :	H	H		artonin J

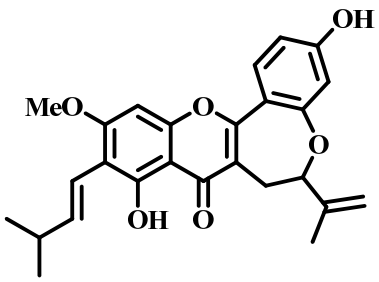


38 : artonin A

k. oxepinoflavones

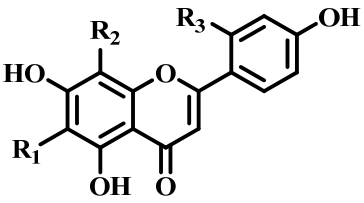


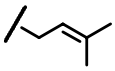
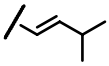
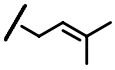
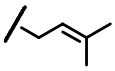
20 : artocommunol CC

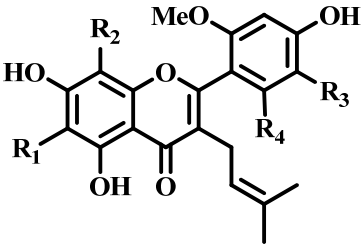


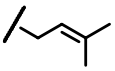
30 : artoindonesianin E1

l. prenylated flavones

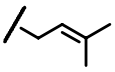


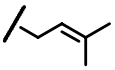
	R_1	R_2	R_3	
1 :		H	OH	artocarpesin
5 :		H	OH	isoartocarpesin
46 :		H	H	6-prenyl-4',5,7-trihydroxyflavone
48 :	H		H	licoflavone C

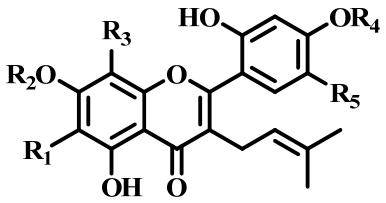


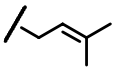
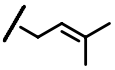
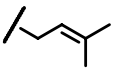
	R_1	R_2	R_3	R_4	
42 :		H	H	OH	cycloheterophyllin
44 :	OMe	H	H	OH	2-(2,4-dihydroxy-6-methoxyphenyl)-5-hydroxy-7-methoxy-6-(3-methyl-l-buten-l-yl)-3-(3-

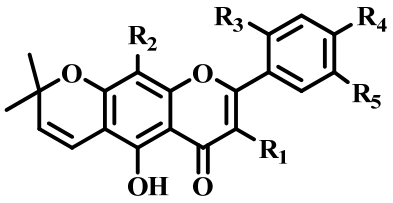
methyl-2-buten-l-yl)-4*H*-1-benzopyran-4-one

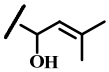
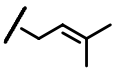
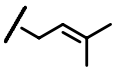
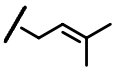
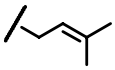
74 : H  OH H artonin V 2'-methylether

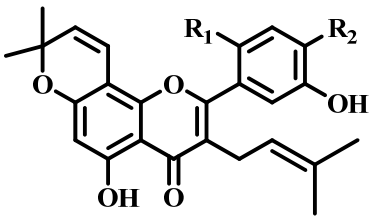
75 :  H OH H dihydroisoartonin E 2'-methylether



	R_1	R_2	R_3	R_4	R_5	
19 :	H	H		Me	OH	artochamin D
29 :		Me	H	H	H	artocarpin
33 :		H	H	H	H	cudraflavones C

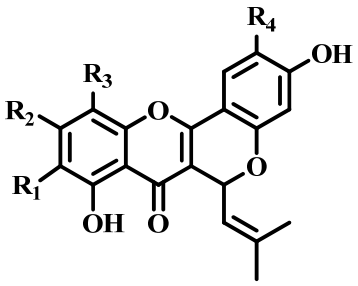


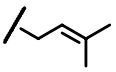
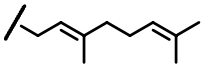
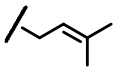
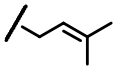
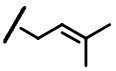
	R_1	R_2	R_3	R_4	R_5	
25 :			OH	OH	OH	artelastoheterol
37 :			OH	OH	H	artoheterophyllin D
76 :		H	OMe	OH	OH	isoartonin E 2'-methylether

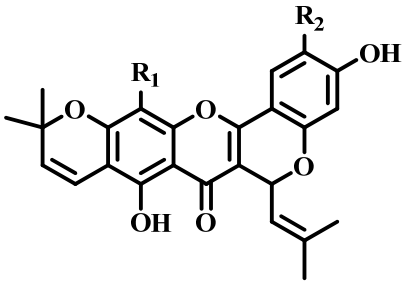


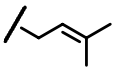
	R_1	R_2	
21 :	OH	OMe	artoflavone A
72 :	OH	OH	artonin E
73 :	OMe	OH	artonin E 2'-methylether

m. pyranoflavones

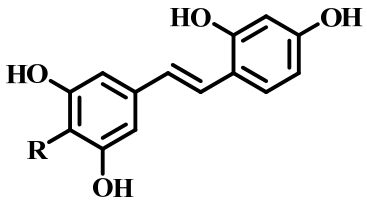


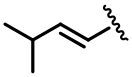
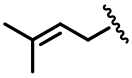
	R_1	R_2	R_3	R_4	
18 :	H	OH		OH	artochamin B
23 :	H	OH		H	cyclogeracommunin
31 :		OMe	H	H	cycloartocarpin
35 :		OH		OH	artoheterophyllin B



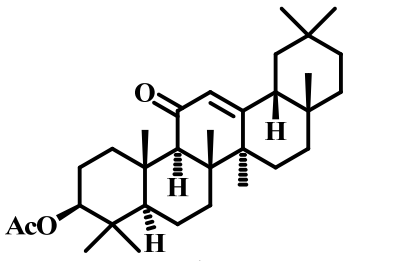
	R_1	R_2	
32 :	H	H	cudraflavones A
41 :		OH	cudraflavones B

n. stilbenoids

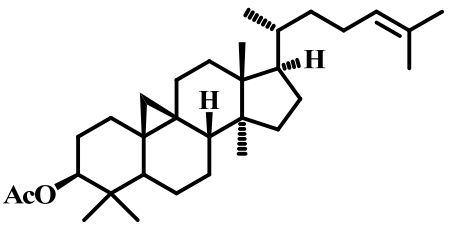


	R	
2 :		artoindonesianin F
6 :		(3-methyl-2-butenyl)-(*E*)-2,3',4,5'-stilbenetetrol
10 :	H	oxyresveratrol

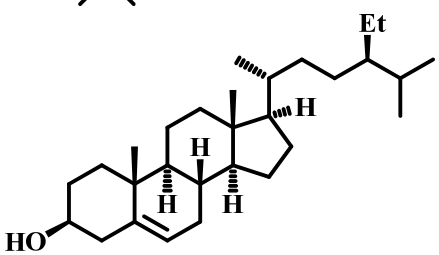
o. terpenoids



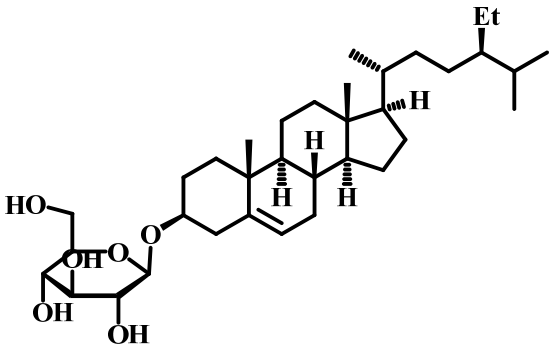
3 : 3β-acetoxyolean-12-en-11-one



4 : cycloartenyl acetate



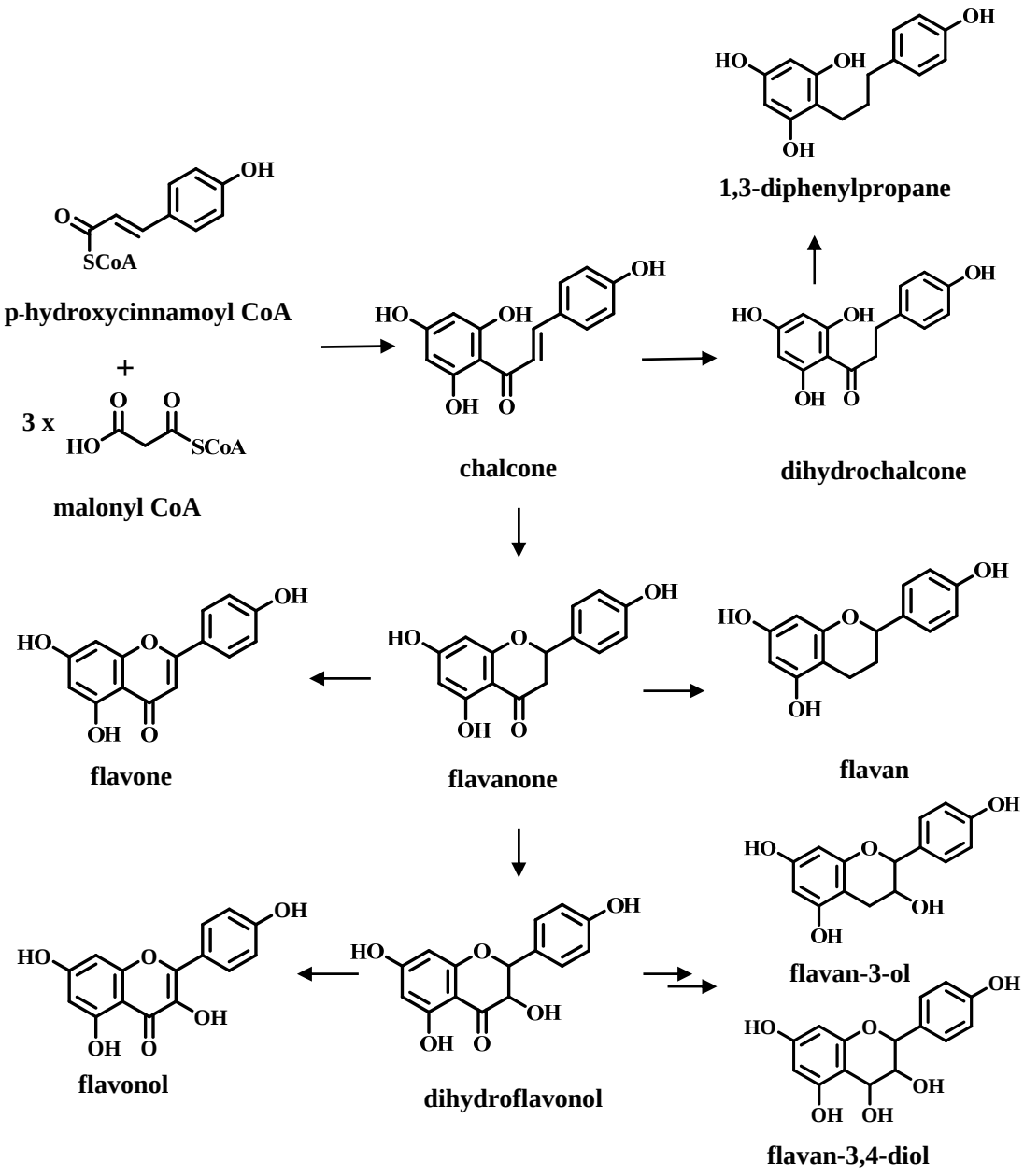
11 : sitosterol



12 : sitosterol-β-D-glucopyranoside

1.2.2 Biogenetic relationship of some flavonoid compounds

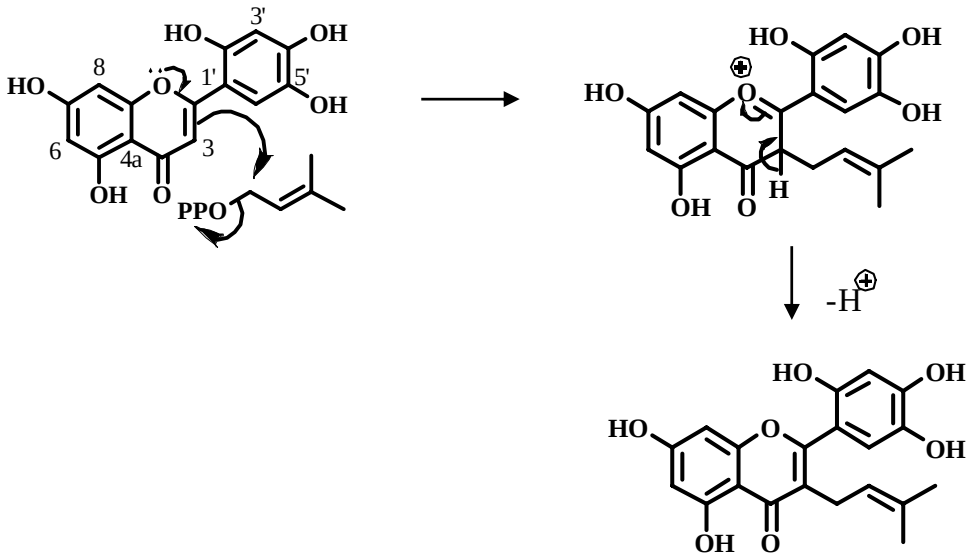
Many phenolic compounds, primarily flavonoids, apart from stilbenoids and 2-arylbenzofuran, have been isolated from *Artocarpus* species. The flavonoid constituents may be further classified according to their skeletons, namely chalcones, flavanones, flavones, flavan-3-ol, and 3-isoprenylflavones. Flavanones represent branch-point intermediates in the biosynthesis of other classes of flavonoids. Biogenetic relationship of the flavonoids compound was shown in **Scheme 1**.



Scheme 1 Biogenetic relationship of the flavonoids compound

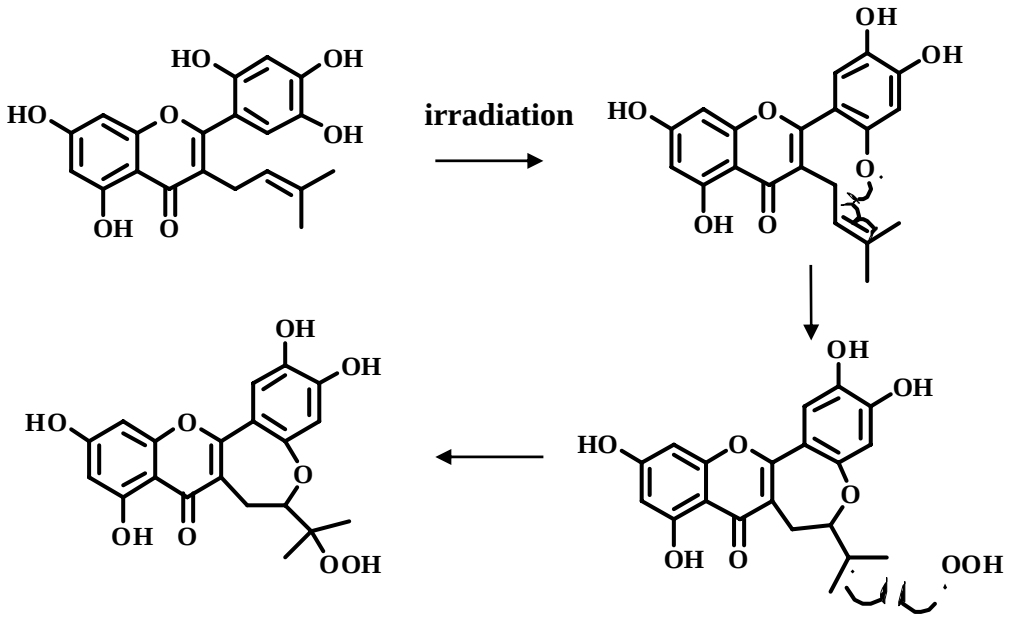
The major chemical compositions of *Artocarpus* plants were prenylated flavonoids**.** Generally, most flavonoids were *C*-prenylted, whereas *O*-prenylation is quite rare. *C*-prenylation take place more frequently on ring A at position 6/8, as well as positions 3'/5' especially in flavanones and flavones (Barron and Ibrahim, 1996). Notable among the prenylated flavones is the frequent substitution at position 3. The formation of 3-prenylflavone derivatives from simple

flavones has been suggested to involve formally selective isoprenylation of the flavones as indicated in **Scheme 2** (Sultanbawa *et al*., 1989).



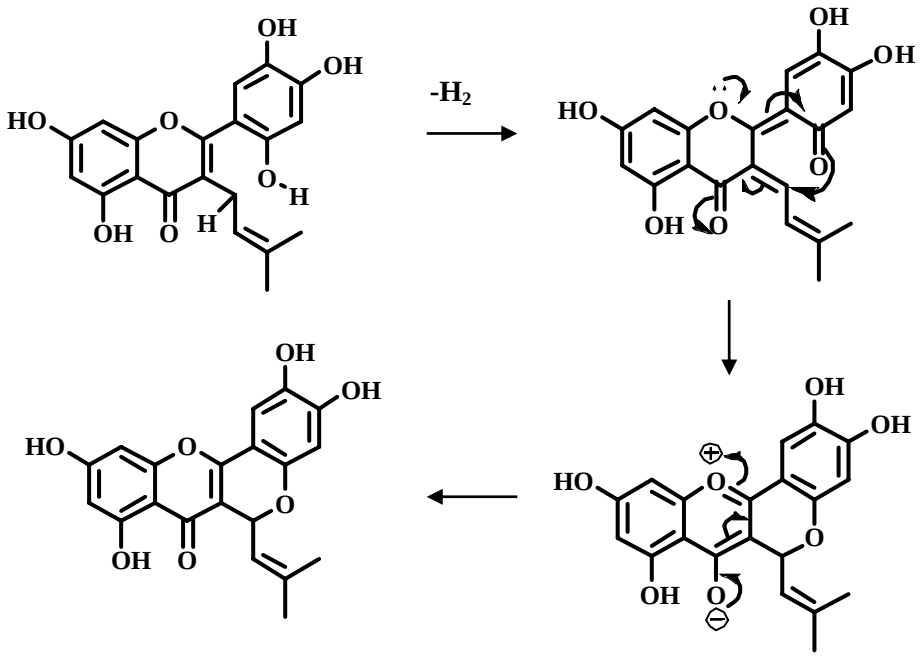
Scheme 2 Prenylation of a flavone at C-3 position

Modification of the isoprenyl side chains may occur by further oxidation, reduction, dehydration and/or cyclization. In common, cyclization of the isoprenyl side chains with adjacent phenolic groups gave the pyrano or furano derivatives. The isoprenyl substituent at C-3 position is always found in the form of a carbocyclic ring or an oxygen-bearing ring fused with rings B and C. Some hypotheses about the biogenesis of the *Artocarpus* flavonoids and related compounds have been reported in the literature (Hakim *et al*., 2006). The 3-prenylflavones serve as precursors for several different structural types of flavonoids. The oxepinoflavone skeleton was provided by photo-oxidative cyclization derived from 3-isoprenyl-2',4',5'-trioxygenatedflavones as presented by **Scheme 3** (Aida *et al*., 1996).



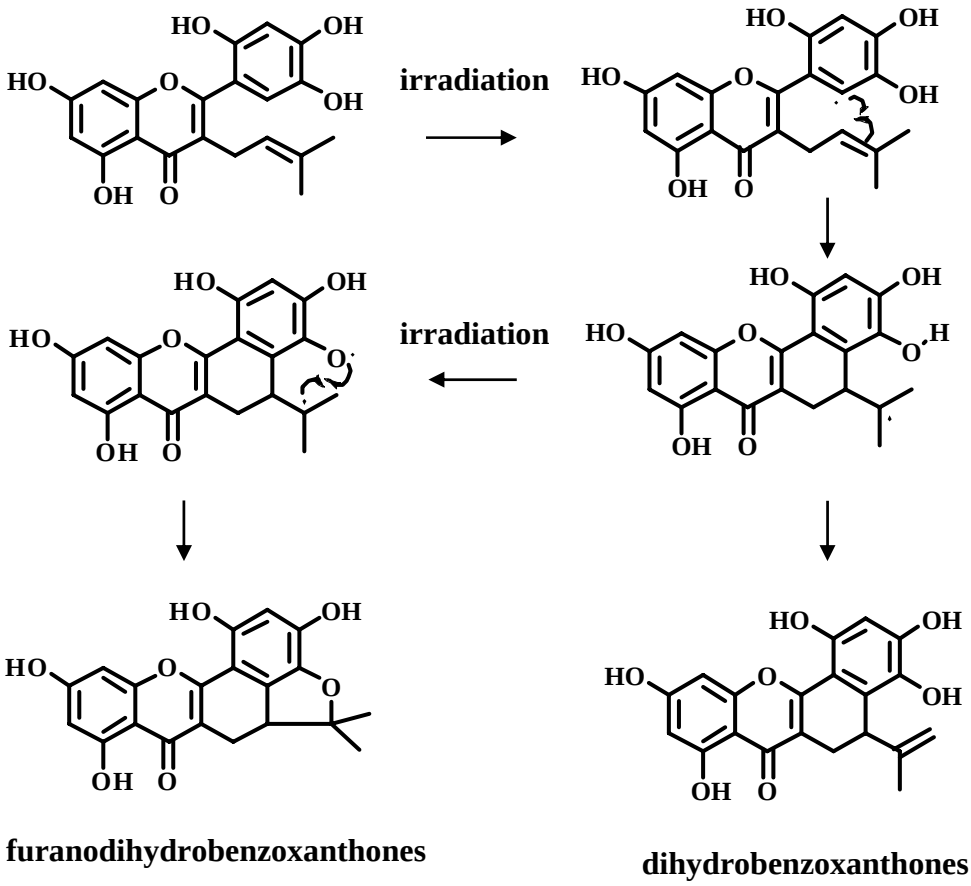
Scheme 3 Radical cyclization of 3-prenylflavone into an oxepinoflavone

In the same way, the pyranoflavone skeleton may proposed that it derived from 3-isoprenyl-2',4',5'-trioxygenated flavones through cyclization as indicated in **Scheme 4** (Hakim *et al*., 2006).



Scheme 4 Cyclization of 3-isoprenylflavone in the formation of pyranoflavone

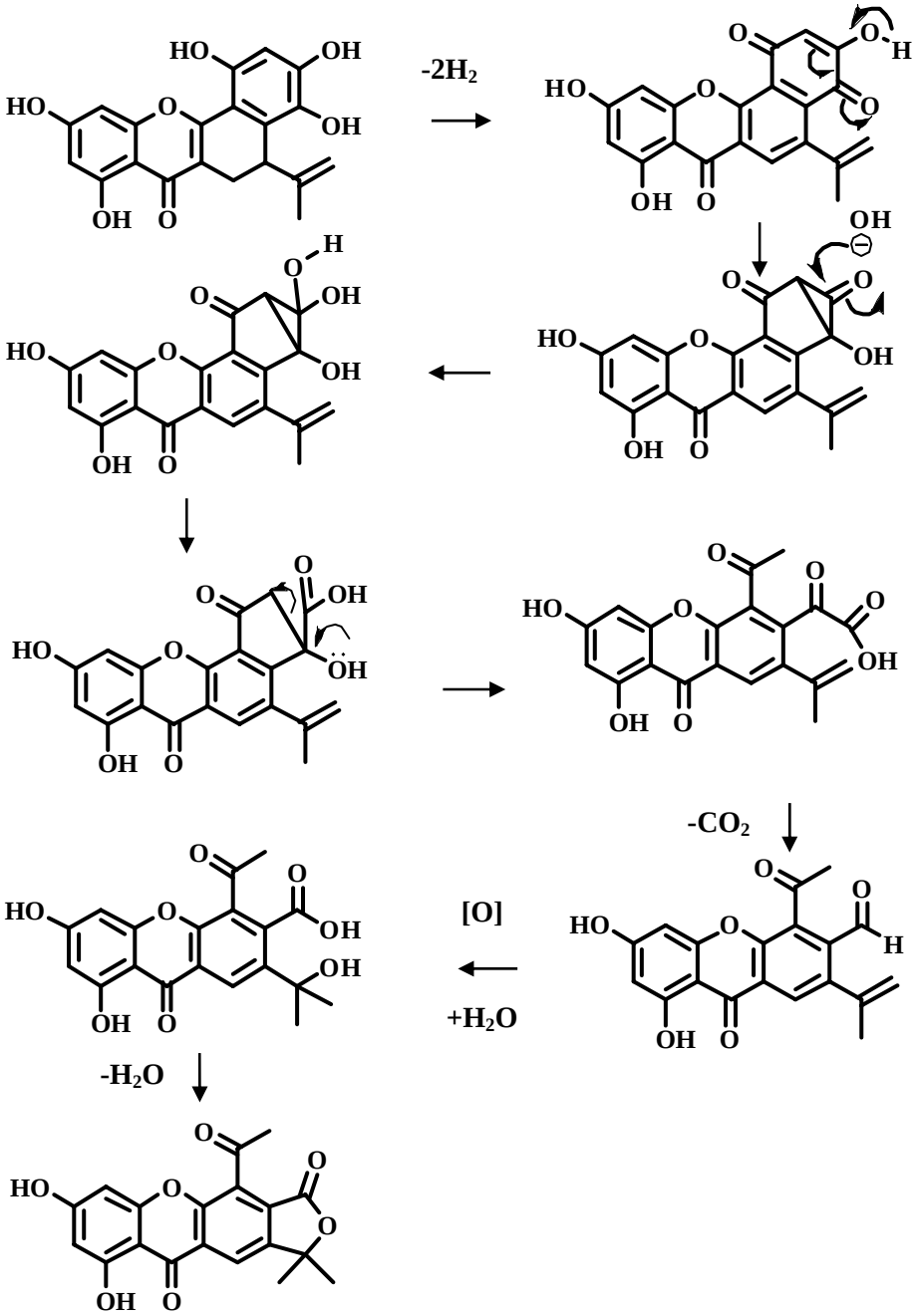
Similarly, it can assume that the dihydrobenzoxanthone skeleton is biologically derived from 3-isoprenyl-2',4',5'-trioxygenated flavones through oxidative cyclization as shown in **Scheme 5**. The hypothesis was confirmed by treatment of artonin E with the radical reagent diphenyl picryl hydrazyl (DPPH) to produce artobiloxanthone and cycloartobiloxanthone (Hano *et al*., 1989; Aida *et al*., 1996).



Scheme 5 Oxidative coupling reaction in the formation of dihydrobenzoxanthone skeleton

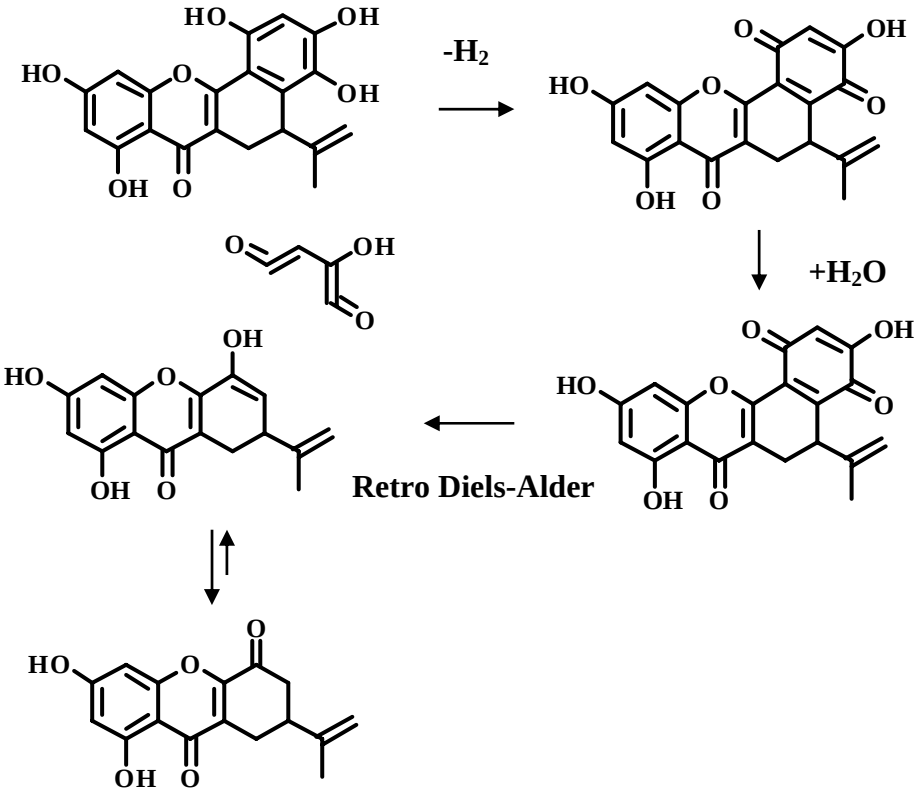
The dihydrobenzoxanthone skeleton may be further rearranged to other xanthone skeletons of quinonobenzoxanthone, cyclopentenoxanthone, xanthonolide, and dihydroxanthone. The quinonobenzoxanthones are biologically assumed to be derived from dihydrobenzoxanthone through oxidation reactions. Favorskii rearrangement of dihydrobenzoxanthone intermediates led to the cyclopente-

noxanthone skeleton, and may be further oxidation into xanthonolide derivatives, as described in **Scheme 6** (Hakim *et al*., 2006).



Scheme 6 Proposed biogenetic route of the cyclopentenoxanthone and xanthonolide types of compounds

Moreover, the dihydroxanthone skeleton may be derived from a dihydrobenzoxanthone hydrate through a retro Diels-Alder reaction, as described in **Scheme 7**. The explanation of this hypothesis was confirmed by Aida and co-worker for the production of artonol A and B (Aida *et al*., 1997).



Scheme 7 Biogenetic route to dihydroxanthone derivative

1.2.3 The Biological Activity of *Artocarpus* genus

Artocarpus plants have been used as traditional medicine in Indonesia against inflammation and malarial fever (Nomura *et al*., 1998). Prenylflavonoids isolated from *Artocarpus elasticus* revealed significant cytotoxic effects against human cancer cell lines (Cidade *et al*., 2001; Ko *et al*., 2005). In the west part of Java, *A. elasticus* has been used to treat inflammation, female contraception (bark), dysentery (latex), and tuberculosis (young leaves) (Musthapa *et al*., 2009). Many members of the *Artocarpus* genus have also been used as traditional folk medicine in Southeast Asia for the treatment of inflammation, malarial fever, and to treat ulcers, absess, and diarrhea (Nomura *et al*., 1998).

