การศึกษาทางพฤกษเคมีของสร้อยนกเขา

นางสาว ปัทมา เหละดุหวี

สถาบนวิทยบริการ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาเภสัชศาสตรมหาบัณฑิต สาขาวิชาเภสัชพฤกษศาสตร์ ภาควิชาเภสัชพฤกษศาสตร์ คณะเภสัชศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ปีการศึกษา 2550 ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PHYTOCHEMICAL STUDY OF

SAUROPUS BACCIFORMIS (L.) AIRY SHAW

Miss Pattama Lekduwee

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Pharmacy Program in Pharmaceutical Botany

Department of Pharmaceutical Botany

Faculty of Pharmaceutical Sciences

Chulalongkorn University

Academic Year 2007

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PHYTOCHEMICAL STUDY OF	
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ป้ทมา เหละดุหวี: การสึกษาทางพฤกษเคมีของสร้อยนกเขา. (PHYTOCHEMICAL STUDY OF *SAUROPUS BACCIFORMIS* (L.) AIRY SHAW) อ. ที่ปรึกษา: รศ.ดร. เอกรินทร์ สายฟ้า, 140 หน้า.

จากส่วนที่อยู่เหนือดินของสร้อขนกเขา (*Sauropus bacciformis* (L.) Airy Shaw) สามารถสกัดแขกสารในกลุ่มฟลาโวนอลกลัยโคไซด์ ได้สารชนิดใหม่ 1 ชนิด คือ rhamnetin-4'-*O-β*-D-glucopyranoside และสารในกลุ่มไตรเทอร์ปีนอยด์ที่เดขมีรายงานมาแล้ว 3 ชนิด คือ friedelin, simiarenol และ glochidonol รวมทั้งได้สารผสมของ β-sitosterol และ stigmasterol การพิสูจน์เอกลักษณ์ของสารเหล่านี้ ทำโดยการวิเคราะห์ข้อมูลทางสเปกโตรสโคปี จาก UV, IR, MS และ NMR ร่วมกับการเปรียบเทียบข้อมูลกับค่าที่ได้มีการรายงานไว้แล้ว

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา เภสัชพฤกษศาสตร์ สาขาวิชา เภสัชพฤกษศาสตร์ ปีการศึกษา 2550

ถายมือชื่อนิสิต	√ัทมา	เพอ: ๆ ทว่	
ลายมือชื่ออาจารย์ที่ป	รึกษา	B	
ลายมือชื่ออาจารข์ที่ป	รึกษาร่วม		

4876583033: MAJOR PHARMACEUTICAL BOTANY

KEY WORD: SAUROPUS BACCIFORMIS/ EUPHORBIACEAE/ FLAVONOL GLYCOSIDE/ TRITERPENOID/ STEROID

PATTAMA LEKDUWEE: PHYTOCHEMICAL STUDY OF *SAUROPUS BACCIFORMIS* (L.) AIRY SHAW. THESIS ADVISOR: ASSOC. PROF. EKARIN SAIFAH, Ph.D., 140 pp.

From the aerial part of *Sauropus bacciformis* (L.) Airy Shaw, one new flavonol glycoside, rhamnetin-4'-O- β -D-glucopyranoside and three known triterpenoids, friedelin, simiarenol and glochidonol, together with a mixture of β -sitosterol and stigmasterol have been isolated. Identification of these compounds was accomplished by analysis of their spectroscopic data (UV, IR, MS and NMR) as well as comparison with reported values.

ุลสาบนวิทยบรกกร จุฬาลงกรณ์มหาวิทยาลัย

Department Pharmaceutical Botany Field of study Pharmaceutical Botany Academic Year 2007

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ACKNOWLEDGEMENTS

I wish to express my deepest gratitude to my thesis advisor, Associate Professor Dr. Ekarin Saifah of the Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for his kindness, proper scientific guidance, suggestion and encouragement throughout the course of this study.

I would like to express my grateful thanks to Associate Professor Dr. Rapepol Bavovada and Associate Professor Dr. Rutt Suttisri, both of the Department of Pharmaceutical Botany, and Dr. Boonchoo Sritularak of the Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for their help on NMR measurements, discussion on structure elucidation, constructive suggestions and valuable critical comment.

My appreciations are extended to Dr. Witchuda Thanakitcharoenpath of the Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for her help, excellent advice, encouragement, kindness and valuable suggestions on several matters, especially on the interpretation of NMR spectrum.

Additional sincere thanks are expressed to all staff members and friends at the departments of Pharmaceutical Botany and Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for their kindness and support during my research work.

Finally, my utmost thanks are due to Ms. Janthima Methaneethorn, Mrs. Rachanee Pongpanit and my family for their love, understanding encouragement and moral support through out my study.

จุฬาลงกรณมหาวทยาลย

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LIST OF ABBREVIATIONS

br	=	Broad (for NMR spectra)
°C	=	Degree Celsius
CC	=	Column Chromatography
CDCl ₃	=	Deuterated chloroform
CH_2Cl_2	=	Dichloromethane
cm	=	Centimeter
cm ⁻¹	=	Reciprocal centimeter (unit of wave number)
¹³ C-NMR	=	Carbon-13 Nuclear Magnetic Resonance
δ	=	Chemical shift
d	= 🧹	Doublet (for NMR spectra)
dd	= 🥖	Doublet of doublets (for NMR spectra)
ddd	=	Doublet of doublets of doublets (for NMR spectra)
DEPT	= _	Distortionless Enhancement by Polarization Transfer
DMSO	=	Dimethyl sulfoxide
DMSO-d ₆	=	Deuterated dimethyl sulfoxide
dt	=	Doublet of triplets (for NMR spectra)
EIMS	=	Electron Impact Mass Spectroscopy
EtOAc	=	Ethyl acetate
3	= 1	Molar absorptivity
g	=	Gram
¹ H NMR	=	Proton Nuclear Magnetic Resonance
¹ H- ¹ H COSY	สถ	Homonuclear (Proton-Proton) Correlation Spectroscopy
HMBC	b] b l	¹ H-detected Heteronuclear Multiple Bond Coherence
HMQC	Ta	¹ H-detected Heteronuclear Multiple Quantum Coherence
H ₂ O	<u>1</u> 61	Water
Hz	=	Hertz
IR	=	Infrared spectrum
J	=	Coupling constant
KBr	=	Potassium bromide
Kg	=	Kilogram
L	=	Liter

λ_{max}	=	Wavelength at maximal absorption
т	=	Multiplet (for NMR spectra)
$[\mathbf{M}]^+$	=	Molecular ion
MeOH	=	Methanol
mg	=	Milligram
MHz	=	Megahertz
mm	=	Millimeter
mp	=	Melting point
MS	=	Mass Spectrometry
MW	=	Molecular weight
m/z.	=	Mass to charge ratio
nm	=	Nanometer
NMR	=	Nuclear Magnetic Resonance Airy Shaw was collected from
ν_{max}	=	Wave Sam number of maximal absorption
ppm	= /	Part-per-million
Pr	=	Propyl
rel. int.	=	Relative intensity
S	=	Singlet (for NMR spectra)
spp.	=	Species
t	=	Triplet (for NMR spectra)
td	=	Triplet of doublets (for NMR spectra)
TLC	=	Thin Layer Chromatography
UV	=	Ultraviolet
UV-VIS	สิด	Ultraviolet and Visible Spectrophotometry

Ultraviolet and Visible Spectrophotometry

CHAPTER I

INTRODUCTION

The genus *Sauropus* belongs to the family Euphorbiaceae. There are at least 50 species of this genus distributed throughout tropical and subtropical parts of the world, ranging from India and Sri Lanka to Southwest China, Southeast Asia (main diversity), Malaysia to Australia (Welzen and Chayamarit, 2006).

Plants in the genus Sauropus are usually herbs to undershrubs, and are monoecious. The stem is often with 4 raised ribs. The stipules are triangular and late caducous. The leaves are simple and distichous. These leaves are symmetric and basally attached. The leaf margin is entire. The leaf blade is without glands and with indistinct venation. The inflorescences are ramiflorous or cauliflorous racemes to usually axillary fascicles of usually one to a few bracteate flowers, all hanging down. These flowers are actinomorphic. The imbricate calyx lobes are 6, petals and disc are absent. The staminate flowers consist of obovoid to obtruncate calyx lobes, often inflexed apically, with erect scale near base. The stamens are 3, united in androphore, the apex of which splits horizontally 3 ways. The anthers are underneath, with (2) 4 thecae. The pistillate flowers consist of ovate sepals, which are persistent in fruit. The ovary is 3-locular, subapically lobed and the real apex emarginated, crater-like. The ovules are 2 per locule. The style is absent. The stigmas are 3, on the wall of crater, split to halfway. The fruits are regmas, not lobed, dehiscent, usually thinwalled and woody when dry. They are smooth, glabrous, with one to many seeds (Welzen and Chayamarit, 2006).

Sauropus species found in Thailand are (ส่วนพฤกษศาสตร์ป่าไม้ สำนักวิชาการป่าไม้ กรมป่าไม้,

Sauropus amabilis Airy Shaw	ใด้ใบใหญ่ Tai bai yai (Nakhon Sawan).
S. amoebiflorus Airy Shaw	กวางหีเปี้ยะ Kwang hi pia (Lampang), ใด้ใบ Tai bai
	(Kanchanaburi), ผักหวานบ้าน Phak wan ban
	(Lamphun).
S. androgynus (L.) Merr.	ก้านตง Kan tong, จ๊าผักหวาน Cha phak wan (Nothern),

2544):

โถหลุ่ขกะนีเด๊าะ Tho lui ka ni do (Karen Mae Hong Son), นานาเซียม Na na siam (Malay Satun), ผักหวาน Phak wan, ผักหวานบ้าน Phak wan ban (General), ผักหวานใด้ใบ Phak wan tai bai (Satun), มะยมป่า Mayom pa (Prachuap Khiri Khan).

มะยมดอน Mayom don (General).

ทองแล้ง Thong laeng (Ubon Ratchathani), มะพร้าว นกเขา Ma phrao nok khao, สร้อยนกเขา Soi nok khao (Bangkok).

ผักหวานแดง Phak wan daeng, มะชมเตี้ข Mayom tia, ชมดง Yom dong (Loei), ผักหวานป่า Phak wan pa (Chiang Mai), สีเสียดแพะ Sisiat phae (Lamphun). กระดูกไก่ดำ Kraduk kai dam (Prachuap Khiri Khan), ข้ามเขา Kham khao (Surat Thani).

มะขมบอน Mayom bon (General).

มะยมอ่างกา Mayom ang ga (General).

โสนรุ่น Sano run (Southeastern), หมากใบ่ลาง

Mak khai lang (Northeastern).

ใคร้หางนาด Khrai hang nak (Northeastern).

กองกอยลอดขอน Kongkoi lot khon (Central), ก่อมก้อย Komkoi (Phetchaburi), ใด้ใบ Tai bai, ผักหวานนก Phak wan nok (Kanchanaburi), ระงับมนุษย์

Ra ngap manut (Chumphon). หญ้ารุ่นไฮ Ya hun hai (Lamphun).

มะขมเขา Mayom khao (General).

กวางเขาขี Kwang khao yi (Lamphun), กล่ำผี Klam phi (Ratchaburi), คำผีน้อย Kham phi noi, สีเสียดโดก Si siat khok (Loei).

- S. asteranthos Airy Shaw S. bacciformis (L.) Airy Shaw
- S. bicolor Craib
- S. brevipes Mull. Arg.
- S. discocalyx Welzen
- S. garrettii Craib
- S. granulosus Airy Shaw
- S. heteroblastus Airy Shaw S. hirsutus Beille
- S. kerrii Airy Shaw S. macranthus Hassk. S. orbicularis Craib

S. poomae Welzen & Chayamarit	ดอกใด้ด้น Dok tai ton (General).
S. pulchellus Airy Shaw	โสนหิน Sano hin (Prachin Buri).
S. quadrangularis (Willd.) Mull. A	Arg. มะยมเกลี้ยง Mayom kliang (General), มะขามป้อมดิน
	Ma kham pom din (Chiangmai), มะชมเถื่อน Mayom
	thuean (Nakhon Sawan), มะขมละมุน Mayom lamun
	(General).
S. rhamnoides Blume	มะขมเหลี่ขม Mayom liam (General).
S. rostratus Miq	หมากบางเบา Mak bang bao (Peninsular).
S. similis Craib	มะขมละม้าย Mayom lamai (General).
S. spatuliifolius Beille	มะยมใบพาย Mayom bai pai (Central), อะจีเจ้า
	A che chao (Chinese).
S. suberosus Airy Shaw	มะขมหยัก Mayom yak (Peninsular).
S. subterblancus (C. E. C. Fisch.) W	Velzen
S. thorelii Beille	สะเลียมหอม Salium hom (Mae Hong Son).
S. thyrsiflorus Welzen	
S. villosus (Blanco) Merr.	งับใช้ Ngap yai, ตานงันเขา Tan ngan khao

(Chumphon).

Sauropus bacciformis vernacular names: "Thong laeng" (Ubon Ratchathani), "Ma phrao nok khao" and "Soi nok khao" (Bangkok) (ส่วนพฤกษศาสตร์ป่าไม้ สำนักวิชาการป่าไม้ กรมป่าไม้, 2544) is a herb to subshrub that can grow up to 50 cm. The branches are 4-ribed, with 1.7-3 by 0.5-1.5 mm triangular stipules. The leaves are simple and distichous. The petiole is less than 1 mm long. The leaf blade is elliptic, 6.5-25 by 1.5-13 mm, with length/width ratio of 1.5-7.8. The leaf base is rounded. The leaf margin is entire, the apex is rounded to acute. The lower surface of the leaf is somewhat papillate and glaucous. The nerves of the leaves are very indistinct. The flowers are green to light purple. The diameter of staminate flowers are 1.2-1.5 mm. Its pedicel is 0.6 mm long. The calyx is deeply lobed and ovate. The size of the calyx lobes are 0.4-0.6 by 0.3-0.4 mm. The apex of calyx is entire and rounded. The stamens consist of androphore (0.2 mm long) and anther (0.2 by 0.2-0.3 mm, 2-locular). The pistillate flowers are 3-5.5 mm in diameter. Its pedicel is 3-4 mm long. The ovary is obtruncate. The size of ovary is 1-1.3 by 0.9-1 mm. The style is erect and 0.5 mm long. The green fruit is ovoid, 5.5-6.5 by 5-5.2 mm, apically lobed around stigmas. The seeds of this plant are triangular-shaped, 4.5-4.9 by 1.2-1.8 by 1.2-1.5 mm in size (Welzen and Chayamarit, 2006) (**Figure 1**).

The plant is distributed at saline sandy or clayey soil, especially along or near beaches, or in wet, grassy roadsides (Airy Shaw, 1980).

Sauropus can be use for a common food and any medical purposes. Two Sauropus species found in China are Sauropus changianus S. Y. Hu, which was found to have antibiotic action on certain bacteria, and S. rostratus Miq., the boiled leaves of which are considered to be bechic expectorant. In Malay Peninsula, a decoction of S. parvifolius Ridl. is drunk to treat colic and diarrhea. In Indonesia, the leaves of S. androgynus (L.) Merr. are mixed with coconut milk and onion, then served as a drink for children with hoarse voices. In Vietnam, its roots are used to treat fever (Perry, 1980).

Sauropus androgynus (L.) Merr. (syn. S. albicans Bl.) is widely used as a kind of vegetable. It is cultivated in India, Malaysia, Indonesia, Southwest China and Vietnam (Chang *et al.*, 1997). The leaves of this plant is comsumed after cooking in Malaysia but never been used for any medical purposes (Luh *et al.*, 1999). It contains large amounts of various nutrients reported to contain 70 g of protein/kg of fresh leaves and 1,000 mg of vitamin C/kg of fresh leaves (Yu and Cheah, 1979). However, the aqueous leaf extract contains traces of the alkaloid papaverine and may cause dizziness, drowsiness and constipation (Bender and Ismail, 1973; Yu and Cheah, 1979; Chang *et al.*, 1997).

In 1994, this plant was imported into Taiwan from the Indo-Malaysia region to make mixed vegetable-fruit juice and consumed for its alleged effects of body weight reduction (Chang *et al.*, 1997). In the following year, an outbreak of its intoxication, causing obliterative bronchiolitis (Lai *et al.*, 1996; Chang *et al.*, 1998; Wang, Tseng and Lai, 1998; Wang *et al.*, 2000), respiratory failure and cardiac arrhythmias (Chen *et al.*, 1996), has been reported.

In Thailand, the roots of *S. androgynus* are used ethnomedically as a remedy for fever and externally for mumps. The leaves and fruits of this plant are common food source (มาโนช วามานนท์ และเพ็ญนภา ทรัพย์เจริญ, 2538).

Sauropus bacciformis has no previous report on phytochemical investigation. Preliminary examination of this plant revealed positive results for triterpenoids, steroids, alkaloids and flavonoids. Therefore, it is the purpose of this investigation to study the nature of the compounds in the aerial part of this plant. The result obtained might provide useful information in the field of phytochemistry and chemotaxonomy.



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Figure 1. Sauropus bacciformis (L.) Airy Shaw

CHAPTER II

HISTORICAL

1. Chemical constituents of plants in the family Euphorbiaceae

A number of compounds have been isolated from plants in the family Euphorbiaceae. They can be classified as terpenoids, steroids, alkaloids, flavonoids, tannins, lignins, lignans, lignan glycosides, phenylpropanoid glucosides, aromatic diglycosides, nucleosides and benzopyran derivatives.

In this topic, reviews of triterpenoids and flavonoids from euphorbiaceous plants, are presented below.