The biological activities of compounds from *A. elasticus* such as norartocarpetin, artocarpesin, isolespeol, artobiloxanthone and cycloartobiloxanthone have been reported to show tyrosinase inhibitory activity (Zheng *et al*., 2009), anti-inflammatory activity (Dang *et al*., 2009; Cerqueira *et al*., 2008; Fang *et al*., 2008), cytotoxic activity (Fang *et al*., 2008; Musthapa *et al*., 2009), anti-oxidant activity (Jamil *et al*., 2008; Jayasinghe *et al*., 2008; Lin *et al*., 2009).

1.2.4 *Artocarpus elasticus*

Artocarpus elasticus (**Figure 1**) that is a perennial plant, is widely found in the southern of Thailand. It can grow as high as 40 meters. Its branches are spreading and its outer bark is smooth dark brown while inner bark is light brown. The leaves are large 12-30 c.m., wide 20-55 c.m. and bright green. Fruits are cylindrical-shaped; at first the rind is green and turning yellow-brown when ripe. It will be mature during July-October. *A. elasticus* is locally known as “Ka-ok”. It is not only found in the southern part of Thailand but also been found in Myanmar, Malaysia, and Indonesia. In the previously report, there are only one report on the chemical constituents from root bark and no report from leaves, so we are motivated to investigate its compositions in detail.

Figure 1 *Artocarpus elasticus*

1.3 Objectives

The objective of this work was to investigate the chemical constituents from the root bark and leaves of *A. elasticus*.

CHAPTER 2
EXPERIMENTAL

2.1 Instruments and Chemicals

Melting points were determined on a digital Electrothermal 9100 Melting Point Apparatus. The UV spectra were measured with a SPECORD S 100 (Analytikjena) and principle bands (λ_{max}) were recorded as wavelengths (nm) and log ε in MeOH solution. The optical rotation $[\alpha]_D$ was measured in chloroform and methanol solution with Sodium D line (590 nm) on a JASCO P-1020 digital polarimeter. The IR spectra were measured with a Perkin-Elmer FTS FT-IR spectrophotometer. The NMR spectral data were recorded using 300 MHz Bruker FTNMR Ultra Shield^{TM} spectrometers in $CDCl_3$, acetone-d_6 and DMSO-d_6 with TMS as the internal standard. Chemical shifts are reported in δ (ppm) and coupling constants (*J*) are expressed in hertz. EI and HREI mass spectra were measured on MAT 95 XL Mass spectrometer. Solvents for extraction and chromatography were distilled at their boiling point ranges prior to use except chloroform was analytical grade reagent. Quick column chromatography (QCC) and column chromatography (CC) were carried out on silica gel 60 H (Merck) and silica gel 100 (Merck), respectively.

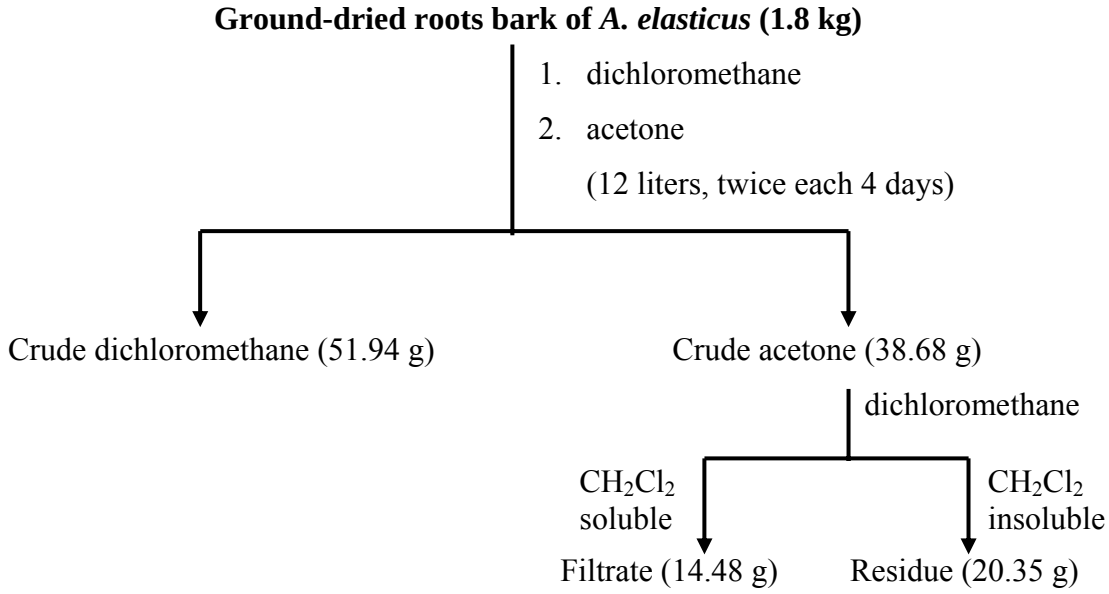
2.2 Plant Material

The root bark of *A. elasticus* was collected from Amphur Kuraburi, Phang Nga province in the southern part of Thailand in May 2008. Identification was made by Mr. Charernsak Saewai, Department of Biology, Faculty of Science, Prince of Songkla University. The specimen (A. Yanya 1Phang-nga: Kuraburi 2/4/2009) have been deposited in the Herbarium of the Department of Biology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, Thailand.

2.3 Extraction and Isolation

A. Root bark

Ground-dried root bark of *Artocarpus elasticus* (1.8 kg) were successively immersed in dichloromethane and acetone at room temperature (each extract 4 days). After removal of solvents, the dark brown viscous dichloromethane extract (51.94 g) and acetone extract (38.68 g) were obtained, respectively. The process of extraction was shown in **Scheme 8**.



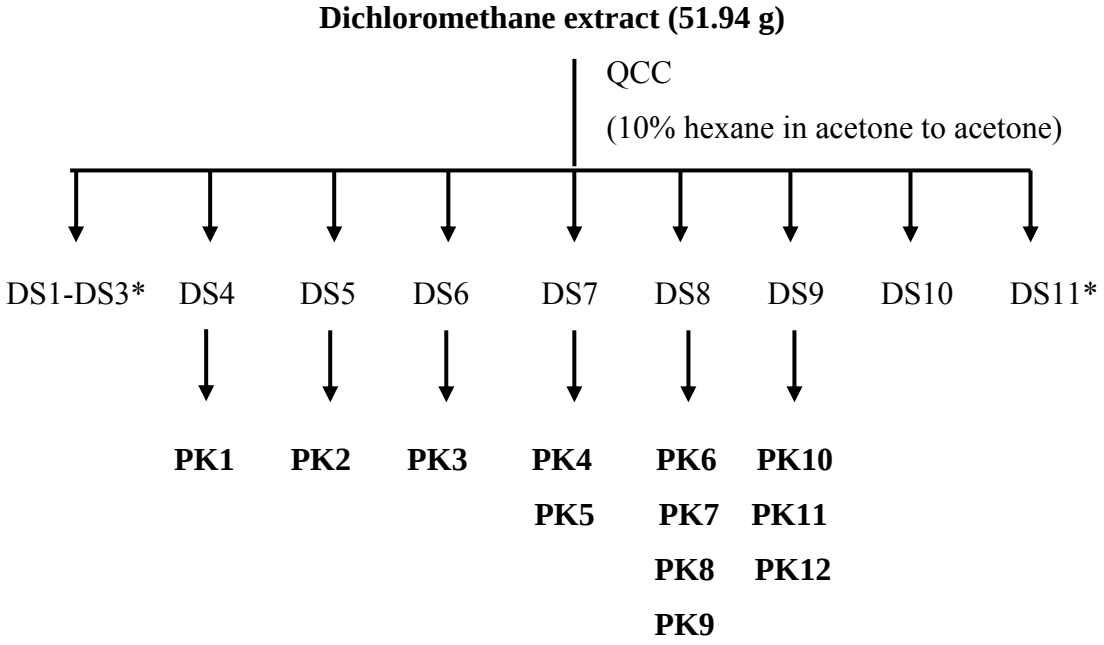
Scheme 8 Extraction of the crude extracts from the root bark of *A. elasticus*

2.3.1 Purification of dichloromethane extract

The dichloromethane extract and the dichloromethane soluble of acetone extract were combined (66.42 g). The extract was chromatographed on quick column chromatography over silica gel 60 using mixed hexane-acetone and acetone as eluent. Fractions with the similar characteristic on TLC were combined to afford 11 fractions (DS1-DS11) **(Table 2)**. Further purification of each fraction gave twelve pure compounds **(Scheme 9)**.

Table 2 Physical characteristic and weights of fractions obtained from QCC of the dichloromethane extract

Fraction	Weight (g)	Physical characteristic
DS1	3.5635	yellow gel
DS2	16.2667	orange gel
DS3	1.8281	yellow-brown viscous liquid
DS4	0.4929	yellow solid
DS5	1.2326	dark-brown viscous liquid
DS6	1.1245	dark-brown viscous liquid
DS7	2.8728	dark-brown viscous liquid
DS8	4.6366	dark-brown viscous liquid
DS9	5.2972	dark-brown viscous liquid
DS10	0.6546	dark-brown viscous liquid
DS11	5.2632	brown solid



* No further investigation

Scheme 9 Isolation of compounds **PK1-PK12** from dichloromethane extract of the root bark of *A. elasticus*

Fraction DS4 (0.4929 g) was purified by column chromatography over silica gel and eluted with 10% dichloromethane in hexane to give fractions DS4A-DS4D**.** Subfraction DS4B (41.2 mg) was recrystallized from methanol to yield a mixture of β-sitosterol and stigmasterol (**PK1**; 32.6 g) as colorless needles.

Fraction DS5 (1.2326 g) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (5% to 20% acetone in hexane) solvent system to give fractions DS5A-DS5F. Fraction DS5D (463.2 mg) was rechromatographed on column chromatography and eluted with 15% acetone in hexane solvent system to give a yellow gum of **PK2** (24.2 mg).

Fraction DS6 (1.1245 g) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (10% to 20% acetone in hexane) solvent system to give fractions DS6A-DS6K. Fraction DS6F (178.7 mg) was rechromatographed by using 15% acetone in hexane as eluent to give a red-brown gum of **PK3** (13.2 mg).

Fraction DS7 (2.8728 g) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (20% to 30% acetone in hexane) solvent system to give fractions DS7A-DS7G. Fraction DS7C (555.0 mg) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (8:1:1) to give fractions DS7C1-DS7C7. Fraction DS7C4 (90.2 mg) was rechromatographed on column chromatography using 20% acetone in hexane as eluent give colorless gum of **PK4** (2.5 mg). Fraction DS7F (134.4 mg) was further purified by column chromatography over silica gel and eluted with 15% acetone in hexane give fractions DS7F1-DS7F7. Fraction DS7F4 (51.2 mg) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to afford an orange solid of **PK5** (7.7 mg) in subfraction DS7F4C.

Fraction DS8 (4.6366 g) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (20% to 30 % acetone in hexane) solvent system to give fractions DS8A- DS8I. Fraction DS8C (334.4 mg) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to give fractions DS8C1-DS8C5. Fraction DS8C4 (169.2 mg) was rechromatographed on

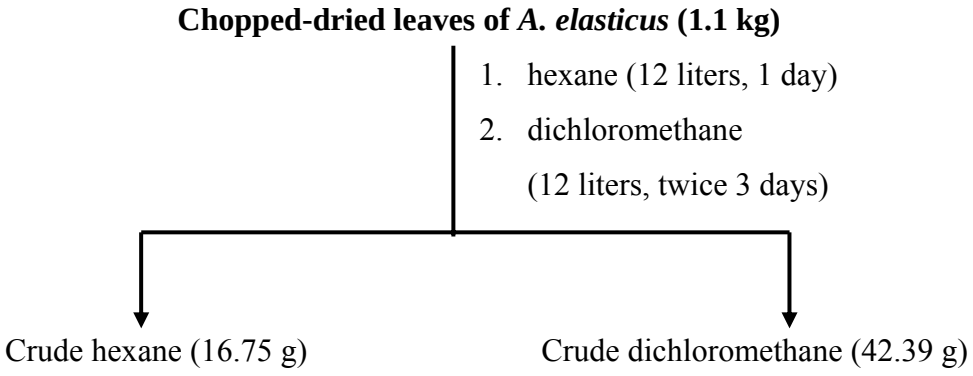
column chromatography and eluted with a mixed solvent of hexane-dichloromethane-acetone (8:1:1) to give a yellow gum of **PK6** (3.4 mg). Fraction DS8D (340.6 mg) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to give fractions DS8D1-DS8D8. Fraction DS8D4 (104.9 mg) was rechromatographed on column chromatography and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to give fractions DS8D4A-DS8D4K. Subfraction DS8D4H was further purified by preparative TLC with 25% acetone in hexane to give a yellow solid of **PK7** (4.8 mg). Fraction DS8D6 was filtered and washed with dichloromethane to give **PK8** (7.2 mg). Fraction DS8F (377.1 mg) was further separated by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to give a yellow solid of **PK9** (29.9 mg).

Fraction DS9 (5.2972 g) was further purified by column chromatography over silica gel and eluted with a gradient of hexane-acetone (10% to 30% acetone in hexane) solvent system to give fractions DS9A-DS9G. Fraction DS9B (197.9 mg) which appears in a yellow solid mixed with yellow viscous liquid, was dissolved in hexane to give a yellow solid of **PK10** (12.6 mg). Fraction DS9C (297.9 mg) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to give fractions DS9C1-DS9C4. Fraction DS9C3 (123.4 mg) was rechromatographed on column chromatography and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to give a brown solid of **PK11** (16.9 mg).

Fraction DS9D (694.1 mg) was further purified by column chromatography over silica gel and eluted with 15% acetone in hexane to give fractions DS9D1-DS9D6. Fraction DS9D3 (26.4 mg) was further purified by column chromatography over silica gel and eluted with 25% acetone in hexane to give a yellow solid of **PK12** (4.1 mg).

B. Leaves

Chopped-dried leaves of *A. elasticus* (1.1 kg) was immersed at room temperature in hexane (extract 1 day) for get rid of chlorophyll compound which have been a major component in this extract. After the solution and the residue were each other isolated, the residue was further immersed in dichloromethane at room temperature (extract 3 days). The solvent was evaporated under reduced pressure to give dichloromethane extract as green-brown viscous gum (42.39 g). The process of extraction was shown in **Scheme 10**.



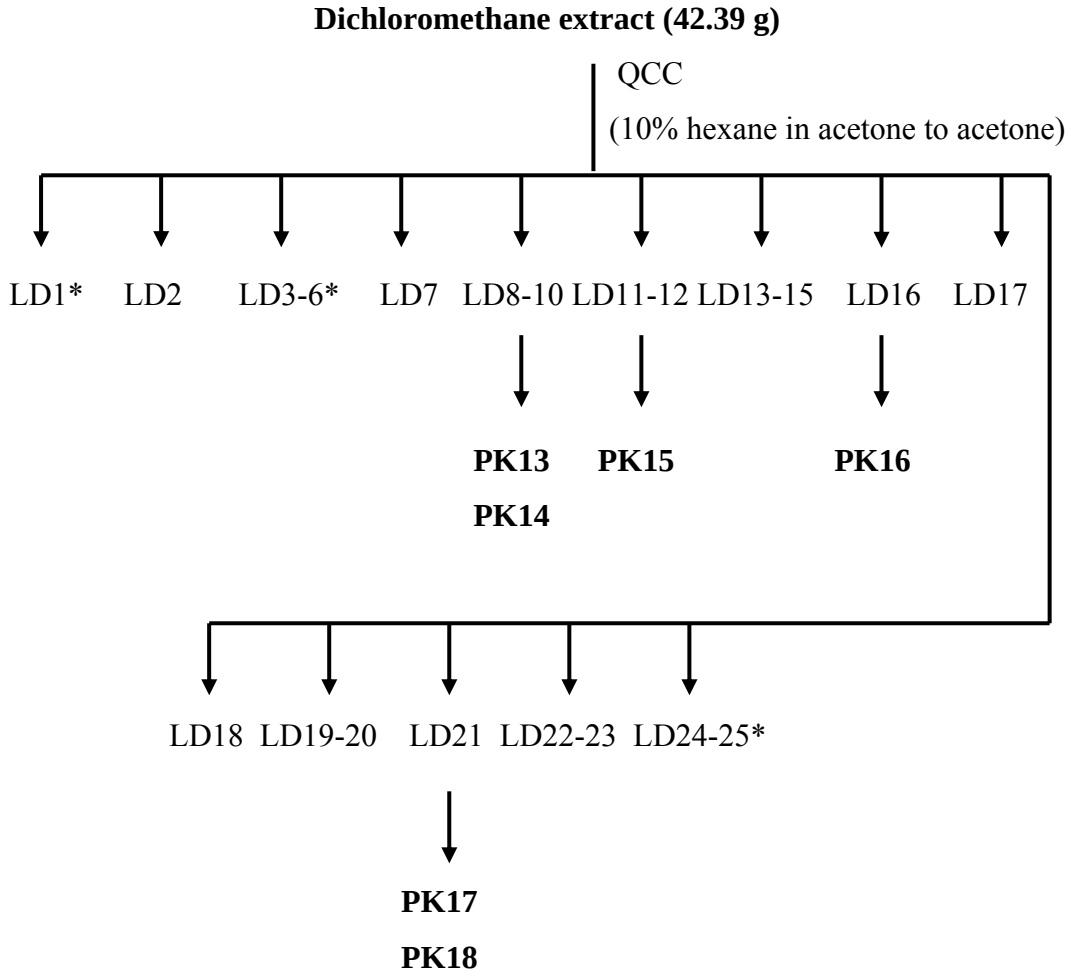
Scheme 10 Extraction of the crude extracts from the leaves of *A. elasticus*

2.3.2 Purification of dichloromethane extract

The dichloromethane extract (42.39 g) was chromatographed on quick column chromatography over silica gel 60 using solvent of increasing polarity from hexane through acetone. Fractions with the similar characteristic on TLC were combined to afford 25 fractions (LD1-LD25) **(Table 3)**. Further purification of each fraction gave six pure compounds **(Scheme 11)**.

Table 3 Physical characteristic and weights of fractions obtained from QCC of the dichloromethane extract

Fraction	Weight (g)	Physical characteristic
LD1	2.8928	yellow gel
LD2	1.8750	orange gum
LD3	1.6742	green viscous liquid
LD4	3.3039	green viscous liquid
LD5	1.2316	green viscous liquid
LD6	0.8712	green viscous liquid
LD7	1.2311	green viscous liquid
LD8	3.3490	brown solid
LD9	1.2562	green-yellow viscous liquid
LD10	0.7602	green-yellow viscous liquid
LD11	1.1365	green-yellow viscous liquid
LD12	0.7605	yellow viscous liquid
LD13	1.3433	yellow viscous liquid
LD14	2.2632	yellow viscous liquid
LD15	1.2109	brown viscous liquid
LD16	1.4309	brown viscous liquid
LD17	0.6549	brown viscous liquid
LD18	1.4390	brown viscous liquid
LD19	1.3412	brown viscous liquid
LD20	0.4256	brown viscous liquid
LD21	2.1172	dark-brown viscous liquid
LD22	1.3411	dark-brown viscous liquid
LD23	1.9134	dark-brown viscous liquid
LD24	1.2122	dark-brown viscous liquid
LD25	2.6129	dark-brown viscous liquid



* No further investigation

Scheme 11 Isolation of compounds **PK13-PK18** from dichloromethane extract of the leaves of *A. elasticus*

Fraction LD8 (3.3490 g) as a solid was filtered and washed with dichloromethane to give **PK13** (1.9213 g) as a major component of dichloromethane extract. Similarly, fraction LD9 (1.2562 g), LD10 (0.7602 g), LD11 (1.1365 g) and LD12 (0.7605 g) was filtered and washed with dichloromethane to give **PK13** (0.9871 g). On the basis of TLC characteristics, the filtrate of LD8, LD9 and LD10 were combined (2.3710 g). In the same, the filtrated of LD11 and LD12 were combined (0.5382 g) before the fraction was further purified.

The filtrate (2.3710 g) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (15% to 25% acetone in hexane) to give fractions LD8.10A-LD8.10H. Fraction LD8.10E (300.7 mg) was further separated by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (8:1:1) to give a green gum of **PK14** (8.4 mg) in fraction LD8.10E4.

The filtrate (538.2 mg) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (15% to 25% acetone in hexane) to give fractions LD11.12A-LD11.12F. Fraction LD11.12D (191.8 mg) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-dichloromethane-acetone (7:2:1) to give fractions LD11.12D1-LD11.12D4. Subfraction LD11.12D2 (50.1 mg) was separated by column chromatography over silica gel using a mixed solvent of hexane-dichloromethane-acetone (7:2:1) as eluent to afford a yellow solid of **PK15** (5.9 mg).

Fraction LD16 (1.4309 g) was purified by column chromatography over silica gel and eluted with 15% acetone in hexane to give fractions LD16A-LD16G. Fraction LD16E (212.3 mg) was further purified by column chromatography over silica gel and eluted with a gradient of acetone-hexane (15% to 25% acetone in hexane) to afford a pale yellow solid of **PK16** (10.2 mg) in subfraction DS16E3.

Fraction LD21 (2.1172 g) was further purified by column chromatography over Sephadex^{TM} LH-20 and eluted with dichloromethane-methanol (4:1) to give fractions LD21A-LD21N. Fraction LD21K (101.2 mg) as a solid was filtered and washed with dichloromethane to give a yellow solid of **PK17** (15.9 mg). The filtrate was collected and combined with LD21J and LD21L based on TLC characteristics to give fraction LD21J.L. This fraction was further purified by column chromatography over Sephadex^{TM} LH-20 and eluted with dichloromethane-methanol (4:1) to give a yellow solid of **PK18** (17.2 mg).

PK1:

a mixture of *β*-sitosterol and stigmasterol, colorless needles

IR (neat) ν_{max} (cm^{-1}): 3425 (O-H stretching) and 1642 (C=C stretching)

^1H NMR spectral data; δ_H 3.57-3.47 (*m*, H-3), δ_H 5.36-5.34 (*br d*, *J* = 5.1 Hz, H-6), 5.16 (*dd*, *J* = 8.4, 15.1 Hz, H-22) and 5.01 (*dd*, *J* = 8.4, 15.1 Hz, H-23)

PK2:

(*E*)-4-(3',4'-dimethoxy-phenyl)-3-butenyl acetate, colorless viscous liquid

UV λ_{max} ($CHCl_3$) (log *ε*): 244 (2.45), 273 (2.40) and 305 (2.42) nm

IR (neat) ν_{max} (cm^{-1}): 1738 (C=O stretching) and 1515 (C=C stretching)

^1H NMR and ^{13}C NMR spectral data, see **Table 4**.

PK3:

5a,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-9-(3-methyl-2-buten-1-yl)-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one, yellow solid

$[\alpha]_D^{28}$ = -31° (*c* 0.1, acetone)

m.p. 249-251 °C

UV λ_{max} (CH_3OH) (log *ε*): 236 (4.46), 256 (4.42), 265 (4.41), 278 (4.50), 335 (4.09) and 391 (4.27) nm

IR (neat) ν_{max} (cm^{-1}): 3371 (O-H stretching) and 1629 (C=O stretching)

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

PK4:

4-hydroxybenzaldehyde, colorless gum

UV λ_{max} (CH_3OH) (log *ε*): 257 (3.68) and 275 (3.04) nm

IR (neat) ν_{max} (cm^{-1}): 3367 (O-H stretching) and 1684 (C=O stretching)

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

PK5:

2,3,8-trihydroxy-11,11-dimethyl-13-(3-methyl-2-butenyl)-6-(2-methyl-1-propenyl)-6*H*,7*H*,11*H*-bis[1]benzopyrano[4,3-*b*:6',7'-*e*]pyran-7-one, orange solid

$[\alpha]_D^{28}$ = -11° (*c* 0.1, acetone)

m.p. 221-222 °C

UV λ_{max} (CH_3OH) (log *ε*): 242 (5.00), 244 (4.98), 300 (5.04) and 384 (4.80) nm

IR (neat) ν_{max} (cm^{-1}): 3345 (O-H stretching) and 1625 (C=O stretching)

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

PK6:

(*E*)-4-(3',4'-dimethoxyphenyl)but-3-en-1-ol, colorless viscous liquid

UV λ_{max} ($CHCl_3$) (log ε): 240 (2.27) and 271 (2.14) nm

IR (neat) ν_{max} (cm^{-1}): 3419 (O-H stretching) and 1515 (C=C stretching)

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

PK7:

8-(2,4-dihydroxyphenyl)-5-hydroxy-2,2-dimethyl-7-(3-methyl-2-butenyl)-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one, yellow solid

m.p. 125-126 ^{o}C

UV λ_{max} (CH_3OH) (log ε): 237 (4.23), 283, (3.59) and 344 (3.34) nm

IR (neat) ν_{max} (cm^{-1}): 3230 (O-H stretching) and 1599 (C=O stretching)

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

PK8:

5a,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one, yellow solid

$[\alpha]_D^{28} = +5^{o}$ (*c* 0.2, CH_2Cl_2)

m.p. 284-285 ^{o}C

UV λ_{max} (CH_3OH) (log ε): 228 (4.56), 257 (4.42), 272 (4.58), 312 (4.19), 330 (4.25) and 391 (4.33) nm

IR (neat) ν_{max} (cm^{-1}): 3405 (O-H stretching) and 1642 (C=O stretching)

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

PK9:

6,7-dihydro-5,9,11,14-tetrahydroxy-3,3-dimethyl-6-(1-methylethenyl)-(-)-3*H*,8*H*-pyrano[3′,2′:4,5]benzo[1,2-*c*]xanthen-8-one, red-brown gum

$[\alpha]_D^{27} = -82^{o}$ (*c* 0.2, acetone)

UV λ_{max} (CH_3OH) (log ε): 263 (4.39), 269 (4.36), 307 (3.71) and 379 (4.11) nm

IR (neat) ν_{max} (cm^{-1}): 3402 (O-H stretching) and 1655 (C=O stretching)

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

PK10:

8,9-dihydro-6,10,11,13-tetrahydroxy-3,3-dimethyl-9-(1-methylethenyl)-3*H*,7*H*-benzo[*c*]pyrano[3,2-*h*]xanthen-7-one, yellow solid

$[\alpha]_D^{26} = +43^o$ (*c* 0.2, CH_2Cl_2)

m.p. 163-164 ^oC

UV λ_{max} (CH_3OH) (log ε): 227 (3.85), 272 (3.93) and 384 (3.56) nm

IR (neat) ν_{max} (cm^{-1}): 3349 (O-H stretching) and 1652 (C=O stretching)

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

PK11:

(*E*)-3-(4'-hydroxy-3'-methoxyphenyl)-2-propenoic acid, brown-yellow gum

UV λ_{max} (CH_3OH) (log ε): 244 (3.39), 273 (3.36), 299 (3.28) and 385 (3.02) nm

IR (neat) ν_{max} (cm^{-1}): 3350 (O-H stretching) 1712 (C=O stretching) and 1513 (C=C stretching)

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

PK12:

5-hydroxy-8,8-dimethyl-3-(3-methyl-2-butenyl)-2-(2,4,5-trihydroxyphenyl)-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one, brown-yellow solid

m.p. 217-219 ^oC

UV λ_{max} (CH_3OH) (log ε): 224 (4.34), 258 (4.41), 266 (4.47), 271 (4.47), 302 (3.90) and 352 (3.89) nm

IR (neat) ν_{max} (cm^{-1}): 3402 (O-H stretching) and 1655 (C=O stretching)

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

PK13:

1-(2,4-dihydroxyphenyl)-3-(8-hydroxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-chromen-6-yl)propan-1-one, brown-yellow gum

UV λ_{max} (CH_3OH) (log ε): 231 (3.19), 273 (3.21) and 313 (2.89) nm

IR (neat) ν_{max} (cm^{-1}): 3383 (O-H stretching) and 1634 (C=O stretching)

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

PK14:

1-(2,4-dihydroxyphenyl)-3-(3,4-dihydroxy-2,5-bis(3-methylbut-2-enyl)phenyl) propan-1-one, yellow solid

m.p. 170 ^{o}C

UV λ_{max} (CH_3OH) (log ε): 237 (3.24), 274 (3.26) and 313 (3.28) nm

IR (neat) ν_{max} (cm^{-1}): 3422 (O-H stretching) and 1629 (C=O stretching)

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

PK15:

1-(2,4-dihydroxyphenyl)-3-(7-((3,3-dimethyloxiran-2-yl)methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)propan-1-one, yellow gum

$[\alpha]_D^{26}$ = -14^{o} (*c* 0.1, acetone)

UV λ_{max} (CH_3OH) (log ε): 245 (3.28), 274 (3.27) and 311 (3.33) nm

IR (neat) ν_{max} (cm^{-1}): 3390 (O-H stretching) and 1631 (C=O stretching)

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

PK16:

(*S*)-2-(2,4-dihydroxyphenyl)-5-hydroxy-7-methoxychroman-4-one, pale yellow solid

$[\alpha]_D^{27}$ = -3^{o} (*c* 0.2, acetone)

m.p. 210-211 ^{o}C

UV λ_{max} (CH_3OH) (log ε): 244 (3.30), 273 (3.28) and 305 (3.32) nm

IR (neat) ν_{max} (cm^{-1}): 3343 (O-H stretching) and 1597 (C=O stretching)

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

PK17:

1-(2,4-dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7*b*-dihydro-1*aH*-oxireno[2,3-*c*]chromen-6-yl)propan-1-one, a yellow solid

$[\alpha]_D^{26}$ = +7^{o} (*c* 0.2, acetone)

m.p. 179-180 ^{o}C

UV λ_{max} (CH_3OH) (log ε): 243 (3.27), 275 (3.26) and 310 (3.32) nm

IR (neat) ν_{max} (cm^{-1}): 3223 (O-H stretching) and 1624 (C=O stretching)

^{1}H NMR and ^{13}C NMR spectral data, see **Table 24**.

PK18:

1-(2,4-dihydroxyphenyl)-3-(7-hydroxy-6-(3-methylbut-2-enyl)benzofuran-5-yl) propan-1-one, yellow gum

UV λ_{max} (CH_3OH) (log ε): 228 (3.18), 276 (3.19) and 314 (2.99) nm

IR (neat) ν_{max} (cm^{-1}): 3352 (O-H stretching) and 1629 (C=O stretching)

^1H NMR and ^{13}C NMR spectral data, see **Table 25**.

CHAPTER 3
RESULTS AND DISCUSSION

3.1 Structure elucidation of compounds from the root bark and leaves of *A. elasticus*

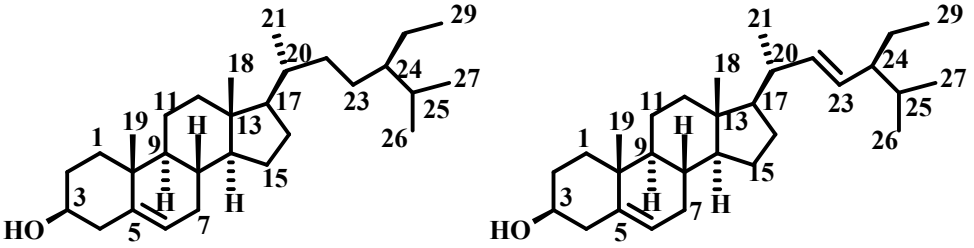
The crude dichloromethane and acetone extracts from the root bark of *A. elasticus* were subjected to repeated quick column and column chromatography over silica gel to furnish twelve known compounds. They were identified as a triterpenoids; a mixture of *β*-sitosterol and stigmasterol **(PK1)**, (*E*)-4-(3',4'-dimethoxy-phenyl)-3-butenyl acetate **(PK2)**, 5a,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-9-(3-methyl-2-buten-1-yl)-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*] xanthen-7-one **(PK3)**, 4-hydroxybenzaldehyde **(PK4)**, 2,3,8-trihydroxy-11,11-dimethyl-13-(3-methyl-2-butenyl)-6-(2-methyl-1-propenyl)-6*H*,7*H*,11*H*-bis[1]benzo pyrano[4,3-b:6',7'-*e*]pyran-7-one **(PK5)**, (*E*)-4-(3',4'-dimethoxyphenyl)but-3-en-1-ol **(PK6)**, 2-(2,4-dihydroxyphenyl)-5-hydroxy-8,8-dimethyl-3-(3-methylbut-2-enyl) pyrano[3,2-*g*]chromen-4(8*H*)-one **(PK7)**, 5a,6-dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one **(PK8)**, 6,7-dihydro-5,9,11,14-tetrahydroxy-3,3-dimethyl-6-(1-methylethenyl)-(-)-3*H*,8*H*-pyrano [3',2':4,5]benzo[1,2-*c*]xanthen-8-one **(PK9)**, 8,9-dihydro-6,10,11,13-tetrahydroxy-3,3-dimethyl-9-(1-methylethenyl)-3*H*,7*H*-benzo[*c*]pyrano[3,2-*h*]xanthen-7-one **(PK10)**, (*E*)-3-(4'-hydroxy-3'-methoxyphenyl)-2-propenoic acid **(PK11)** and 5-hydroxy-8,8-dimethyl-3-(3-methyl-2-butenyl)-2-(2,4,5-trihydroxyphenyl)-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one **(PK12)**. Purification of the crude dichloromethane from the leaves furnish five new prenylated dihydrochalcones; 1-(2,4-dihydroxyphenyl)-3-(8-hydroxy 2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-chromen-6-yl)propan-1-one **(PK13)**, 1-(2,4-dihydroxyphenyl)-3-(3,4-dihydroxy-2,5-bis(3-methylbut-2-enyl)phenyl)propan-1-one **(PK14)**, 1-(2,4-dihydroxyphenyl)-3-(7-((3,3-dimethyloxiran-2-yl)methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)propan-1-one **(PK15)**, 1-(2,4-dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7*b*-dihydro-1*aH*-oxireno[2,3-*c*]chromen-6-yl)propan-1-one **(PK17)** and 1-(2,4-dihydroxyphenyl)-3-(7-hydroxy-6-(3-

methylbut-2-enyl)benzofuran-5-yl)propan-1-one **(PK18)**, and one known compound; (*S*)-2-(2,4-dihydroxyphenyl)-5-hydroxy-7-methoxychroman-4-one **(PK16)**.

Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data: ^{1}H, ^{13}C NMR, DEPT 135°, DEPT 90°, HMQC, HMBC, COSY and NOESY. The physical data of the known compounds were also compared with the reported values.

PK1

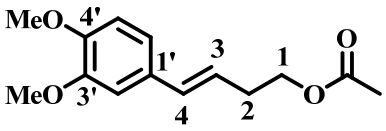
Mixture of *β*–sitosterol and sigmasterol



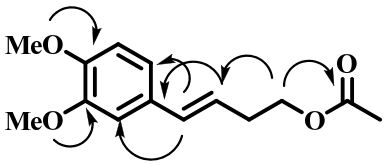
The mixture of **PK1** was obtained as colorless needles. The ^{1}H NMR spectrum exhibited the characteristic resonances of an oxymethine protons at δ_H 3.57-3.47 (*m*, H-3), three olefinic protons at δ_H 5.36-5.34 (*br d*, *J* = 5.1 Hz, H-6), 5.16 (*dd*, *J* = 8.4, 15.1 Hz, H-22) and 5.01 (*dd*, *J* = 8.4, 15.1 Hz, H-23). These spectral data were in agreement with that of the mixture of *β*–sitosterol and sigmasterol (**PK1**) (Boonnak, 2006).

PK2

(*E*)-4-(3',4'-Dimethoxyphenyl)-3-butenyl acetate



PK2 was obtained as colorless viscous liquid. The UV spectrum showed maximum absorption bands at 244, 273 and 305 nm. The IR spectrum showed the stretching of C=O of ester group at 1738 cm^{-1} and C=C at 1515 cm^{-1}. The ^{1}H NMR spectral data (**Table 4**) displayed an ABX signal of aromatic protons at δ_H 6.81 (*d*, *J* = 8.1 Hz, H-5'), 6.87 (*dd*, *J* = 8.1, 1.8 Hz, H-6') and 6.90 (*d*, *J* = 1.8 Hz, H-2') indicating a trisubstituted benzene ring. A substituent group was assigned for 3-butenyl acetate side chain which the resonances of *trans*-vinylic protons H-3 and H-4 were at δ_H 6.02 and 6.41 (*J* = 15.9 Hz), methylene protons H-1 and H-2 were at δ_H 4.18 (*t*, *J* = 6.9 Hz) and 2.53 (*qd*, *J* = 6.9, 1.8 Hz), and acetyl proton was at δ_H 2.06 (*s*). The HMBC correlations of H-1 to C=O and vinylic carbon C-3 confirmed the structure of that side chain. The side chain was positioned at C-1' according to the HMBC correlations of H-4 to C-2' (δ_C 108.8) and C-6' (δ_C 119.1) and of H-3 to C-1' (δ_C 130.5). The *ortho*-methoxyl groups which resonated at δ_H 3.90 (*s*, 3H) and δ_H 3.88 (*s*, 3H) were proposed for 3'-OCH_3 and 4'-OCH_3, respectively. Therefore, **PK2** was identified as (*E*)-4-(3',4'-dimethoxyphenyl)-3-butenyl acetate (Han *et al.*, 2003).



Major HMBC of **PK2**

Table 4 ^{1}H, ^{13}C and HMBC spectral data of **PK2**

Position	**δ_H (*mult*, J_{Hz})**	**δ_C (C-Type)**	**HMBC**
1	4.18 (2H, *t*, 6.9)	63.8 (CH_2)	1-O<u>C</u>(O)CH_3, C-3, C-2
2	2.53 (2H, *qd*, 6.9, 1.8)	32.3 (CH_2)	C-1, C-3, C-4
3	6.02 (1H, *dt*, 15.9, 6.9)	128.3 (CH)	C-1, C-2, C-1'
4	6.41 (1H, *d*, 15.9)	132.0 (CH)	C-2, C-1', C-2', C-6'
1'	-	130.5 (C)	-
2'	6.90 (1H, *d*, 1.8)	108.8 (CH)	C-4, C-4', C-6'
3'	-	149.1 (C)	-
4'	-	148.6 (C)	-
5'	6.81 (1H, *d*, 8.1)	111.2 (CH)	C-1', C-3', C-4', C-6'
6'	6.87 (1H, *dd*, 8.1, 1.8)	119.1 (CH)	C-4, C-2', C-4'
3'-OCH_3	3.90 (3H, *s*)	56.0 (OCH_3)	C-3'
4'-OCH_3	3.88 (3H, *s*)	55.8 (OCH_3)	C-4'
1-O<u>C</u>(O)CH_3	-	171.1 (C=O)	-
1-OC(O)<u>C</u>H_3	2.06 (3H, *s*)	21.0 (CH_3)	1-O<u>C</u>(O)CH_3

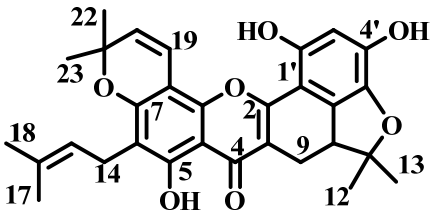
recorded in $CDCl_3$

Table 5 ^{1}H-^{1}H COSY spectral data of **PK2**

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-4 (6.41)	⟷	H-3 (6.02)
H-3 (6.02)	⟷	H-4 (6.41), H-2 (2.53)
H-2 (2.53)	⟷	H-3 (6.02), H-1 (4.18)

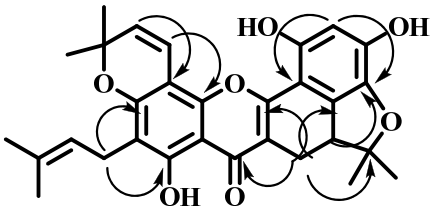
PK3

5*a*,6-Dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-9-(3-methyl-2-buten-1-yl)-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one : artonin F



PK3 is a yellow solid, m.p. 249-251 ^{o}C, $[\alpha]_D^{28}$ = -31^{o} (*c* 0.1, acetone). The UV spectrum showed maximum absorption bands at 236, 256, 265, 278, 335 and 391 nm. Its IR spectrum showed absorption bands for hydroxyl (3371 cm^{-1}) and conjugated carbonyl (1629 cm^{-1}). The ^{1}H NMR spectrum (**Table 6**) indicated the presence of three hydroxyl groups (5-OH, δ_H 13.42, *s*; 2'-OH, δ_H 7.78, *s*; and 4'-OH, δ_H 9.23, *s*) and one aromatic proton (H-3', δ_H 6.38, *s*). The ^{1}H-NMR spectrum also indicated the resonances of two methyl groups at δ_H 1.35 and 1.66 (each 3H, *s*) and an ABX spin system at δ_H 2.40 (H_α-9, *t*, *J* = 15.0 Hz), 3.23 (H_β-9, *dd*, *J* = 15.0, 7.2 Hz), and 3.41 (H-10, *dd*, *J* = 15.0, 7.2 Hz), assignable to a furanodihydrobenzoxanthone skeleton (Hakim *et al*., 2006). In the HMBC experiments, the protons resonated at δ_H 3.41 had correlations with carbons resonated at δ_C 131.8 (C-6'), 137.2 (C-5'), 93.5 (C-11), 22.7 (C-12) and 28.1 (C-13), confirming the cyclic was formed between C-3 and C-6' whereas the furan moiety was formed at C-5' and C-6' of the aromatic ring. Moreover, a 2,2-dimethylchromene ring was detected from the characteristic signals at δ 6.76 (*d*, *J* = 9.9 Hz, H-19), 5.57 (*d*, *J* = 9.9 Hz, H-20) and 1.46 (*s*, 22-CH_3 and 23-CH_3). The correlations of H-19 to C-7 and C-8a and of H-20 to C-8 confirmed the orientation of a chromene ring at C-7 and C-8 position. The spectrum further showed the resonances of methylene protons (H-14, δ_H 3.33, *d, J* = 7.2 Hz), an olefinic proton (H-15, δ_H 5.24, *mt*, *J* = 7.2 Hz) and methyl protons (CH_3-17, δ_H 1.81, *s* and CH_3-18, δ_H 1.68, *s*), indicating the presence of a prenyl group. The HMBC correlations of H-14 to C-5 (δ_C 158.7) and C-7 (δ_C 156.4) confirmed the location of the isoprenyl group

at C-6. The HMBC experiments (**Table 6**) supported the assignment. **PK3** was then identified to be artonin F (Hano *et al*., 1990).



Major HMBC of **PK3**

Table 6 ^{1}H, ^{13}C and HMBC spectral data of **PK3**

Position	**δ_H (*mult*, J_{Hz})**	**δ_C (C-Type)**	**HMBC**
2	-	160.3 (C)	-
3	-	111.5 (C)	-
4	-	180.7 (C=O)	-
4a	-	104.3 (C)	-
5	-	158.7 (C)	-
6	-	112.5 (C)	-
7	-	156.4 (C)	-
8	-	100.5 (C)	-
8a	-	149.2 (C)	-
9	3.23 ($1H_\beta$, *dd*, 15.0, 7.2)	19.9 (CH_2)	C-2, C-3, C-4, C-10 , C-6'
	2.40 ($1H_\alpha$, *t*, 15.0)		C-2, C-3, C-4, C-10, C-11, C-6'
10	3.41 (1H, *dd*, 15.0, 7.2)	46.6 (CH)	C-9, C-11, C-12, C-13, C-1', C-5', C-6'
11	-	93.5 (C)	-
12	1.35 (3H, *s*)	22.7 (CH_3)	C-10, C-11, C-13
13	1.66 (3H, *s*)	28.1 (CH_3)	C-10, C-12
14	3.33 (2H, *d*, 7.2)	21.3 (CH_2)	C-5, C-6, C-7, C-15, C-16
15	5.24 (1H, *mt*, 7.2)	122.1 (CH)	C-6, C-14, C-17, C-18
16	-	131.3 (C)	-
17	1.81 (3H, *s*)	17.9 (CH_3)	C-15, C-16, C-18

Table 6 (continued)

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
18	1.68 (3H, *s*)	25.8 (CH_3)	C-15, C-16, C-17
19	6.76 (1H, *d*, 9.9)	115.3 (CH)	C-7, C-8, C-8a, C-20, C-21
20	5.57 (1H, *d*, 9.9)	127.1 (CH)	C-8, C-21, C-22, C-23
21	-	77.3 (C)	-
22	1.46 (3H, *s*)	28.0 (CH_3)	C-20, C-21, C-23
23	1.46 (3H, *s*)	28.0 (CH_3)	C-20, C-21, C-22
1'	-	103.4 (C)	-
2'	-	150.1 (C)	-
3'	6.38 (1H, *s*)	104.6 (CH)	C-2, C-1', C-2', C-4', C-5'
4'	-	146.4 (C)	-
5'	-	137.2 (C)	-
6'	-	131.8 (C)	-
5-OH	13.42 (1H, *s*)	-	C-4, C-4a, C-5, C-6
2'-OH	7.78 (1H, *s*)	-	C-1', C-2', C-3'
4'-OH	9.23 (1H, *s*)	-	C-5'

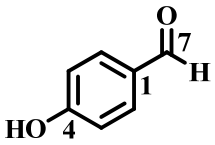
recorded in $CDCl_3$+DMSO-d_6

Table 7 ^{1}H-^{1}H COSY spectral data of **PK3**

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H_α-9 (2.40)	⟷	H_β-9 (3.23), H-10 (3.41)
H_β-9 (3.23)	⟷	H_α-9 (2.40), H-10 (3.41)
H-10 (3.41)	⟷	H_α-9 (2.40), H_β-9 (3.23)
H-14 (3.33)	⟷	H-15 (5.24), H-17 (1.81), H-18 (1.68)
H-15 (5.24)	⟷	H-14 (3.33), H-17 (1.81), H-18 (1.68)
H-17 (1.81)	⟷	H-14 (3.33), H-15 (5.24), H-18 (1.68)
H-18 (1.68)	⟷	H-14 (3.33), H-15 (5.24), H-17 (1.81)
H-19 (6.76)	⟷	H-20 (5.57)

PK4

4-hydroxybenzaldehyde



PK4 was obtained as a colorless gum. The UV spectrum showed absorption bands at λ_{max} 257 and 275 nm, indicating the presence of a benzene chromophore. Its IR spectrum showed absorption bands for hydroxyl and carbonyl groups at 3367 and 1684 cm^{-1}, respectively. The ^{1}H NMR spectrum displayed characteristic signals of a *para*-disubstituted benzene at δ_H 7.81 (*d*, *J* = 8.4 Hz, 2H) and 6.96 (*d*, *J* = 8.4 Hz, 2H) and a singlet of an aldehyde proton at δ_H 9.88 (1H, *s*, CHO). The ^{13}C NMR spectrum exhibited the signal of a carbonyl carbon of aldehyde group at δ_C 190.6. The HMBC experiments were summarized in **Table 8**. Accordingly, the structure of **PK4** was assigned as 4-hydroxybenzaldehyde (Jang *et al*., 2004).

Table 8 ^{1}H, ^{13}C and HMBC spectral data of **PK4**

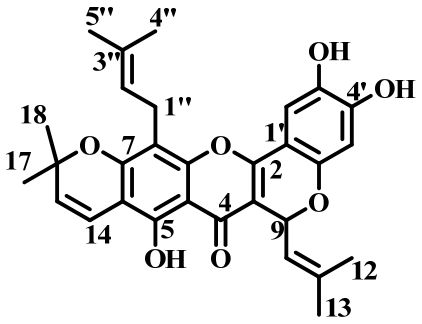
Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1	-	130.0 (C)	-
2/6	7.81 (2H, *d*, 8.4)	132.5 (CH)	C-3, C-4, C-7
3/5	6.96 (2H, *d*, 8.4)	116.1 (CH)	C-1, C-2
4	-	161.0 (C)	-
7	9.88 (1H, *s*)	190.6 (C)	-

recorded in $CDCl_3$

PK5

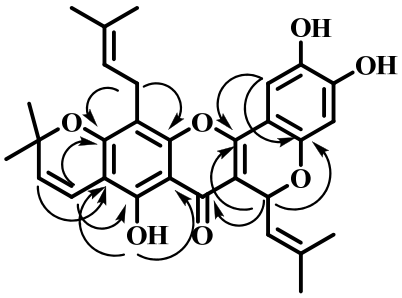
2,3,8-Trihydroxy-11,11-dimethyl-13-(3-methyl-2-butenyl)-6-(2-methyl-1-propenyl)-6*H*,7*H*,11*H*-bis[1]benzopyrano[4,3-*b*:6',7'-*e*]pyran-7-one

: cycloheterophyllin



PK5 is an orange solid, m.p. 221-222 ^{o}C (220 ^{o}C; Wei *et al*., 2005), $[\alpha]_D^{28}$ = -11^{o} (*c* 0.1, acetone) ($[\alpha]_D^{23}$ = -2^{o} (*c* 0.1, acetone); Wei *et al*., 2005). The UV spectrum showed maximum absorption bands at 242, 244, 300 and 384 nm. The IR spectrum showed the O-H and C=O stretching at 3345 and 1625 cm^{-1}, respectively. The ^{13}C NMR revealed the presence of 30 carbons, including a carbonyl group (δ_C 178.8) and six methyl groups, corresponding to a triprenylated flavonoid. The ^{1}H NMR spectral data (**Table 9**) displayed a hydrogen-bonded hydroxyl group at δ_H 12.96 (5-OH) and two isolated aromatic protons at δ_H 6.50 (H-3') and 7.26 (H-6'). The spectrum further showed the characteristic signals of 2,2-dimethylchromene ring (δ_H 6.72, *d*, *J* = 10.2 Hz, H-14; δ_H 5.62, *d*, *J* = 10.2 Hz, H-15; δ_H 1.46, *s*, CH_3-17 and δ_H 1.47, *s*, CH_3-18) and a prenyl side chain (δ_H 5.24, *mt*, *J* = 7.2 Hz, H-2", 1H; δ_H 3.49, *d*, *J* = 7.2 Hz, H-1", 2H; δ_H 1.86, *s*, H-4", 3H; δ_H 1.69, *s*, H-5", 3H). In the HMBC experiment, proton H-14 (δ_H 6.72) correlated to quaternary carbons C-5 (δ_C 154.4), C-6 (δ_C 105.4), C-7 (δ_C 156.5), indicating that a 2,2-dimethylchromene ring was fused to C-6 and C-7 in the A ring. The HMBC correlations of H-1" to C-7 (δ_C 156.5), C-8 (δ_C 107.6) and C-8a (δ_C 153.6) confirmed the location of the isoprenyl group at C-6. The oxidative cyclization between the allylic methylene of a C-3 prenyl side chain with the C-2' hydroxyl group of the B ring led to 2*H* benzopyran ring system. It exhibited signals of two vinyl methyl groups at δ_H 1.95 (*s*, H-12) and δ_H 1.69 (*s*, H-13), an olefinic proton at δ_H 5.46 (*d*, *J* = 9.0 Hz, H-10) and an oxy-methine proton at δ_H 6.20

(*d*, *J* = 9.0 Hz, H-9). The oxidative cyclization was confirmed by the long-range cross peaks of H-9 (δ_H 6.20) to C-2 (δ_C 155.3), C-3 (δ_C 109.9), C-4 (δ_C 178.8), C-2' (δ_C 151.7). Thus, this compound was 2,3,8-trihydroxy-11,11-dimethyl-13-(3-methyl-2-butenyl)-6-(2-methyl-1-propenyl)-6*H*,7*H*,11*H*-bis[1]benzopyrano[4,3-*b*:6',7'-*e*]pyran-7-one which was corresponded to the previously isolated, cycloheterophyllin (Wei *et al*., 2005).



Major HMBC of **PK5**

Table 9 ^{1}H, ^{13}C and HMBC spectral data of **PK5**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
2	-	155.3 (C)	-
3	-	109.9 (C)	-
4	-	178.8 (C=O)	-
4a	-	105.4 (C)	-
5	-	154.4 (C)	-
6	-	105.4 (C)	-
7	-	156.5 (C)	-
8	-	107.6 (C)	-
8a	-	153.6 (C)	-
9	6.20 (1H, *d*, 9.0)	69.4 (CH)	C-2, C-3, C-4, C-11, C-2'
10	5.46 (1H, *d*, 9.0)	121.0(CH)	C-12, C-13
11	-	139.4 (C)	-
12	1.95 (3H, *s*)	18.6 (CH_3)	C-10, C-11, C-13
13	1.69 (3H, *s*)	25.9 (CH_3)	C-10, C-11, C-12

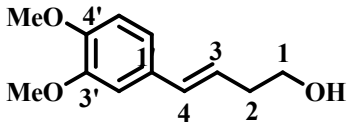
Table 9 (continued)

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
14	6.72 (1H, *d*, 10.2)	115.9 (CH)	C-5, C-7, C-16
15	5.62 (1H, *d*, 10.2)	127.9 (CH)	C-6, C-16, C-17, C-18
16	-	77.7 (C)	-
17	1.46 (3H, *s*)	28.1 (CH_3)	C-15, C-16
18	1.47 (3H, *s*)	28.2 (CH_3)	C-15, C-16
1'	-	108.1 (C)	-
2'	-	151.7 (C)	-
3'	6.50 (1H, *s*)	104.8 (CH)	C-9, C-1', C-2', C-4', C-5'
4'	-	149.5 (C)	-
5'	-	138.6 (C)	-
6'	7.26 (1H, *s*)	109.4 (CH)	C-2, C-1', C-2', C-4', C-5'
1"	3.49 (2H, *d*, 7.2)	21.5 (CH_2)	C-7, C-8, C-8a, C-2", C-3"
2"	5.24 (1H, *mt*, 7.2)	122.1 (CH)	C-1", C-4", C-5"
3"	-	131.7 (C)	-
4"	1.86 (3H, *s*)	18.1 (CH_3)	C-3", C-5"
5"	1.69 (3H, *s*)	25.8 (CH_3)	C-3", C-4"
5-OH	12.96 (1H, *s*)	-	C-4a, C-5, C-6

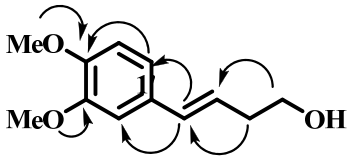
recorded in $CDCl_3$

PK6

(*E*)-4-(3',4'-Dimethoxyphenyl)but-3-en-1-ol



PK6 was obtained as colorless viscous liquid. The UV spectrum showed maximum absorption bands at 240 and 271 nm. The IR spectrum showed the O-H and C=C stretching at 3419 cm^{-1} and 1515 cm^{-1}, respectively. Its ^{1}H NMR spectral data showed the resonances of H-5' (δ_H 6.82, *d*), H-6' (δ_H 6.90, *dd*), H-2' (δ_H 6.93, *d*), 3'-OCH_3 (δ_H 3.92, *s*), 4'-OCH_3 (δ_H 3.89, *s*), H-4 (δ_H 6.46, *d*, J = 15.6 Hz), H-3 (δ_H 6.09, *dt*, J = 15.6, 6.6 Hz), H-2 (δ_H 2.50, *qd*, J = 6.6, 1.2 Hz) and H-1 (δ_H 3.78, *t*, J = 6.6 Hz). Its ^{1}H NMR, ^{13}C NMR and HMBC spectral data were similar to those of **PK2**, except the absence of a C=O carbon signal. Therefore, **PK6** was identified as (*E*)-4-(3',4'-dimethoxyphenyl)but-3-en-1-ol (Han *et al.*, 2003). The HMBC correlations (**Table 10**) confirmed the assigned structure.



Major HMBC of **PK6**

Table 10 ^{1}H, ^{13}C and HMBC spectral data of **PK6**

Position	**δ_H (*mult*, J_{Hz})**	**δ_C (C-Type)**	**HMBC**
1	3.78 (2H, *t*, 6.6)	62.1 (CH_2)	C-2, C-3
2	2.50 (2H, *qd*, 6.6, 1.2)	36.4 (CH_2)	C-1, C-3, C-4
3	6.09 (1H, *dt,* 15.6, 6.6)	128.4 (CH)	C-1, C-2, C-1'
4	6.46 (1H, *d,* 15.6)	132.5 (CH)	C-2, C-1', C-2', C-6'
1'	-	130.4 (C)	-
2'	6.93 (1H, *d*, 1.8)	108.7 (CH)	C-4, C-4', C-6'
3'	-	148.6 (C)	-
4'	-	149.1 (C)	-
5'	6.82 (1H, *d*, 8.1)	111.2 (CH)	C-1', C-3', C-4'
6'	6.90 (1H, *dd,* 8.1, 1.8)	119.1 (CH)	C-4, C-2', C-4'
3'-OCH_3	3.92 (3H, *s*)	55.8 (OCH_3)	C-3'
4'-OCH_3	3.89 (3H, *s*)	55.9 (OCH_3)	C-4'

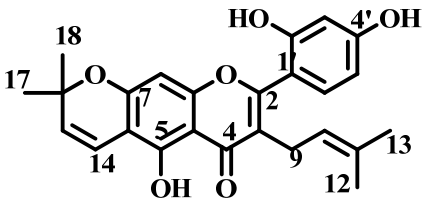
recorded in $CDCl_3$

Table 11 ^{1}H-^{1}H COSY spectral data of **PK6**

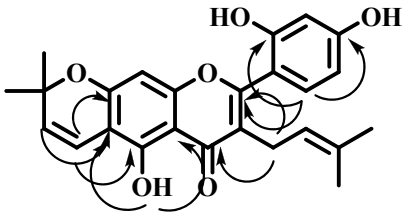
Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-4 (6.46)	⟷	H-3 (6.09)
H-3 (6.09)	⟷	H-4 (6.46), H-2 (2.50)
H-2 (2.50)	⟷	H-3 (6.09), H-1 (3.78)

PK7

2-(2,4-Dihydroxyphenyl)-5-hydroxy-8,8-dimethyl-3-(3-methylbut-2-enyl)pyrano [3,2-*g*]chromen-4(8*H*)-one : cudraflavone B



PK7 is a yellow solid, m.p. 125-126 ^{o}C (126 ^{o}C; Ryu *et al.,* 2009). The UV spectrum showed maximum absorption bands at 237, 283, and 344 nm. The IR spectrum exhibited the absorption bands of hydroxyl group at 3230 cm^{-1}. The ^{1}H NMR spectral data (**Table 12**) revealed the presence of a chelated hydroxyl group (δ_H 13.18, *s*), an isolated aromatic proton (δ_H 6.27, *s*), and a 1,2,4-trisubstituted benzene [δ_H 7.21 (*d*, *J* = 9.0 Hz, H-6'), 6.52 (*d*, *J* = 9.0 Hz, H-5') and 6.51 (*s*, H-3')]. The spectrum further showed signals corresponded to a prenyl group [δ_H 3.13 (*d*, *J* = 6.6 Hz, 2H, H-9), 5.17 (*mt*, *J* = 6.6 Hz, 1H, H-10), 1.66 (*s*, 3H, H-13) and 1.48 (*s*, 3H, H-12)] and a 2,2-dimethylchromene ring [δ_H 6.73 (*d*, *J* = 10.2 Hz, 1H, H-14), 5.48 (*d*, *J* = 10.2 Hz, 1H, H-15), 1.46 (*s*, 6H, H-17 and H-18]. The HMBC correlations of H-9 to carbonyl carbon (δ_C 182.2), C-2 (δ_C 159.3) indicated that a prenyl side chain was at C-3 position. While the correlations of H-14 to C-5 (δ_C 156.5), C-7 (δ_C 159.2) and of H-15 to C-6 (δ_C 105.4) indicated that a chromene ring was fused at C-6 and C-7 position. Thus **PK7** was assigned as 2-(2,4-dihydroxyphenyl)-5-hydroxy-8,8-dimethyl-3-(3-methylbut-2-enyl)pyrano[3,2-*g*]chromen-4(8*H*)-one which corresponded to cudraflavone B (Ryu *et al.,* 2009).