1.1 Triterpenoids

The triterpenoids types reported as chemical constituents within this family are all pentacyclic, belonging to the oleanane (A), taraxerane (B), friedelane (C), glutinane (D), multiflorane (E), ursane (F), lupane (G), hopane (H), filicane (I), adianane (J) and fernane (K) types. Some of these possess interesting pharmacological activities such as anti-tumor [betulinic acid (Yan *et al.*, 1989), glochidiol (Tanaka *et al.*, 2004; Puapairoj *et al.*, 2005), glochidonol and lup-20(29)-ene- 3α ,23-diol (Puapairoj *et al.*, 2005), lupeol (Kuo *et al.*, 1997)], anti-inflammatory [β -amyrin (Akihisa *et al.*, 1996), taraxerol (Singh, Sahu and Sharma, 2002), friedelin (Shimizu and Tomoo, 1994), α -amyrin and lupeol (Recio *et al.*, 1995b; Akihisa *et al.*, 1996), betulin and betulinic acid (Recio *et al.*, 1995a)], anti-tuberculosis [betulin, betulinic acid, lupeol and lupenone (Wachter *et al.*, 1999)], antiviral [lupenone (Madureira *et al.*, 2003)], anti-dermatophytic [betulinic acid (Kuiate *et al.*, 2007)], antiangiogenic [lupeol (You *et al.*, 2003)], antiplasmodial [lupeol (Alves *et al.*, 1997)], antimicrobial [lupeol (Ajaiyeoba *et al.*, 2003)] and diuretic activities [friedelin (Rizvi *et al.*, 1980a)].

Of the eleven triterpene skeletal types found in the family Euphorbiaceae, the lupane skeleton is the most common. Major compounds of this type are lupeol, glochidonol, glochidiol and glochidone. Two other classes of triterpenoids which are prevalent in the family Euphorbiaceae are the friedelane and the oleanane skeleton. Friedelin, epifriedelinol and friedelinol are major compounds of the friedelane type while β -amyrin and germanicol are of the oleanane type. For the last eight skeletal types only taraxerane, glutinane, multiflorane, ursane, hopane, filicane, adianane and fernane have so far been isolated from this family as summarized in **Table 1**.



Figure 2. Basic skeleton of pentacyclic triterpenoids







Hopane (H)





Figure 2. Basic skeleton of pentacyclic triterpenoids (continued)

Compounds	Sources	Plant part	References
1. Oleanane type			
β-Amyrin [1]	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
	E. cyparissias	Latex	Starratt, 1966
	E. pulcherrima	Latex	Biesboer et al., 1982
	Excoecaria agallocha	Leaves and	Hui and Sung, 1968
		stems	
	Glochidion heyneanum	Stems	Srivastava and Kulshrestha, 1988
	Macaranga tanarius	Leaves and	Hui, Li and Kai, 1975
		stems	
	Phyllanthus acidus	Bark	Sengupta and Mukhopadhyay,
			1966
	P. flexuosus	Stem bark	Tanaka and Matsunaga, 1988a
	Ricinus communis	Leaves	Khafagy, Mahmoud and Salam,
			1979
	Senefelderopsis	Stems	Canelon et al., 2005
	chiribiquet <mark>e</mark> nsis	216	
β -Amyrin acetate	Euphorbia maculata	Whole plant	Matsunaga, Tanaka and Akagi,
[2]	121-21-21-2	NULS- FOR	1988
	E. pulcherrima	Latex	Biesboer et al., 1982
	Phyllanthus flexuosus	Stem bark	Tanaka and Matsunaga, 1988a
δ-Amyrin [3]	Euphorbia supina	Whole plant	Tanaka and Matsunaga, 1988b
δ -Amyrin formate	E. supina	Whole plant	Tanaka and Matsunaga, 1988b
[4]			
Drypechevalin A	Drypetes chevalieri	Stems	Wansi et al., 2006
[5]	م	9	0
Epimachaerinic	Glochidion heyneanum	Stems	Srivastava and Kulshrestha,
acid [6]			1988
Germanicol [7]	Euphorbia pulcherrima	Latex	Biesboer et al., 1982
	E. supina	Whole plant	Tanaka and Matsunaga, 1988b
Germanicol	E. pulcherrima	Latex	Biesboer et al., 1982
acetate [8]			
Glochidioside N	Glochidion heyneanum	Stems	Srivastava and Kulshrestha,
[9]			1988

Table 1. Distribution of triterpenoids in the family Euphorbiaceae

Compounds	Sources	Plant part	References
Glochidioside Q	G. heyneanum	Stems	Srivastava and Kulshrestha,
[10]			1988
Kamaladiol-3-acetate	Mallotus philippinensis	Stem bark	Nair and Rao, 1993
[11]			
Oleana-9(11),12-	Phyllanthus flexuosus	Stem bark	Tanaka and Matsunaga, 1988a
dien-3β-ol [12]	Soft De		
Oleana-11,13(18)-	Euphorbia supina	Whole plant	Tanaka and Matsunaga, 1988b
dien-3 <i>β</i> -ol [13]	Phyllanthus flexuosus	Stem bark	Tanaka and Matsunaga, 1988a
Oleana-11,13(18)-	P. flexuosus	Stem bark	Tanaka, Tabuse and
dien-3 <i>β</i> ,24-diol [14]			Matsunaga, 1988
Olean-12-en-3β,24-	P. flexuosus	Stem bark	Tanaka <i>et al.</i> , 1988
diol [15]	b Cal		
Olean-12-en-3β,15α-	P. flexuosus	Stem bark	Tanaka <i>et al.</i> , 1988
diol [16]			
Olean-12-en- 3β ,15 α ,	P. flexuosus	Stem bark	Tanaka <i>et al.</i> , 1988
24-triol [17]		4	
Olean-12-en-3 β ,9 α ,	Euphorbia supina	Whole plant	Tanaka and Matsunaga, 1989a
11 <i>α</i> -triol [18]		15-5-	
2. Taraxerane type			2
Epitaraxerol [19]	Excoecaria agallocha	Leaves and	Hui and Sung, 1968
		stems	
	Macaranga triloba	Leaves	Jang et al., 2004
Euphorginol [20]	Euphorbia tirucalli	Stem bark	Rasool, Khan and Malik, 1989
$11\alpha, 12\alpha$ -Oxido	E. supina	Whole plant	Tanaka and Matsunaga, 1988b
taraxerol [21]	- Maraniu		
3,4-Seco-4(23),14-	E. broteri	Aerial part	Teresa et al., 1987
taraxeradien-3-oic			
acid methyl ester			
[22]			
Taraxerol [23]	Bridelia micrantha	Bark and	Pegel and Rogers, 1968
		wood	
	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
	E. indica	Aerial part	Rizk and Rimpler, 1977

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Taraxerol [23]	Excoecaria agallocha	Leaves and	Hui and Sung, 1968
		stems	
	Macaranga triloba	Leaves	Jang et al., 2004
	Sapium discolor	Leaves and	Hui and Sung, 1968
		stems	
Taraxerone [24]	Bridelia micrantha	Bark	Pegel and Rogers, 1968
	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
	Excoecaria agallocha	Leaves	Hui and Sung, 1968
	Sapium discolor	Stems	Hui and Sung, 1968
Taraxeryl acetate	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
[25]	E. maculata	Whole plant	Matsunaga et al., 1988
	Excoecaria agallocha	Leaves	Hui and Sung, 1968
3. Friedelane type			
30-Acetoxyfriedelan-	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
3 <i>β</i> -ol [26]	3. 15 to () 100		
3β-Acetoxy	E. antiquorum	Stems	Anjaneyulu and Ravi, 1989
friedelan-30-ol [27]	Charles Contraction	120	
Antidesmanol [28]	Antidesma menasu	Aerial part	Rizvi <i>et al.</i> , 1980a
Canophyllal [29]	A. menasu	Aerial part	Rizvi et al., 1980b
Canophyllol [30]	A. menasu	Aerial part	Rizvi et al., 1980b
1β,22β-Dihydroxy	Phyllanthus	Bark	Adesida, Girgis and Taylor,
friedelin [31]	muellerianus		1972
Drypechevalin B	Drypetes chevalieri	Stems	Wansi et al., 2006
[32]		116 U L	
Drypemolundein B	D. armoracia	Stem bark	Wandji et al., 2003
[33]	กงกรณม	หาวข	ยาลย
Epifriedelinol [34]	Antidesma bunius	Leaves and	Hui and Sung, 1968
		stems	
	Aporosa cardiosperma	Bark	Carpenter et al., 1980
	Bischofia trifoliata	Leaves and	Hui and Ho, 1968
		stems	
	Bridelia crenulata	Bark	Ramesh et al., 2001
	B. micrantha	Bark	Pegel and Rogers, 1968

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Epifriedelinol [34]	B. moonii	Bark	Carpenter et al., 1980
	Drypetes armoracia	Stem bark	Wandji et al., 2003
	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
	Fluggea virosa	Stems	Hui, Li and Lee, 1977
	Glochidion	Leaves and	Hui et al., 1970
	macrophyllum	stems	
	G. puberum	Leaves and	Hui and Li, 1978
		stems	
	G. wrightii	Leaves and	Hui and Fung, 1969
		stems	
	Jatropha maheshwarii	Stems	Viswanathan et al., 2004
	Macaranga tanarius	Stems	Hui et al., 1975
	Mallotus hookerianus	Leaves and	Hui and Li, 1976b
		stems	
	Phyllanthus reticulatus	Leaves and	Hui, Li and Wong, 1976
	12/2/2/2	stems	
	P. watsonii	Leaves and	Matsunaga et al., 1993
	131-23-49 IN 31 M	stems	
	Suregada angustifolia	Stems	Venkatesan et al., 2005
Euphorcinol [35]	Euphorbia tirucalli	Stem bark	Khan et al., 1989
Friedelan-3 <i>β</i> ,30-diol	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
diacetate [36]			
Friedelan-3β-yl	E. antiquorum	Stems	Anjaneyulu and Ravi, 1989
acetate [37]	ถาบนวท	ยปวก	15
Friedelin [38]	Antidesma bunius 🚽	Leaves and	Hui and Sung, 1968
ฉพำ	ลงกรณบ	stems	ยาลย
9	A. menasu	Aerial part	Rizvi <i>et al.</i> , 1980a
	Aporosa cardiosperma	Bark	Carpenter et al., 1980
	Bischofia trifoliata	Leaves and	Hui and Ho, 1968
		stems	
	Bridelia crenulata	Bark	Ramesh et al., 2001

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Friedelin [38]	B. micrantha	Bark and	Pegel and Rogers, 1968
		wood	
	B. moonii	Bark	Carpenter et al., 1980
	Claoxylon polot	Leaves and	Hui et al., 1977
		stems	
	Drypetes armoracia	Stem bark	Wandji et al., 2003
	D. chevalieri	Stems	Wansi et al., 2006
	Euphorbia supina	Whole plant	Tanaka and Matsunaga, 1988b
	Excoecaria agallocha	Leaves	Hui and Sung, 1968
	Fluggea virosa	Leaves and	Hui et al., 1977
		stems	
	<i>Glochidion</i>	Leaves and	Hui et al., 1970
	macrophyllum	stems	
	G. puberum	Leaves and	Hui and Li, 1978
	3.44.000	stems	
	G. wrightii	Leaves and	Hui and Fung, 1969
	Carlos and a second	stems	
	Jatropha maheshwarii	Stems	Viswanathan et al., 2004
	Macaranga tanarius	Leaves and	Hui et al., 1975
	1	stems	
	Mallotus hookerianus	Leaves and	Hui and Li, 1976b
		stems	
6	M. philippinensis	Stem bark	Nair and Rao, 1993
Friedelinol [39]	Bischofia trifoliata	Leaves	Hui and Ho, 1968
	Bridelia moonii	Bark	Carpenter et al., 1980
จพา	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
9	Fluggea virosa	Leaves and	Hui et al., 1977
		stems	
21 <i>a</i> -Hydroxyfriedel-	Phyllanthus reticulatus	Leaves and	Hui et al., 1976
4(23)-en-3-one [40]		stems	
21 <i>α</i> -Hydroxy	P. reticulatus	Leaves and	Hui et al., 1976
friedelan-3-one [41]		stems	

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
22β -Hydroxy-3-oxo-	P. muellerianus	Bark	Adesida et al., 1972
friedel-1-ene [42]			
Pentatronol [43]	Alchornea sidifolia	Leaves	Barbo <i>et al.</i> , 2002
Putranjivadione [44]	Drypetes armoracia	Stem bark	Wandji et al., 2003
	D. chevalier	Stems	Wansi et al., 2006
4. Glutinane type			
3- <i>Epi</i> -glutinol [45]	Euphorbia cyparissias	Latex	Starratt, 1966
Glutinone [46]	E. cyparissias	Latex	Starratt, 1966
Glutinyl acetate [47]	E. maculata	Whole plant	Matsunaga et al., 1988
1 <i>β</i> -Hydroxyglut-	Andrachne cordifolia	Aerial part	Mukherjee et al., 1986
5(10)-ene [48]		and roots	
5. Multiflorane type	1/1/3.50		
16α-Acetoxy-3-keto			
isomultiflorene [49]	Antidesma menasu	Aerial part	Rizvi et al., 1980b
3β -Acetoxy-16-keto	A. menasu	Aerial part	Rizvi et al., 1980b
isomultiflorene [50]			
3α ,16 α -Dihydroxy	A. menasu	Aerial part	Rizvi et al., 1980b
isomultiflorene [51]	11-2-1-2/N	1 second	
3,16-Diketo	A. menasu	Aerial part	Rizvi et al., 1980b
isomultiflorene [52]	24		
16α-Hydroxy-3-keto	A. menasu	Aerial part	Rizvi et al., 1980b
isomultiflorene [53]			
3β -Hydroxy-16-keto	A. menasu	Aerial part	Rizvi et al., 1980b
isomultiflorene [54]	նլլությու	116 U U	
Isomultiflorenol [55]	A. menasu	Aerial part	Rizvi et al., 1980b
AW1	Euphorbia supina	Whole plant	Tanaka and Matsunaga, 1988b
16-Keto	Antidesma menasu	Aerial part	Rizvi et al., 1980b
isomultiflorene [56]			
6. Ursane type			
<i>α</i> -Amyrin [57]	Aleurites moluccana	Leaves and	Hui and Ho, 1968
		stems	
	Bridelia crenulata	Bark	Ramesh et al., 2001
	Mallotus repandus	Stems	Hui and Li, 1977

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
<i>α</i> -Amyrin [57]	Suregada angustifolia	Stem bark	Venkatesan et al., 2005
3β,20ε-Dihydroxy-	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
ψ-taraxastane [58]			
3β-Hydroxyurs-	E. maculata	Whole plant	Matsunaga et al., 1988
9(11),12-diene [59]			
3α -Hydroxy-1 3α -	Mallotus repandus	Stems	Hui and Li, 1977
ursan-28,12β-olide			
[60]			
3β -Hydroxy-13 α -	M. repandus	Leaves	Hui and Li, 1977
ursan-28,12 <i>β</i> -olide			
[61]			
Phyllanthol [62]	Phyllanthus acidus	Bark	Sengupta and Mukhopadhyay,
	1 1 1 1 10		1966
	P. engleri	Root bark	Alberman and Kipping, 1951
	P. sellowianus	Stem bark	Hnatyszyn and Ferraro, 1985
7. Lupane type			
3β -Acetoxy-20-oxo-	Euphorbia maculata	Whole plant	Matsunaga et al., 1988
30-norlupane [63]	25220214	635	
Betulin [64]	Euphorbia broteri	Aerial part	Teresa et al., 1987
	E. trigona	Stems	Anjaneyulu, Rao and
			Connolly, 1985
	Phyllanthus flexuosus	Stem bark	Tanaka, Tabuse and
র	อาบับวิท	แมริก	Matsunaga, 1988
61	Mallotus philippinensis	Stems	Bandopadhyay et al., 1972
0000	Senefelderopsis	Stems	Canelon et al., 2005
NN	chiribiquetensis	NIJV	12 10 2
Betulin-3-acetate	Claoxylon polot	Leaves	Hui et al., 1977
[65]	Fluggea virosa	Stems	Hui et al., 1977
Betulinic acid [66]	Phyllanthus reticulatus	Stems	Hui et al., 1976
Betulinic acid methyl	Glochidion	Leaves and	Hui and Li, 1978
ester [67]	macrophyllum	stems	
Canaric acid [68]	Euphorbia broteri	Aerial part	Teresa et al., 1987

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
1 <i>β</i> ,3 <i>β</i> -Dihydroxy	Glochidion eriocarpum	Roots and	Puapairoj et al., 2005
lup-20(29)-ene [69]		stems	
	G. heyneanum	Stems	Srivastava and Kulshrestha,
			1988
	G. macrophyllum	Stems	Hui et al., 1970
	G. puberum	Stems	Hui and Li, 1978
	G. zeylanicum	Stem bark	Tanaka et al., 2004
	Phyllanthus watsonii	Leaves and	Matsunaga et al., 1993
		stems	
3α ,23-Dihydroxy	Glochidion macrophyllum	Stems	Hui and Lee, 1971
lup-20(29)-ene [70]	G. moonii	Bark	Carpenter et al., 1980
	G. sphaerogynum	Roots and	Puapairoj et al., 2005
		stems	
	Glochidion spp.	Bark	Carpenter et al., 1980
3β,24-Dihydroxy	Phyllanthus flexuosus	Stem bark	Tanaka et al., 1988
lup-20(29)-ene [71]			
1,3-Dioxolup-	Glochidion puberum	Leaves	Hui and Li, 1978
20(29)-ene [72]	15-18-21X-21X-21X-2	Trister	
3- <i>Epi</i> -lupeol [73]	G. eriocarpum	Roots and	Puapairoj et al., 2005
	Ú.	stems	
	G. hongkongense	Stems	Hui et al., 1970
Glochidiol [74]	G. dasyphyllum	Stems	Hui et al., 1970
	G. eriocarpum	Roots and	Puapairoj et al., 2005
6	61 1012 3718	stems	
	G. heyneanum	Stems	Srivastava and Kulshrestha,
จหา	ลงกรณม	หาวข	1988
9	G. hongkongense	Stems	Hui et al., 1970
	G. macrophyllum	Stems	Hui et al., 1970
	G. moonii	Bark	Carpenter et al., 1980
	G. multiloculare	Whole plant	Talapatra et al., 1973
	G. puberum	Stems	Hui and Li, 1978
	G. sphaerogynum	Roots and	Puapairoj et al., 2005
		stems	