Major HMBC of **PK7**

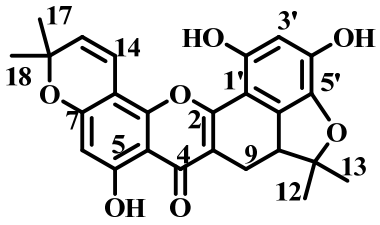
Table 12 ^{1}H, ^{13}C and HMBC spectral data of **PK7**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
2	-	159.3 (C)	-
3	-	121.4 (C)	-
4	-	182.2 (C=O)	-
4a	-	103.6 (C)	-
5	-	156.5 (C)	-
6	-	105.4 (C)	-
7	-	159.2 (C)	-
8	6.27 (1H, *s*)	94.6 (CH)	C-4a, C-6, C-7, C-8a
8a	-	157.0 (C)	-
9	3.13 (2H, *d*, 6.6)	24.4 (CH_2)	C-2, C-3, C-4, C-10, C-11
10	5.17 (1H, *mt*, 6.6)	120.9 (CH)	-
11	-	133.3 (C)	-
12	1.48 (3H, *s*)	17.7 (CH_3)	C-10, C-11, C-13
13	1.66 (3H, *s*)	25.6 (CH_3)	C-10, C-11, C-12
14	6.73 (1H, *d*, 10.2)	115.6 (CH)	C-5, C-7, C-16
15	5.48 (1H, *d*, 10.2)	128.0 (CH)	C-6
16	-	77.9 (C)	-
17	1.46 (3H, *s*)	28.2 (CH_3)	C-15, C-18
18	1.46 (3H, *s*)	28.2 (CH_3)	C-15, C-17
1'	-	112.6 (C)	-
2'	-	155.2 (C)	-
3'	6.51 (1H, *s*)	103.8 (CH)	C-1', C-2', C-5'
4'	-	159.0 (C)	-
5'	6.52 (1H, *d*, 9.0)	108.4 (CH)	C-1', C-3', C-4'
6'	7.21 (1H, *d*, 9.0)	131.6 (CH)	C-2, C-2', C-4'
5-OH	13.18 (1H, *s*)	-	C-4a, C-5, C-6

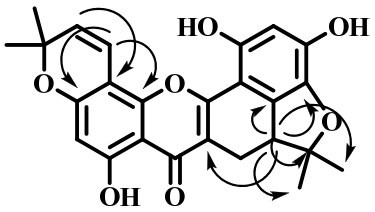
recorded in $CDCl_3$

PK8

5a,6-Dihydro-1,3,8-trihydroxy-5,5,11,11-tetramethyl-5*H*,7*H*,11*H*-benzofuro[3,4-*bc*]pyrano[3,2-*h*]xanthen-7-one : cycloartobiloxanthone



PK8 is a yellow solid, m.p. 284-285 ^{o}C (285-287 ^{o}C; Sultanbawa *et al*., 1989), $[\alpha]_D^{28}$ = +5^{o} (*c* 0.2, CH_2Cl_2) ($[\alpha]_D^{20}$ = +80^{o} (*c* 0.2, CH_2Cl_2); Ren *et al*., 2010). The UV spectrum showed maximum absorption bands at 228, 257, 272, 312, 330 and 391 nm. Its IR spectrum showed the stretching of hydroxyl (3405 cm^{-1}) and conjugated carbonyl group (1642 cm^{-1}). The ^{1}H NMR spectrum (**Table 13**) exhibited the signals of a chelated hydroxyl proton (5-OH) at δ_H 13.22 and non-chelated hydroxyl protons (4'-OH and 2'-OH) at δ_H 9.17 and δ_H 7.86. Two singlet signals at δ_H 6.25 and δ_H 6.38 were assigned for isolated aromatic protons H-6 and H-3'. The ^{1}H-NMR spectrum also indicated the resonances of two methyl groups at δ_H 1.35 and 1.67 (each 3H, *s*) and an ABX spin system at δ_H 2.41, 3.22, and 3.39, assignable to a furanodihydrobenzoxanthone skeleton (Hakim *et al*., 2006) as those of **PK3**. The difference was the disappearance of a prenyl group signal but instead the resonances of aromatic protons (H-6, δ_H 6.25, *s*). Moreover, a 2,2-dimethylchromene ring was detected from the characteristic signals at δ_H 6.75 (*d*, H-14), 5.57 (*d*, H-15) and 1.42 (*s*, 17-CH_3 and 18-CH_3). The correlations of H-14 to C-7 and C-8a and of H-15 to C-8 confirmed the orientation of a chromene ring at C-7 and C-8 position. The assigned structure of **PK8** was in agreement with cycloartobiloxanthone (Sultanbawa *et al*., 1989).



Major HMBC of **PK8**

Table 13 ^{1}H, ^{13}C and HMBC spectral data of **PK8**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
2	-	160.9 (C)	-
3	-	112.0 (C)	-
4	-	181.0 (C=O)	-
4a	-	105.1 (C)	-
5	-	162.0 (C)	-
6	6.25 (1H, *s*)	100.4 (CH)	C-4a, C-5, C-7, C-8
7	-	159.1 (C)	-
8	-	101.3 (C)	-
8a	-	151.2 (C)	-
9	3.22 ($1H_\beta$, *dd*, 15.0, 7.2)	20.2 (CH_2)	C-2, C-3, C-4, C-10, C-6'
	2.41 ($1H_\alpha$, *t*, 15.0)		C-2, C-3, C-10, C-11, C-6'
10	3.39 (1H, *dd*, 15.0, 7.2)	46.9 (CH)	C-3, C-9, C-11, C-12, C-13, C-5', C-6'
11	-	93.9 (C)	-
12	1.35 (3H, *s*)	23.0 CH_3)	C-10, C-11, C-13
13	1.67 (3H, *s*)	28.4 (CH_3)	C-10, C-11, C-12
14	6.75 (1H, *d*, 9.9)	115.3 (CH)	C-7, C-8, C-8a, C-16
15	5.57 (1H, *d*, 9.9)	127.7 (CH)	C-8, C-16, C-17, C-18
16	-	78.2 (C)	-
17	1.42 (3H, *s*)	28.5 (CH_3)	C-14, C-15, C-16, C-18
18	1.42 (3H, *s*)	28.5 (CH_3)	C-14, C-15, C-16, C-17
1'	-	103.7 (C)	-
2'	-	150.5 (C)	-
3'	6.38 (1H, *s*)	105.1 (CH)	C-1', C-2', C-4', C-5'

Table 13 (continued)

Position	**δ_H (*mult*, J_{Hz})**	**δ_C (C-Type)**	**HMBC**
4'	-	146.8 (C)	-
5'	-	137.6 (C)	-
6'	-	132.2 (C)	-
5-OH	13.22 (1H, *s*)	-	C-4, C-4a, C-5, C-6
2'-OH	7.86 (1H, *s*)	-	C-1', C-2', C-3'
4'-OH	9.17 (1H, *s*)	-	C-3', C-4', C-5'

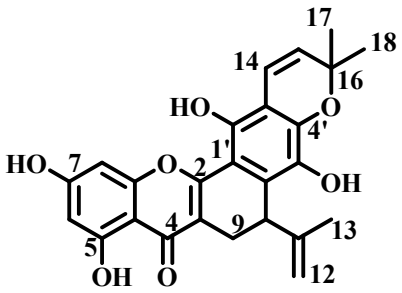
recorded in $CDCl_3$+DMSO-d_6

Table 14 ^{1}H-^{1}H COSY spectral data of **PK8**

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H_α-9 (2.41)	⟷	H_β-9 (3.22), H-10 (3.39)
H_β-9 (3.22)	⟷	H_α-9 (2.41), H-10 (3.39)
H-10 (3.39)	⟷	H_α-9 (2.41), H_β-9 (3.22)
H-14 (6.75)	⟷	H-15 (5.57)

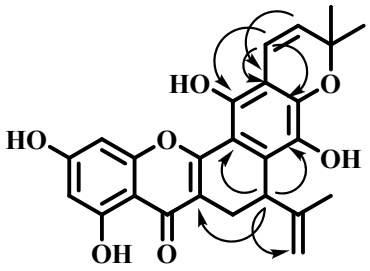
PK9

6,7-Dihydro-5,9,11,14-tetrahydroxy-3,3-dimethyl-6-(1-methylethenyl)-(-)-3*H*,8*H*-pyrano[3′,2′:4,5]benzo[1,2-*c*]xanthen-8-one : artelastoxanthone



PK9 is a red-brown gum, $[\alpha]_D^{27}$ = -82° (*c* 0.2, acetone) ($[\alpha]_D^{28}$ = -67° (*c* 0.2, acetone); Ko *et al*., 2005). The UV spectrum showed maximum absorption bands at 263, 269, 307 and 379 nm. The IR spectrum showed the stretching of hydroxyl group at 3402 cm^{-1} and carbonyl group at 1655 cm^{-1}. The ^{1}H NMR spectral data **(Table 15)** showed the signals of a chelated hydroxyl proton 5-OH at δ_H 12.98, phenolic hydroxyl groups 2'-OH, 5'-OH at δ_H 7.78, 5.46 and *meta*-aromatic protons H-6, H-8 at δ_H 6.35, 6.40 with J = 1.8 Hz. The characteristic signals of 2, 2-dimethylchromene ring were shown at δ_H 5.64 (*d*, H-15), δ_H 6.74 (*d*, H-14), δ_H 1.49 (*s*, CH_3-18) and δ_H 1.52 (*s*, CH_3-17). It was placed at C-3' and C-4' position due to the HMBC correlation of H-14 to C-2', C-3', C-4' and of H-15 to C-3'. The ^{1}H NMR spectrum further showed an ABX system signal of non-equivalent methylene protons H_α-9 (δ_H 2.58, *dd*, J = 16.2, 6.9 Hz), H_β-9 (δ_H 3.39, *dd*, J = 16.2, 1.5 Hz) and a methine proton H-10 (δ_H 3.96, *d*, J = 6.9 Hz). The signal of non-equivalent vinylic protons (δ_H 4.34, *s*, H_α-12 and δ_H 4.71, *s*, H_β-12) and methyl proton (δ_H 1.81, *s*, H-13), corresponding to an isopropenyl group, were shown in the spectrum. The ^3J HMBC correlations of H-10 to C-3, C-12, C-1', C-5' and C-6' suggested the point of attachment of C-10 to isoproprenyl group and to C-6' of the aromatic ring. This evidence indicated that the cyclic was formed between C-3 and C-6' position, whereas the isoprenyl group was linked at C-10. The coupling constant value of 6.9 Hz suggested the *trans*-axial position of protons H_α-9 and H-10, consequently. These signals are the characteristic signals of a dihydrobenzoxanthone skeleton (Hakim *et*

al., 2006). The spectral data and assignments corresponded to the previously isolated, artelastoxanthone (Ko *et al*., 2005).



Major HMBC of **PK9**

Table 15 ^{1}H, ^{13}C and HMBC spectral data of **PK9**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
2	-	159.7 (C)	-
3	-	111.5 (C)	-
4	-	180.0 (C=O)	-
4a	-	104.5 (C)	-
5	-	162.4 (C)	-
6	6.35 (1H, *d*, 1.8)	99.8 (CH)	C-4a, C-5, C-7, C-8
7	-	163.0 (C)	-
8	6.40 (1H, *d*, 1.8)	93.6 (CH)	C-4a, C-6, C-7, C-8a
8a	-	155.9 (C)	-
9	3.39 ($1H_\beta$, *dd*, 16.2, 1.5)	21.5 (CH_2)	C-2, C-3, C-4, C-10, C-11, C-6'
	2.58 ($1H_\alpha$, *dd*, 16.2, 6.9)		C-2, C-3, C-10, C-11
10	3.96 (1H, *d*, 6.9)	36.5 (CH)	C-3, C-9, C-11, C-12, C-13, C-1', C-5', C-6'
11	-	144.3 (C)	-
12	4.71 ($1H_\beta$, *s*)	111.7 (CH_2)	C-10, C-13
	4.34 ($1H_\alpha$, *s*)		C-10, C-13
13	1.81 (3H, *s*)	21.6 (CH_3)	C-10, C-11, C-12
14	6.74 (1H, *d*, 10.0)	116.3 (CH)	C-2', C-3', C-4', C-16
15	5.64 (1H, *d*, 10.0)	128.5 (CH)	C-3', C-16, C-17, C-18
16	-	78.3 (C)	-

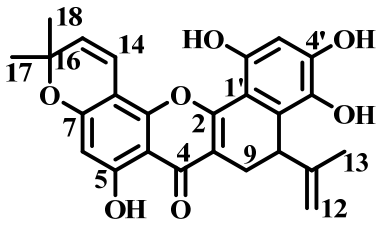
Table 15 (continued)

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
17	1.52 (3H, *s*)	28.2 (CH_3)	C-15, C-16, C-18
18	1.49 (3H, *s*)	28.1 (CH_3)	C-15, C-16, C-17
1'	-	105.2 (C)	-
2'	-	144.9 (C)	-
3'	-	108.8 (C)	-
4'	-	143.8 (C)	-
5'	-	135.6 (C)	-
6'	-	126.7 (C)	-
5-OH	12.98 (1H, *s*)	-	C-4, C-4a, C-5, C-6
2'-OH	7.78 (1H, *s*)	-	C-1', C-2', C-3'
5'-OH	5.46 (1H, *s*)	-	C-4', C-5', C-6'

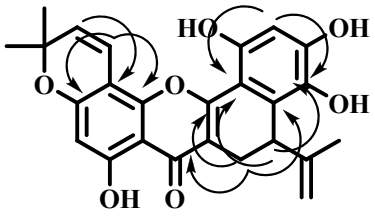
recorded in $CDCl_3$+DMSO d_6

PK10

8,9-Dihydro-6,10,11,13-tetrahydroxy-3,3-dimethyl-9-(1-methylethenyl)-3*H*,7*H*-benzo[*c*]pyrano[3,2-*h*]xanthen-7-one : artobiloxanthone



PK10 is a yellow solid, m.p. 163-164 ^{o}C (162-164 ^{o}C; Sultanbawa *et al*., 1989), $[\alpha]_D^{26}$ = +43^{o} (*c* 0.2, CH_2Cl_2) ($[\alpha]_D^{20}$ = +60^{o} (*c* 0.2, CH_2Cl_2); Ren *et al*., 2010). The UV spectrum showed maximum absorption bands at 227, 272 and 384 nm. The IR spectrum showed O-H stretching and C=O stretching at 3349 and 1652 cm^{-1}, respectively. The ^{1}H NMR spectrum had resonances associated with a chelated hydroxyl group at δ_H 13.01 (5-OH) and an ABX spin system at δ_H 2.59 (1H, *dd*, *J* = 16.2, 6.9 Hz, H_α-9), δ_H 3.36 (1H, *dd*, *J* = 16.2, 1.5 Hz, H_β-9) and δ_H 3.88 (1H, *dd*, *J* = 6.9, 1.5 Hz, H-10), attributed to the isoprenyl moiety located at the C-3 position, similar to the arrangement found for related compound, **PK9**. The ^{1}H NMR spectrum also indicated the presence of a 2,2-dimethylchromene ring by the resonance of two vinylic methine protons H-14 (δ_H 6.54, *d*, *J* = 10.2 Hz), H-15 (δ_H 5.64, *d*, *J* = 10.2 Hz), and two methyl groups 17-CH_3 (δ_H 1.46, *s*), 18-CH_3 (δ_H 1.48, *s*). This moiety was placed at C-7 and C-8 of the flavone skeleton due to the HMBC correlations of H-14 to C-7 (δ_C 159.2), C-8 (δ_C 104.8), and C-8a (δ_C 149.8) and of H-15 to C-8 (δ_C 104.8). Two isolated aromatic protons were indicated from the resonances at δ_H 6.29 (H-6, *s*) and δ_H 6.51 (H-3', *s*). The HMBC experiments (**Table 16**) showed long-range correlations between the singlet at δ_H 6.29 (H-6) and the quaternary carbon signals at δ_C 112.5 (C-4a) and δ_C 104.8 (C-8), locating of H-6 on the A-ring. Another aromatic proton (δ_H 6.51) was assigned in according with 1,2,4,5,6-pentasubstituted B-ring based on the biogenetic pattern of constituents in *Artocarpus* genus (Hakim *et al*., 2006). Consequently, artobiloxanthone was assigned the structure **PK10** (Jayasinghe *et al*., 2008).



Major HMBC of **PK10**

Table 16 ^{1}H, ^{13}C and HMBC spectral data of **PK10**

Position	δ_C (C-Type)	δ_H (*mult*, J_{Hz})	HMBC
2	159.7 (C)	-	-
3	110.9 (C)	-	-
4	180.1 (C=O)	-	-
4a	112.5 (C)	-	-
5	161.7 (C)	-	-
6	100.7 (CH)	6.29 (1H, *s*)	C-4a, C-5, C-7, C-8
7	159.2 (C)	-	-
8	104.8 (C)	-	-
8a	149.8 (C)	-	-
9	21.8 (CH_2)	3.36 ($1H_\beta$, *dd*, 16.2, 1.5)	C-2, C-3, C-4, C-10, C-11, C-6'
		2.59 ($1H_\alpha$, *dd*, 16.2, 6.9)	C-2, C-3, C-4, C-10, C-11, C-6'
10	37.9 (CH)	3.88 (1H, *dd*, 6.9, 1.5)	C-9, C-11, C-12, C-13, C-1', C-5', C-6'
11	144.7 (C)	-	-
12	112.6 (CH_2)	4.78 ($1H_\beta$, *br s*)	C-10, C-13
		4.46 ($1H_\alpha$, *br s*)	C-10, C-11, C-13
13	21.0 (CH_3)	1.79 (3H, *s*)	C-10, C-11, C-12
14	114.0 (CH)	6.54 (1H, *d*, 10.2)	C-7, C-8a, C-15, C-16
15	128.6 (CH)	5.64 (1H, *d*, 10.2)	C-8, C-16, C-17, C-18
16	78.3 (C)	-	-
17	27.9 (CH_3)	1.46 (3H, *s*)	C-15, C-16, C-18
18	28.1 (CH_3)	1.48 (3H, *s*)	C-15, C-16, C-17
1'	105.2 (C)	-	-

Table 16 (continued)

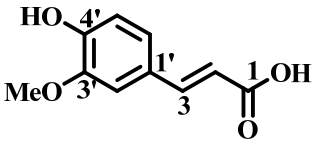
Position	δ_C (C-Type)	δ_H (*mult*, J_{Hz})	HMBC
2'	150.8 (C)	-	-
3'	103.0 (CH)	6.51 (1H, *s*)	C-1', C-2', C-4', C-5'
4'	150.4 (C)	-	-
5'	135.0 (C)	-	-
6'	127.7 (C)	-	-
5-OH	-	13.01 (1H, *br*)	-
*OH	-	7.50 (1H, *br*)	-

recorded in $CDCl_3$

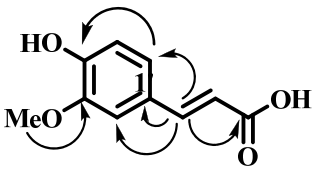
*The position not identified

PK11

(*E*)-3-(4'-Hydroxy-3'-methoxyphenyl)-2-propenoic acid



PK11 was obtained as a brown-yellow gum. The UV spectrum showed maximum absorption bands at 244, 273, 299 and 385 nm. The IR spectrum showed the O-H, C=O and C=C stretching at 3350, 1712 and 1513 cm^{-1}, respectively. The ^1H NMR spectral data (**Table 17**) displayed an ABX signal of aromatic protons at δ_H 6.94 (*d*, *J* = 8.4 Hz, H-5'), δ_H 7.05 (*d*, *J* = 1.8 Hz, H-2') and δ_H 7.13 (*dd*, *J* = 8.4, 1.8 Hz, H-6'). The spectrum further showed the resonance of vinylic proton H-3 at δ_H 7.59 and H-2 at δ_H 6.48. Their large coupling constant (*J* = 15.9 Hz) indicated *trans* configuration. In addition, the spectrum also showed the signal of a methoxyl group at δ_H 3.95. The high field signal of *ortho*-oxygenated aromatic carbons had resonated at δ_C 146.8 and 147.9 due to a mesomeric effect. The HMBC correlations of H-3 to C-1' (δ_C 127.8), C-2' (δ_C 109.7) and C-6' (δ_C 122.8) and of H-2 to C-1' (δ_C 127.8) correctly determined that the side chain was connected at C-1'. The correlations of H-6' to an oxygenated aromatic carbons (δ_C 147.9) whereas of a methoxyl group to another one, confirming the methoxyl group and the hydroxyl group were at C-3' and C-4', respectively. The structure of **PK11** was identified as (*E*)-3-(4'-hydroxy-3'-methoxyphenyl)-2-propenoic acid. It was corresponded to *trans*-feluric acid (Kelley *et al.*, 1976).



Major HMBC of **PK11**

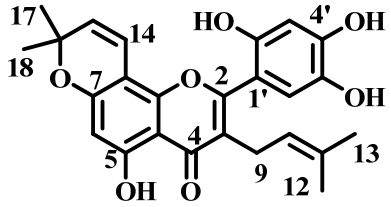
Table 17 ^{1}H, ^{13}C and HMBC spectral data of **PK11**

Position	**δ_H (*mult*, J_{Hz})**	**δ_C (C-Type)**	**HMBC**
1	-	183.4 (C=O)	-
2	6.48 (1H, *d,* 15.9)	121.8 (CH)	C-3, C-1'
3	7.59 (1H, *d,* 15.9)	140.5 (CH)	C-1, C-2, C-1', C-2', C-6'
1'	-	127.8 (C)	-
2'	7.05 (1H, *d*, 1.8)	109.7 (CH)	C-3, C-3', C-4', C-6'
3'	-	146.8 (C)	-
4'	-	147.9 (C)	-
5'	6.94 (1H, *d*, 8.4)	114.8 (CH)	C-1', C-3', C-4'
6'	7.13 (1H, *dd,* 8.4, 1.8)	122.8 (CH)	C-3, C-2', C-5'
3'-OCH_3	3.95 (3H, *s*)	56.0 (OCH_3)	C-3'
4-OH	8.09 (1H, *s*)	-	-

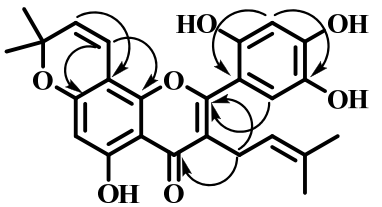
recorded in $CDCl_3$

PK12

5-Hydroxy-8,8-dimethyl-3-(3-methyl-2-butenyl)-2-(2,4,5-trihydroxyphenyl)-4*H*, 8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one : artonin E



PK12 is a brown-yellow solid, m.p. 217-219 ^{o}C. The UV spectrum showed maximum absorption bands at 224, 258, 266, 271, 302 and 352 nm. The IR spectrum exhibited the absorption bands of hydroxyl group (3402 cm^{-1}) and carbonyl group (1655 cm^{-1}). The ^{1}H NMR spectral data (**Table 18**) revealed the presence of a hydrogen bonded hydroxyl group (δ_H 13.21, *s*), three non-bonded hydroxyl groups (δ_H 8.56, 8.38, and 7.54), and three isolated aromatic protons (δ_H 6.19, *s*, H-6; δ_H 6.58, *s*, H-3' and δ_H 6.79, *s*, H-6'). The presence of a prenyl group was observed from characteristic signals of methylene protons (H-9, δ_H 3.14, *d*), an olefinic methine proton (H-10, δ_H 5.12, *mt*) and methyl protons (CH_3-12, δ_H 1.47, *s* and CH_3-13, δ_H 1.61, *s*). The correlation of H-9 to carbonyl group (δ_C 182.5) indicated that a prenyl side chain connected to C-3 position. The characteristic signals of a 2,2-dimethylchromene ring were shown at δ_H 5.48 (*d*, H-15), δ_H 6.62 (*d*, H-14), and δ_H 1.44 (*s*, CH_3-17 and *s*, CH_3-18). It was placed at C-7 and C-8 position due to the HMBC correlation of H-14 to C-7, C-8, C-8a and of H-15 to C-8. Thus **PK12** was assigned as artonin E (Jayasinghe *et al.,* 2008).



Major HMBC of **PK12**

Table 18 ^{1}H, ^{13}C and HMBC spectral data of **PK12**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
2	-	161.2 (C)	-
3	-	120.8 (C)	-
4	-	182.5 (C=O)	-
4a	-	105.0 (C)	-
5	-	161.5 (C)	-
6	6.19 (1H, *s*)	99.2 (CH)	C-4a, C-5, C-7, C-8
7	-	158.8 (C)	-
8	-	100.8 (C)	-
8a	-	152.4 (C)	-
9	3.14 (2H, *d*, 6.6)	24.2 (CH_2)	C-2, C-3, C-4, C-10, C-11
10	5.12 (1H, *mt*, 6.6)	121.5 (CH)	-
11	-	132.0 (C)	-
12	1.47 (3H, *s*)	17.5 (CH_3)	C-10, C-11, C-13
13	1.61 (3H, *s*)	25.7 (CH_3)	C-10, C-11, C-12
14	6.62 (1H, *d*, 9.9)	115.2 (CH)	C-7, C-8, C-8a, C-16
15	5.48 (1H, *d*, 9.9)	126.5 (CH)	C-8, C-16, C-17, C-18
16	-	77.7 (C)	-
17	1.44 (3H, *s*)	28.0 (CH_3)	C-15, C-16, C-18
18	1.44 (3H, *s*)	28.0 (CH_3)	C-15, C-16, C-17
1'	-	110.7 (C)	-
2'	-	148.8 (C)	-
3'	6.58 (1H, *s*)	104.0 (CH)	C-1', C-2', C-5'
4'	-	147.9 (C)	-
5'	-	137.6 (C)	-
6'	6.79 (1H, *s*)	116.2 (CH)	C-2, C-4', C-5'

Table 18 (continued)

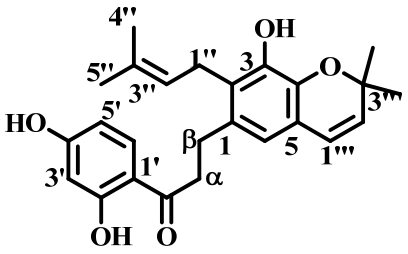
Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
5-OH	13.21 (1H, *s*)	-	C-4a, C-5, C-6
*OH	8.56 (1H, *s*)	-	-
*OH	8.38 (1H, *s*)	-	-
*OH	7.54 (1H, *s*)	-	-

recorded in $CDCl_3$+DMSO-d_6

* The position not identified

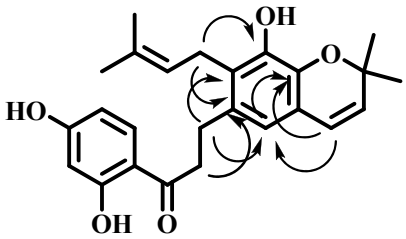
PK13

1-(2,4-Dihydroxyphenyl)-3-(8-hydroxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-chromen-6-yl)propan-1-one



PK13 was obtained as a green-yellow gum. The UV spectrum showed maximum absorption bands at 231, 273 and 313 nm. The IR spectrum exhibited absorption bands at 3383 and 1634 cm^{-1} for a hydroxyl group and a carbonyl group. The ^{1}H NMR spectral data (**Table 19**) showed singlet resonance of a hydroxyl proton (2'-OH) at δ_H 12.83, isolated aromatic proton (H-6) at δ_H 6.42 and aromatic protons attributed to 1,2,4-trisubstitued benzene at δ_H 7.58 (*d*, *J* = 8.7 Hz, H-6'), 6.35 (*dd*, *J* = 8.7, 2.1 Hz, H-5') and 6.38 (*d*, *J* = 2.1 Hz, H-3'). The aromatic proton (H-6') resonated at low field because of mesomeric effect of carbonyl group in *ortho* position. The spectrum further showed signals of two methylene groups which were coupled to each other (*J* = 9.6, 6.9 Hz) at δ_H 3.11 (α-CH_2) and 2.93 (β-CH_2). The HMBC correlations of α-CH_2 to C-1 (δ_C 131.5) while β-CH_2 to C-2 (δ_C 126.4), C-6 (δ_C 117.7) suggested that they were the α- and β- methylene proton of dihydrochalcone skeleton (Wang, *et al*., 2007). The characteristic signals of a prenyl side chain [δ_H 3.37 (*d*, *J* = 6.6 Hz, H-1''), 5.14 (*mt*, *J* = 6.6 Hz, H-2''), 1.72 (*s*, H-4''), 1.66 (*s*, H-5'')] and of a 2,2-dimethylchromene ring [δ_H 6.25 (*d*, *J* = 8.7 Hz, H-1'''), 5.56 (*d*, *J* = 8.7 Hz, H-2'''), 1.44 (*s*, H-4''' and H-5''')] were displayed in the spectrum. The prenyl group was placed at C-2 according to the correlation of H-2'' to C-2 (δ_C 126.4) and of H-1'' to C-1 (δ_C 131.5), C-3 (δ_C 142.4). The correlations of H-1''' to C-4 (δ_C 137.5), C-6 (δ_C 117.7) and of H-6 to C-4 (δ_C 137.5), C-1''' (δ_C 121.9) correctly determined that the chromene ring was at C-4 and C-5 position. The ^{13}C NMR spectrum showed 25 carbon signals separated by DEPT experiment into 11 quaternary, 7 methine, 3 methylene and 4 methyl carbons. The proposed structure of **PK13** was in agreement with molecular ion of *m/z* 408.1932 ($C_{25}H_{28}O_5$). Consequently, a new

dihydrochalcone derivative, 1-(2,4-dihydroxyphenyl)-3-(8-hydroxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*-chromen-6-yl)propan-1-one, was assigned for **PK13**.



Major HMBC of **PK13**

Table 19 ^{1}H, ^{13}C and HMBC spectral data of **PK13**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1	-	131.5 (C)	-
2	-	126.4 (C)	-
3	-	142.4 (C)	-
4	-	137.5 (C)	-
5	-	118.7 (C)	-
6	6.42 (1H, *s*)	117.7 (CH)	C_β, C-2, C-4, C-5, C-1'''
C=O	-	204.0 (C=O)	-
α	3.11 (2H, *dd*, 9.6, 6.9)	39.5 (CH_2)	C_β, C-1
β	2.93 (2H, *dd*, 9.6, 6.9)	27.2 (CH_2)	C_α, C-1, C-2, C-6
1'	-	113.5 (C)	-
2'	-	163.1(C)	-
3'	6.38 (1H, *d*, 2.1)	103.4 (CH)	C-1', C-2', C-4', C-5'
4'	-	165.1 (C)	-
5'	6.35 (1H, *dd*, 8.7, 2.1)	107.8 (CH)	C-1', C-3'
6'	7.58 (1H, *d*, 8.7)	132.1 (CH)	C-1', C-2', C-4'
1"	3.37 (2H, *d*, 6.6)	25.3 (CH_2)	C-1, C-2, C-3, C-2", C-3"
2"	5.14 (1H, *mt*, 6.6)	122.8 (CH)	C-2, C-1", C-4", C-5"
3"	-	131.8 (C)	-
4"	1.72 (3H, *s*)	17.8 (CH_3)	C-2", C-3", C-5"
5"	1.66 (3H, *s*)	25.6 (CH_3)	C-2", C-3"

Table 19 (continued)

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1'''	6.25 (1H, *d*, 8.7)	121.9 (CH)	C-4, C-5, C-6, C-3'''
2'''	5.56 (1H, *d*, 8.7)	129.9 (CH)	C-5, C-4''', C-5'''
3'''	-	77.1 (C)	-
4'''	1.44 (3H, *s*)	28.0 (CH_3)	C-2''', C-3'''
5'''	1.44 (3H, *s*)	28.0 (CH_3)	C-2''', C-3'''
2'-OH	12.83 (1H, *s*)	-	-

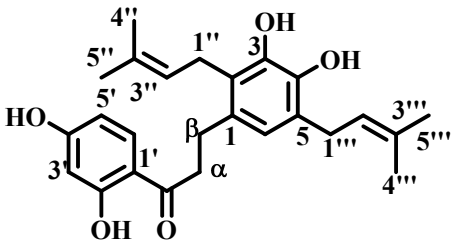
recorded in $CDCl_3$

Table 20 ^{1}H-^{1}H COSY spectral data of **PK13**

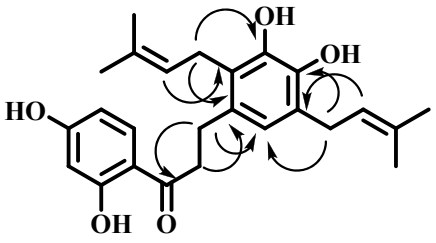
Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-α (3.11)	⟷	H-β (2.93)
H-3' (6.38)	⟷	H-5' (6.35)
H-5' (6.35)	⟷	H-3' (6.38), H-6' (7.58)
H-6' (7.58)	⟷	H-5' (6.35)
H-1'' (3.37)	⟷	H-2'' (5.14)
H-1''' (6.25)	⟷	H-2''' (5.56)

PK14

1-(2,4-dihydroxyphenyl)-3-(3,4-dihydroxy-2,5-bis(3-methylbut-2-enyl)phenyl) propan-1-one



PK14 was obtained as a yellow solid, m.p. 170 C°. The UV spectrum showed maximum absorption bands at 237, 274 and 313 nm. The IR spectrum showed absorption band of a hydroxyl group at 3422 cm^{-1} and a carbonyl group at 1629 cm^{-1}. Its ^{1}H NMR spectral data (**Table 21**) showed signals corresponded to the α- and β- methylene protons (δ_H 3.29, *dd*, *J* = 8.1, 7.2 Hz; δ_H 2.91 (*dd*, *J* = 8.1, 7.2 Hz), a 1,2,4-trisubstitued benzene (δ_H 7.54, *d*, *J* = 9.3 Hz, H-6'; δ_H 6.36, *d*, *J* = 9.3 Hz, H-5'; δ_H 6.38, *s*, H-3'), an aromatic proton (δ_H 6.49, H-6) on ring B, a hydrogen bonded hydroxyl group (δ_H 12.84), two prenyl groups (δ_H 3.36, *d*, *J* = 7.2 Hz, H-1"; δ_H 5.14, *mt*, *J* = 7.2 Hz, H-2"; δ_H 1.65, *s*, H-4"; δ_H 1.71, *s*, H-5" and δ_H 3.28, *d*, *J* = 7.2 Hz, H-1'''; δ_H 5.28, *mt*, *J* = 7.2 Hz, H-2'''; δ_H 1.70, *s*, H-4'''; δ_H 1.71, *s*, H-5'''). The ^{13}C NMR spectral data and HMBC correlations suggested that it was a dihydrochalcone with a prenylated side chain at C-2 as for **PK13**. The second prenyl group was placed at C-5 position according to the HMBC correlations of H-1''' to C-4 (δ_C 140.2), C-6 (δ_C 120.6) and of olefinic proton (H-2''') to C-5 (δ_C 125.9) indicated that this side chain was at C-5 position. The molecular ion of *m/z* 410.2087 ($C_{25}H_{30}O_5$) was in agreement with the proposed structure. Therefore a new dihydrochalcone structure, 1-(2,4-dihydroxyphenyl)-3-(3,4-dihydroxy-2,5-bis(3-methylbut-2-enyl)phenyl)propan-1-one, was assigned for **PK14**.



Major HMBC of **PK14**

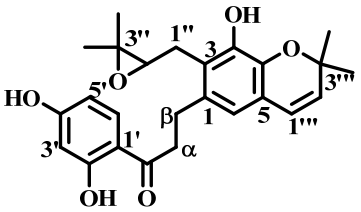
Table 21 ^{1}H, ^{13}C and HMBC spectral data of **PK14**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1	-	130.4 (C)	-
2	-	124.2 (C)	-
3	-	142.6 (C)	-
4	-	140.2 (C)	-
5	-	125.9 (C)	-
6	6.49 (1H, *s*)	120.6 (CH)	C-2, C-4
C=O	-	203.6 (C=O)	-
α	3.29 (2H, *dd*, 8.1, 7.2)	38.8 (CH_2)	C=O, C_β, C-1
β	2.91 (2H, *dd*, 8.1, 7.2)	27.1 (CH_2)	C=O, C_α, C-2, C-6
1'	-	112.4 (C)	-
2'	-	164.2 (C)	-
3'	6.38 (1H, *s*)	102.8 (CH)	C-1', C-4', C-5'
4'	-	164.7 (C)	-
5'	6.36 (1H, *d*, 9.3)	107.8 (CH)	C-1', C-3'
6'	7.54 (1H, *d*, 9.3)	131.6 (CH)	C-1', C-4', C=O
1"	3.36 (2H, *d*, 7.2)	25.0 (CH_2)	C-1, C-2, C-3, C-2", C-3"
2"	5.14 (1H, *mt*, 7.2)	123.0 (CH)	C-2, C-1", C-4", C-5'
3"	-	131.0 (C)	-
4"	1.65 (3H, *s*)	17.3 (CH_3)	C-2", C-3"
5"	1.71 (3H, *s*)	25.2 (CH_3)	C-2", C-3"
1"'	3.28 (2H, *d*, 7.2)	28.1 (CH_2)	C-4, C-5, C-6, C-2"', C-3"'
2"'	5.28 (1H, *mt*, 7.2)	122.1 (CH)	C-5, C-1"', C-4"', C-5"'
3"'	-	132.0 (C)	-
4"'	1.71 (3H, *s*)	17.4 (CH_3)	C-2"', C-3"'
5"'	1.70 (3H, *s*)	25.3 (CH_3)	C-2"', C-3"'
3-OH	6.86 (1H, *s*)	-	C-2, C-3, C-4
4-OH	6.98 (1H, *s*)	-	C-3, C-4, C-5
2'-OH	12.84 (1H, *s*)	-	C-1', C-2', C-3'
4'-OH	9.86 (1H, *s*)	-	C-3', C-4', C-5'

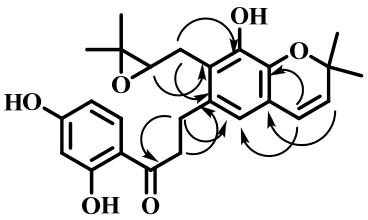
recorded in $CDCl_3$+DMSO-d_6

PK15

1-(2,4-Dihydroxyphenyl)-3-(7-((3,3-dimethyloxiran-2-yl)methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)propan-1-one



PK15 was obtained as a yellow gum, $[\alpha]_D^{26}$ = -14^o (*c* 0.1, acetone). The UV spectrum showed maximum absorption bands at 245, 274 and 311 nm. The IR spectrum showed absorption band of a hydroxyl group at 3390 cm^{-1} and a carbonyl group at 1631 cm^{-1}. The ^{1}H NMR spectral data **(Table 22)** disclosed the signals of a 1,2,4-trisubstitued benzene (δ_H 7.58, *d*, *J* = 8.4 Hz, H-6'; 6.35, *dd*, *J* = 8.4, 1.8 Hz, H-5'; 6.37, *d*, *J* = 1.8 Hz, H-3'), an aromatic proton (δ_H 6.45, H-6) on ring B, α- and β-methylene protons (δ_H 3.13, *dd*, *J* = 8.4, 6.6 Hz; 2.87, *dd*, *J* = 8.4, 6.6 Hz), hydrogen bonded hydroxyl group (δ_H 12.83, s, 2'-OH) and a chromene ring at C-4/C-5 position (δ_H 6.27; *d*, *J* = 9.6 Hz, H-1'''; 5.57, *d*, *J* = 9.6 Hz, H-2'''; 1.43, *s*, H-4'''; 1.44, *s*, H-5''') as for **PK13**. The replacement of the prenyl side chain at C-3 by 3,3-dimethyloxiran-2-yl-methyl group was indicated by the resonances of non-equivalent methylene protons (δ_H 2.96, *dd*, *J* =11.7, 5.4 Hz; 2.70, *dd*, *J* = 11.7, 5.4 Hz), an oxy-methine proton (δ_H 3.82, *t*, *J* = 5.4 Hz) and two methyl groups (δ_H 1.37, *s*; δ_H 1.32, *s*).). The appearing of non-equivalent methylene proton H-1'' suggested that it connected to a chiral carbon C-2''. In ^{13}C NMR spectrum, oxy-methine carbon (C-2'') and oxy-quarternary carbon (C-3'') resonated at δ_C 69.8 at δ_C 76.4, respectively. A molecular ion in the HREI-MS at *m/z* 424.1880 which corresponded to a molecular formula of $C_{25}H_{28}O_6$ confirmed that **PK15** was 1-(2,4-dihydroxyphenyl)-3-(7-((3,3-di methyloxiran-2-yl)methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl)propan-1-one, a new dihydrochalcone.



Major HMBC of **PK15**

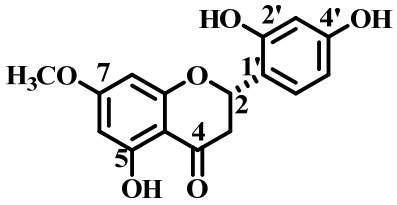
Table 22 ^{1}H, ^{13}C and HMBC spectral data of **PK15**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1	-	131.9 (C)	-
2	-	118.7 (C)	-
3	-	141.7 (C)	-
4	-	140.0 (C)	-
5	-	120.4 (C)	-
6	6.45 (1H, *s*)	118.1 (CH)	C_β, C-2, C-4, C-1'''
C=O	-	203.8 (C=O)	-
α	3.13 (2H, *dd*, 8.4, 6.6)	38.4 (CH_2)	C=O, C_β, C-1
β	2.87 (2H, *dd*, 8.4, 6.6)	26.6 (CH_2)	C=O, C_α, C-6
1'	-	113.7 (C)	-
2'	-	165.2 (C)	-
3'	6.37 (1H, *d*, 1.8)	103.6 (CH)	C-1', C-2', C-5'
4'	-	163.0 (C)	-
5'	6.35 (1H, *dd*, 8.4, 1.8)	107.9 (CH)	C-1', C-3', C-4'
6'	7.58 (1H, *d*, 8.4)	132.2 (CH)	C=O, C-2', C-4'
1''	2.96 (1H, *dd*, 11.7, 5.4)	29.6 (CH_2)	C-1, C-2, C-3, C-2'', C-3''
	2.70 (1H, *dd*, 11.7, 5.4)		C-1, C-2, C-3, C-2'', C-3''
2''	3.82 (1H, *t*, 5.4)	69.8 (CH)	C-2, C-4'', C-5''
3''	-	76.4 (C)	-
4''	1.37 (3H, *s*)	21.8 (CH_3)	C-2'', C-3'', C-5''
5''	1.32 (3H, *s*)	24.4 (CH_3)	C-2'', C-3'', C-4''
1'''	6.27 (1H, *d*, 9.6)	122.2 (CH)	C-4, C-5, C-6, C-3'''
2'''	5.57 (1H, *d*, 9.6)	130.9 (CH)	C-5, C-1''', C-3''', C-4''', C-5'''
3'''	-	76.3 (C)	-
4'''	1.43 (3H, *s*)	27.7 (CH_3)	C-2''', C-3''', C-5'''
5'''	1.44 (3H, *s*)	27.5 (CH_3)	C-2''', C-3''', C-4'''
2'-OH	12.83 (1H, *s*)	-	C-1', C-2', C-3'

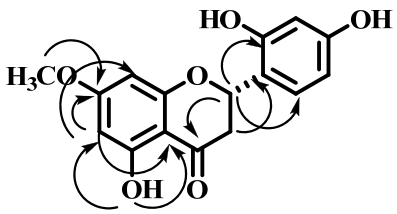
recorded in $CDCl_3$

PK16

(*S*)-2-(2,4-Dihydroxyphenyl)-5-hydroxy-7-methoxychroman-4-one



PK16 is a pale yellow solid, m.p. 210-211 ^{o}C (210-212 ^{o}C); Wei *et al*., 2005), $[\alpha]_D^{27}$ = -3^{o} (*c* 0.2, acetone) ($[\alpha]_D^{24}$ = -2^{o} (*c* 0.2, acetone); Wei *et al*., 2005). The UV spectrum showed maximum absorption bands at 244, 273 and 305 nm. Its IR spectrum showed the stretching of hydroxyl (3343 cm^{-1}) and carbonyl group (1697 cm^{-1}). The ^{13}C NMR revealed the presence of 16 carbons separated by DEPT experiment into 8 quaternary, 6 methine, 1 methylene and 1 methyl carbons. The ^{1}H NMR spectral data (**Table 23**) displayed an ABX signal of aromatic protons at δ_H 7.32 (*d*, *J* = 8.1 Hz, H-6'), δ_H 6.48 (*d*, *J* = 2.4 Hz, H-3') and δ_H 6.44 (*dd*, *J* = 8.1, 2.4 Hz, H-5'), and *meta*-aromatic protons at δ_H 6.03 (H-6) and δ_H 6.05 (H-8) with *J* = 2.4 Hz. The spectrum further showed the doublet of doublet resonance of an oxy-methine proton at δ_H 5.73 (*J* = 13.2, 3.0, H-2) and the doublet of doublet resonance of the adjacent non-equivalent methylene protons (H-3) at δ_H 3.21 (*J* = 17.1, 13.2 Hz; H_α) and δ_H 2.74 (*J* = 17.1, 3.0 Hz, H_β). The signals at δ 3.21 and 2.74 were ascribed to the *trans*- and *cis*- orientation with H-2, respectively. The spectrum also exhibited the resonances of methoxyl group at δ_H 3.84. It was placed at C-7 by HMBC correlations of the methoxyl group (δ_H 3.84), H-6 (δ_H 6.03) and H-8 (δ_H 6.05) to C-7 (δ_C 167.8). The correlations of oxy-methine proton (H-2) to C-2' (δ_C 155.5) and C-6' (δ_C 128.1) confirmed the linkage of C-2 and C-1'. This compound was flavanones, named (*S*)-2-(2,4-dihydroxyphenyl)-5-hydroxy-7-methoxychroman-4-one. These assignment indicated that **PK16** was artocarpanone (Wei *et al*., 2005).



Major HMBC of **PK16**

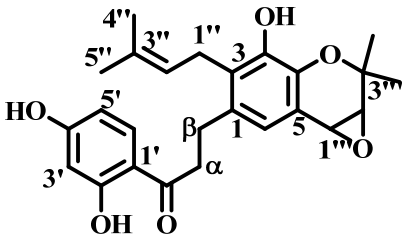
Table 23 ^{1}H, ^{13}C and HMBC spectral data of **PK16**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
2	5.73 (1H, *dd*, 13.2, 3.0)	74.6 (CH)	C-4, C-1', C-2', C-6'
3	3.21 ($1H_\alpha$, *dd*, 17.1, 13.2)	41.7 (CH_2)	C-2, C-4, C-1'
	2.74 ($1H_\beta$, *dd*, 17.1, 3.0)		C-4, C-4a, C-1'
4	-	197.2 (C=O)	-
4a	-	102.8 (C)	-
5	-	164.1 (C)	-
6	6.03 (1H, *d*, 2.4)	94.5 (CH)	C-4a, C-5, C-7, C-8
7	-	167.8 (C)	-
8	6.05 (1H, *d*, 2.4)	93.6 (CH)	C-4a, C-6, C-7, C-8a
8a	-	163.8 (C)	-
1'	-	116.4 (C)	-
2'	-	155.5 (C)	-
3'	6.48 (1H, *d*, 2.4)	102.6 (CH)	C-1', C-2', C-4', C-5'
4'	-	158.7 (C)	-
5'	6.44 (1H, *dd*, 8.1, 2.4)	107.2 (CH)	C-1', C-3', C-4'
6'	7.32 (1H, *d*, 8.1)	128.1 (CH)	C-2, C-2', C-4'
5-OH	12.17 (1H, *s*)	-	C-4a, C-5, C-6
7-OMe	3.84 (3H, *s*)	55.3 (CH_3)	C-7

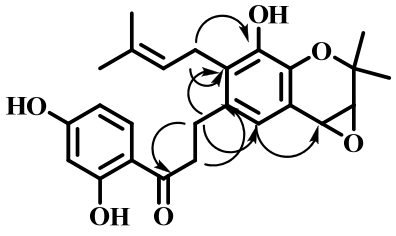
recorded in acetone-d_6

PK17

1-(2,4-Dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7*b*-dihydro-1*aH*-oxireno[2,3-*c*]chromen-6-yl)propan-1-one



PK17 was obtained as a yellow solid, m.p. 179-180 C°, $[\alpha]_D^{26}$ = +7° (*c* 0.2, acetone). The UV spectrum showed maximum absorption bands at 243, 275 and 310 nm. The IR spectrum exhibited the presence of hydroxyl (3223 cm^{-1}) and carbonyl (1624 cm^{-1}) groups. The ^1H NMR spectral data and HMBC correlation (**Table 24**) were much closely to those of **PK13** with the replacement of olefinic proton signals at δ_H 6.25 (*d*, *J* = 8.7 Hz, H-1''') and δ_H 5.56 (*d*, *J* = 8.7 Hz, H-2''') by signals of oxy-methine proton at δ_H 4.47 and 3.54 (2 x *br d*, *J* = 7.8 Hz, H-1''' and H-2'''). The signals of dihydrochalcone skeleton disclosed the signals of α- and β-methylene proton (δ_H 3.15-3.21, *m*; 2.92-2.95, *m*), a 1,2,4-trisubstitued benzene (δ_H 7.77 (*d*, *J* = 8.7 Hz, H-6'); 6.42 (*d*, *J* = 8.7, 2.4 Hz, H-5'); 6.33 (*d*, *J* = 2.4 Hz, H-3')), an aromatic proton (δ_H 6.86, H-6) on ring B, a hydrogen bonded hydroxyl group (δ_H 12.83), a prenyl group (δ_H 3.39 (*d*, *J* = 6.6 Hz, H-1''); 5.14 (*mt*, *J* = 6.6 Hz, H-2''); 1.71 (*s*, H-4''); 1.63 (*s*, H-5'')). The HMBC correlation of H-1''' to C-3''' (δ_C 78.9) and of H-2''' to C-1''' (δ_C 69.0) confirm that the epoxy group was at C-1''' and C-2'''. A molecular ion in the HREI-MS at *m/z* 424.1865, corresponding to a molecular formula of $C_{25}H_{28}O_6$, so this compound have been epoxide structure. Thus a new dihydrochalcone structure, 1-(2,4-dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7b-dihydro-1a*H*-oxireno[2,3-*c*] chromen-6-yl) propan-1-one, was assigned for **PK17**.



Major HMBC of **PK17**

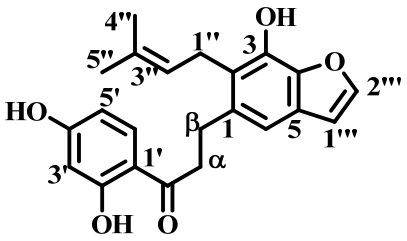
Table 24 ^{1}H, ^{13}C and HMBC spectral data of **PK17**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1	-	131.4 (C)	-
2	-	124.8 (C)	-
3	-	142.9 (C)	-
4	-	138.1 (C)	-
5	-	123.8 (C)	-
6	6.86 (1H, *s*)	118.1 (CH)	C_β, C-2, C-4, C-5, C-1'''
C=O	-	204.3 (C=O)	-
α	3.15-3.21 (2H, *m*)	39.3 (CH_2)	C=O, C_β, C-1
β	2.92-2.95 (2H, *m*)	27.3 (CH_2)	C=O, C_α, C-1, C-2, C-6
1'	-	113.0 (C)	-
2'	-	165.4 (C)	-
3'	6.33 (1H, *d*, 2.4)	102.7 (CH)	C-1', C-2', C-5'
4'	-	164.6 (C)	-
5'	6.42 (1H, *dd*, 8.7, 2.4)	107.8 (CH)	C-1', C-3', C-4'
6'	7.77 (1H, *d*, 8.7)	132.7 (CH)	C=O, C-4'
1''	3.39 (2H, *d*, 6.6)	24.9 (CH_2)	C-2, C-3, C-3''
2''	5.14 (1H, *mt*, 6.6)	122.4 (CH)	C-1'', C-4'', C-5''
3''	-	130.2 (C)	-
4''	1.71 (3H, *s*)	17.1 (CH_3)	C-2'', C-3'', C-5''
5''	1.63 (3H, *s*)	24.9 (CH_3)	C-2'', C-3'', C-4''
1'''	4.47 (1H, *br d*, 7.8)	69.0 (CH)	C-3'''
2'''	3.54 (1H, *br d*, 7.8)	76.2 (CH)	C-1'''
3'''	-	78.9 (C)	-
4'''	1.44 (3H, *s*)	26.1 (CH_3)	C-3''', C-5'''
5'''	1.19 (3H, *s*)	18.7 (CH_3)	C-3''', C-4'''
3-OH	7.18 (1H, *s*)	-	C-2, C-3
2'-OH	12.83 (1H, *s*)	-	C-1', C-2', C-3'

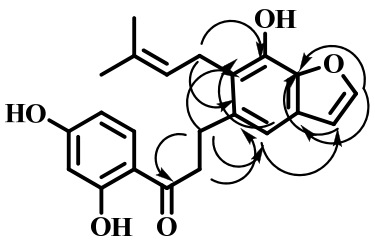
recorded in acetone-d_6

PK18

1-(2,4-Dihydroxyphenyl)-3-(7-hydroxy-6-(3-methylbut-2-enyl)benzofuran-5-yl)propan-1-one



PK18 was obtained as a yellow gum. The UV spectrum showed maximum absorption bands at 228, 276 and 314 nm. The IR spectrum exhibited the presence of hydroxyl (3352 cm^{-1}) and carbonyl (1629 cm^{-1}) groups. Its ^{1}H NMR spectral data and HMBC correlations (**Table 25**) suggested that it had the same dihydrochalcone core as for **PK13**, showing signals of α- and β- methylene protons [δ_H 3.17-3.22 (*m*, 2H) and 3.08-3.14 (*m*, 2H)], aromatic protons of a 1,2,4-trisubstitued benzene (δ_H 7.60 (*d*, *J* = 8.7 Hz, H-6'); 6.36 (*dd*, *J* = 8.7, 2.4 Hz, H-5'); 6.40 (*d*, *J* = 2.4 Hz, H-3')), an aromatic proton (δ_H 7.02, H-6) on ring B, a hydrogen bonded hydroxyl group (δ_H 12.78), a prenyl group (δ_H 3.52 (*d*, *J* = 6.6 Hz, H-1"); 5.19 (*mt*, *J* = 6.6 Hz, H-2"); 1.79 (*s*, H-4"); 1.70, *s*, H-5")), without the signals of a 2,2-dimethylchromene ring. The assignment of a furan ring was indicated from the resonances of olefinic protons at δ_H 6.68 (*d*, *J* = 2.1 Hz, H-1''') and 7.55 (*d*, *J* = 2.1 Hz, H-2'''). The later one was shown at the lower field due to deshielding effect by oxygen atom. The correlations of olefinic protons H-1''' and H-2''' to C-4 (δ_C 142.7), C-5 (δ_C 126.6) correctly determined that the furan ring was at C-4 and C-5 position. In ^{13}C NMR spectrum, oxy-sp^2 carbon (C-2''') and sp^2 carbon (C-1''') resonated at δ_C 144.6 at δ_C 106.9, respectively. A molecular ion in the HREI-MS at *m/z* 366.1461 which corresponded to a molecular formula of $C_{22}H_{22}O_5$ confirmed that **PK18** was 1-(2,4-dihydroxyphenyl)-3-(7-hydroxy-6-(3-methylbut-2-enyl)benzofuran-5-yl)propan-1-one, a new dihydrochalcone.



Major HMBC of **PK18**

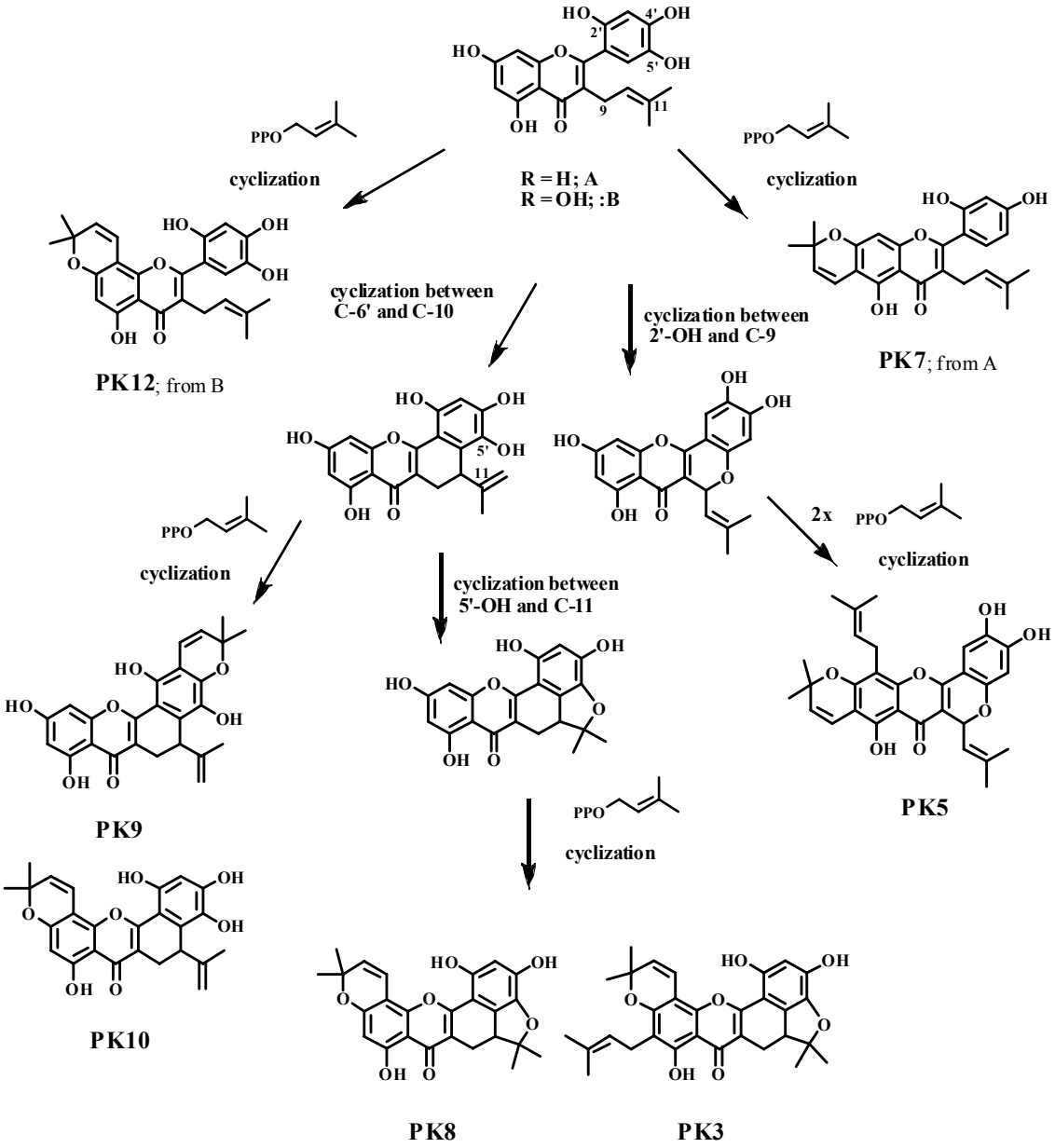
Table 25 ^{1}H, ^{13}C and HMBC spectral data of **PK18**

Position	δ_H (*mult*, J_{Hz})	δ_C (C-Type)	HMBC
1	-	135.1 (C)	-
2	-	121.6 (C)	-
3	-	139.4 (C)	-
4	-	142.7 (C)	-
5	-	126.6 (C)	-
6	7.02 (1H, *s*)	112.9 (CH)	C_β, C-2, C-4, C-1'''
C=O	-	203.7 (C=O)	-
α	3.17-3.22 (2H, *m*)	39.8 (CH_2)	C=O, C_β, C-1
β	3.08-3.14 (2H, *m*)	28.2 (CH_2)	C=O, C_α, C-2, C-6
1'	-	113.6 (C)	-
2'	-	165.3 (C)	-
3'	6.40 (1H, *d*, 2.4)	103.6 (CH)	C-2', C-4', C-5'
4'	-	163.1 (C)	-
5'	6.36 (1H, *dd*, 8.7, 2.4)	107.9 (CH)	C-1', C-3'
6'	7.60 (1H, *d*, 8.7)	132.1 (CH)	C=O, C-1', C-4'
1''	3.52 (2H, *d*, 6.6)	25.2 (CH_2)	C-1, C-2, C-3, C-2'', C-3''
2''	5.19 (1H, *t*, 6.6)	122.8 (CH)	-
3''	-	133.1 (C)	-
4''	1.79 (3H, *s*)	17.9 (CH_3)	C-2'', C-3'', C-5''
5''	1.70 (3H, *s*)	25.7 (CH_3)	C-2'', C-3'', C-4''
1'''	6.68 (1H, *d*, 2.1)	106.9 (CH)	C-4, C-5, C-2'''
2'''	7.55 (1H, *d*, 2.1)	144.6 (CH)	C-4, C-5, C-1''
2'-OH	12.78 (1H, *s*)	-	C-1', C-2', C-3'

recorded in $CDCl_3$

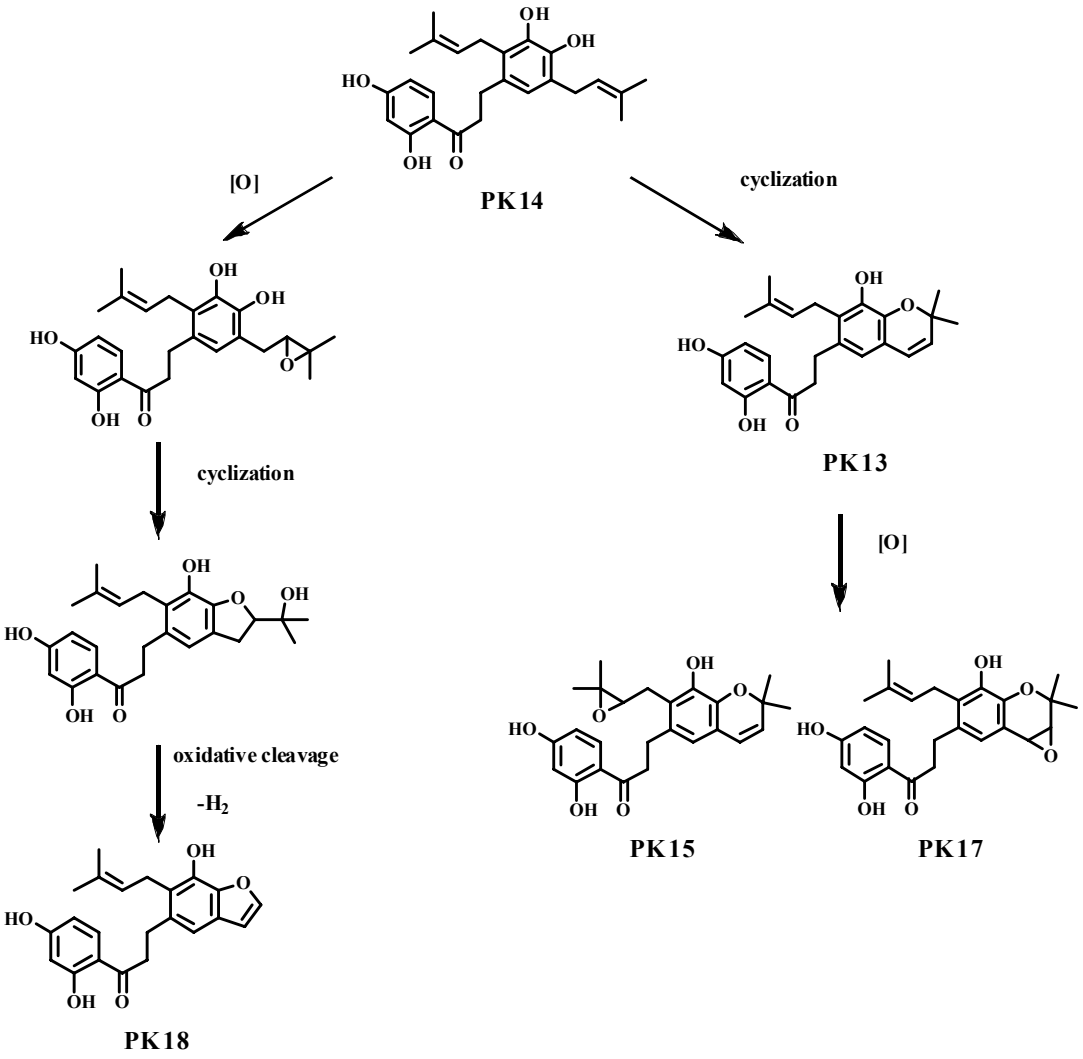
3.2 Relationship of flavonoids in this study

Investigation of *A. elasticus* has revealed that flavonoids is main components in this plant. The various classes of flavonoids is in agreement with the biogenetic relationship involving a 3-prenylatedflavone as a key intermediate. The relationship of flavones in this study can be discussed in **Scheme 12**.