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Glochidiol [74]	G. wrightii	Leaves and	Hui and Fung, 1969
		stems	
	G. zeylanicum	Stem bark	Tanaka et al., 2004
	Glochidion spp.	Bark	Carpenter et al., 1980
Glochidiol-1-acetate	G. puberum	Stems	Hui and Li, 1978
[75]			
Glochidiol-3-acetate	G. puberum	Stems	Hui and Li, 1978
[76]			
Glochidiol diacetate	G. puberum	Stems	Hui and Li, 1978
[77]			
Glochidol [78]	G. eriocarpum	Roots and	Puapairoj et al., 2005
		stems	
	G. zeylanicum	Stem bark	Tanaka <i>et al.</i> , 2004
Glochidone [79]	Bridelia moonii	Bark	Carpenter et al., 1980
	Glochidion dasyphyllum	Stems	Hui et al., 1970
	G. eriocarpum	Roots and	Puapairoj et al., 2005
	The first and the second	stems	
	G. heyneanum	Stems	Srivastava and Kulshrestha,
			1988
	G. hongkongense	Stems	Hui et al., 1970
	G. macrophyllum	Stems	Hui et al., 1970
	G. multiloculare	Whole plant	Talapatra et al., 1973
	G. puberum	Stems	Hui and Li, 1978
ิล	G. wrightii	Leaves and	Hui and Fung, 1969
	с ⁺	stems	2
ิ ลเทำ	Glochidion spp.	Bark	Carpenter et al., 1980
	Phyllanthus flexuosus	Stem bark	Tanaka and Matsunaga, 1988a
	P. watsonii	Leaves and	Matsunaga et al., 1993
		stems	
Glochidonol [80]	Fluggea virosa	Stems	Hui et al., 1977
	Glochidion eriocarpum	Roots and	Puapairoj et al., 2005
		stems	

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Glochidonol [80]	G. heyneanum	Stems	Srivastava and Kulshrestha,
			1988
	G. hongkongense	Stems	Hui et al., 1970
	G. macrophyllum	Stems	Hui et al., 1970
	G. moonii	Bark	Carpenter et al., 1980
	G. puberum	Stems	Hui and Li, 1978
	G. sphaerogynum	Roots and	Puapairoj et al., 2005
		stems	
	G. wrightii	Leaves and	Hui and Fung, 1969
		stems	
	G. zeylanicum	Stem bark	Tanaka et al., 2004
	Glochidion spp.	Bark	Carpenter et al., 1980
	Phyllanthus reticulatus	Leaves and	Hui et al., 1976
		stems	
	P. watsonii	Leaves and	Matsunaga et al., 1993
	23/2/2	stems	
Glochidonyl acetate	Glochidion puberum	Stems	Hui and Li, 1978
[81]	11-13-14 JAN	Tool State	
Glochilocudiol [82]	Fluggea virosa	Stems	Hui et al., 1977
	Glochidion multiloculare	Whole plant	Talapatra et al., 1973
	G. puberum	Stems	Hui and Li, 1978
3 <i>β</i> -Hydroxy-20-	Claoxylon polot	Leaves and	Hui et al., 1977
oxo-30-norlupane	e e	stems	
[83]	Ricinus communis	Leaves	Thompson and Bowers, 1968
Lupenone [84]	Drypetes chevalieri	Stems	Wansi et al., 2006
ลเท้า	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
	Glochidion dasyphyllum	Stems	Hui et al., 1970
	G. eriocarpum	Roots and	Puapairoj et al., 2005
		stems	
	G. hongkongense	Stems	Hui et al., 1970
	G. puberum	Stems	Hui and Li, 1978
	G. wrightii	Stems	Hui and Fung, 1969
	Phyllanthus emblica	Stems	Hui and Sung, 1968

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Lupenyl acetate	Euphorbia maculata	Whole plant	Matsunaga et al., 1988
[85]			
Lupeol [86]	Drypetes chevalieri	Stems	Wansi et al., 2006
	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989
	E. lateriflora	Leaves and	Lavie and Jain, 1968
		stems	
	Fluggea virosa	Stems	Hui et al., 1977
	Glochidion eriocarpum	Stems	Hui and Li, 1976a
	G. hongkongense	Stems	Hui et al., 1970
	G. puberum	Leaves	Hui and Li, 1978
	G. wrightii	Stems	Hui and Fung, 1969
	Mallotus philippinensis	Stems	Bandopadhyay et al., 1972
	M. repandus	Stems	Hui and Li, 1977
	Phyllanthus emblica	Leaves and	Hui and Sung, 1968
	3. 4. C. W.	stems	
	P. flexuosus	Stem bark	Tanaka and Matsunaga, 1988a
	P. watsonii	Leaves and	Matsunaga et al., 1993
	13-22+21×21×	stems	
	Ricinus communis	Leaves	Thompson and Bowers, 1968
	Senefelderopsis	Stems	Canelon et al., 2005
	chiribiquetensis	- Fin	
Lupeolactone [87]	Antidesma pentandrum	Aerial part	Kikuchi et al., 1983
1α,3α,23-	Glochidion spp.	Bark	Carpenter et al., 1980
Trihydroxylup-	เลาบนวท	ปปรก	15
20(29)-ene [88]	с ⁺	-	0
8. Hopane type	ลงกรณบ	18779	ยาลย
Moretenol [89]	Aleurites moluccana	Leaves and	Hui and Ho, 1968
		stems	
	Euphorbia lateriflora	Leaves and	Lavie and Jain, 1968
		stems	
	E. supina	Whole plant	Matsunaga and Morita, 1983
	E. trigona	Stems	Anjaneyulu et al., 1985

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References	
Moretenone [90]	Aleurites moluccana	Leaves and	Hui and Ho, 1968	
		stems		
	Euphorbia antiquorum	Stems	Anjaneyulu and Ravi, 1989	
	E. cyparissias	Stems	Starratt, 1969	
	E. lateriflora	Leaves and	Lavie and Jain, 1968	
	SALL AND A	stems		
29-Nor-21 <i>a</i> H-hopane-	Mallotus paniculatus	Stems	Hui and Li, 1976b	
3,22-dione [91]				
9. Filicane type				
Trisnorisoespinenoxide	Euphorbia supina	Whole plant	Tanaka <i>et al.</i> , 1989	
[92]				
10. Adianane type	1/1/56			
Espinendiol-A [93]	E. supina	Whole plant	Tanaka and Matsunaga, 1988b	
Espinendiol-B [94]	E. supina	Whole plant	Tanaka and Matsunaga, 1988b	
Espinenoxide [95]	E. supina	Whole plant	Tanaka <i>et al.</i> , 1989	
Simiarenol [96]	E. supina	Whole plant	Tanaka and Matsunaga,	
	(Section of the section of the secti	177 A	1988b; Tanaka <i>et al.</i> , 1989	
11. Fernane type	A CONTRACTOR	150		
Arundoin [97]	E. supina	Whole plant	Tanaka and Matsunaga, 1988b	
Fern-8-en-3β-ol [98]	E. supina	Whole plant	Tanaka and Matsunaga, 1988b	
3β-Hydroxyfern-	E. supina	Whole plant	Tanaka and Matsunaga, 1988b	
7,9(11)-diene [99]				
Isomotiol [100]	E. supina	Whole plant	Tanaka and Matsunaga, 1988b	
Motiol [101]	E. supina	Whole plant	Matsunaga and Morita, 1983	
Supinenolone-A [102]	E. supina	Whole plant	Tanaka and Matsunaga, 1989b	
Supinenolone-B [103]	E. supina	Whole plant	Tanaka and Matsunaga, 1989b	
Supinenolone-C [104]	E. supina	Whole plant	Tanaka and Matsunaga, 1989b	

Table 1. Distribution of triterpenoids in the family Euphorbiaceae (continued)



	\mathbf{R}_1	\mathbf{R}_2
β -Amyrin [1]	ОН	CH ₃
β-Amyrin acetate [2]	OCOCH ₃	CH ₃
Olean-12-en-3 <i>β</i> ,24-diol [15]	ОН	CH ₂ OH



Drypechevalin A [5]








Oleana-9(11),12-dien-3β-ol [**12**]



Oleana-11,13(18)-dien-3 β -ol [13] $R = CH_3$ Oleana-11,13(18)-dien-3 β ,24-diol [14] $R = CH_2OH$



Olean-12-en- 3β ,15 α -diol [16]	$R = CH_3$
Olean-12-en-3β,15α,24-triol [17]	$R = CH_2OH$







Olean-12-en- 3β , 9 α , 11 α -triol [**18**]



 11α , 12α -Oxidotaraxerol [**21**]





3,4-Seco-4(23),14-taraxeradien-3-oic acid methyl ester [**22**]



Figure 3. Chemical structures of triterpenoids in the family Euphorbiaceae (continued)



	R_1	R_2	\mathbf{R}_3
30-Acetoxyfriedelan-3β-ol [26]	<i>β</i> -ОН	CH ₃	CH ₂ OCOCH ₃
3β-Acetoxyfriedelan-30-ol [27]	β-OCOCH ₃	CH ₃	CH ₂ OH
Canophyllal [29]	=0	СНО	CH ₃
Canophyllol [30]	=0	OH	CH ₃
Epifriedelinol [34]	<i>β</i> -OH	CH ₃	CH ₃
Friedelan-3 β ,30-diol diacetate [36]	β-OCOCH ₃	CH ₃	CH ₂ OCOCH ₃
Friedelan-3 β -yl acetate [37]	β-OCOCH ₃	CH ₃	CH ₃
Friedelin [38]	=0	CH ₃	CH ₃
Friedelinol [39]	α-ОН	CH ₃	CH ₃







Figure 3. Chemical structures of triterpenoids in the family Euphorbiaceae (continued)





22β-Hydroxy-3-oxo-friedel-1-ene [42]

Pentatronol [43]



1*β*-Hydroxyglut-5(10)-ene [**48**]





	\mathbf{R}_1	\mathbf{R}_2
16α -Acetoxy-3-ketoisomultiflorene [49]	=O	α -OCOCH ₃
3β -Acetoxy-16-ketoisomultiflorene [50]	β-OCOCH ₃	=0
3α , 16 α -Dihydroxyisomultiflorene [51]	α- ΟΗ	α-ОН
3,16-Diketoisomultiflorene [52]	=O	=0
16α -Hydroxy-3-ketoisomultiflorene [53]	=O	α-ОН
3β -Hydroxy-16-ketoisomultiflorene [54]	β-ОН	=0
Isomultiflorenol [55]	<i>β</i> -OH	Н
16-Ketoisomultiflorene [56]	Н	=0



α-Amyrin [**57**]

 3β ,20 ε -Dihydroxy- ψ -taraxastane [**58**]

Figure 3. Chemical structures of triterpenoids in the family Euphorbiaceae (continued)





3α -Hydroxy-1 3α -ursan-28,12 β -olide [60]	$R = \alpha$ -OH
3β -Hydroxy-13 α -ursan-28,12 β -olide [61]	$R = \beta$ -OH



Figure 3. Chemical structures of triterpenoids in the family Euphorbiaceae (continued)



	\mathbf{R}_1	R_2
Betulin [64]	<i>β</i> -ОН	CH ₂ OH
Betulin-3-acetate [65]	β-OCOCH ₃	CH ₂ OH
Betulinic acid [66]	β-ОН	COOH
Betulinic acid methyl ester [67]	β-ОН	OCOCH ₃
3- <i>Epi</i> -lupeol [73]	α-ОН	CH ₃
Lupenone [84]	=0	CH ₃
Lupenyl acetate [85]	β-OCOCH ₃	CH ₃
Lupeol [86]	<i>β</i> -ОН	CH ₃



Canaric acid [68]





	\mathbf{R}_1	\mathbf{R}_2
1β , 3β -Dihydroxylup-20(29)-ene [69]	<i>β</i> -ОН	<i>β</i> -OH
1,3-Dioxolup-20(29)-ene [72]	=O	=0
Glochidiol [74]	β-ОН	α-ОН
Glochidiol-1-acetate [75]	β-OCOCH ₃	α-ОН
Glochidiol-3-acetate [76]	β-ОН	α -OCOCH ₃
Glochidiol diacetate [77]	β-OCOCH ₃	α -OCOCH ₃
Glochidonol [80]	<i>β</i> -ОН	=0
Glochidonyl acetate [81]	β-OCOCH ₃	=0
Glochilocudiol [82]	α-ОН	<i>β</i> -OH



Figure 3. Chemical structures of triterpenoids in the family Euphorbiaceae (continued)







29-Nor-21*a*H-hopane-3,22-dione [**91**]



Trisnorisoespinenoxide [92]









Arundoin [97]







Isomotiol [100]





Fern-8-en- 3β -ol [98]	Н	Н
Supinenolone-A [102]	α-ОН	=0
Supinenolone-B [103]	=0	<i>β</i> -OH
Supinenolone-C [104]	=O	=0



1.2 Flavonoids

The flavonoids, one of the most diverse and widespread groups of natural products, occupy a prominent position among the natural phenols. Interest in flavonoids results particularly from the conspicuously vivid and beautiful colors these pigments impart to various parts of plants. Some of these compounds from euphorbiaceous plants are found to possess interesting pharmacological activities such as anti-inflammatory [artemesin (Sertie *et al.*, 1990), hyperoside and quercitrin (Manga *et al.*, 2004)], antibacterial [bonannione A, euchrestaflavanone A, macaranga flavanones A and B (Schutz *et al.*, 1995)], antiulcer [myricetin and quercetin (Lacasa *et al.*, 2000)], vasorelaxant [quercetin-3,7-dimethyl ether (Guerrero *et al.*, 2002)] and hypoglycemic activities [isoquercitrin and rutin (Hnatyszyn *et al.*, 2002)].

In plants, flavonoid aglycones occur in a variety of structural forms. All contain fifteen carbon atoms in their basic nucleus and these are arranged in a C_6 - C_3 - C_6 configuration. Each C_6 represents an aromatic ring. These aromatic rings are linked by a three carbon unit which forms a third heterocyclic ring via cyclization with one of the aromatic ring via an oxygen atom. The aromatic rings are labeled as ring A and B and heterocyclic ring as ring C (Agrawal, 1989). Flavonoids can be classified according to their biosynthetic origin. Some flavonoid types are both intermediates in biosynthesis as well as end-product, which can accumulate in plant tissue. These include chalcone (the first formed C_{15} structure derived from cinnamoyl-coenzyme A and three malonyl-coenzyme A), flavanone, flavanon-3-ol, flavan-3,4-diol and flavan-3-ol. Other classes are only known as end-products of biosynthesis i.e. flavone, flavonol, anthocyanidin and flavan. Two classes of flavonoids are those in which the position 2-phenyl side chain of flavanone isomerizes to the position 3 (giving rise to isoflavone and related isoflavonoids) and then to the position 4 (giving rise to the neoflavonoids) as shown in **Scheme 1** (Dewick, 1997).

Flavonoids are associated with sugars in conjugated form and within any one class may be characterized as monoglycosidic, diglycosidic, triglycosidic, etc. Glycosidic complexity is considerable. There are over 1,500 glycosides of the flavone and flavonol isolated to date. Mono, di and trisaccharides may be linked through a phenolic hydroxyl and one or more hydroxyl groups may carry a sugar substitution. Acylated O-glycosides are known, where aliphatic acids or aromatic are linked through the 6-hydroxyl of a glucose moiety. A special group of mainly flavone-based C-glycosides also occurs in plants (Hocking, 1997).



Scheme 1. Biosynthetic relationship of flavonoids

 \mathbf{a} = cyclization, \mathbf{b} = bioreduction, \mathbf{c} = aryl migration, \mathbf{d} = dehydrogenation, \mathbf{e} = hydroxylation, \mathbf{f} = dehydroxylation

The near ubiquitous distribution of flavonoids in green plants, their relative chemical stability and the ease with which most can be identified have made them particularly useful as taxonomic markers in plant classification (Agrawal, 1989).

The literature reviews of flavonoids in the family Euphorbiaceae are summarized in **Table 2**.