Scheme 12 Relationship of prenylated flavones from *A. elasticus*

The major component isolated from the leaves of *A. elasticus* is **PK14** which has the relationship with other compounds as shown in **Sheme 13**.

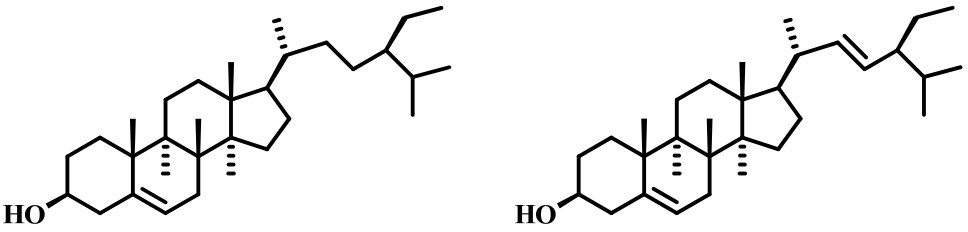


Scheme 13 Relationship of prenylated dihydrochalcones from *A. elasticus*

Conclusion

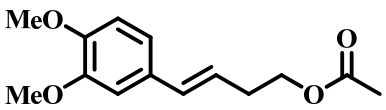
Investigation of the chemical constituents from the root bark and leaves of *A. elasticus* led to the isolation of various types of compounds. A triterpenoids **(PK1)**, two phenylbutenoids **(PK2** and **PK6)**, two furanodihydrobenzoxanthones **(PK3** and **PK8)**, a benzaldehyde derivatives (**PK4**), a pyranoflavones **(PK5)**, two 3-prenylated flavones **(PK7** and **PK12)**, two dihydrobenzoxanthones **(PK9** and **PK10)**, a phenylpropanoids **(PK11)** were obtained from the root. A flavanone **(PK16)** and five new prenylated dihydrochalcones **(PK13**, **PK14**, **PK15**, **PK17** and **PK18)** were isolated from the leaves. **PK13**, **PK14**, **PK15**, **PK17** and **PK18** are new compounds. **PK2, PK4, PK5, PK6, PK7, PK9, PK10** and **PK16** were obtained for the first time from this plant. Since this plant has been reported to have anti-inflammatory activity and cytotoxicity, further study on the antibacterial and antiprotozoa activity of the isolated compound should be performed.

Triterpenoids

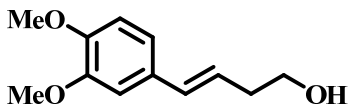


PK1 : a mixture of *β*-sitosterol and stigmasterol

Phenylbutenoids

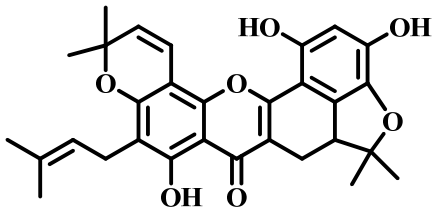


PK2 : (*E*)-4-(3',4'-dimethoxyphenyl)-butenyl acetate

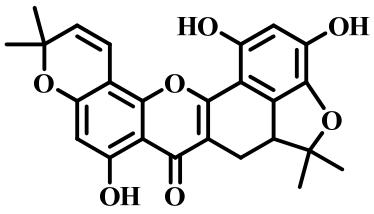


PK6 : (*E*)-4-(3',4'-dimethoxyphenyl) but-3-en-1-ol

Furanodihydrobenzoxanthones

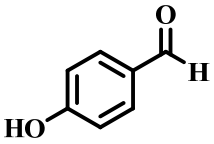


PK3 : artonin F



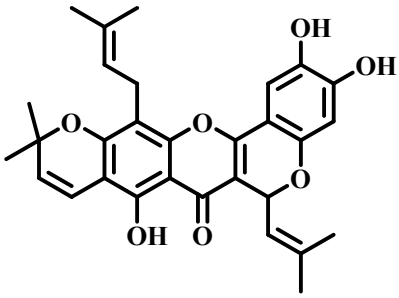
PK8 : cycloartobiloxanthone

Benzaldehyde derivatives



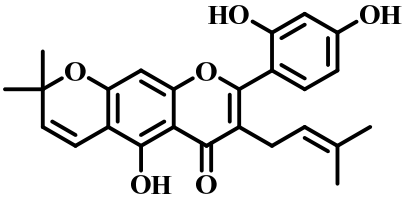
PK4 : 4-hydroxybenzaldehyde

Pyranoflavones

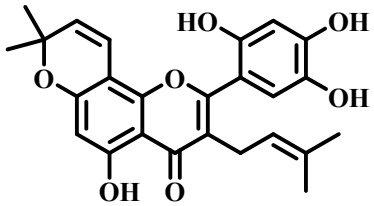


PK5 : cycloheterophyllin

3-Prenylated flavones

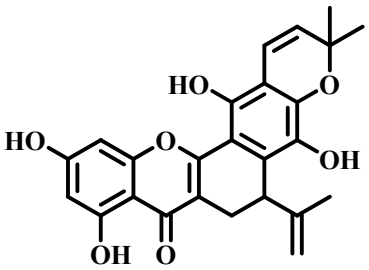


PK7 : cudraflavone B

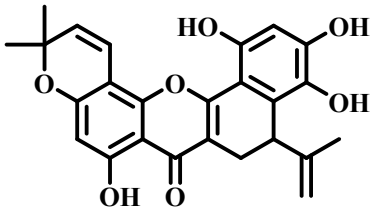


PK12 : artonin E

Dihydrobenzoxanthones

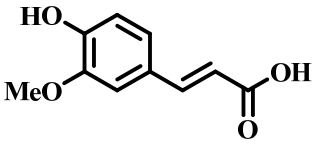


PK9 : artelastoxanthone



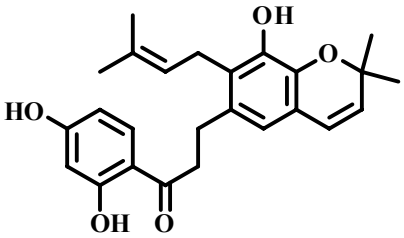
PK10 : artobiloxanthone

Phenylpropanoids

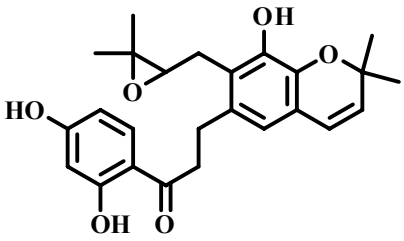


PK11 : *trans*-feluric acid

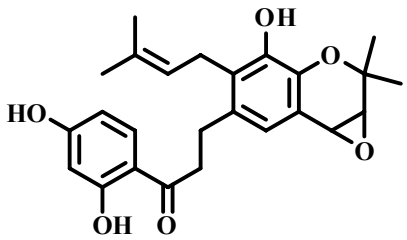
Prenylated dihydrochalcones



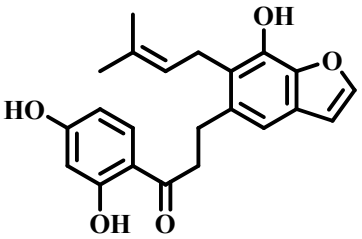
PK14 : 1-(2,4-dihydroxyphenyl)-3-(3,4- dihydroxy-2,5-bis(3-methylbut-2- enyl) phenyl)propan-1-one



PK15 : 1-(2,4-dihydroxyphenyl)-3-(7- ((3,3-dimethyloxiran-2-yl) methyl)-8-hydroxy-2,2-dimethyl-2*H*-chromen-6-yl) propan-1-one

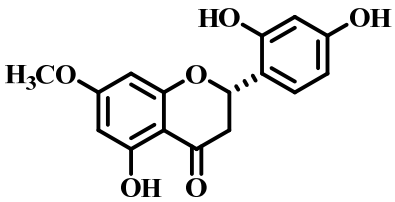


PK17 : 1-(2,4-dihydroxyphenyl)-3-(4-hydroxy-2,2-dimethyl-5-(3-methylbut-2-enyl)-2,7*b*-dihydro-1*aH*-oxireno[2,3-*c*] chromen-6-yl)propan-1-one



PK18 : 1-(2,4-dihydroxyphenyl)-3-(7-hydroxy-6-(3-methylbut-2-enyl) benzofuran-5-yl)propan-1-one

Flavonones



PK16 : artocarpanone

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APPENDIX

1. ^{1}H-NMR and ^{13}C-NMR spectrum of compounds PK1-PK18

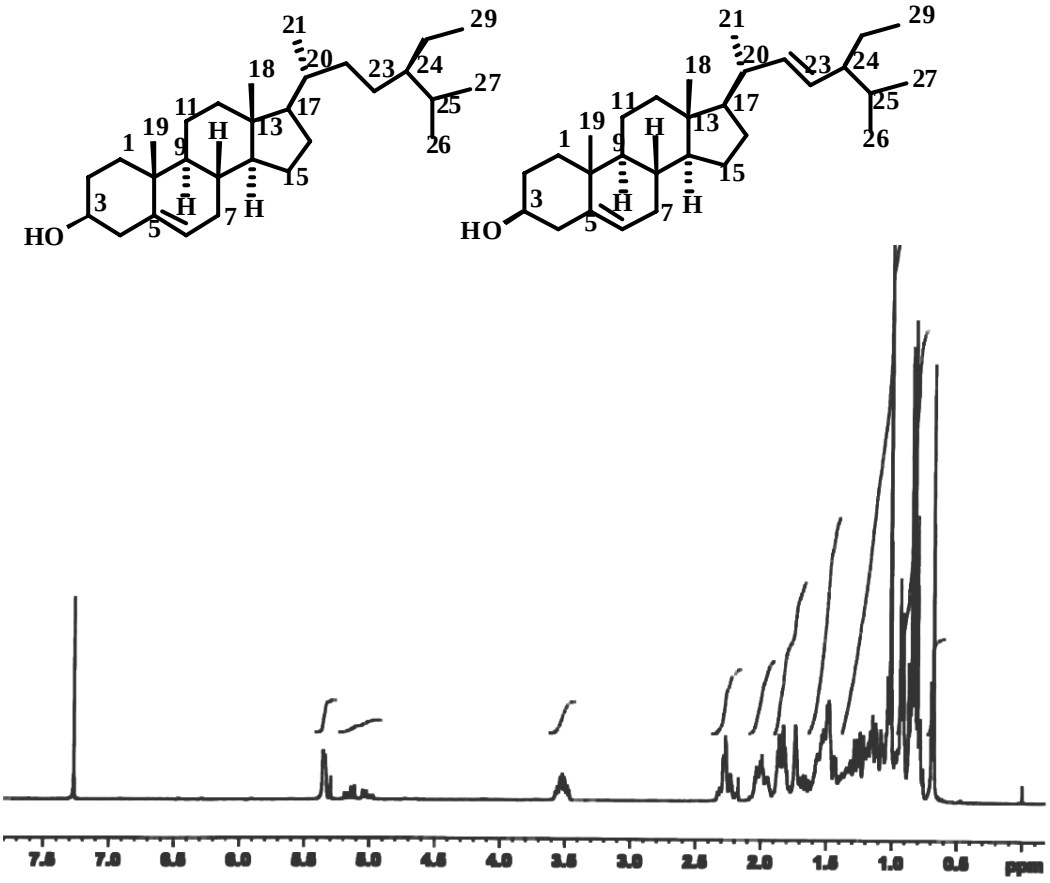

Figure A-1 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK1**

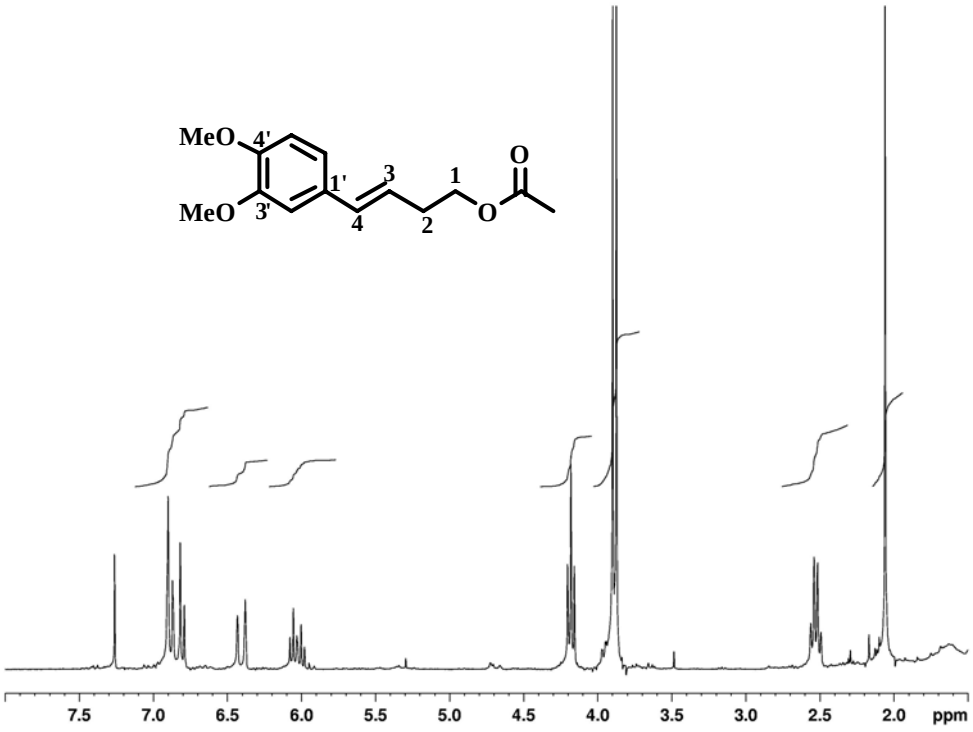

Figure A-2 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK2**

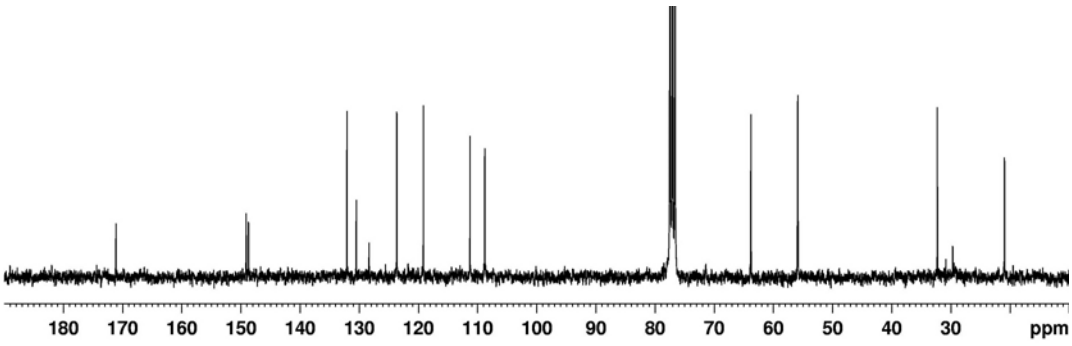

Figure A-3 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK2**

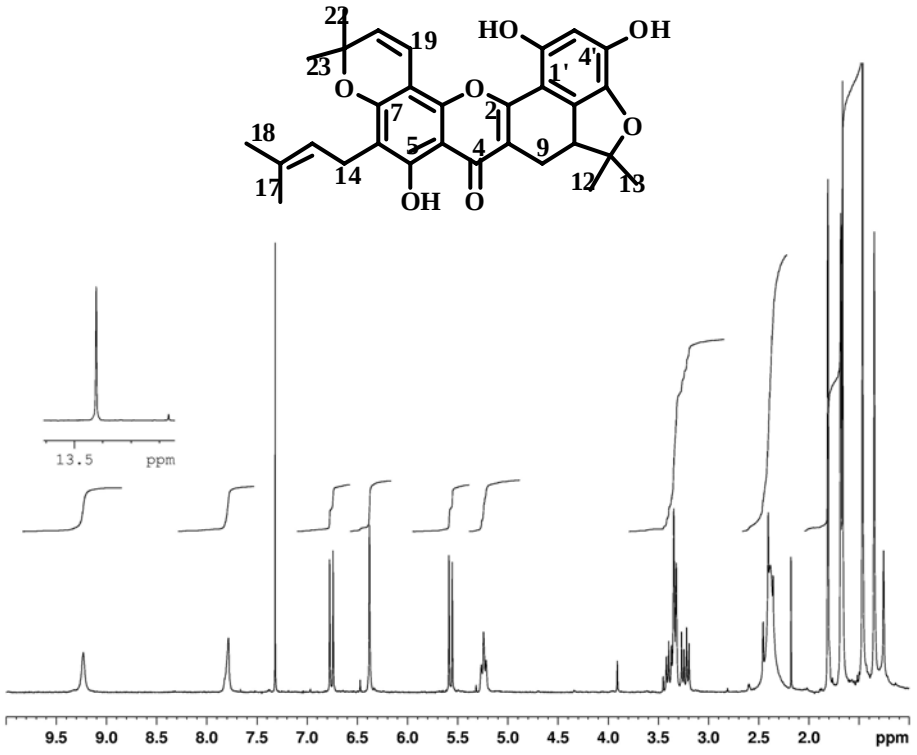

Figure A-4 ^{1}H-NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK3**

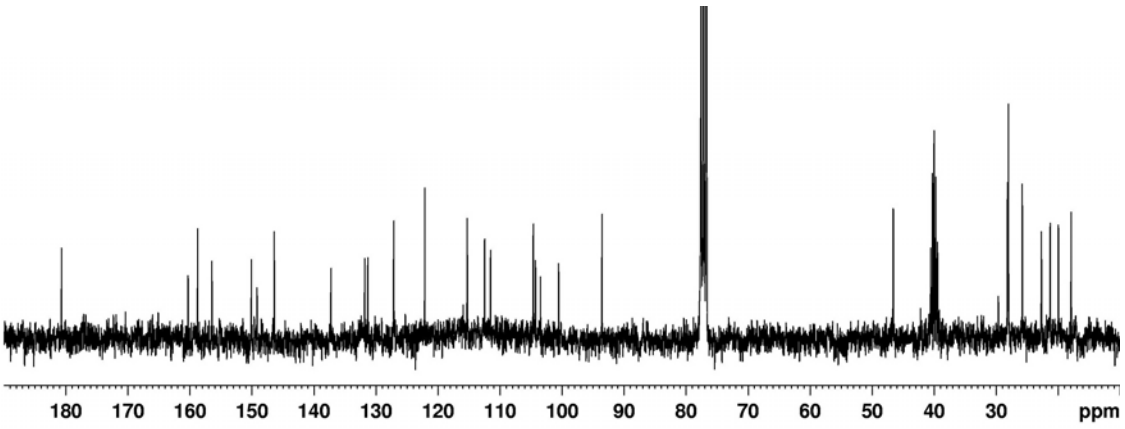

Figure A-5 ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK3**

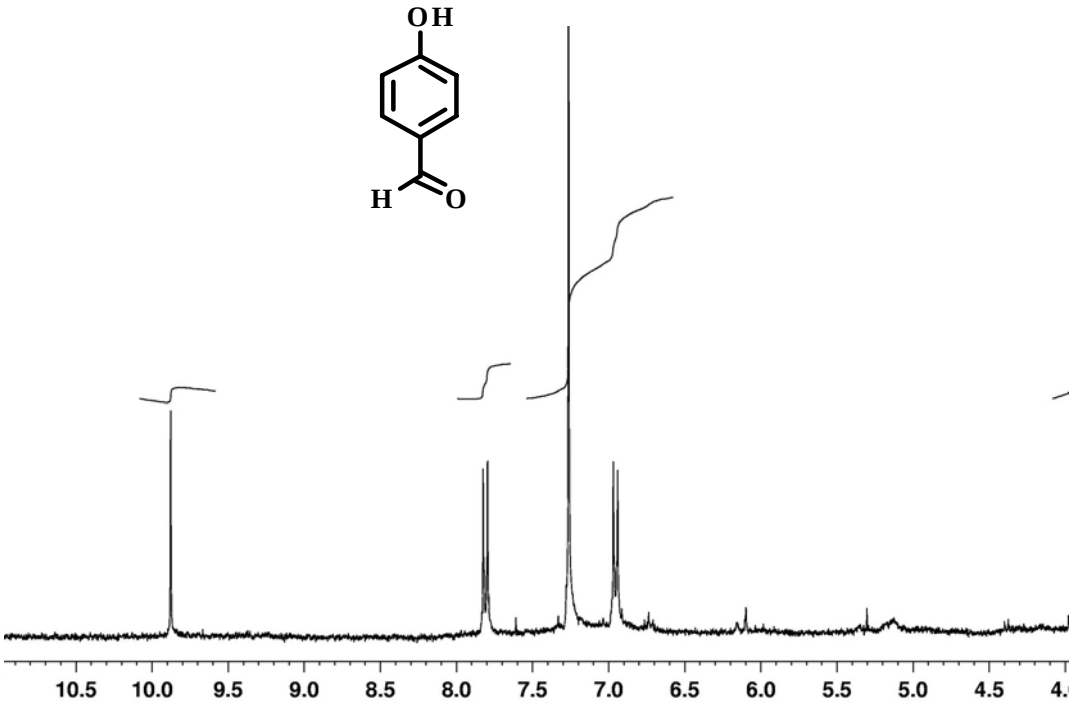

Figure A-6 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK4**

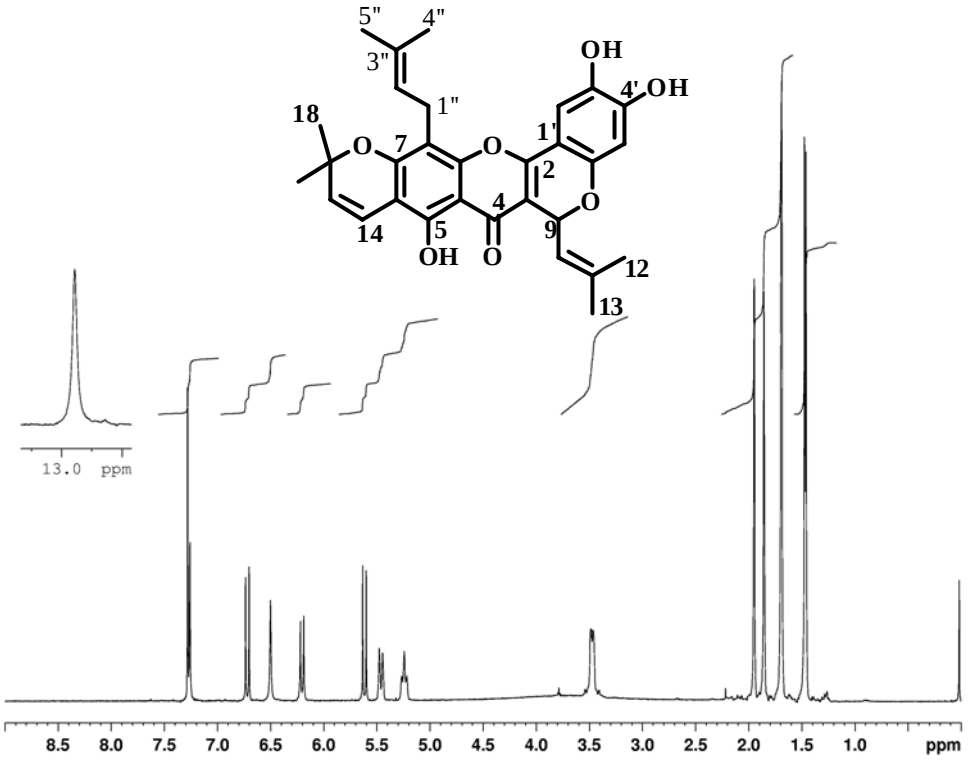

Figure A-7 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK5**

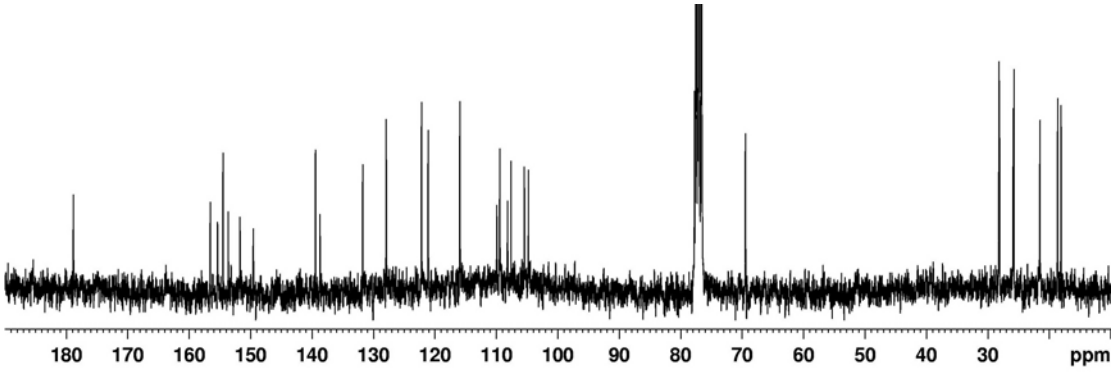

Figure A-8 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK5**

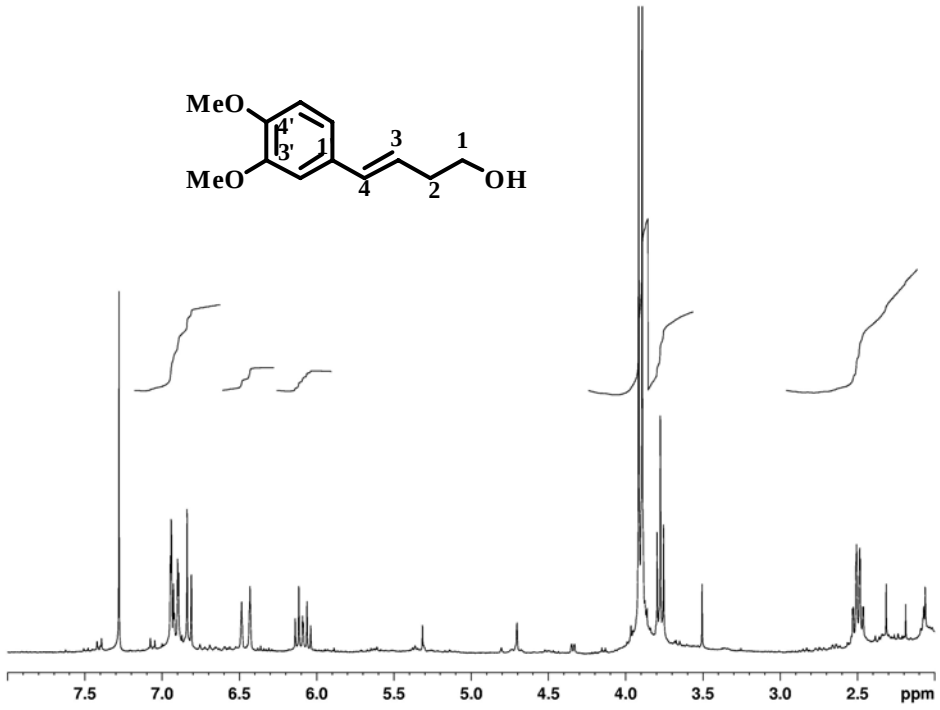

Figure A-9 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK6**

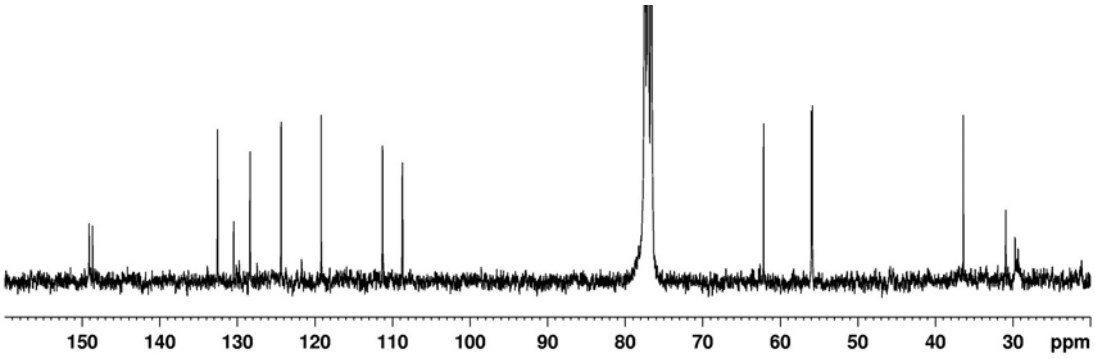

Figure A-10 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK6**

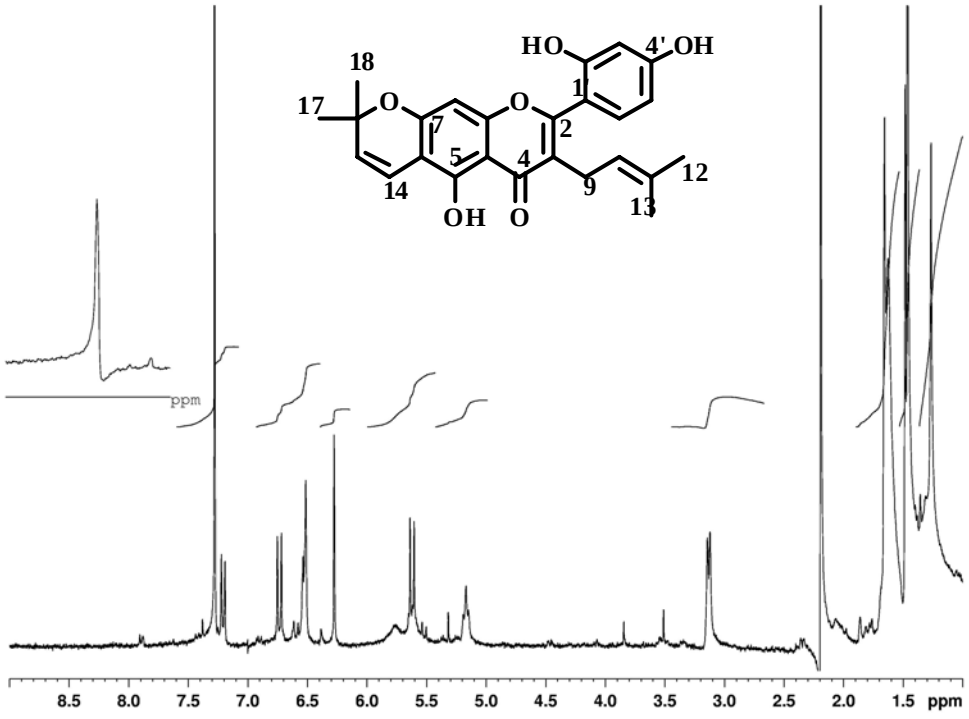

Figure A-11 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK7**

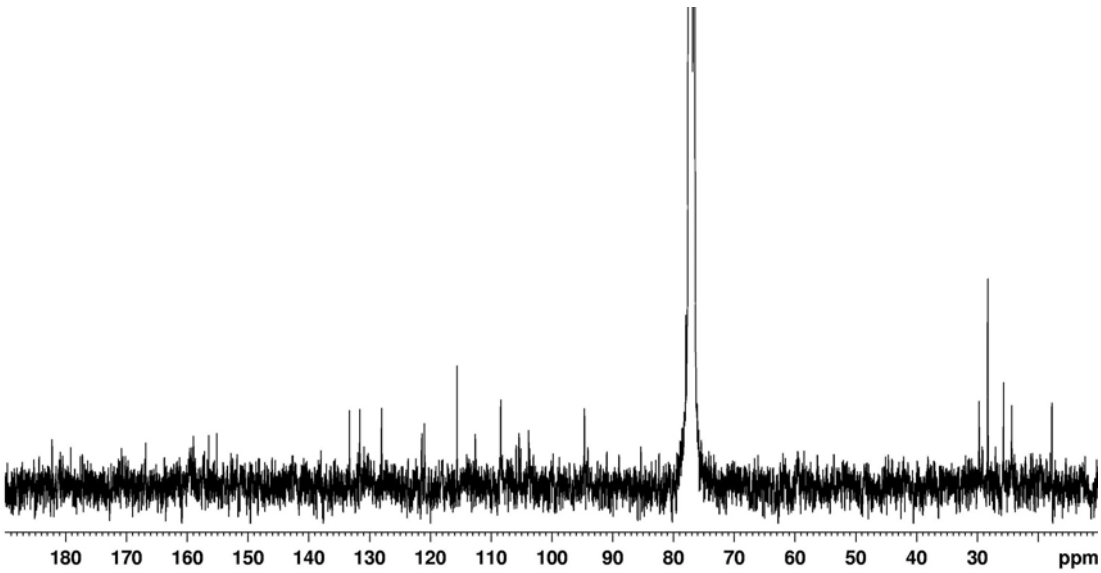

Figure A-12 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK7**

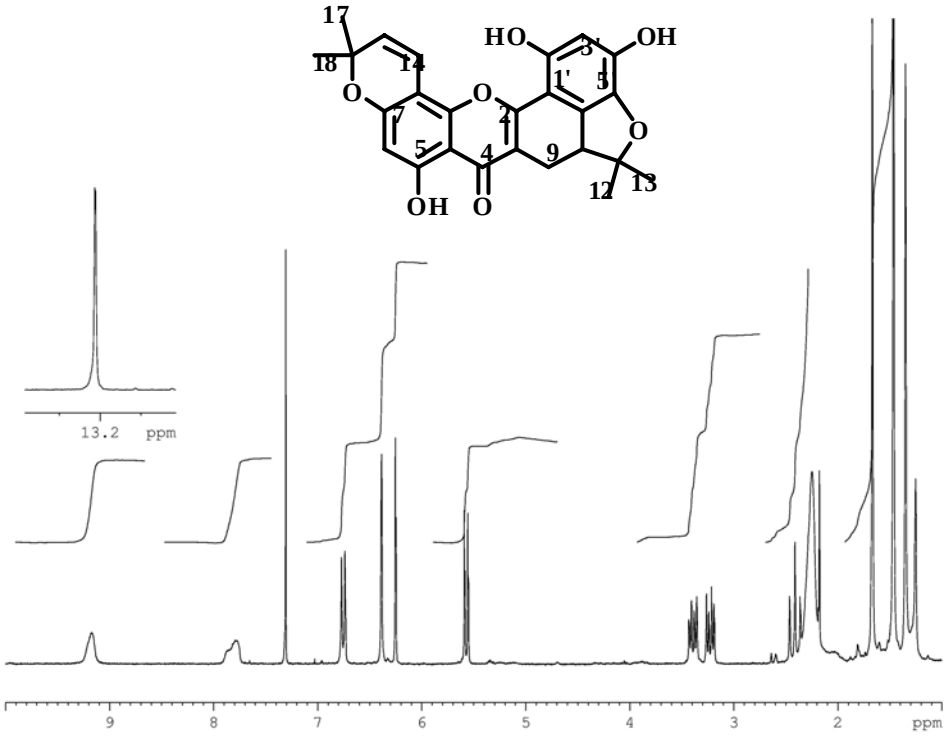

Figure A-13 ^{1}H-NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK8**

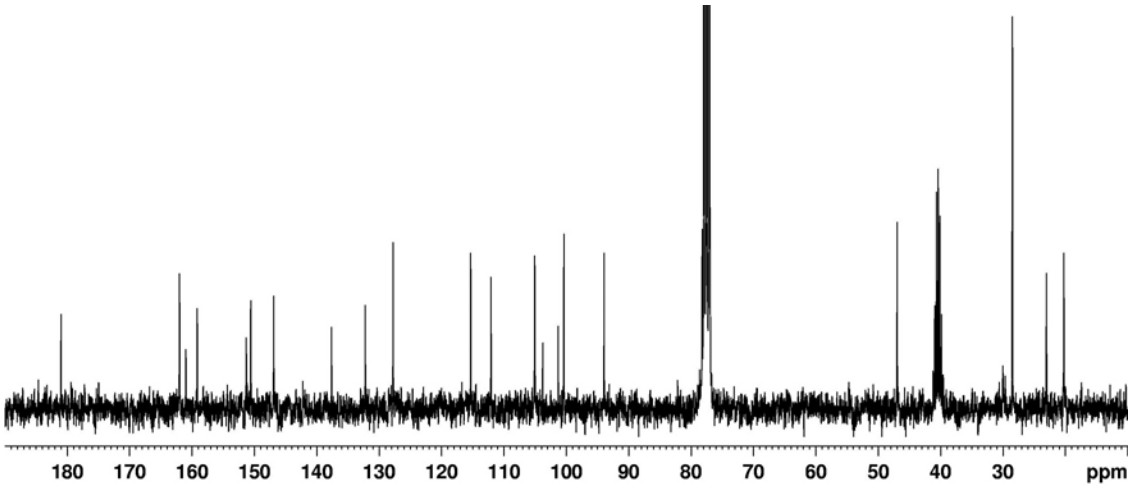

Figure A-14 ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK8**

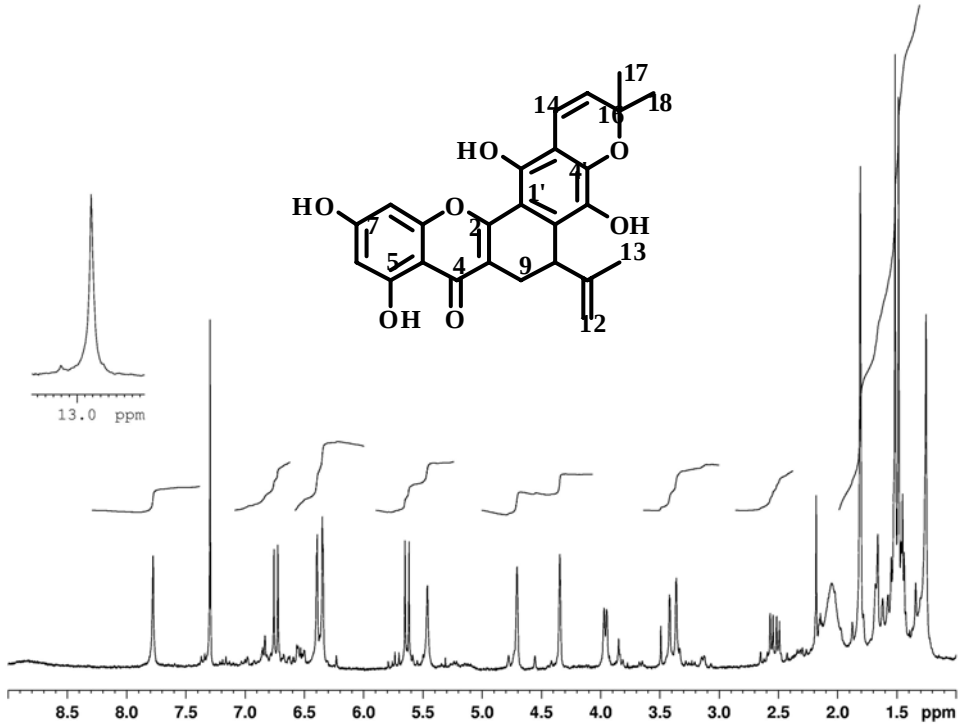

Figure A-15 ^{1}H-NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK9**

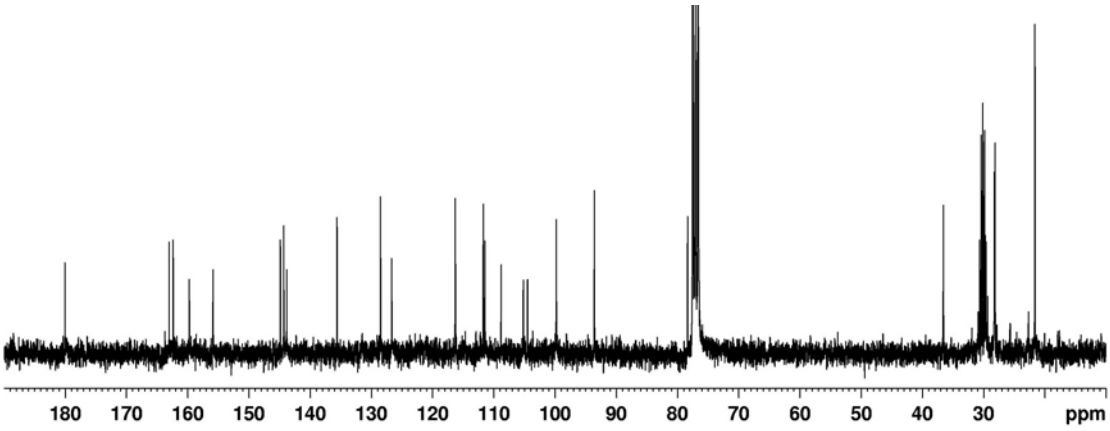

Figure A-16 ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK9**

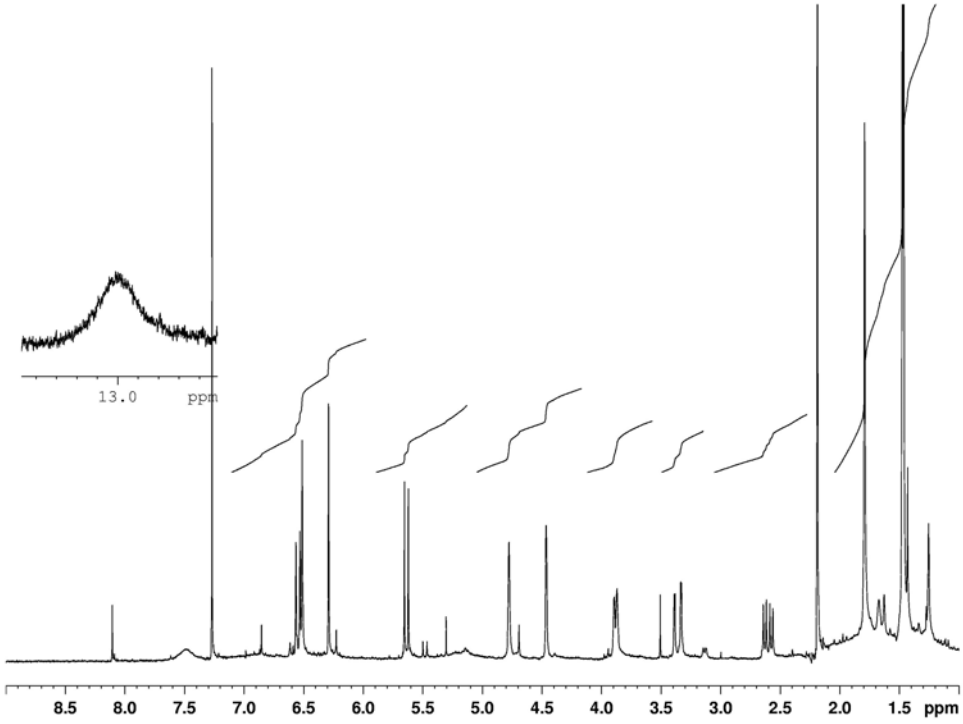

Figure A-17 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK10**

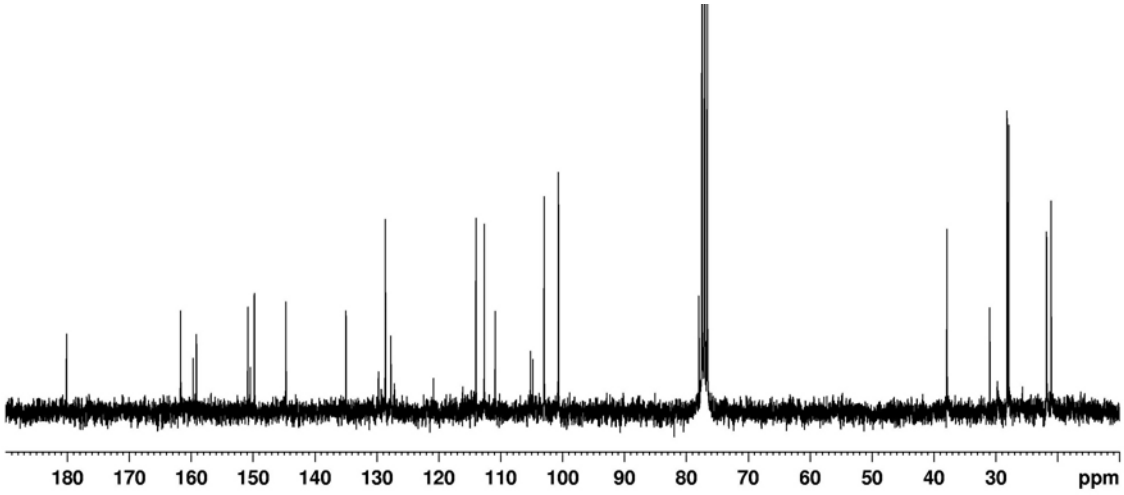

Figure A-18 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK10**

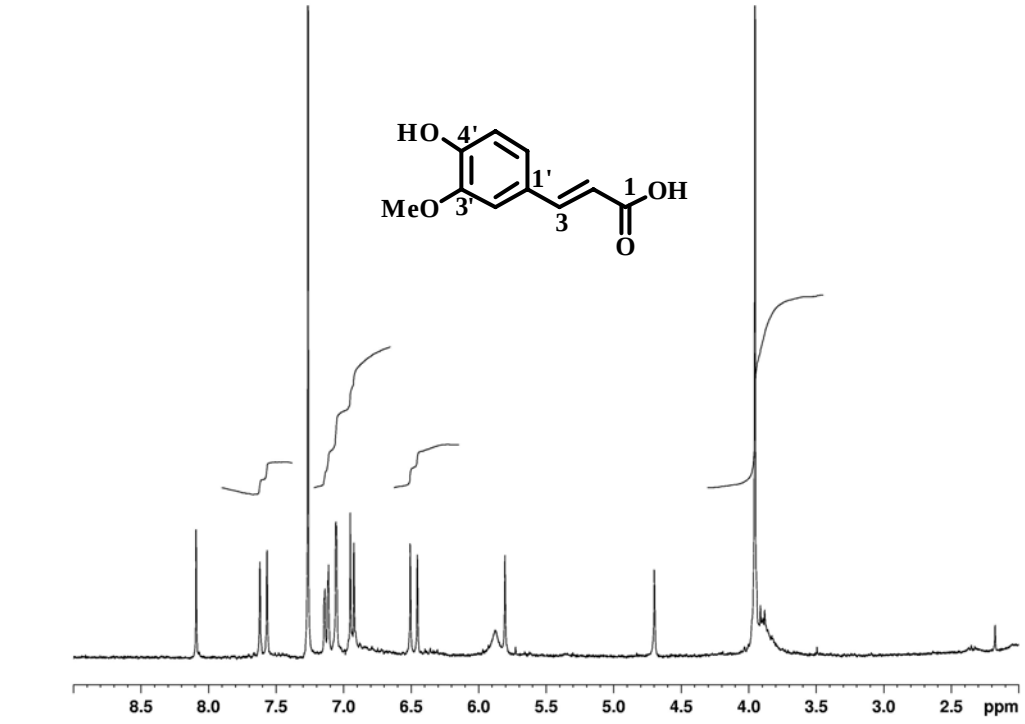

Figure A-19 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK11**

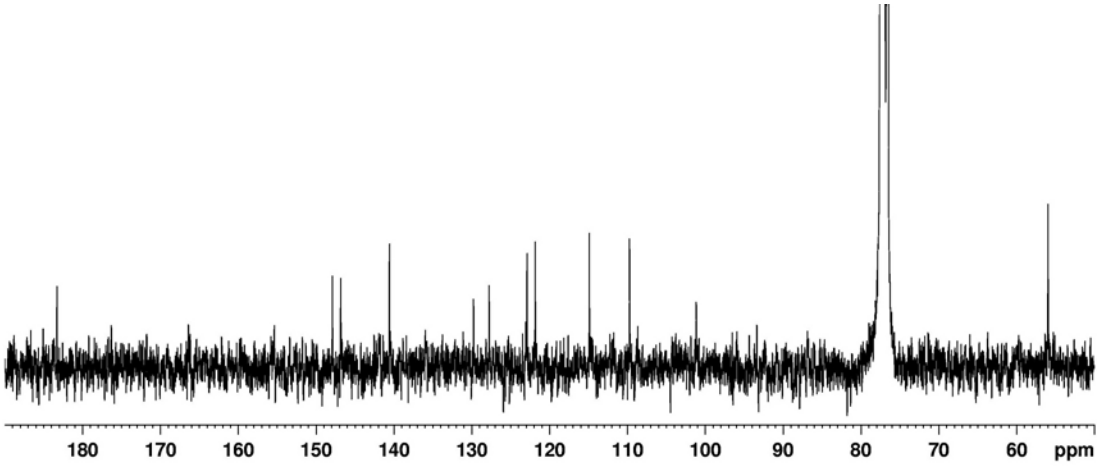

Figure A-20 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK11**

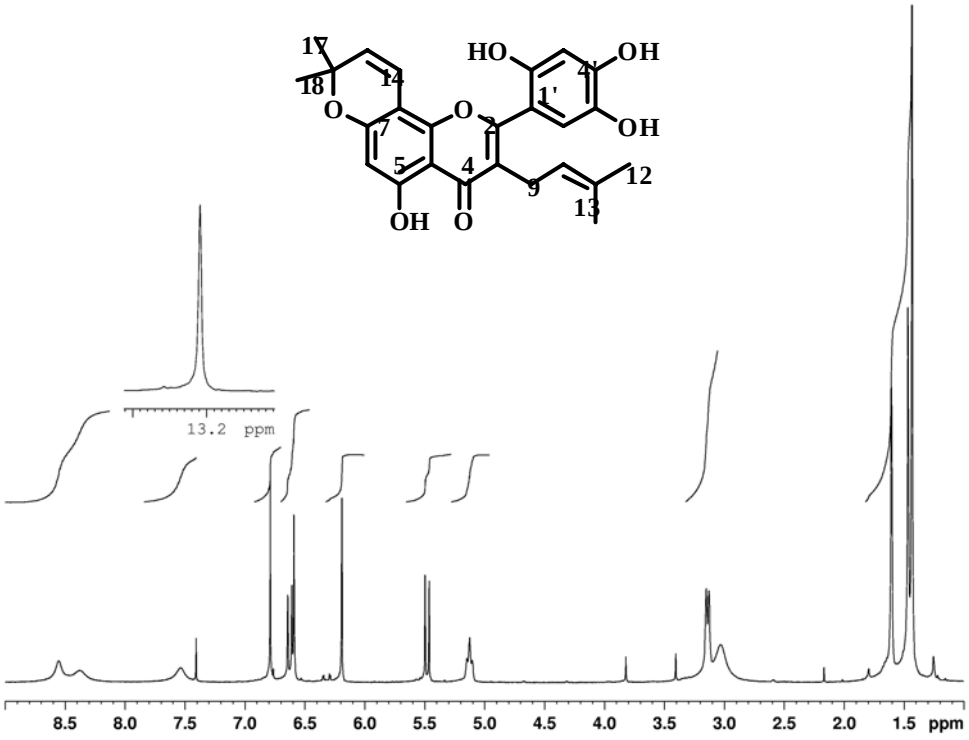

Figure A-21 ^{1}H-NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK12**

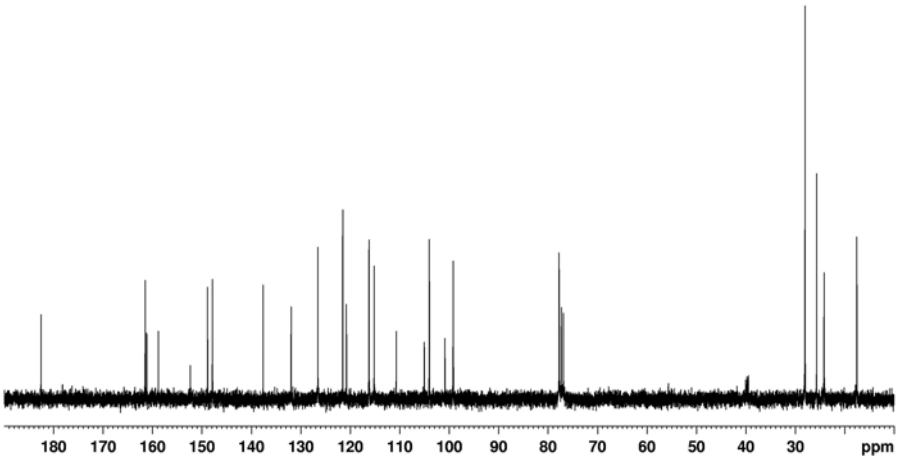

Figure A-22 ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK12**

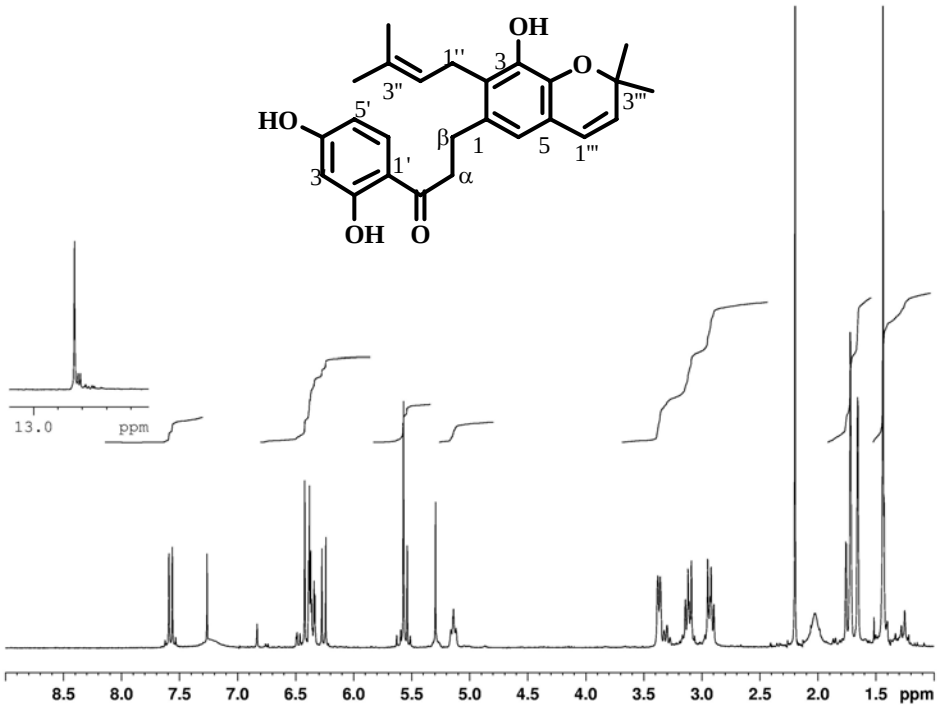

Figure A-23 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK13**

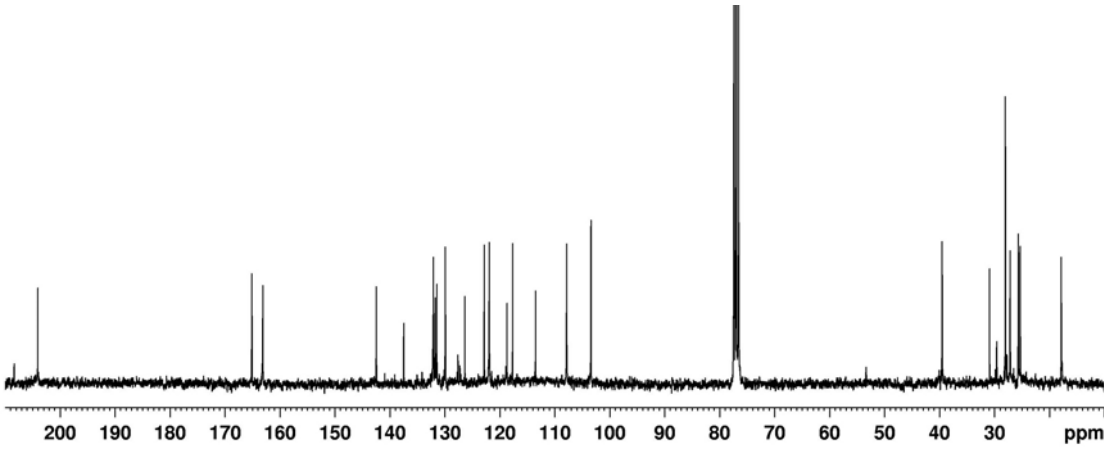

Figure A-24 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK13**

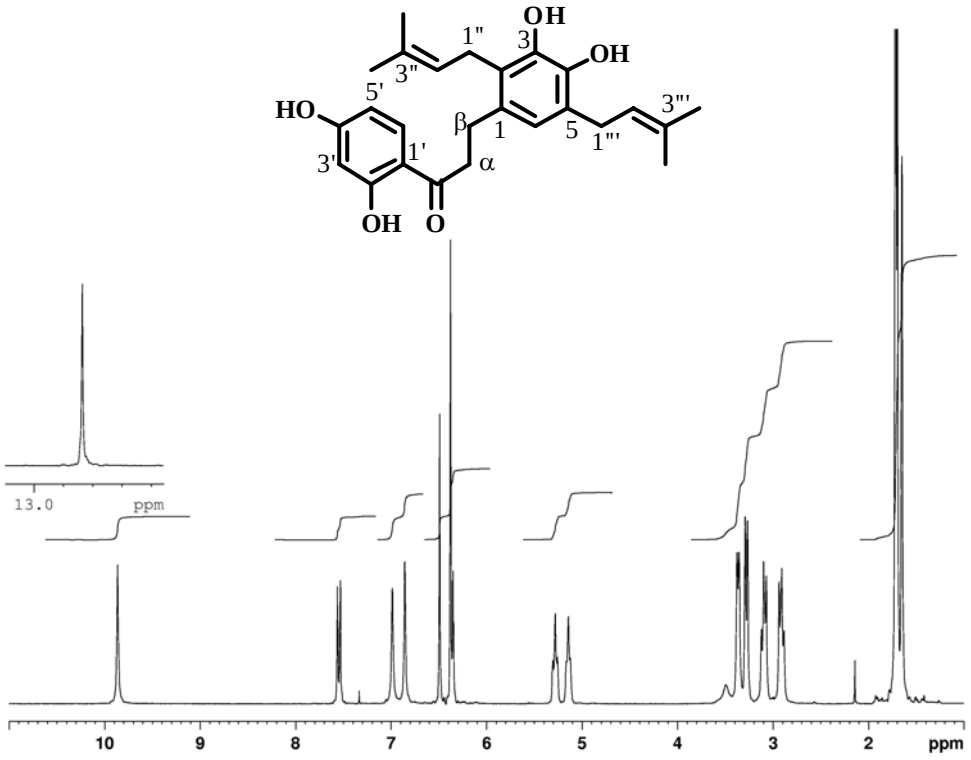

Figure A-25 ^{1}H-NMR (300 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK14**