Compounds	Sources	Plant part	References
1. Flavanone		2	
Bonannione A [105]	Macaranga alnifolia	Leaves	Schutz et al., 1995;
		Fruits	Yoder <i>et al.</i> , 2007
	M. pleiostemona	Leaves	Schutz et al., 1995
5,4'-Dihydroxy-[2"-(1-	M. conifera	Leaves	Jang et al., 2002
hydroxy-1-methylethyl)			
dihydrofurano]-			
(7,8:5",4") flavanone	Sala al		
[106]			
5,7-Dihydroxy-4'-	M. conifera	Leaves	Jang et al., 2002
methoxy-8-(2-hydroxy-			
3-methylbut-3-enyl)			
flavanone [107]			
5,7-Dihydroxy-4'-	M. conifera	Leaves	Jang et al., 2002
methoxy-8-(3-methyl			
but-2-enyl) flavanone	2 2	A	
[108]	111731819	รการ	
6,7-Dimethoxy-3',4'-	M. indica	Leaves	Sultana and Ilyas, 1987
methylenedioxy	กรถไปเห	กิจภย	าลย
flavanone [109]	1 9 10 10 11		1610
Euchrestaflavanone A	M. pleiostemona	Leaves	Schutz et al., 1995
[110]			
5-Hydroxy-4'-methoxy-	M. conifera	Leaves	Jang et al., 2002
2",2"-dimethylpyrano-			
(7,8:6",5") flavanone			
[111]			

Table 2. Distribution of flavonoids in the family Euphorbiaceae

Compounds	Sources	Plant part	References
Lonchocarpol A [112]	M. conifera	Leaves	Jang et al., 2002
Macaranga flavanone A [113]	M. pleiostemona	Leaves	Schutz et al., 1995
Macaranga flavanone B [114]	M. pleiostemona	Leaves	Schutz et al., 1995
Nymphaeol-A [115]	M. alnifolia	Fruits	Yoder et al., 2007
	M. tanarius	Leaves	Phommart et al., 2005
Nymphaeol-B [116]	M. tanarius	Leaves	Phommart et al., 2005
Nymphaeol-C [117]	M. tanarius	Leaves	Tseng et al., 2001;
			Phommart et al., 2005
Sophoraflavanone B [118]	M. conifera	Leaves	Jang et al., 2002
	M. denticulata	Leaves	Sutthivaiyakit et al.,
			2002
Tanariflavanone A [119]	M. tanarius	Leaves	Tseng et al., 2001
Tanariflavanone B [120]	M. tanarius	Leaves	Tseng et al., 2001;
			Phommart et al., 2005
Tanariflavanone C [121]	M. tanarius	Leaves	Phommart et al., 2005
Tanariflavanone D [122]	M. tanarius	Leaves	Phommart et al., 2005
Tomentosanol D [123]	M. conifera	Leaves	Jang et al., 2002
2. Flavanonol	acon win sin with the		
Alnifoliol [124]	M. alnifolia	Fruits	Yoder et al., 2007
Bonanniol A [125]	M. alnifolia	Fruits	Yoder et al., 2007
Diplacol [126]	M. alnifolia	Fruits	Yoder et al., 2007
Lupinifolinol [127]	M. conifera	Leaves	Jang et al., 2002
3. Isoflavone			
7-Methyltectorigenin [128]	M. indica	Leaves	Sultana and Ilyas, 1987
4. Flavone	e		2
Amentoflavone [129]	Alchornea	Leaves	Lima et al., 2006
9	castaneaefolia		
	Chrozophora	Leaves and	Hashim <i>et al.</i> , 1990
	brocchiana	stems	
	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
Apigenin [130]	Jatropa curcas	Leaves	Subramanian, Nagarajan
			And Sulochana, 1971a

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Apigenin [130]	J. gossypifolia	Leaves	Subramanian, Nagarajan
			And Sulochana, 1971b
Artemetin [131]	Croton brasiliensis	Leaves and	Palmeira, Conserva and
		stems	Silveira, 2005
Casticin [132]	C. brasiliensis	Leaves and	Palmeira et al., 2005
	Sold Bar	stems	
Chrysosplenol-D [133]	C. brasiliensis	Leaves and	Palmeira et al., 2005
		stems	
Desmethoxykanugin [134]	Gelonium multiflorum	Roots	Das et al., 1994
Kanugin [135]	G. multiflorum	Roots	Das et al., 1994
Penduletin [136]	Croton brasiliensis	Leaves and	Palmeira et al., 2005
	1624	stems	
Pinnatin [137]	Gelonium multiflorum	Roots	Das et al., 1994
5. Flavone glycoside			
Apigenin-5- <i>O</i> -glucoside [138]	Chrozophora	Leaves and	Hashim <i>et al.</i> , 1990
	brocchiana	stems	
	C. obliqua	Leaves and	Hashim <i>et al.</i> , 1990
	and with a frances	stems	
	C. plicata	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
20		stems	
(C. verbascifolia	Leaves and	Hashim <i>et al.</i> , 1990
ิ สถาเ	111 วาทยา	stems	
Apigenin-7-O-glucoside [139]	C. brocchiana	Leaves and	Hashim <i>et al.</i> , 1990
ลหำลงก	ารถโบเหา	stems	าลย
Q	C. obliqua	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	C. plicata	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
		stems	

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Apigenin-7- <i>O</i> -glucoside [139]	C. verbascifolia	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	Euphorbia forskaolii	Leaves and	Kawashty et al., 1990
		stems	
	E. prostrata	Leaves and	Kawashty et al., 1990
		stems	
Isovitexin [140]	Hevea brasiliensis	Leaves	Subramanian et al., 1971a
	Jatropha curcas	Leaves	Subramanian et al., 1971a
	J. gossypifolia	Leaves	Subramanian et al., 1971b
	J. heynii	Leaves and	Subramanian et al., 1971a
		stems	
Luteolin-3- <i>O</i> -glucoside [141]	Chrozophora	Leaves and	Hashim <i>et al.</i> , 1990
	brocchiana	stems	
	C. obliqua	Leaves and	Hashim <i>et al.</i> , 1990
	a late O marked	stems	
	C. plicata	Leaves and	Hashim <i>et al.</i> , 1990
	Jacobs Chippeling and A	stems	
	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
	a sussidier Augusta	stems	
	C. verbascifolia	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
Luteolin-7- <i>O</i> -glucoside [142]	C. brocchiana	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
ิ ลถาเ	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
	с ⁻	stems	0
ฉฬาลงก	Euphorbia forskaolii	Leaves and	Kawashty et al., 1990
9		stems	
	E. prostrata	Leaves and	Kawashty et al., 1990
		stems	
	Senefelderopsis	Leaves and	Canelon et al., 2005
	chiribiquetensis	stems	
Vitexin [143]	Croton hovarum	Leaves	Krebs and Ramiarantsoa,
			1997

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Vitexin [143]	Hevea brasiliensis	Leaves	Subramanian et al., 1971a
	Jatropha curcas	Leaves	Subramanian et al., 1971a
	J. gossypifolia	Leaves	Subramanian et al., 1971b
	J. heynii	Leaves and	Subramanian et al., 1971a
		stems	
6. Flavonol			
Ayanin [144]	Croton schiedeanus	Aerial part	Guerrero et al., 2002
	Macaranga triloba	Leaves	Jang et al., 2004
Denticulaflavonol [145]	Macaranga	Leaves	Sutthivaiyakit et al., 2002
	denticulata		
Ferrugin [146]	Bridelia ferruginea	Stem bark	Cimanga et al., 2001
Isolicoflavonol [147]	Macaranga conifera	Leaves	Jang et al., 2002
Isorhamnetin [148]	Croton oblongifolius	Leaves	Subramanian et al., 1971a
Kaempferol [149]	Euphorbia paralias	Leaves and	Rizk, Ahmad and Diab,
	a ha onit h	stems	1979
	Phyllanthus	Aerial part	Miean and Mohamed,
	androgynus		2001
	P. emblica	Leaves	Subramanian et al., 1971a
Kaempferol-3,6-dimethyl ether	Chamaesyce	Aerial part	Rojas et al., 1999
[150]	prostrata		
	Macaranga conifera	Leaves	Jang et al., 2002
Kaempferol-3,7-dimethyl ether	Croton cajucara	Leaves	Maciel et al., 2000
[151]	Y	<u>A</u>	
Kaempferol-3,4',7-trimethyl	C. cajucara	Leaves	Maciel et al., 2000
ether [152]	o-		
Macarangin [153]	Macaranga	Leaves	Sutthivaiyakit et al., 2002
9	denticulata		
3-O-Methylmacarangin [154]	M. denticulata	Leaves	Sutthivaiyakit et al., 2002
3-O-Methylquercetin [155]	Bridelia ferruginea	Stem bark	Cimanga et al., 2001
Myricetin [156]	B. ferruginea	Stem bark	Cimanga et al., 2001
Quercetin [157]	Alchornea	Leaves	Lima et al., 2006
	castaneaefolia		

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References		
Quercetin [157]	Bridelia ferruginea	Leaves	Mensah and Achenbach, 1985		
	Croton oblongifolius	Leaves	Subramanian et al., 1971a		
	Euphorbia paralias	Leaves and stems	Rizk et al., 1979		
	Jatropha heynii	Leaves	Subramanian et al., 1971a		
	Manihot utilissima	Aerial part	Miean and Mohamed, 2001		
	Ricinus communis	Leaves	Khafagy, Mahmoud and Salam, 1979		
	Sauropus androgynus	Aerial part	Miean and Mohamed, 2001		
Quercetin-3,7-dimethyl ether [158]	Croton schiedeanus	Aerial part	Guerrero et al., 2002		
	Macaranga triloba	Leaves	Jang et al., 2004		
Rutisin [159]	Bridelia ferruginea	Stem bark	Cimanga et al., 2001		
	Macaranga conifera	Leaves	Jang et al., 2002		
3,3',4',5'-Tetra- <i>O</i> -methyl myricetin [160]	B. ferruginea	Stem bark	Cimanga et al., 2001		
6. Flavonol glycoside					
Astragalin [161]	Adenopeltis colliguaya	Leaves	Ugarte and Silva, 1972		
สถาเ	Chrozophora brocchiana	Leaves and stems	Hashim <i>et al.</i> , 1990		
ลหำลงก	C. obliqua	Leaves and stems	Hashim <i>et al.</i> , 1990		
9	C. plicata	Leaves and stems	Hashim <i>et al.</i> , 1990		
	C. tinctoria	Leaves and stems	Hashim <i>et al.</i> , 1990		
	C. verbascifolia	Leaves and stems	Hashim <i>et al.</i> , 1990		

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Astragalin [161]	Euphorbia arguta	Leaves and	Kawashty et al., 1990
		stems	
	E. chamaescye	Leaves and	Kawashty et al., 1990
		stems	
	E. dentroides	Leaves and	Kawashty et al., 1990
		stems	
	E. geniculata	Leaves and	Kawashty et al., 1990
		stems	
	E. isthmian	Leaves and	Kawashty et al., 1990
		stems	
	E. maculata	Aerial part	Agata <i>et al.</i> , 1991
	E. paralias	Leaves and	Kawashty et al., 1990
		stems	
	E. peplus	Leaves and	Kawashty et al., 1990
	3.440000	stems	
	E. supina	Aerial part	Agata <i>et al.</i> , 1991
	Phyllanthus emblica	Leaves	Subramanian <i>et al.</i> , 1971a
Biorobin [162]	Acalypha indica	Flowers	Nahrstedt, Hungeling and
		and leaves	Petereit, 2006
Clitorin [163]	A. indica	Flowers	Nahrstedt et al., 2006
		and leaves	
$3-O-\beta$ -D-Glucosyl- $(1\rightarrow 6)$ -	Sauropus	Aerial part	Wang and Lee, 1997;
β -D-glucosyl kaempferol [164]	androgynus	200	Yu <i>et al.</i> , 2006
$3-O-\beta$ -D-Glucosyl- $(1\rightarrow 6)$ -	S. androgynus	Aerial part	Wang and Lee, 1997;
β -D-glucosyl-7- O - α -L-	σ	-	Yu et al., 2006
rhamnosyl kaempferol [165]	ารณมหา	าวทย	าลย
$3-O-\beta$ -D-Glucosyl-7- $O-\alpha$ -L-	S. androgynus	Aerial part	Wang and Lee, 1997
rhamnosyl kaempferol [166]			
6-Hydroxykaempferol-7-	Sapium	Leaves	Ahmad <i>et al.</i> , 1991
rutinoside [167]	eugeniaefolium		
Hyperoside [168]	Croton oblongifolius	Leaves	Subramanian et al., 1971a
	Euphorbia arguta	Leaves and	Kawashty et al., 1990
		stems	

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Hyperoside [168]	E. helioscopia	Leaves and	Kawashty et al., 1990
		stems	
	E. hypericifolia	Leaves and	Kawashty et al., 1990
		stems	
	E. paralias	Leaves and	Rizk et al., 1979;
		stems	Kawashty et al., 1990
	E. prostrata	Leaves and	Kawashty et al., 1990
		stems	
	Jatropha heynii	Leaves	Subramanian et al., 1971a
Isoquercitrin [169]	Acalypha indica	Flowers	Nahrstedt et al., 2006
		and leaves	
	Bridelia ferruginea	Stem bark	Cimanga et al., 2001
	Chrozophora	Leaves and	Hashim <i>et al.</i> , 1990
	brocchiana	stems	
	C. obliqua	Leaves and	Hashim <i>et al.</i> , 1990
	122/21/21/21	stems	
	C. plicata	Leaves and	Hashim <i>et al.</i> , 1990
	ACONUN UN UN UN	stems	
	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	C. verbascifolia	Leaves and	Hashim et al., 1990
20		stems	
	Euphorbia arabica	Leaves and	Kawashty et al., 1990
ิลถาเ	แนวทยา	stems	
	E. arguta	Leaves and	Kawashty et al., 1990
ลเท้าลงก	ารถเบเห	stems	าลย
9	E. chamaescye	Leaves and	Kawashty et al., 1990
		stems	
	E. dentroides	Leaves and	Kawashty et al., 1990
		stems	
	E. dracunculoides	Leaves and	Kawashty et al., 1990
		stems	

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Isoquercitrin [169]	E. forskaolii	Leaves and	Kawashty et al., 1990
		stems	
	E. geniculata	Leaves and	Kawashty et al., 1990
		stems	
	E. hirta	Leaves and	Kawashty et al., 1990
		stems	
	E. hypericifolia	Leaves and	Kawashty et al., 1990
		stems	
	E. hyssopifolia	Leaves and	Kawashty et al., 1990
		stems	
	E. isthmia	Leaves and	Kawashty et al., 1990
	1 19 200 6	stems	
	E. maculata	Aerial part	Agata et al., 1991
	E. paralias	Leaves and	Kawashty et al., 1990
	a hate price h	stems	
	E. peplus	Leaves and	Kawashty et al., 1990
	Marthal Contractor	stems	
	E. prostrata	Leaves and	Kawashty et al., 1990
		stems	
	E. retusa	Aerial part	Saleh, 1985
		Leaves and	Kawashty et al., 1990
20		stems	
	E. scordifolia	Leaves and	Kawashty et al., 1990
ิลลาเ	เนวทยา	stems	
	E. supina	Aerial part	Agata et al., 1991
ฉฬาลงก	Phyllanthus	Stem bark	Hnatyszyn et al., 2002
9	sellowianus		
Isorhamnetin-3- <i>O</i> -β-	Chrozophora obliqua	Aerial part	Mohamed, 2001
glucopyranoside-7- <i>O</i> -α-			
rhamnopyranoside [170]			
Kaempferol-3-arabinoside	Euphorbia paralias	Leaves and	Kawashty et al., 1990
[171]		stems	

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Kaempferol-3-galactoside	E. paralias	Leaves and	Kawashty et al., 1990
[172]		stems	
Kaempferol-3-O-(2'-O-	E. maculata	Aerial part	Agata <i>et al.</i> , 1991
galloyl)- β -D-glucoside [173]			
Kaempferol-7-O-glucoside	Chymaesyce	Aerial part	Rojas <i>et al.</i> , 1999
[174]	prostrata		
	Euphorbia	Leaves and	Kawashty et al., 1990
	helioscopia	stems	
	E. isthmia	Leaves and	Kawashty et al., 1990
		stems	
Kaempferol-3-O-rutinoside	Acalypha indica	Flowers	Nahrstedt et al., 2006
[175]		and leaves	
	Chrozophora	Leaves and	Hashim <i>et al.</i> , 1990
	brocchiana	stems	
	C. obliqua	Leaves and	Hashim <i>et al.</i> , 1990
	12/2/2/2/2	stems	
	C. plicata	Leaves and	Hashim <i>et al.</i> , 1990
	acon un un un	stems	
0	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	C. verbascifolia	Leaves and	Hashim <i>et al.</i> , 1990
		stems	
	Euphorbia	Leaves and	Kawashty et al., 1990
ลลาเ	chamaescye	stems	3
	E. geniculata	Leaves and	Kawashty et al., 1990
ฉฬาลงก	ารถเบห	stems	าลย
9	Mnihot esculenta	Leaves	Prawat et al., 1995
	Ricinus communis	Roots	Kang et al., 1985
Mauritianin [176]	Acalypha indica	Flowers	Nahrstedt et al., 2006
		and leaves	
Myricetin-3- <i>O</i> -α-L-	Alchrnea	Leaves	Lima <i>et al.</i> , 2006
arabinopyranoside [177]	castaneaefolia		

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Myricetin-3- <i>O</i> -glucoside [178]	Bridelia ferruginea	Leaves	Mensah and Achenbach, 1985
Myricetin-3-O-rhamnoside	B. ferruginea	Leaves	Mensah and Achenbach,
[179]			1985
Quercetin-3-arabinoside [180]	Alchornea	Leaves	Lima <i>et al.</i> , 2006
	castaneaefolia		
	Euphorbia	Leaves and	Kawashty et al., 1990
	hypericifolia	stems	
	E. paralias	Leaves and	Rizk et al., 1979;
		stems	Kawashty et al., 1990
Quercetin-3- O - β -D-galacto	Alchornea	Leaves	Lima <i>et al.</i> , 2006
pyranoside [181]	castaneaefolia		
Quercetin-3-O-(2"-O-galloyl)-	Euphorbia maculata	Aerial part	Agata et al., 1991
β-D-glucoside [182]			
Quercetin-3- <i>O</i> -β-	Chrozophora obliqua	Aerial part	Mohamed, 2001
glucopyranoside-7- <i>Ο</i> -α-	A SIZIS IN		
rhamnopyranoside [183]	(The Charles of Control of Charles of Charle		
Quercetin-7-O-glucoside [184]	Euphorbia	Leaves and	Kawashty et al., 1990
A	helioscopia	stems	
Quercetin-3-xyloside [185]	E. paralias	Leaves and	Kawashty et al., 1990
		stems	
Quercitrin [186]	Adenopeltis	Leaves	Ugarte and Silva, 1972
6000	colliguaya	200	
616111	Euphorbia arguta	Leaves and	Kawashty et al., 1990
	σ	stems	0
จฬาลงก	E. forskaolii	Leaves and	Kawashty et al., 1990
9		stems	
	E. hirta	Leaves	Yoshida et al., 1988
		Leaves and	Kawashty et al., 1990
		stems	
	E. hypericifolia	Leaves and	Kawashty et al., 1990
		stems	

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Quercitrin [186]	E. retusa	Aerial part	Saleh, 1985
		Leaves and	Kawashty et al., 1990
		stems	
	Senefelderopsis	Leaves and	Canelon et al., 2005
	chiribiquetensis	stems	
Rutin [187]	Acalypha indica	Flowers	Nahrstedt et al., 2006
		and leaves	
	Bridelia ferruginea	Leaves	Mensah and Achenbach,
			1985
	Chrozophora	Leaves and	Hashim <i>et al.</i> , 1990
	brocchiana	stems	
	C. obliqua	Leaves and	Hashim et al., 1990
		stems	
	C. plicata	Leaves and	Hashim <i>et al.</i> , 1990
	The fitte Streak of	stems	
	C. tinctoria	Leaves and	Hashim <i>et al.</i> , 1990
	(Jackson and a start and a	stems	
	C. verbascifolia	Leaves and	Hashim <i>et al.</i> , 1990
	and a start	stems	
	Euphorbia arguta	Leaves and	Kawashty et al., 1990
		stems	
	E. chamaescye	Leaves and	Kawashty et al., 1990
		stems	
สถาเ	E. geniculata	Leaves and	Kawashty et al., 1990
		stems	
ลหำลงก	E. hyssopifolia	Leaves and	Kawashty et al., 1990
9		stems	
	E. peplus	Leaves and	Kawashty et al., 1990
		stems	
	E. retusa	Aerial part	Saleh, 1985
		Leaves and	Kawashty et al., 1990
		stems	
	Mcaranga triloba	Leaves	Jang et al., 2004

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)

Compounds	Sources	Plant part	References
Rutin [187]	Manihot esculenta	Leaves	Prawat et al., 1995
	Phyllanthus	Stem bark	Hnatyszyn et al., 2002
	sellowianus		
	Ricinus communis	Leaves	Khafagy et al., 1979
	Senefelderopsis	Leaves and	Canelon et al., 2005
	chiribiqu <mark>etens</mark> is	stems	
8. Flavan			
Epicatechin [188]	Sauropus hirsutus	Aerial part	Lohakol, 2003
Gallocatechin-(4'-O-7)-	Bridelia ferruginea	Stem bark	Cimanga et al., 2001
epigallocatechin [189]			
9. Rotenoid			
4,5-Dihydro-5'α-hydroxy-4'α-	Macaranga triloba	Leaves	Jang et al., 2004
methoxy-6a,12a-dehydro-α-			
toxicarol [190]			
Sumatrol [191]	M. indica	Leaves	Sultana and Ilyas, 1987

Table 2. Distribution of flavonoids in the family Euphorbiaceae (continued)





Bonannione A [105]

Macaranga flavanone A [113]





5,4'-Dihydroxy-[2"-(1-hydroxy-1-methylethyl) dihydrofurano]-(7,8:5",4") flavanone [106]



Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae



	\mathbf{R}_1	\mathbf{R}_2
5,7-Dihydroxy-4'-methoxy-8-(3-methyl	Н	CH ₃
but-2-enyl) flavanone [108]		
Lonchocarpol A [112]	Prenyl	Η
Sophoraflavanone B [118]	Н	Η



6,7-Dimethoxy-3',4'-methylenedioxy flavanone [109]



Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae (continued)



5-Hydroxy-4'-methoxy-2",2"-dimethylpyrano-(7,8:6",5") flavanone [111]



Tanariflavanone A [**119**]

Tanariflavanone B [120]





Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae (continued)





Lupinifolinol [127]

7-Methyltectorigenin [128]





	R ₁	R ₂	R ₃	\mathbf{R}_4
Apigenin [130]	Н	Н	H	Н
Apigenin-5-O-glucoside [138]	Н	Glc	Н	Н
Apigenin-7-O-glucoside [139]	Н	Н	Glc	Н
Luteolin-3-O-glucoside [141]	OGlc	Н	Н	OH
Luteolin-7-O-glucoside [142]	Н	Н	Glc	OH

Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae (continued)









Pinnatin [137]









Denticulaflavonol [145]







 $\begin{array}{ccc} R_1 & R_2 \\ H & H \end{array}$

Isorhamnetin [148]

Isorhamnetin-3-O- β -glucopyranoside-7-O- α -rhamnopyranoside [**170**] β -Glc α -Rha



Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae (continued)


	\mathbf{R}_1	\mathbf{R}_2	\mathbf{R}_3
Astragalin [161]	Glc	Н	Н
Biorobin [162]	- ∟-Rha-(1→6)-β- D-Gal	Н	Н
Clitorin [163] α -L-Rha-(1 \rightarrow 2)- α	-L-Rha-(1→6)-β-D-Glc	Н	Н
3- O - β -D-Glucosyl-(1 \rightarrow 6)- β -D-	β -Glc ⁶ - β -Glc	Н	Н
glucosyl kaempferol [164]			
3- <i>O</i> - β -D-Glucosyl-(1→6)- β -D-	β -Glc ⁶ - β -Glc	Н	α-Rha
glucosyl-7- O - α -L-rhamnosyl kaempferol	[165]		
3- <i>O</i> -β-D-Glucosyl-7- <i>O</i> - α -L-	β-Glc	Н	α-Rha
rhamnosyl kaempferol [166]			
6-Hydroxykaempferol-7-rutinoside [167]	Н	OH	Glc ⁶ -Rha
Kaempferol-3-arabinoside [171]	Ara	Н	Н
Kaempferol-3-galactoside [172]	Gal	Н	Н
Kaempferol-3- <i>O</i> -(2"- <i>O</i> -galloyl)-β-D-	2"- O -galloyl- β -Glc	Н	Н
glucoside [173]			
Kaempferol-7- <i>O</i> -glucoside [174]	Н	Н	Glc
Kaempferol-3-O-rutinoside [175]	Glc ⁶ -Rha	Н	Н
Mauritianin [176] α -L-Rha-(1 \rightarrow 2)- α -	L-Rha- $(1\rightarrow 6)$ - β -D-Gal	Н	Н

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Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae (continued)



	R_1	R_2
Hyperoside [168]	Gal	Н
Isoquercitrin [169]	Glc	Н
3-O-Methylquercetin [155]	CH ₃	Н
Quercetin [157]	Н	Н
Quercetin-3,7-dimethyl ether [158]	CH ₃	CH_3
Quercetin-3-arabinoside [180]	Ara	Н
Quercetin-3- O - β -D-galactopyranoside [181]	β-Gal	Н
Quercetin-3- O -(2"- O -galloyl)- β -D-glucoside [182]	2"- <i>O</i> -galloyl-β-Glc	Н
Quercetin-3- O - β -D-glucopyranoside-7- O - α -	β-Glc	α -Rha
rhamnopyranoside [183]		
Quercetin-7- <i>O</i> -glucoside [184]	Н	Glc
Quercetin-3-xyloside [185]	Xyl	Н
Quercitrin [186]	Rha	Н
Rutin [187]	Glc ⁶ -Rha	Н

Epicatechin [188]

Figure 4. Chemical structures of flavonoids in the family Euphorbiaceae (continued)



Gallocatechin-[4'-0-7]-epigallocatechin [189]



4,5-Dihydro-5' α -hydroxy-4' α -methoxy-6a,12a-dehydro- α -toxicarol [**190**]



Sumatrol [191]



2. Chemical constituents of plants in the genus Sauropus

Of the 27 species of genus *Sauropus* found in Thailand, only 3 species, i.e. *Sauropus androgynus* (L.) Merr., *S. hirsutus* Beille and *S. quadrangularis* (Willd.) Mull. Arg., have been chemically investigated and a wide range of constituents, including terpenoids, steroids, alkaloids, flavonoids, lignans, lignan glycosides and nucleosides, have been reported as shown in **Table 3**.

Plants	Plant part	Chemical	Name	References
		type		
Sauropus androgynus	Aerial part	Terpenoids	Corchoionoside C	Kanchanapoom
(L.) Merr.			[192]	et al.,2003
_		100 A	Sauroposide [193]	Kanchanapoom
				et al.,2003
	Leaves	Alkaloids	Papaverine [194]	Bender and
/		COMP.		Ismail, 1973;
		avala In		Cordell et al.,
	1555	aseren and		1989
	Aerial part	Flavonoids	$3-O-\beta$ -D-Glucosyl-	Wang and Lee,
0.			$(1\rightarrow 6)$ - β -D-glucosyl	1997; Yu et al.,
5			kaempferol [164]	2006
			$3-O-\beta$ -D-Glucosyl-	Wang and Lee,
			$(1\rightarrow 6)$ - β -D-glucosyl-	1997; Yu et al.,
60		0.0.010	7- O - α -L-rhamnosyl	2006
6161	11น เ	INEU	kaempferol [165]	
		5°	$3-O-\beta$ -D-Glucosyl-	Wang and Lee,
จพาลง	เกรเ	AL N	7- O - α -L-rhamnosyl	1997
9			kaempferol [166]	
			Quercetin [157]	Miean and
				Mohamed,
				2001
		Lignan	(+)-Isolariciresinol-	Kanchanapoom
		glycosides	3α - <i>O</i> - β -gluco	et al.,2003
			pyranoside [195]	

Table 3. Chemical constituents of plants in the genus Sauropus

Plants	Plant part	Chemical	Name	References
		type		
S. androgynus	Aerial part	Lignan	(-)-Isolariciresinol- 3α -	Kanchanapoom
(L.) Merr.		glycosides	O - β -glucopyranoside	et al.,2003
			[196]	
			(-)-Isolariciresinol- 3α -	Kanchanapoom
			<i>O-β</i> -apiofuranosyl-	et al.,2003
			$(1\rightarrow 2)$ - <i>O</i> - β -gluco	
			pyranoside [197]	
			Liriodendrin [198]	Kanchanapoom
_				<i>et al.</i> ,2003
		Nucleosides	Adenosine [199]	Wang and Lee,
				1997
	1115		5'-Deoxy-5'-methyl	Wang and Lee,
		STARL .	sulphinyl adenosine	1997
	1 24	COMP A	[200]	
		alasa In	Guanosine [201]	Kanchanapoom
	0266	an series and a series of the		et al.,2003
	1524	WY ANDER	Uridine [202]	Wang and Lee,
				1997
S. hirsutus Beille	Aerial part	Steroids	β -Sitosterol [203]	Lohakol, 2003
		Alkaloids	4-Methoxy-2-methyl-	Lohakol, 2003
	01		7,8-methylenedioxy-	
สก	הופופר	9/1619	1-isoquinolone [204]	
61 6 1	IU IA	יומע	4,6-Dimethoxy-2-	Lohakol, 2003
20022	0050	5" 0 0 0"	methyl-7,8-methylene	
NN 16 1	11196	PHU	dioxy-1-isoquinolone	
9			[205]	
		Flavonoids	Epicatechin [188]	Lohakol, 2003
S. quadrangularis	Aerial part	Lignans	Diphyllin [206]	Satyanarayana
(Willd.) Mull. Arg.				and Ramu,
				1995

 Table 3. Chemical constituents of plants in the genus Sauropus (continued)

Plants	Plant part	Chemical	Name	References
		type		
S. quadrangularis	Aerial part	Lignans	Benzoyl diphyllin	Satyanarayana
(Willd.) Mull. Arg.			[207]	and Ramu,
				1995
			6-Bromo-3,4-	Satyanarayana
			dimethoxybenzoyl	and Ramu,
			diphyllin [208]	1995
			6-Bromo-3,4-	Satyanarayana
			methylenedioxy	and Ramu,
			benzoyl diphyllin	1995
			[209]	
			Cinnamoyl diphyllin	Satyanarayana
			[210]	and Ramu,
				1995
/	3.6		3,4-Methylenedioxy	Satyanarayana
		NAVA	benzoyl diphyllin	and Ramu,
		and a start	[211]	1995
	and the	114/114/2	4-Nitro-benzoyl	Satyanarayana
		ad adda	diphyllin [212]	and Ramu,
				1995
			3,4,5-Trimethyl	Satyanarayana
			benzo <mark>yl</mark> diphyllin	and Ramu,
	2 6	A	[213]	1995
สถ'	191917	19/1919	<i>Tran-(3R,4S)</i> bis	Satyanarayana
1010			(3',4'-methylenedioxy	and Ramu,
ລາທາລ	ากรก	191921	benzyl) tetrahydro	1995
N N 161	1196	γЧЛ	furan [214]	J

Table 3. Chemical constituents of plants in the genus Sauropus (continued)



Figure 5. Chemical structures of plants in the genus Sauropus



Figure 5. Chemical structures of plants in the genus Sauropus (continued)



4,6-Dimethoxy-2-methyl-7,8-methylene dioxy-1-isoquinolone [**205**] $R = OCH_3$



Figure 5. Chemical structures of plants in the genus Sauropus (continued)





6-Bromo-3,4-dimethoxybenzoyl diphyllin [208]



NO₂

6-Bromo-3,4-methylenedioxybenzoyl diphyllin [209]

Cinnamoyl diphyllin [210]



4-Nitro-benzoyl diphyllin [212]







Trans-(3R,4S) bis (3',4'-methylenedioxy benzyl) tetrahydrofuran [**214**]

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Figure 5. Chemical structures of plants in the genus Sauropus (continued)

CHAPTER III

EXPERIMENTAL

1. Source of plant material

Sauropus bacciformis (L.) Airy Shaw was collected from Sam Roi Yot National Park, Prachuap Khiri Khan province, Thailand in October 2006. The plant was identified by Professor Dr. Thawatchai Santisuk of Botanical Section, Royal Forest Department, Ministry of Agriculture and Co-operatives, Bangkok, Thailand. A voucher specimen, BKF. No. 148136, is deposited at the Forest Herbarium (BKF), Royal Forest Department, Ministry of Agriculture and Co-operative, Bangkok, Thailand.

2. General techniques

2.1 Chromatographic technique

2.1.1 Analytical thin-layer chromatography (TLC)

Technique	:	One dimension, ascending
Adsorbent	:	Silica gel 60 F ₂₅₄ (E. Merck) precoated plate
Layer thickness	:	0.2 mm
Solvent system	:	Various solvent systems depending on materials
Distance	-:	5.0 cm
Temperature	<u>.</u>	Laboratory temperature 30-35 °C
Detection	: 9	1) UV light at the wavelengths of 254 and 365 nm
		2) 10% Sulfuric acid in ethanol, heating at 110 $^{\circ}$ C for
		5-10 minutes
2.1.2	2 Colun	nn chromatography (CC)
Column	:	Flat bottom glass column (various diameters)
Adsorbent	:	1) Silica gel 60 (No. 7734, E. Merck) particle size 0.063
		-0.200 nm (70-230 mesh ASTM)
	:	2) Silica gel 60 (No. 9385, E. Merck) particle size 0.040
		-0.063 nm (230-400 mesh ASTM)
Packing method	:	Wet packing

Sample loading	:	1) Dry packing
		The sample was dissolved in a small volume of
		organic solvent, mixed with a small quantity of
		adsorbents, triturated, dried and then loaded on top of
		the column.
	:	2) Wet packing
		The sample was dissolved in a small volume
		of the eluent, then loaded on top of the column.
Solvent system	:	Various solvent systems depending on materials
Detection : Fractions we		Fractions were examined by TLC technique in the same
		manner as described in section 2.1.1

2.1.3 Gel filtration chromatography

Gel Filter	:	Sephadex LH-20
Packing method	:	Gel filter was suspended in the eluent and left standing
		to swell for 24 hours prior to use. It was then poured
		into the column and allowed to set tightly.
Sample loading	: /	The sample was dissolved in a small volume of the
		eluent and then applied gently on top of the column.
Detection	:	Fractions were examined by TLC technique in the same
		manner as described in section 2.1.1
Solvent system	:	CH ₂ Cl ₂ -MeOH (1:1)

 CH_2Cl_2 -MeOH (1:4)

2.2 Crystallization technique

The compounds were crystallized from various solvents. Each compound was dissolve in selected solvent until saturated and left standing at room temperature until amorphous powder or crystals were formed.

2.3 Spectroscopy

2.3.1 Ultraviolet (UV) absorption spectra

UV spectra (in DMSO) were obtained on a Shimadzu UV-1601 spectrophotometer (Scientific Equipment Center, Prince of Songkla University).

2.3.2 Infrared (IR) absorption spectra

IR spectra (KBr disc and thin film) were recorded on a Perkin Elmer FT-IR1760X spectrophotometer (Scientific and Technological Research Equipment Center, Chulalongkorn University).

2.3.3 Mass spectra (MS)

Electron impact mass spectra (EIMS) were obtained on a Thermo Finnigan MAT 95 XL mass spectrometer (Scientific Equipment Center, Prince of Songkla University).