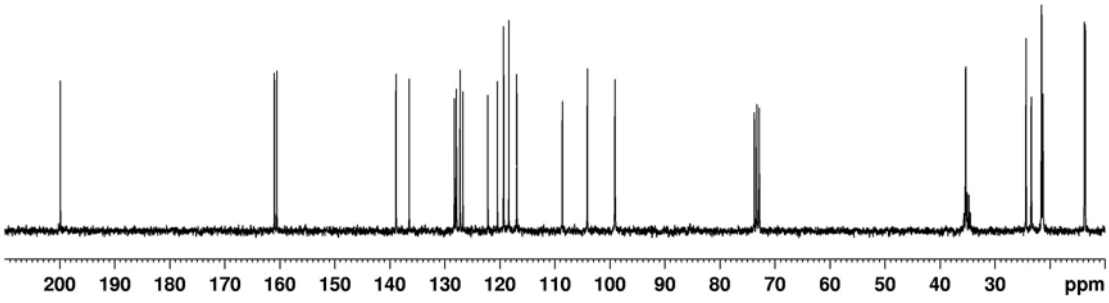

Figure A-26 ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6) spectrum of **PK14**

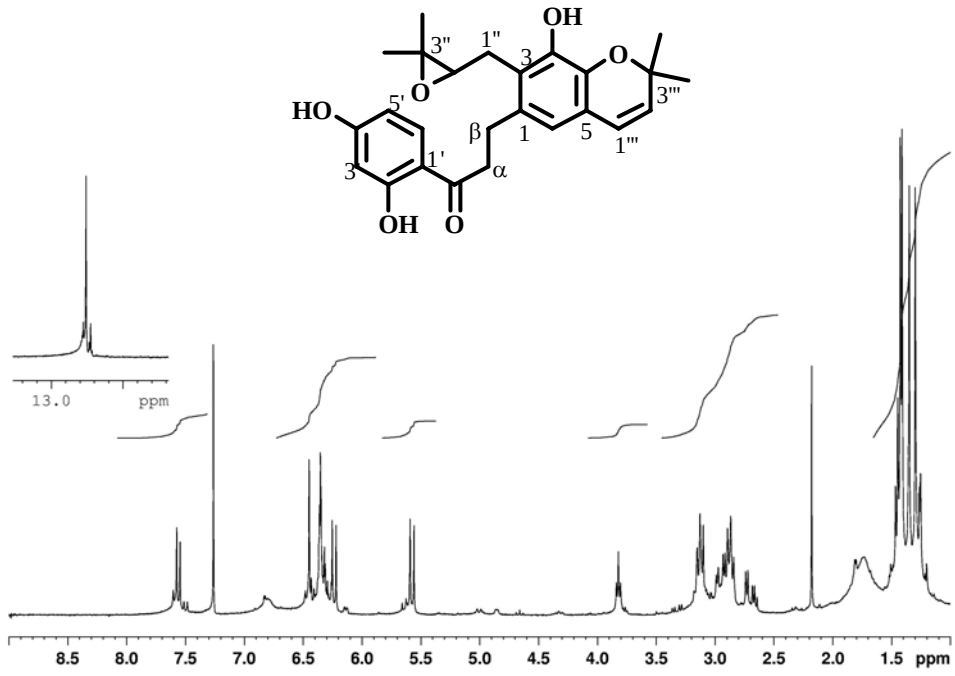

Figure A-27 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK15**

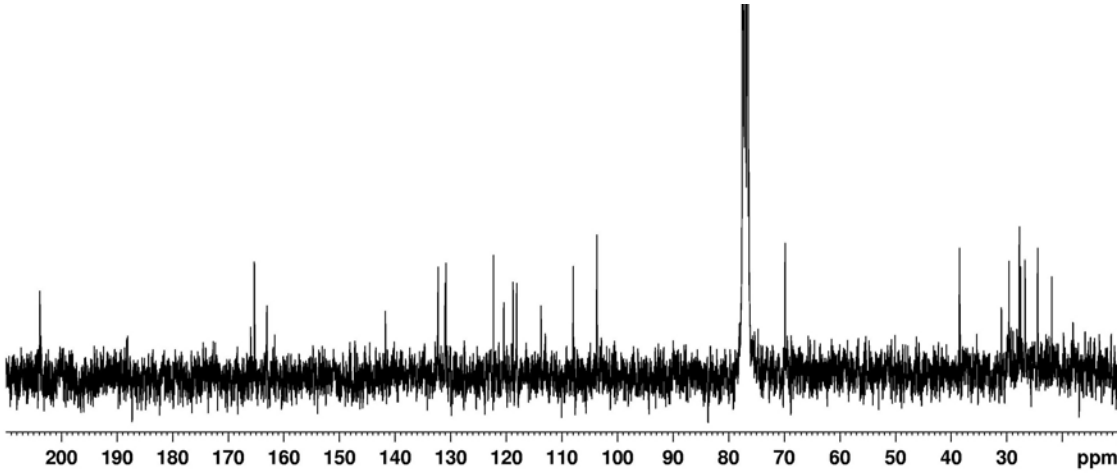

Figure A-28 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK15**

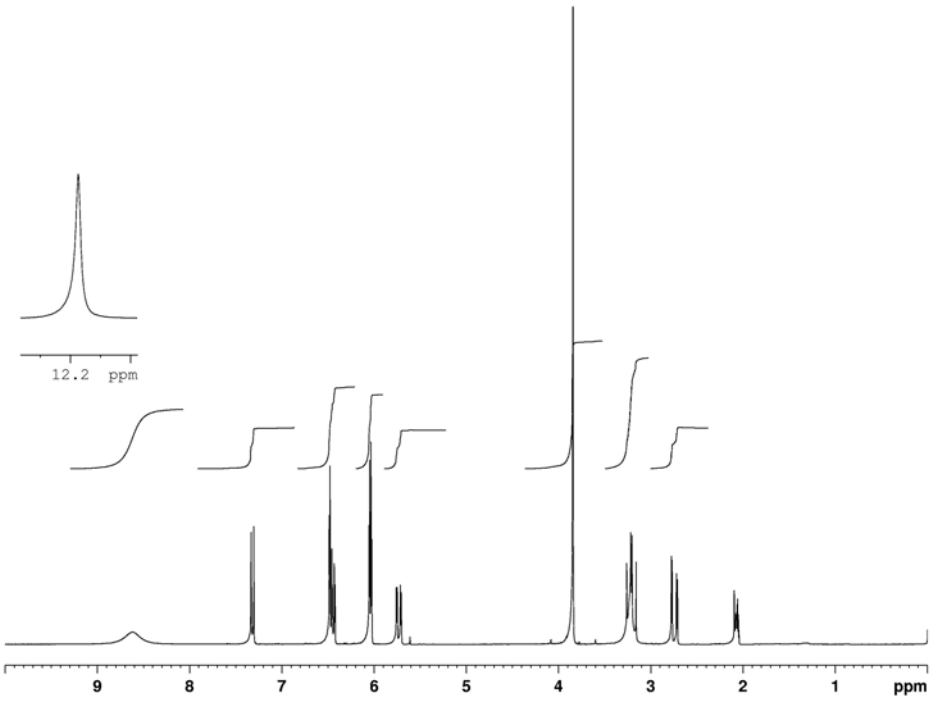

Figure A-29 ^{1}H-NMR (300 MHz) (acetone-d_6) spectrum of **PK16**

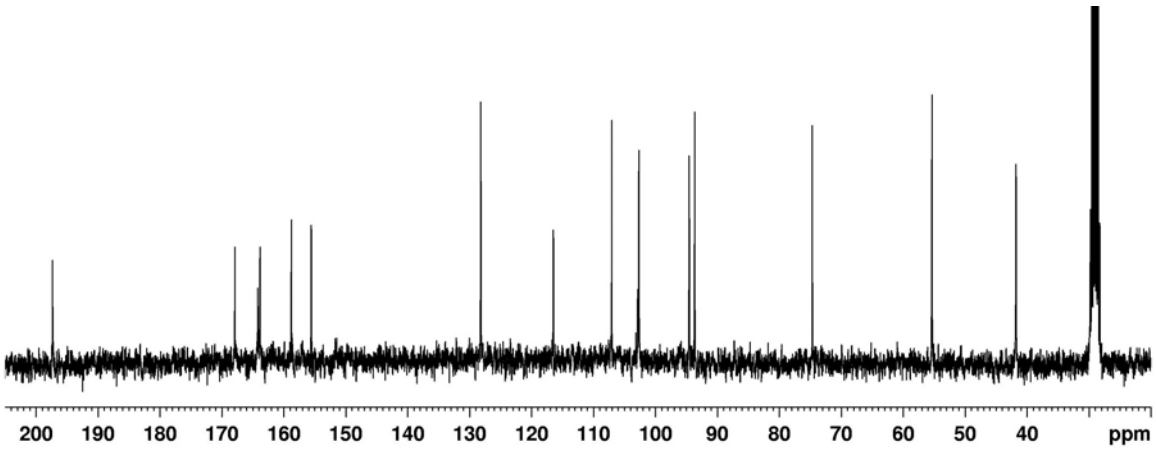

Figure A-30 ^{13}C-NMR (75 MHz) (acetone-d_6) spectrum of **PK16**

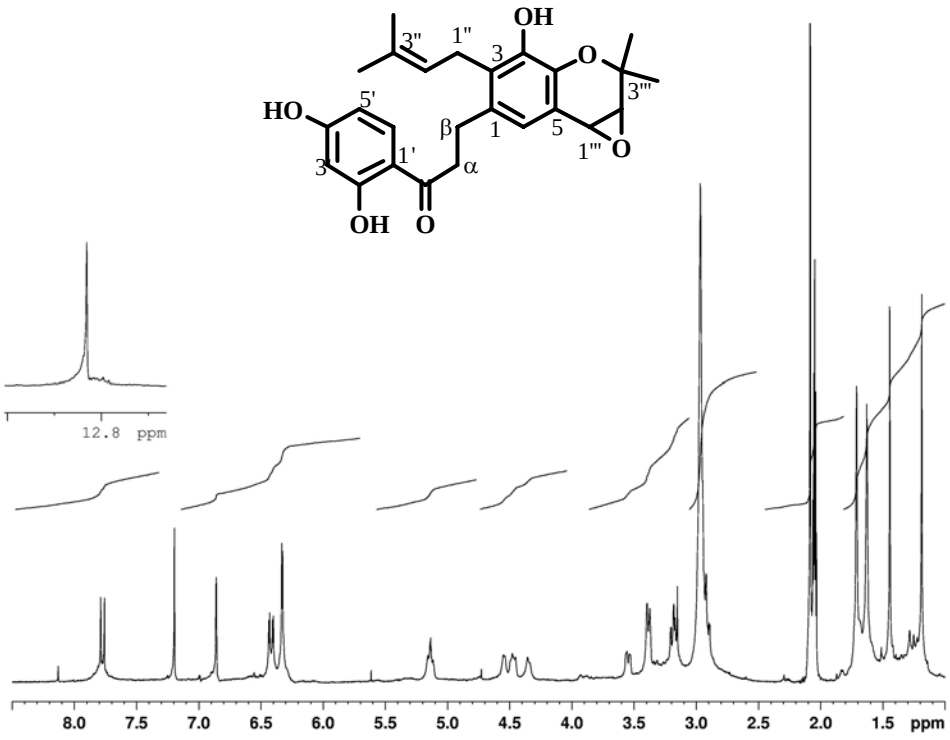

Figure A-31 ^{1}H-NMR (300 MHz) (acetone-d_6) spectrum of **PK17**

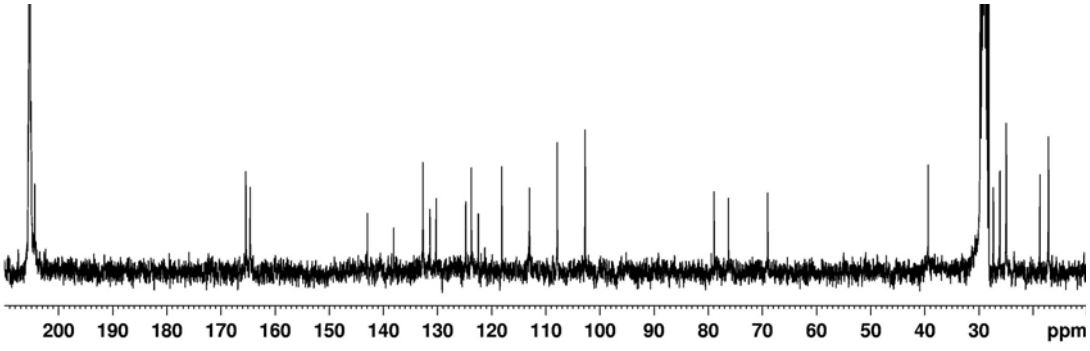

Figure A-32 ^{13}C-NMR (75 MHz) (acetone-d_6) spectrum of **PK17**

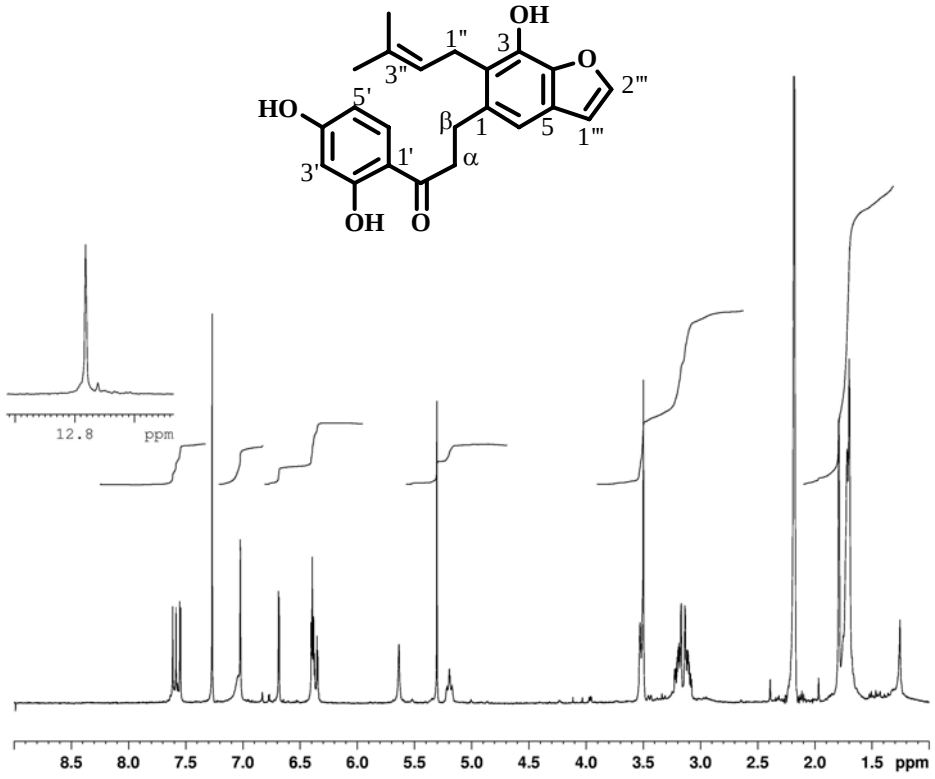

Figure A-33 ^{1}H-NMR (300 MHz) ($CDCl_3$) spectrum of **PK18**

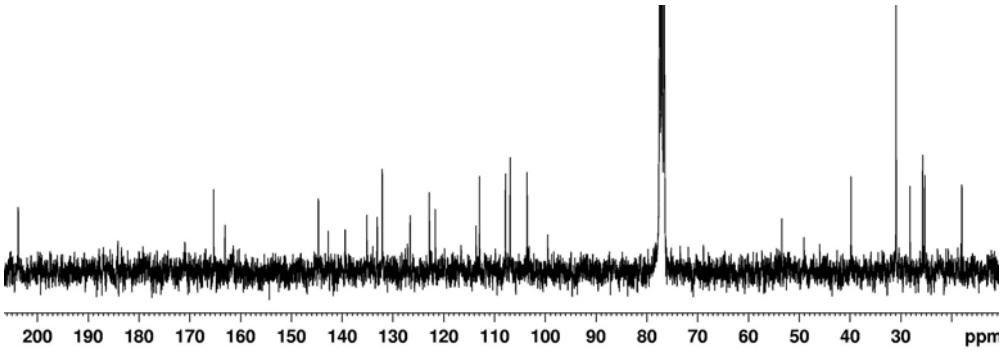

Figure A-34 ^{13}C-NMR (75 MHz) ($CDCl_3$) spectrum of **PK18**

2. ^{13}C-NMR and ^{1}H-NMR spectral data of known compounds from literatures

Table A-1 ^{1}H and ^{13}C NMR spectral data of (*E*)-4-(3',4'-dimethoxyphenyl)-3-butenyl acetate (Han *et al.*, 2003)

Position	δ_H (*mult*, J_{Hz})	δ_C
1	4.18 (2H, *t*, 6.8)	64.1
2	2.53 (2H, *qd*, 6.8, 1.2)	32.5
3	6.03 (1H, *dt*, 16.0, 6.8)	123.8
4	6.41 (1H, *d*, 16.0)	132.3
1'	-	130.6
2'	6.91 (1H, *d*, 1.8)	108.8
3'	-	149.3
4'	-	148.8
5'	6.81 (1H, *d*, 8.0)	111.4
6'	6.88 (1H, *dd*, 8.0, 1.8)	119.3
3'-OCH_3	3.90 (3H, *s*)	56.2
4'-OCH_3	3.88 (3H, *s*)	56.0
1-O<u>C</u>(O)CH_3	-	171.3
1-OC(O)<u>C</u>H_3	2.06 (3H, *s*)	21.2

recorded in $CDCl_3$

Table A-2 ^{1}H and ^{13}C NMR spectral data of 4-hydroxybenzaldehyde (Jang *et al.*, 1990)

Position	δ_H (*mult*, J_{Hz})	δ_C
1	-	129.9
2/6	7.82 (2H, *d*, 8.6)	132.5
3/5	6.98 (2H, *d*, 8.6)	116.0
4	-	161.6
7	9.86 (1H, *s*)	191.2

recorded in $CDCl_3$

Table A-3 ^{1}H and ^{13}C NMR spectral data of cycloheterophyllin (Wei *et al*., 2005)

Position	δ_H (*mult*, J_{Hz})	δ_C	**Position**	δ_H (*mult*, J_{Hz})	δ_C
2	-	157.4	16	-	79.3
3	-	110.7	17	1.46 (3H, *s*)	28.9
4	-	180.1	18	1.48 (3H, *s*)	29.0
4a	-	106.5	1'	-	108.5
5	-	156.1	2'	-	153.1
6	-	106.7	3'	6.47 (1H, *s*)	106.1
7	-	158.7	4'	-	152.8
8	-	109.1	5'	-	142.1
8a	-	155.1	6'	7.29 (1H, *s*)	110.6
9	6.14 (1H, *d*, 9.4)	70.6	1"	3.49 (2H, *dd*, 7.2, 3.2)	22.8
10	5.51 (1H, *d*, 9.4)	123.8	2"	5.28 (1H, *m*)	122.8
11	-	139.2	3"	-	132.8
12	1.93 (3H, *s*)	19.3	4"	1.68 (3H, *s*)	26.2
13	1.68 (3H, *s*)	26.2	5"	1.87 (3H, *s*)	19.0
14	6.65 (1H, *d*, 10.0)	116.9	5-OH	13.25 (1H, *s*)	-
15	5.74 (1H, *d*, 10.0)	129.8			

recorded in $CDCl_3$

Table A-4 ^{1}H and ^{13}C NMR spectral data of (*E*)-4-(3',4'-dimethoxyphenyl) but-3-en-1-ol (Han *et al.*, 2003)

Position	δ_H (*mult*, J_{Hz})	δ_C
1	3.75 (2H, *t*, 6.4)	62.1
2	2.47 (2H, *qd*, 6.4, 7.2)	36.4
3	6.07 (1H, *dt*, 15.6, 7.2)	124.4
4	6.43 (1H, *d*, 15.6)	132.5
1'	-	130.4
2'	6.92 (1H, *d*, 1.8)	108.6
3'	-	149.0
4'	-	148.6
5'	6.81 (1H, *d*, 8.2)	111.2
6'	6.89 (1H, *dd*, 8.2, 1.8)	119.1
3'-OCH_3	3.90 (3H, *s*)	55.8
4'-OCH_3	3.84 (3H, *s*)	55.9

recorded in $CDCl_3$

Table A-5 ^{1}H and ^{13}C NMR spectral data of cudraflavone B (Ryu *et al.*, 2009)

Position	δ_H (*mult*, J_{Hz})	δ_C
2	-	159.7
3	-	121.4
4	-	182.3
4a	-	105.4
5	-	156.4
6	-	105.1
7	-	159.2
8	6.25 (1H, s)	94.7
8a	-	157.2
9	3.11 (2H, *brd*, 6.7)	24.3
10	5.11 (1H, *m*)	121.0
11	-	133.2
12	1.44 (3H, *s*)	17.7
13	1.52 (3H, *s*)	25.7
14	6.70 (1H, *d*, 10.0)	115.6
15	5.59 (1H, *d*, 10.0)	128.0
16	-	78.0
17	1.44 (3H, *s*)	28.3
18	1.44 (3H, *s*)	28.3
1'	-	112.5
2'	-	155.2
3'	6.49 (1H, *d*, 0.3)	103.8
4'	-	159.5
5'	6.50 (1H, *dd*, 8.9, 0.3)	108.4
6'	7.17 (1H, *d*, 8.9)	131.6
5-OH	13.10 (1H, *s*)	-

recorded in $CDCl_3$

Table A-6 ^{1}H and ^{13}C NMR spectral data of cycloartobiloxanthone (Sultanbawa *et al*., 1989)

Position	δ_H (*mult*, J_{Hz})	δ_C
2	-	162.8/163.1
3	-	102.1
4	-	181.9
4a	-	105.2
5	-	152.4
6	6.14 (1H, *s*)	102.2
7	-	162.8/163.1
8	-	105.2
8a	-	158.6
9	3.21 ($1H_\beta$, *dd*, 14.5, 7.0)	20.5
	2.36 ($1H_\alpha$, *t*, 14.5)	
10	3.43 (1H, *dd*, 14.0, 7.0)	47.7
11	-	93.9
12	1.34 (3H, *s*)	22.9
13	1.67 (3H, *s*)	29.1
14	6.92 (1H, *d*, 10.0)	116.3
15	5.64 (1H, *d*, 10.0)	128.2
16	-	78.9
17	1.47 (3H, *s*)	28.3
18	1.47 (3H, *s*)	28.3
1'	-	113.0
2'	-	151.9
3'	6.43 (1H, *s*)	106.8
4'	-	147.8
5'	-	138.6
6'	-	134.0
5-OH	13.33 (1H, *s*)	-
2'-OH	8.70 (1H, *s*)	-
4'-OH	8.85 (1H, *s*)	-

recorded in acetone d_6

Table A-7 ^{1}H and ^{13}C NMR spectral data of artelastoxanthone (Ko *et al*., 2005)

Position	δ_H (*mult*, J_{Hz})	δ_C
2	-	161.9
3	-	112.7
4	-	181.6
4a	-	105.6
5	-	163.8
6	6.28 (1H, *d*, 2.4)	100.4
7	-	165.1
8	6.58 (1H, *d*, 2.4)	95.6
8a	-	158.1
9	3.38 ($1H_\beta$, *dd*, 16.0, 2.0)	22.8
	2.45 ($1H_\alpha$, *dd*, 16.0, 6.4)	
10	3.98 (1H, *d*, 6.4)	38.4
11	-	145.9
12	4.64 ($1H_\beta$, *s*)	112.5
	4.31 ($1H_\alpha$, *s*)	
13	1.77 (3H, *s*)	22.6
14	6.76 (1H, *d*, 10.0)	117.9
15	5.75 (1H, *d*, 10.0)	130.4
16	-	78.9
17	1.47 (3H, *s*)	28.7
18	1.45 (3H, *s*)	28.7
1'	-	107.8
2'	-	146.1
3'	-	111.1
4'	-	146.0
5'	-	137.9
6'	-	129.2

Table A-7 (continued)

Position	δ_H (*mult*, J_{Hz})	δ_C
5-OH	13.17 (1H, *s*)	-
7-OH	9.63 (1H, *s*)	-
2'-OH	8.02 (1H, *s*)	-
5'-OH	7.58 (1H, *s*)	-

recorded in $CDCl_3$

Table A-8 ^{13}C NMR spectral data of *trans*-feluric acid (Kelley *et al.*, 1976)

Position	δ_C
1	175.8
2	121.1
3	141.3
1'	127.7
2'	110.5
3'	147.1
4'	146.4
5'	115.3
6'	121.9
3'-OCH_3	55.6
4-OH	-

recorded in acetone d_6-D_2O (9:1)

Table A-9 ^{1}H and ^{13}C NMR spectral data of artobiloxanthone (Jayasinghe *et al*., 2008)

Position	δ_H (*mult*, J_{Hz})	δ_C
2	-	161.7
3	-	110.8
4	-	180.1
4a	-	104.8
5	-	159.5
6	6.-9 (1H, *s*)	100.6
7	-	159.2
8	-	100.4
8a	-	151.0
9	3.36 ($1H_\beta$, *dd*, 16.6, 1.7)	21.7
	2.63 ($1H_\alpha$, *dd*, 16.6, 7.8)	
10	3.86 (1H, *br d*, 7.0)	38.1
11	-	149.8
12	4.80 ($1H_\alpha$, *br s*)	112.8
	4.51 ($1H_\alpha$, *br s*)	
13	1.79 (3H, *s*)	20.9
14	6.54 (1H, *d*, 10.2)	113.9
15	5.64 (1H, *d*, 10.2)	128.7
16	-	77.9
17	1.46 (3H, *s*)	27.9
18	1.48 (3H, *s*)	28.1
1'	-	105.2
2'	-	150.4
3'	6.51 (1H, *s*)	103.0
4'	-	144.8
5'	-	134.7
6'	-	127.7
5-OH	13.01 (1H, *s*)	-

recorded in $CDCl_3$

Table A-10 ^{1}H and ^{13}C NMR spectral data of artonin E (Jayasinghe *et al.*, 2008)

Position	δ_H (*mult*, J_{Hz})	δ_C
2	-	163.2
3	-	122.0
4	-	183.9
4a	-	105.9
5	-	162.7
6	6.14 (1H, *s*)	100.1
7	-	160.5
8	-	102.2
8a	-	153.8
9	3.11 (2H, *br d*, 7.0)	24.9
10	5.10 (1H, *m*)	122.6
11	-	133.0
12	1.59 (3H, *br s*)	17.6
13	1.41(3H, *br s*)	25.9
14	6.61 (1H, *d*, 10.0)	115.8
15	5.59 (1H, *d*, 10.0)	128.2
16	-	79.1
17	1.43 (3H, *s*)	28.4
18	1.43 (3H, *s*)	28.4
1'	-	111.7
2'	-	150.1
3'	6.45 (1H, *s*)	104.7
4'	-	150.0
5'	-	-
6'	6.69 (1H, *s*)	-

recorded in CD_3OD

Table A-11 ^{1}H and ^{13}C NMR spectral data of artocarpanone (Wei *et al*., 2005)

Position	δ_H (*mult*, J_{Hz})	δ_C
2	5.73 (1H, *dd*, 14.0, 3.0)	75.9
3	3.21 (1H, *dd*, 17.0, 14.0)	43.0
	2.74 (1H, *dd*, 17.0, 3.0)	
4	-	198.5
4a	-	104.1
5	-	160.0
6	6.02 (1H, *d*, 2.2)	95.7
7	-	169.1
8	6.05 (1H, *d*, 2.2)	94.8
8a	-	165.1
1'	-	117.7
2'	-	156.7
3'	6.47 (1H, *d*, 2.0)	103.9
4'	-	165.4
5'	6.43 (1H, *dd*, 8.0, 2.0)	108.3
6'	7.32 (1H, *d*, 8.0)	129.4
5-OH	12.17 (1H, *s*)	-
7-OMe	3.85 (3H, *s*)	56.6

recorded in acetone-d_6

VITAE

Name Mr. Prakit Chaithada

Student ID 5110220115

Educational Attainment

Degree	Name of Institution	Year of Graduation
B.SC. (Chemistry)	Chulalongkorn University	2004

Scholarship Awards during Enrolment

Center for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education

Publication and Proceedings

Prakit Chaithada and Wilawan Mahabusarakam. "Prenylated flavones, phenylbutenoids and phenylpropanoids from the root bark of *Artocarpus elasticus*" The 1st Current Drug Development International Conference, Woraburi Phuket Resort & Spa, Phuket, Thailand, May 6-8, 2010. (Poster Presentation)