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

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

The ¹H-NMR (500 MHz) and ¹³C-NMR (125 MHz) spectra were obtained on an INOVA-500 500 MHz NMR spectrometer (Scientific and Technological Research Equipment Center, Chulalongkorn University).

Solvents for NMR spectra were deuterated chloroform (CDCl₃) and deuterated dimethylsulfoxide (DMSO- d_6). Chemical shifts were reported in ppm scale using the chemical shift of the solvent as the reference signal.

2.4 Physical property

2.4.1 Melting points

Melting points were obtained on a Fisher-John melting point apparatus (Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

2.5 Solvents

Throughout this work, all organic solvents used in the extraction and isolation procedure were of commercial grade and were redistilled prior to use.

3. Extraction procedure

The dried aerial part of *Sauropus bacciformis* (1.9 kg) was ground and extracted with hexane (7 × 6 L) in a percolator to give, on evaporation, 95.00 g of crude hexane extract (5.00% of dried weight). The remaining marc was air-dried and consequently extracted with CH_2Cl_2 (7 × 6 L), EtOAc (7 × 6 L) and MeOH (7 × 6 L) in the same manner to give, on evaporation, 17.20 g of crude CH_2Cl_2 extract (0.91% of dried weight), 11.11 g of crude EtOAc extract (0.58% of dried weight) and 472.00 g of crude MeOH extract (24.84% of dried weight), respectively.



Dried Sauropus bacciformis aerial part (1.9 kg)

Scheme 2. Extraction of Sauropus bacciformis aerial part

4. Isolation procedure

4.1 Fractionation of the hexane extract

The hexane extract (15.00 g) was subjected to a silica gel column chromatography (450 g, 10×15 cm) eluted with hexane-acetone (49:1). Two hundred and forty-nine 30-ml fractions were collected and combined according to their TLC patterns into eleven major fractions (H01-H11) as shown in **Table 4.**

Fraction	Number of eluates	Weight (g)
H01	1-16	0.38
H02	17-55	2.43
H03	56-62	0.39
H04	63-72	0.62
H05	73-83	0.52
H06	84-106	1.56
H07	107-129	1.13
H08	130-167	0.75
H09	168-215	0.82
H10	216-249	1.67
H11	MeOH eluate	4.23

Table 4. Combined fractions from the hexane extract

4.1.1 Isolation of compound SB1

Fraction H03 (0.39 g), which showed one main spot on TLC plate, was further separated by gel filtration chromatography using a Sephadex LH-20 column (1.5×82 cm) eluted with CH₂Cl₂-MeOH (1:1). Twenty-four 2-ml fractions were collected and combined based on their TLC patterns into three major fractions (H12-H14). Fraction H13 (78.6 mg) was crystallized in MeOH to give compound SB1 as colorless needles (6.8 mg, 0.0004% yield). Fraction H04 (0.62 g), was subjected to a silica gel column chromatography (25 g, 2×28 cm) eluted with hexane-acetone (97:3), to give forty-six fractions (5 ml each). These fractions were combined based on their TLC pattern to afford four fractions (H15-H18). Fraction H16 (108.4 mg) was futher fractionated by gel filtration chromatography using a Sephadex LH-20 column (1.5×82 cm) eluted with CH₂Cl₂-MeOH (1:1) to give three combined

fractions (H19-H21). Fraction H20 (34.5 mg) was purified by crystallization in MeOH to give an additional amount of compound SB1 (2.9 mg, 0.0002% yield).

4.1.2 Isolation of compound SB2

Fraction H05 (0.52 g) was chromatographed on a silica gel column (20 g, 2×22 cm) eluted with hexane-acetone (97:3). Twenty-six fractions (5 ml each) were combined based on their similar TLC pattern into five fractions (H22-H26). Fraction H25 (42.2 mg), which gave one pink-violet spot on TLC plate, was recrystallized in MeOH to give compound SB2 as white amorphous powder (29.0 mg, 0.002% yield)

4.1.3 Isolation of compound SB3

Fraction H07 (1.13 g) was separated on a silica gel column (50 g, 3×20 cm) eluted with hexane-acetone (9:1) to give fifty-nine fractions (5 ml each). Similarity of TLC pattern led to combination of these fractions into four combined fractions (H27-H30). Fraction H29 (231.8 mg), which gave one purple spot on TLC plate, was recrystallized in MeOH to give compound SB3 as colorless needles (72.5 mg, 0.004% yield).

4.1.4 Isolation of compound SB4

Fraction H09 (0.82 g) was separated on a silica gel column (30 g, 3×15 cm) eluted with hexane-acetone (22:3). Sixty-seven fractions (5 ml each) were collected and combined based on their TLC pattern to give four fractions (H31-H34). Fraction H33 (250.4 mg) was fractionated on a silica gel column (20 g, 2×22 cm) eluted with hexane-acetone (41:9) to give four combined fractions (H35-H38). Fraction H36 (117.7 mg) was further separated by gel filtration chromatography using a Sephadex LH-20 column (1.5 × 82 cm) eluted with CH₂Cl₂-MeOH (1:1) to give three combined fractions (H39-H41). Fraction H40 (53.2 mg), which showed one pink-violet spot on TLC plate, was further purified by crystallization in methanol. White amorphous powder (9.3 mg, 0.001% yield) was obtained and designated as compound SB4.



Sheme 3. Isolation of the hexane extract from Sauropus bacciformis aerial part

4.2 Fractionation of the EtOAc extract

The EtOAc extract (11.11 g) was subjected to a silica gel column (350 g, 10×10 cm) eluted with CH₂Cl₂-acetone (7:3). One hundred and forty-seven 30-ml fractions were collected and combined according to their TLC patterns into seven major fractions (E01-E07) as shown in **Table 5.**

Fraction	Number of eluates	Weight (g)
E01	1-6	0.63
E02	7-15	0.41
E03	16-36	0.35
E04	37-93	0.41
E05	94-119	0.42
E06	120-147	1.46
E07	MeOH eluate	7.33

Table 5. Combined fractions from the EtOAc extract

4.2.1 Isolation of compound SB5

Fraction E06 (1.46 g), was separated on a silica gel column (70 g, 3×29 cm) eluted with CH₂Cl₂-acetone (2:3) to give seventy-five 2-ml fractions (10 ml each), which were then combined according to their TLC patterns into five fractions (E08-E12). Fraction E11 (167.5 mg), which exhibited one yellow spot when detected with 10% ethanolic sulfuric acid, was separated by gel filtration chromatography using a Sephadex LH-20 column (1.5 × 82 cm), with CH₂Cl₂-MeOH (1:4) as the eluent, to yield compound SB5 as yellowish amorphous powder (26.4 mg, 0.001% yield).

Compound SB5 was tested with Shinoda's reagent (0.5 ml HCl + Mg ribbon). Positive result (orange color bubble) was obtained.



Sheme 4. Isolation of the EtOAc extract from Sauropus bacciformis aerial part

5.1 Compound SB1

Appearance	: Colorless needles
Solubility	: Soluble in hexane and CH ₂ Cl ₂
Melting point	: 263-264 °C

IR v_{max} (KBr disc) cm⁻¹ (**Figure 6**, page 116)

: 2925, 2868, 2848, 1715, 1462, 1389, 1363, 1073, 1045 and 794

EIMS m/z (% relative intensity) (Figure 7, page 116)

: 426 (M⁺, 75), 411 (27), 341 (15), 302 (48), 273 (80), 246 (49),

205 (76), 125 (100) and 109 (93)

¹H-NMR (δ ppm, 300 MHz, CDCl₃) (**Figure 8**, page 117)

: 0.70 (3H, s), 0.85 (3H, s), 0.86 (3H, d, J = 6.0 Hz), 0.93 (3H, s), 0.98 (6H, s), 1.03 (3H, s), 1.16 (3H, s), 1.26-1.75 (18H, m), 1.35 (1H, dd, J = 9.3, 4.8 Hz), 1.48 (1H, dd, J = 6.0, 3.0 Hz), 1.66 (1H, dd, J = 13.0, 5.7 Hz), 1.91-1.98 (2H, m), 2.21-2.36 (2H, m) and 2.27 (1H, dt, J = 18.6, 6.9 Hz)

¹³C-NMR (δ ppm, 75 MHz, CDCl₃) (**Figure 9**, page 118)

: 6.8, 14.7, 17.9, 18.2, 18.6, 20.3, 22.3, 28.2, 30.0, 30.5, 31.8,
32.1, 32.4, 32.8, 35.0, 35.4, 35.6, 36.0, 37.5, 38.3, 39.3, 39.7,
41.3, 41.5, 42.1, 42.8, 53.1, 58.2, 59.5 and 213.1

5.2 Compound SB2

Appearance	: White amorphous powder
Solubility	: Soluble in hexane and CH ₂ Cl ₂
Melting point	: 213-214 °C
IR υ _{max} (KBr disc) cm	n ⁻¹ (Figure 11 , page 120)
	: 3511, 2929, 2868, 2850, 1732, 1463, 1455, 1384, 1364, 1173
	and 738
EIMS m/z (% relative	e intensity) (Figure 12, page 120)
	: 426 (M ⁺ , 8), 411 (5), 393 (4), 274 (100), 259 (81), 245 (10),
	231 (22), 205 (14), 189 (13), 152 (24) and 134 (34)

¹H-NMR (δ ppm, 500 MHz, CDCl₃) (**Figure 13**, page 121)

: 0.76 (3H, s), 0.81 (3H, d, J = 6.5 Hz), 0.87 (3H, d, J = 6.5 Hz), 0.87 (3H, s), 0.90 (3H, s), 0.98 (3H, s), 1.02 (3H, s), 1.12 (3H, s), 1.31-1.38 (1H, m), 1.42-1.47 (2H, m), 1.42-1.52 (6H, m), 1.52-1.59 (6H, m), 1.64-1.74 (2H, m), 1.79 (1H, t, J = 3.0 Hz), 1.86-1.96 (2H, m), 1.89 (1H, dd, J = 3.7, 2.0 Hz), 1.95 (1H, dd, J = 3.5, 2.0 Hz), 2.06 (1H, ddd, J = 12.4, 5.2, 3.5 Hz), 3.45 (1H, br t, J = 2.5 Hz) and 5.59 (1H, dd, J = 3.5, 2.0 Hz)

¹³C-NMR (δ ppm, 125 MHz, CDCl₃) (Figure 14, page 121)

: 15.0, 15.7, 16.1, 17.8, 18.0, 19.9, 21.9, 22.9, 24.0, 25.5, 27.8, 28.3, 29.0, 29.0, 29.1, 30.8, 34.1, 34.8, 35.4, 38.6, 39.3, 40.8, 42.8, 44.2, 50.2, 51.7, 60.0, 76.3, 122.0 and 141.9

5.3 Compound SB3

Appearance	: Colorless needles
Solubility	: Soluble in hexane and CH ₂ Cl ₂
IR v _{max} (KBr dise	c) cm ⁻¹ (Figure 18 , page 126)
	: 3418, <mark>2935, 2867, 2850</mark> , 1716, 1667, 1463, 1381, 1332, 1049,
	1022, 800 and 738
¹ H-NMR (δ ppm	, 300 MHz, CDCl ₃) (Figure 19 , page 126)
	: 0.66 (3H, <i>s</i>), 0.67 (3H, <i>d</i> , <i>J</i> = 5.4 Hz), 0.80 (3H, <i>t</i> , <i>J</i> = 6.3 Hz),
	0.90 (3H, d, J = 6.3 Hz), 1.00 (3H, d, J = 6.9 Hz), 1.23 (3H,
	s), 3.47 (1H, m), 4.99 (1H, dd, J = 15.3, 8.4 Hz), 5.13 (1H, dd,
	J = 15.3, 8.4 Hz) and 5.33 (1H, br s)
¹³ C-NMR (δ ppn	n, 75 MHz, CDCl ₃) (Figure 20 , page 127)
	: 11.9, 12.0, 12.0, 12.2, 18.8, 19.0, 19.0, 19.4, 19.8, 21.1, 21.2,
	23.1, 24.3, 25.4, 26.1, 28.2, 28.9, 29.2, 31.7, 31.9, 34.0, 36.1,
	36.5, 37.3, 39.7, 39.8, 40.5, 42.2, 42.3, 45.9, 50.1, 51.2, 56.0,
	56.1, 56.8, 56.9, 71.8, 121.7, 129.3, 138.3 and 140.8

5.4 Compound SB4

Appearance	: White amorphous powde
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- Solubility : Soluble in CH₂Cl₂
- Melting point $: 228-229 \degree C$
- IR v_{max} (KBr disc) cm⁻¹ (Figure 22, page 128)
 - : 3418, 2950, 2873, 2855, 1713, 1641, 1456, 1414, 1379, 1357,

1345, 1110, 883 and 739

EIMS m/z (% relative intensity) (Figure 23, page 129)

: 440 (M⁺, 4), 422 (17), 407 (5), 327 (8), 285 (5), 229(18), 203

(12), 189 (13), 175 (9), 149 (13), 135 (16) and 114 (100)

¹H-NMR (δ ppm, 500 MHz, CDCl₃) (**Figure 24**, page 129)

: 0.78 (3H, *s*), 0.82 (3H, *s*), 0.96 (3H, *s*), 1.02 (3H, *s*), 1.04 (6H, *s*), 1.06-1.23 (4H, *m*), 1.33 (1H, *dd*, J = 10.0, 5.0 Hz), 1.35 (1H, *dd*, J = 4.5, 2.0 Hz), 1.46 (1H, *dd*, J = 4.5, 2.5 Hz), 1.48-1.53 (8H, *m*), 1.63-1.71 (1H, *m*), 1.64 (2H, *dd*, J = 6.2, 4.5 Hz), 1.79-1.93 (2H, *m*), 2.20 (1H, *dd*, J = 14.2, 4.0 Hz), 2.98 (1H, *dd*, J = 14.2, 8.0 Hz), 2.36 (1H, *td*, J = 11.0, 5.5 Hz), 3.88 (1H, *dd*, J = 8.0, 4.0 Hz), 4.54 (1H, *dd*, J = 2.5, 1.0 Hz), and 4.66 (1H, *d*, J = 2.5 Hz)

¹³C-NMR (δ ppm, 125 MHz, CDCl₃) (Figure 25, page 130)

: 11.8, 14.4, 15.9, 18.0, 19.3, 19.6, 19.8, 23.0, 25.1, 27.5, 27.9, 29.8, 32.9, 35.5, 37.9, 40.0, 41.1, 42.9, 42.9, 42.9, 45.1, 47.1, 47.9, 48.2, 50.7, 51.3, 79.6, 109.5, 150.7 and 215.7

5.5 Compound SB5

Appearance	: Yellowish amorphous powder
Solubility	: Soluble in DMSO
Melting point	: 176-177 °C
EIMS m/z (% relative	e intensity) (Figure 31, page 135)

: 478 (M⁺, 1), 441 (2), 361 (6), 316 (100), 286 (11), 273 (12),

259 (3), 168 (7), 149 (7), 137 (14), 111 (4) and 73 (8)

UV λ max nm (log ε), in DMSO (Figure 29, page 134)

: 260 (3.88), 309 (3.51) and 372 (3.86)

IR v_{max} (KBr disc) cm⁻¹ (**Figure 30**, page 135)

: 3329, 2924, 2854, 1656, 1622, 1603, 1506, 1208 and 1071

¹H-NMR (δ ppm, 500 MHz, DMSO-*d*₆) (**Figure 32**, page 136)

: 3.86 (3H, OMe, *s*), 6.35 (1H, *d*, J = 2.5 Hz), 6.77 (1H, *d*, J = 2.5 Hz), 7.25 (1H, *d*, J = 9.0 Hz), 7.66 (1H, *dd*, J = 9.0, 2.0 Hz), 7.74 (1H, *d*, J = 2.0 Hz), 3.17 (1H, *dd*, J = 9.0, 3.0 Hz), 3.29 (1H, *dd*, J = 9.5, 5.0 Hz), 3.33 (1H, *s*), 3.37 (1H, *dt*, J = 7.9, 1.5 Hz), 3.48 (1H, *dd*, J = 12.0, 6.0 Hz), 3.73 (1H, *dd*, J = 11.7, 5.5 Hz) and 4.84 (1H, *d*, J = 7.5 Hz)

¹³C-NMR (δ ppm, 125 MHz, DMSO-*d*₆) (Figure 34, page 137)

: 56.0, 92.0, 97.5, 104.1, 115.2, 115.8, 119.6, 125.0, 136.7, 146.3, 146.4, 146.9, 156.2, 160.3, 165.0, 176.2, 60.7, 69.8, 73.3, 75.9, 77.3 and 101.4

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CHAPTER IV

RESULTS AND DISCUSSION

Chromatographic separation of the hexane and EtOAc extracts of *Sauropus bacciformis* aerial part led to the isolation of five chemical constituents. The identification and structure elucidation of these compounds were based on analysis of their spectroscopic data and comparison with the literature. The details can be discussed as follows.

1. Identification of compound SB1

Compound SB1 was crystallized as colorless needles from methanol (9.7 mg, 0.001% yield). This compound gave purple color to Liebermann-Burchard reagent, suggesting that it is a triterpenoid. Its IR absorption band (**Figure 6**) at 1715 cm⁻¹ was indicative of the presence of keto carbonyl group (C=O stretching). Its EIMS (**Figure** 7) exhibited the molecular ion peak at m/z 426, indicating the molecular formula of $C_{30}H_{50}O$. The index of hydrogen deficiency for this compound, which equals six, and the remaining index of one is attributed to the unsaturation in the keto carbonyl group in the structure.

The ¹H-NMR spectrum (**Figure 8**) exhibited the signals due to one doublet of secondary methyl at δ 0.86 ppm (3H, *J* = 6.0 Hz, H-23), and seven singlets of tertiary methyls at δ 0.70 (3H, H-24), 0.85 (3H, H-25), 0.93 (3H, H-29), 0.98 (6H, H-26, H-30), 1.03 (3H, H-27) and 1.16 ppm (3H, H-28).

The ¹³C-NMR spectrum (**Figure 9**) showed 30 carbon peaks, supportive of a triterpenoid structure. These peaks were classified, according to DEPT experiment (**Figure 10**), into those of eight methyl carbons at δ 6.8 (C-23), 14.7 (C-24), 17.9 (C-25), 18.6 (C 27), 20.3 (C-26), 31.8 (C-30), 32.1 (C-28) and 35.0 ppm (C-29), eleven methylene carbons at δ 18.2 (C-7), 22.3 (C-1), 30.5 (C-12), 32.4 (C-15), 32.8 (C-21), 35.4 (C-19), 35.6 (C-11), 36.0 (C-16), 39.3 (C-22), 41.3 (C-6) and 41.5 ppm (C-2), four methine carbons at δ 42.8 (C-18), 53.1 (C-8), 58.2 (C-4) and 59.5 ppm (C-10), and seven quaternary carbons at δ 28.2 (C-20), 30.0 (C-17), 37.5 (C-9), 38.3 (C-14), 39.7 (C-13), 42.1 (C-5) and 213.1 ppm (C-3). The last signal represented the keto carbonyl group in the molecule.

The mass fragment peaks at m/z 273, 302 and 341 were the results of cleavage at different positions across the skeleton, which have been shown to have the keto group on the ring A (**Scheme 5**) (Ogunkoya, 1981).

The ¹³C-NMR data of compound SB1 (**Table 6**) were found to be in full agreement with those values previously reported for friedelin (Akihisa *et al.*, 1992), a friedelane-type triterpenoid with 3-keto substituent.



Scheme 5. Mass fragmentation of compound SB1



Friedelin was previously isolated from 20 species out of 13 euphorbiaceous genera. However, this is the first report of its occurrence in the genus *Sauropus*.

Friedelin has been reported as possessing cytotoxic (Zheng, 1994; Chilpa *et al.*, 2004), anti-inflammatory (Shimizu and Tomoo, 1994) and diuretic activities (Rizvi *et al.*, 1980a).



Position	Compour	nd SB1	Friedelin
	δH (ppm)	δC (ppm)	δC (ppm)
1	1.91-1.98 (<i>m</i>)	22.3	22.3
2	2.21-2.36 (<i>m</i>)	41.5	41.5
3	-	213.1	213.2
4	2.27 (dt, J = 18.6, 6.9 Hz)	58.2	58.2
5	-	42.1	42.1
6	1.26-1.75 (<i>m</i>)	41.3	41.3
7	1.26-1.75 (m)	18.2	18.2
8	1.35 (dd, J = 9.3, 4.8 Hz)	53.1	53.1
9	- / / =	37.5	37.4
10	1.48 (dd, J = 6.0, 3.0 Hz)	59.5	59.4
11	1.26-1.75 (<i>m</i>)	35.6	35.6
12	1.26-1.75 (m)	30.5	30.5
13	- / 2014	39.7	39.7
14	-	38.3	38.3
15	1.26-1.75 (<i>m</i>)	32.4	32.4
16	1.26-1.75 (<i>m</i>)	36.0	36.0
17	Q -	30.0	30.0
18	1.66 (<i>dd</i> , <i>J</i> = 13.0, 5.7 Hz)	42.8	42.8
19	1.26-1.75 (<i>m</i>)	35.4	35.3
20	- 0 _	28.2	28.1
21	1.26-1.75 (<i>m</i>)	32.8	32.7
22	1.26-1.75 (<i>m</i>)	39.3	39.2
23	0.86 (d, J = 6.0 Hz)	6.8	6.8
24	0.70 (s)	14.7	14.6
25	0.85 (s)	17.9	17.9
26	0.98 (s)	20.3	20.2
27	1.03 (s)	18.6	18.6
28	1.16 (s)	32.1	32.1
29	0.93 (s)	35.0	35.0
30	0.98 (s)	31.8	31.8

Table 6. ¹H-NMR data and comparision of the ¹³C-NMR assignments of compound SB1 and friedelin (in CDCl₃)

2. Identification of compound SB2

Compound SB2 was obtained as white amorphous powder (29.0 mg, 0.002% yield). The compound gave purple color to Liebermann-Burchard reagent, suggesting that it is a triterpenoid. The IR spectrum (**Figure 11**) exhibited absorption bands at 3511 (OH stretching) and 1173 (C-O stretching) cm⁻¹, suggesting the presence of hydroxyl substituent. Its EIMS (**Figure 12**) displayed a molecular ion peak at m/z 426 which corresponded to the molecular formula of $C_{30}H_{50}O$. The base peak at m/z 274 should be due to the ion resulting directly from retro-Diels-Alder fission of ring B, in which the charge remains with the monoalkene instead of the diene. This is suggestive of a C-5 unsaturated pentacyclic triterpenoid in which there is no substitution in ring C, D, or E and that the compound has a skeleton structure of the adianane type (Ogunkoya, 1981). The peaks at m/z 259 (274-CH₃) and 231 (274-Pr) for those with isopropyl group in ring E, and the [M-CH₃]⁺ and [M-CH₃-H₂O]⁺ peaks at m/z 411 and 393, respectively, were also observed (**Scheme 6**).

The ¹H-NMR spectrum (**Figure 13**) exhibited signals due to two doublet of secondary methyls at δ 0.81 (3H, J = 6.5 Hz, H-30), and δ 0.87 ppm (3H, J = 6.5 Hz, H-29), and six tertiary methyls singlets at δ 0.76 (3H, H-28), 0.87 (3H, H-25), 0.90 (3H, H-27), 0.98 (3H, H-26), 1.02 (3H, H-23) and 1.12 ppm (3H, H-24). The proton signal at δ 3.45 ppm (1H, *br t*, J = 2.5 Hz, H-3) confirmed the presence of hydroxyl substituent. The most downfield signal at δ 5.59 ppm (1H, *dd*, J = 3.5, 2.0 Hz), represents H-6 of a C-6 unsaturated triterpenoid.

The ¹³C-NMR spectrum (**Figure 14**) showed 30 carbon signals, supportive of a triterpenoid structure. The DEPT (**Figure 15**) and HMQC (**Figure 16**) experiments were performed to differentiate these signals into eight methyl carbons at δ 15.0 (C-27), 15.7 (C-26), 16.1 (C-28), 17.8 (C-25), 21.9 (C-29), 22.9 (C-30), 25.5 (C-24) and 29.0 ppm (C-23), nine methylene carbons at δ 18.0 (C-1), 19.9 (C-19), 24.0 (C-7), 27.8 (C-2), 28.3 (C-20), 29.0 (C-12), 29.1 (C-15), 34.1 (C-11) and 35.4 ppm (C-16), seven methine carbons at δ 30.8 (C-22), 44.2 (C-8), 50.2 (C-10), 51.7 (C-18), 60.0 (C-21), 76.3 (C-3) and 122.0 ppm (C-6), and six quaternary carbons at δ 34.8 (C-9), 38.6 (C-13), 39.3 (C-14), 40.8 (C-4), 42.8 (C-17) and 141.9 ppm (C-5). The downfield carbon signals at δ 122.0 and 141.9 ppm represent the characteristic double bond between C-5 and C-6 in the adianane skeleton (Ahmad and Rahman, 1994). The HMBC experiment (**Figure 17**) was useful in confirming the structure of compound SB2. The proton signal at δ 3.45 ppm (H-3) displayed three-bond correlations with C-5 (δ 141.9 ppm) and C-1 (δ 18.0) (**Figure 17a**). HMBC correlations of H-23 (δ 1.02) and H-24 methyl signals (δ 1.12) with C-3 (δ 76.3 ppm) (**Figure 17b**), confirmed the presence of hydroxyl substituent at this carbon, while the signal of the olefinic H-6 (δ 5.59) showed three-bond correlations with C-10 (δ 50.2), C-8 (δ 44.2) and C-4 (δ 40.8 ppm) (**Figure 17c**), confirming the position of double bond as between C-5 and C-6.

Compound SB2 was therefore proven to be a C-5 unsaturated triterpenoid of the adianane type. Comparison of the ¹³C-NMR data of compound SB2 with those reported for simiarenol (Tanaka *et al*, 1989), a known adian-5-ene, previously isolated from *Euphorbia supina*, indicated the structures of both compounds to be identical. The ¹H and ¹³C-NMR assignments and HMBC (correlation with ¹³C) of compound SB2 and the reported ¹³C-NMR data of simiarenol are shown in **Table 7**.



Simiarenol

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย



Scheme 6. Mass fragmentation of compound SB2

Position	Compound SB2		Simiarenol	HMBC
	δH (ppm)	δC (ppm)	δC (ppm)	correlation with ¹³ C
1	1.42-1.47 (<i>m</i>)	18.0	18.1	C-2*, C-3, C-10*
2	1.64-1.74 (<i>m</i>)	27.8	27.8	C-1*
3	3.45 (<i>br t</i> , <i>J</i> = 2.5 Hz)	76.3	76.4	C-1, C-5
4	-	40.8	41.0	_
5	-	141.9	142.0	_
6	5.59 (dd, J = 3.5, 2.0 Hz)	122.0	122.0	C-4, C-7*, C-8, C-10
7	1.86-1.96 (<i>m</i>)	24.0	24.0	C-5, C-6*, C-8*
8	1.89 (dd, J = 3.7, 2.0 Hz)	44.2	44.3	C-7*
9	-	34.8	34.8	_
10	1.95 (<i>dd</i> , <i>J</i> = 3.5, 2.0 Hz)	50.2	50.0	C-5*, C-6, C-8
11	1.42-1.52 (m)	34.1	34.2	C-8, C-9*, C-10, C-12*, C-13
12	1.42-1.52 (<i>m</i>)	29.0	28.9	C-27
13	- / / 3	38.6	38.6	_
14	-	39.3	40.3	_
15	1.52-1.59 (m)	29.1	29.1	C-13, C-14*, C-17
16	1.52-1.59 (<i>m</i>)	35.4	35.4	C-14, C-17*
17	E.	42.8	42.4	-
18	1.79 (t, J = 3.0 Hz)	51.7	51.8	C-17*, C-19*
19	1.42-1.52 (<i>m</i>)	19.9	19.9	C-18*
20	1.52-1.59 (<i>m</i>)	28.3	28.3	C-17, C-19*
21	2.06 (<i>ddd</i> , <i>J</i> = 12.4, 5.2, 3.5 Hz)	60.0	60.0	C-20*, C-22*
22	1.31-1.38 (<i>m</i>)	30.8	30.8	C-17, C-20
23	1.02 (s)	29.0	29.1	C-3, C-5
24	1.12 (s)	25.5	25.5	C-3, C-5
25	9 0.87 (<i>s</i>)	17.8	17.9	C-8, C-9*, C-10, C-11
26	0.98 (s)	15.7	15.8	C-8, C-14*, C-15
27	0.90 (s)	15.0	15.0	C-12, C-13*, C-14, C-18
28	0.76 (<i>s</i>)	16.1	16.1	C-16, C-17*, C-18, C-21
29	0.87 (<i>d</i> , <i>J</i> = 6.5 Hz)	21.9	21.9	C-21
30	0.81 (<i>d</i> , <i>J</i> = 6.5 Hz)	22.9	22.9	C-21
		•	•	

Table 7. The ¹H and ¹³C-NMR data, HMBC correlation of compound SB2 and comparison of the ¹³C-NMR assignments with those similarenol (in CDCl₃)

* Two-bond correlation

3. Identification of compound SB3

Compound SB3 was recrystallized as colorless needles from methanol (72.5 mg, 0.004% yield). This compound gave green color to Liebermann-Burchard reagent, suggesting the presence of the steroid nucleus. The IR spectrum (**Figure 18**) exhibited absorption bands at 3418 (OH stretching), 1049 and 1022 (C-O stretching) cm⁻¹, suggesting the presence of hydroxyl substituent .

The ¹H-NMR spectrum (**Figure 19**) gave evidences which suggested this compound is a mixture of β -sitosterol (SB3B) and stigmasterol (SB3S). The olefinic proton at δ 5.33 ppm (2H, *d*, *J* = 4.5 Hz) was assignable to H-6 of both β -sitosterol and stigmasterol, while two signals at δ 4.99 (1H, *dd*, *J* = 15.3, 8.4 Hz) and 5.13 ppm (1H, *dd*, *J* = 15.3, 8.4 Hz) were assigned as olefinic protons at H-22 and H-23 of stigmasterol, respectively. The ratio of SB3B and SB3S in the mixture was deduced from the integration value between H-6 and H-22 or H-23 to be 1:0.5:0.4. The multiplet signal at δ 3.47 ppm was attributable to the methine proton of hydroxyl substituted position 3 of both β -sitosterol and stigmasterol. The ¹H-NMR spectrum of both β -sitosterol and stigmasterol displayed signals due to one primary methyl at δ 0.80 ppm (3H, *t*, *J* = 6.3 Hz, H-29), three secondary methyls doublets at δ 0.67 (3H, *J* = 5.4 Hz, H-21), 0.90 (3H, *J* = 6.3 Hz, H-27) and 1.00 ppm (3H, *J* = 6.9 Hz, H-26), and two tertiary methyls singlets at δ 0.66 (3H, H-18) and 1.23 ppm (3H, H-19), suggestive of the steroidal skeleton (De-Eknamkul and Potduang, 2003).

The ¹³C-NMR (**Figure 20**) and DEPT spectrum (**Figure 21**) showed 29 carbon signals easily assigned to β -sitosterol. However, four olefinic carbon signals were observed at δ 140.8, 138.3, 129.3 and 121.7 ppm. The two signals at δ 140.8 and 121.7 ppm were assignable to C-5 and C-6 of both β -sitosterol and stigmasterol. The other two signals which resonated at δ 138.3 and 129.3 ppm were due to C-22 and C-23 of stigmasterol, respectively. The carbon signal at δ 71.8 ppm represents the oxygenated C-3 of both β -sitosterol and stigmasterol.

Comparison of the ¹³C-NMR assignment of compound SB3 (a mixture of SB3B and SB3S) with those previously reported data for a mixture of β -sitosterol and stigmasterol (De Eknamkul and Potduang, 2003), is shown in **Table 8**.



 β -Sitosterol and stigmasterol were the most common phytosterols in plant kingdom (Li, Beveridge and Drover, 2007). β -Sitosterol has been reported as possessing antimicrobial (Ajaiyeoba *et al.*, 2003), antihyperglycemic (Ivorra *et al.*, 1988), anti-inflammatory and antipyretic activities (Gupta *et al.*, 1980).



Position	δ C (ppm)				
	SB3B	SB3S	SB3S <i>β</i> -sitosterol		
1	37.3	37.3	37.2	37.2	
2	31.7	31.7	31.6	31.6	
3	71.8	71.8	71.8	71.8	
4	42.2	42.3	42.2	42.3	
5	140.8	140.8	140.7	140.7	
6	121.7	121.7	121.7	121.7	
7	31.9	31.9	31.9	31.9	
8	31.9	31.9	31.9	31.9	
9	50.1	50.1	50.1	50.1	
10	36.5	36.5	36.5	36.5	
11	21.1	21.1	21.1	21.1	
12	39.8	39.7	39.7	39.7	
13	42.3	42.3	42.3	42.3	
14	56.8	56.9	56.7	56.8	
15	24.3	24.3	24.3	24.3	
16	28.2	28.9	28.2	28.9	
17	56.1	56.0	56.0	55.9	
18	11.9	12.0	11.8 12.0		
19	19.4	19.4	19.4	19.4	
20	36.1	40.5	36.1	36.1 40.5	
21	18.8	21.1	18.8 21.1		
22	34.0	138.3	33.9	138.3	
23	26.1	129.3	26.0	129.2	
24	45.9	51.2	45.8	51.2	
25	29.2	31.9	29.1 31.9		
26	19.8	21.2	19.8 21.2		
27	19.0	19.0	19.0	19.0 19.0	
28	23.1	25.4	23.0	25.4	
29	12.0	12.2	12.0 12.2		

Table 8. Comparison of the ¹³C-NMR assignment of compound SB3 (a mixture of SB3B and SB3S, β -sitosterol and stigmasterol (in CDCl₃)

4. Identification of compound SB4

Compound SB4 was crystallized as white amorphous powder from methanol (9.3 mg, 0.001% yield). This compound gave purple color to Liebermann Burchard reagent, suggesting that it is a triterpenoid. Its IR spectrum (**Figure 22**) exhibited absorption bands at 3418 (OH stretching), 1110 (C-O stretching), suggesting the presence of hydroxyl substituent, and displayed keto carbonyl absorption (C=O stretching) at 1713 cm⁻¹. Its EIMS (**Figure 23**) showed a molecular ion peak at m/z 440 which corresponded to the molecular formula of $C_{30}H_{48}O_2$. The mass fragment peaks at m/z 285, 229, 203 and 189 were the results of cleavage at different positions across the lupane skeleton (Hui and Fung, 1969) as shown in **Scheme 7**.

The ¹H-NMR spectrum (**Figure 24**) showed signals due to seven tertiary methyls singlets at δ 0.78 (3H, H-28), 0.82 (3H, H-25), 0.96 (3H, H-27), 1.02 (3H, H-24), 1.04 (6H, H-23, H-26) and 1.66 ppm (3H, *br s*, H-30). The proton signal at δ 3.88 ppm (1H, *dd*, *J* = 8.0, 4.0 Hz, H-1) confirmed the presence of hydroxyl group substituent. The most downfield signals at δ 4.54 (1H, *dd*, *J* = 2.5, 1.0 Hz) and δ 4.66 ppm (1H, *d*, *J* = 2.5 Hz) could be assigned as those of exomethylene protons at position 29.

The ¹³C-NMR spectrum (**Figure 25**) showed 30 carbon signals supportive of a triterpenoid structure. These peaks were classified, according to DEPT (**Figure 26**) and HMQC (**Figure 27**) experiments, into those of seven methyl carbons at δ 11.8 (C-25), 14.4 (C-27), 15.9 (C-26), 18.0 (C-28), 19.3 (C-30), 19.8 (C-24) and 27.9 ppm (C-23), ten methylene carbons at δ 19.6 (C-6), 23.0 (C-11), 25.1 (C-12), 27.5 (C-15), 29.8 (C-21), 32.9 (C-7), 35.5 (C-16), 40.0 (C-22), 45.1 (C-2) and 109.5 ppm (C-29), six methine carbons at δ 37.9 (C-13), 47.9 (C-19), 48.2 (C-18), 50.7 (C-9), 51.3 (C-5) and 79.6 ppm (C-1), seven quaternary carbons at δ 41.1 (C-8), 42.9 (C-10, C-14, C-17), 47.1 (C-4), 150.7 (C-20) and 215.7 ppm (C-3). The last signal represented keto carbonyl group in the molecule.

The HMBC experiment (**Figure 28**) was useful to confirm the structure of compound SB4. The proton signal at δ 3.88 ppm (H-1) displayed three-bond correlations with C-3 (δ 215.7) (**Figure 28a**), C-9 (δ 50.7) and C-25 (δ 11.8) (**Figure 28b**), confirming the presence of hydroxyl substituent at C-1. The proton signals at δ 1.02 (H-24), δ 1.04 (H-23) (**Figure 28c**), and δ 3.88 ppm (H-1) all exhibited three-bond correlations with C-3 (δ 215.7 ppm) (**Figure 28a**), confirming that the keto
carbonyl was at position 3. Correlations between both exomethylene protons at position 29 with C-30 (δ 19.3) and between H-30 methyl protons and C-19 (δ 47.9) could also be observed (**Figure 28b**).

The ¹³C-NMR data of compound SB4 were found to be in full agreement with those values previously reported for glochidonol (Ayer, Flanagan and Reffstrup, 1984), a lupane-type triterpenoid with 3-keto substituent, as shown in **Table 9**.



Glochidonol MW 440

Scheme 7. Mass fragmentation of compound SB4



Glochidonol was previously isolated from 13 species out of 3 euphorbiaceous genera. However, this is the first report of its occurrence in the genus *Sauropus*.

Glochidonol has been reported as possessing anti-tumor activity against three human tumor cell lines, including MCF-7 (breast adenocarcinoma), NCI-H-460 (non-small cell lung cancer) and SF-268 (CNS cancer) (Puapairoj *et al.*, 2005).



Position	Compound SB4		Glochidonol	HMBC
	δ H (ppm)	δC (ppm)	δC (ppm)	correlation with ¹³ C
1	3.88 (<i>dd</i> , <i>J</i> = 8.0, 4.0 Hz)	79.6	79.6	C-3, C-9, C-25
2a	2.20 (<i>dd</i> , <i>J</i> = 14.2, 4.0 Hz)	45.1	45.2	C-1*, C-3*, C-10
2b 3	2.98 (dd, J = 14.2, 8.0 Hz)	215.7	216.1	_
4	_	47.1	47.1	_
5	- 1 33 (dd I - 100 50 Hz)	51.3	51.4	
5	1.55 (uu, 5 = 10.0, 5.0 Hz)	51.5	51.4	C-1, C-0 , C-23, C-24, C-23
6	1.48-1.53 (<i>m</i>)	19.6	19.6	C-5*, C-7*, C-8, C-10
7	1.48-1.53 (<i>m</i>)	32.9	33.0	C-5, C-8*, C-14, C-26
8	-	41.1	41.2	_
9	1.46 (<i>dd</i> , <i>J</i> = 4.5, 2.5 Hz)	50.7	50.8	C-1, C-10*, C-25, C-26
10	-	42.9	43.0	-
11	1.48-1.53 (<i>m</i>)	23.0	23.0	C-8, C-10
12	1.48-1.53 (m)	25.1	25.2	C-11*, C-14
13	1.63-1.71 (<i>m</i>)	37.9	38.0	C-8, C-17, C-18*
14	- //	42.9	43.0	_
15	1.64 (dd, J = 6.2, 4.5 Hz)	27.5	27.5	C-16*, C-17
16	1.06-1.23 (<i>m</i>)	35.5	35.6	C-17*, C-28
17	-	42.9	43.0	_
18	1.35 (dd, J = 4.5, 2.0 Hz)	48.2	48.3	C-13*, C-16, C-17*, C-19*, C-20
19	2.36 (<i>td</i> , <i>J</i> = 11.0, 6.0 Hz)	47.9	48.0	C-13, C-18*, C-21*, C-29, C-30
20		150.7	150.7	-
21	1.79-1.93 (m)	29.8	29.8	C-18, C-19*, C-22*
22	1.06-1.23 (<i>m</i>)	40.0	40.4	C-16, C-17*, C-28
23	1.04 (s)	27.9	28.0	C-3, C-4*, C-5, C-24
24	1.02 (s)	19.8	19.9	C-3, C-4*, C-5, C-23
25	0.82 (s)	11.8	11.8	C-1, C-5, C-9, C-10*
26	1.04 (s)	15.9	16.0	C-7, C-8*, C-14
27	9 0.96 (s)	14.4	14.5	C-8, C-13, C-14*, C-15
28	0.78 (s)	18.0	18.1	C-16, C-17*, C-18, C-22
29	4.54 (<i>dd</i> , <i>J</i> = 2.5, 1.0 Hz) 4.66 (<i>d</i> , <i>J</i> = 2.5 Hz)	109.5	109.5	C-19, C-30
30	0.81 (d, J = 6.5 Hz)	19.3	19.3	C-19, C-20* and C-29

Table 9. The ¹H and ¹³C-NMR data, HMBC correlation of compound SB4 and comparison of the ¹³C-NMR assignments with those glochidonol (in CDCl₃)

* Two-bond correlation

5. Structure elucidation of compound SB5

Compound SB5 was obtained as yellowish amorphous powder (26.4 mg, 0.001% yield). This compound gave orange color bubble to Shinoda's reagent, suggesting that it is a flavonoid. The IR spectrum (**Figure 30**) displayed absorption bands at 3329 (OH stretching), 1071 (C-O stretching), suggesting the presence of hydroxyl substituent, at 1208 (CH₂ bending), 1506 (C=C aromatic), 1603 and 1622 (conjugated C=C), and at keto carbonyl absorption (C=O stretching) at 1656 cm⁻¹. Its EIMS (**Figure 31**) showed base peak at m/z 316 which suggested that SB5 has an aglycone of rhamnetin (Wagner and Chari, 1976). The UV absorption showed maxima (**Figure 29**) at 260, 309 and 372 nm [Band I 350-385, Band II 250-280 nm for flavonols (3-OH free)] and the presence of three carbon in the ¹³C-NMR spectrum (**Figure 34**) at δ 146.3 (C-2), δ 136.7 (C-3) and δ 176.2 ppm (C-4) [C-2 (δ 140.0-151.2), C-3 (δ 133.5-140.0), C-4 (δ 167.9-179.6 ppm) for flavonols] were indicative of a flavonol skeleton (Agrawal, 1989).

The ¹H-NMR spectrum (**Figure 32**) exhibited a methoxyl signal at δ 3.86 (3H, *s*), three hydroxyl signals including one chelated hydroxyl was observed at δ 12.39 (5-OH) and two hydroxyl groups at δ 8.95 and δ 9.65 ppm. The presence of two doublets at δ 6.35 (1H, *J* = 2.5 Hz) and δ 6.77 ppm (1H, *J* = 2.5 Hz) were assignable to the two *meta*-coupled H-6 and H-8 aromatic protons of ring A.

Substitution pattern on ring B was deduced from the *meta*-coupling of aromatic proton signals at δ 7.74 (1H, *d*, *J* = 2.0 Hz, H-2') and δ 7.66 ppm (1H, *dd*, *J* = 9.0, 2.0 Hz, H-6'), whereas the latter signal also *ortho*-coupled to a doublet at δ 7.25 ppm (1H, *J* = 9.0 Hz, H-5') indicated a *meta* or *para*-substituted for ring B. A set of proton signal of a sugar moiety [δ 3.17 (1H, *dd*, *J* = 9.0, 3.0 Hz, H-4"), 3.29 (1H, *dd*, *J* = 9.5, 5.0 Hz, H-3"), 3.33 (1H, *s*, H-2"), 3.37 (1H, *dt*, *J* = 7.9, 1.5 Hz, H-5"), 3.48 (1H, *dd*, *J* = 12.0, 6.0 Hz, H-6a"), 3.73 (1H, *dd*, *J* = 11.7, 5.5 Hz, H-6b"), 4.84 (1H, *d*, *J* = 7.5 Hz, H-1") were also observed. In addition, the presence of one anomeric proton signal at δ 4.84 (1H, *d*, *J* = 7.5 Hz, H-1") suggested that compound SB5 should be a monoglycoside of rhamnetin.

The ¹³C-NMR (**Figure 34**), DEPT (**Figure 35**) and HMQC (**Figure 36**) spectrum showed 22 carbon signals, supporting the assignment of this compound as a flavonoid glycoside, and exhibited 6 signals for sugar carbons including one anomeric carbon at δ 101.4 ppm (C-1"), in addition to fifteen carbons and one

methoxyl at δ 56.0 ppm (7-OMe) of rhamnetin nucleus. The anomeric carbon was attached to rhamnetin with *O*-linkage (δ 59-110 ppm for *O*-glycoside and δ 60-85 ppm for *C*-glycoside) (Agrawal, 1989).

To identify the sugar unit, Compound SB5 was hydrolysed with 10% H₂SO₄ acid to give aglycone and sugar. These sugar was identified as β -D-glucose by TLC analysis, comparison with sugar standards, and the ¹³C-NMR assignment with those previously reported data for β -D-glucose (Mahmoud *et al.*, 1989; Kojima *et al.*, 1990, Champavier *et al.*, 1999; Kim *et al.*, 2006; Mizushina *et al.*, 2006). The connectivity of these sugar protons and the assignment of ¹³C-NMR signals were determined by ¹H-¹H COSY (**Figure 33**) and HMQC (**Figure 36**) experiments, as shown in **Table 10**. The observed vicinal coupling constants of J = 7.5 Hz between the *trans* diaxial H-1" and H-2" suggested that H-1" (δ 4.84 ppm) was β -anomeric proton (Agrawal, 1992).

The HMBC experiment (**Table 10** and **Figure 37**) was useful to confirm the structure of compound SB5. The methoxyl signal at δ 3.86 ppm should be placed on ring A at C-7, as shown by the HMBC correlation with C-7 (δ 165.0 ppm) (**Figure 37a**), confirming that the rhamnetin nucleus. The anomeric proton signal at δ 4.84 ppm (d, J = 7.5 Hz, H-1") displayed three-bond correlation with C-4' (**Figure 37b**), suggesting that the β -D-glucose was at position 4'.

According to all information mentioned above, compound SB5 was proposed as a rhamnetin-4'-O- β -D-glucopyranoside. The ¹³C-NMR data of compound SB5 were found to be in full agreement with those values previously reported for rhamnetin (Wagner and Chari, 1976), as shown in **Table 10**.

On the basis of the above spectroscopic studies, Compound SB5 was thus identified as a new compound and has been given the name Rhamnetin-4'-O- β -D-glucopyranoside, the structure of which is shown below.



Rhamnetin-4'-*O*-β-D-glucopyranoside

Position	Compound SB5	5	Rhamnetin	НМВС
	δH (ppm)	δC (ppm)	δC (ppm)	correlation with ¹³ C
2	_	146.3	147.3	_
3	_	136.7	136.0	_
4	-	176.2	175.9	_
5		160.3	160.4	_
6	6.35 (<i>d</i> , <i>J</i> = 2.5 Hz)	97.5	97.4	C-8, C-10, C-5*, C-7*
7	-	165.0	164.9	-
8	6.77 (d , J = 2.5 Hz)	92.0	91.8	C-6, C-10, C-7*, C-9*
9	-	156.2	156.0	
10	-///	104.1	103.7	
1'	- / / 5	125.0	124.9	
2'	7.74 ($d, J = 2.0$ Hz)	115.2	115.2	C-2, C-1'*, C-6'
3'	- / / 5	146.4	145.0	_
4'	- / (146	146.9	147.8	_
5′	7.25 (d, J = 9.0 Hz)	115.8	115.6	C-1', C-3', C-4'*
6′	7.66 (dd, J = 9.0, 2.0 Hz)	119.6	120.1	C-2' and C-2
1"	4.84 (d, J = 7.5 Hz)	101.4	Ē	C-4', C-3", C-5"
2"	3.33 (s)	73.3		C-1"*, C-3"*
3"	3.29 (dd, J = 9.5, 5.0 Hz)	75.9	วกาว	C-2"*, C-4"*
4"	3.17 (dd, J = 9.0, 3.0 Hz)	69.8	กิจักย	C-3"*, C-5"*
5"	3.37 (<i>dt</i> , <i>J</i> = 7.9, 1.5 Hz)	77.3	1 <u>0 ř</u> l C	C-1", C-6"*
ба"	3.48 (<i>dd</i> , <i>J</i> = 12.0, 6.0 Hz)	60.7	_	C-5″*
6b"	3.73 (<i>dd</i> , <i>J</i> = 11.7, 5.5 Hz)			C-4″
7-OMe	3.86 (s)	56.0	_	C-7
5-OH	12.39 (s)	-	-	C-5*, C-6, C-10

Table 10. The ¹H and ¹³C-NMR data, HMBC correlation of compound SB5 and comparison of the ¹³C-NMR assignments with those rhamnetin (in DMSO-*d*₆)

* Two-bond correlation

CHAPTER V

CONCLUSION

In this investigation, four compounds and a mixture of two compounds were isolated from the aerial part of *Sauropus bacciformis* (L.) Airy Shaw by chromatographic techniques. From the EtOAc extract, a new flavonol glycoside named rhamnetin-4'-O- β -D-glucopyranoside was isolated and its structure elucidated. From the hexane extract, three known triterpenoids, i.e. friedelin, similarenol and glochidonol, and a mixture of β -sitosterol and stigmasterol were identified.

This is the first report of chemical constituents of *Sauropus bacciformis* (L.) Airy Shaw. Glochidonol is considered a chemotaxonomic marker found only in several genus of Euphorbiaceae Subtribe Flueggeinae such as *Fluggea*, *Glochidion* and *Phyllanthus*.

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APPENDIX



Figure 6. IR spectrum of compound SB1 (KBr disc)



Figure 7. EIMS of compound SB1



Figure 8a. The 300 MHz ¹H-NMR spectrum of compound SB1 (in CDCl₃)



Figure 8b. The 300 MHz ¹H-NMR spectrum of compound SB1 (expanded)



Figure 9a. The 75 MHz ¹³C-NMR spectrum of compound SB1 (in CDCl₃)



Figure 9b. The 75 MHz ¹³C-NMR spectrum of compound SB1 (expanded)



Figure 9c. The 75 MHz ¹³C-NMR spectrum of compound SB1 (expanded)



Figure 10. The 75 MHz ¹³C-DEPT spectra of compound SB1 (in CDCl₃)



Figure 11. IR spectrum of compound SB2 (KBr disc)



Figure 12. EIMS of compound SB2



Figure 13. The 500 MHz ¹H-NMR spectrum of compound SB2 (in CDCl₃)



Figure 14a. The 125 MHz ¹³C-NMR spectrum of compound SB2 (in CDCl₃)



Figure 14b. The 125 MHz ¹³C-NMR spectrum of compound SB2 (expanded)



Figure 15. The 125 MHz ¹³C-DEPT spectra of compound SB2 (in CDCl₃)



Figure 16a. The 500 MHz ¹H-¹³C HMQC NMR spectrum of compound SB2 (in CDCl₃)



Figure 16b. The 500 MHz ¹H-¹³C HMQC NMR spectrum of compound SB2 (expanded)



Figure 17a. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB2 (in CDCl₃)



Figure 17b. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB2 (expanded)



Figure 17c. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB2 (expanded)



Figure 17d. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB2 (expanded)



Figure 18. IR spectrum of compound SB3 (KBr disc)



Figure 19a. The 300 MHz ¹H-NMR spectrum of compound SB3 (in CDCl₃)



Figure 20a. The 75 MHz ¹³C-NMR spectrum of compound SB3 (in CDCl₃)



Figure 20b. The 75 MHz ¹³C-NMR spectrum of compound SB3 (in CDCl₃)



Figure 21. The 75 MHz ¹³C-DEPT spectra of compound SB3 (in CDCl₃)



Figure 22. IR spectrum of compound SB4 (KBr disc)



Figure 23. EIMS of compound SB4



Figure 24. The 500 MHz ¹H-NMR spectrum of compound SB4 (in CDCl₃)



Figure 25a. The 125 MHz ¹³C-NMR spectrum of compound SB4 (in CDCl₃)



Figure 25b. The 125 MHz ¹³C-NMR spectrum of compound SB4 (expanded)


Figure 26a. The 125 MHz ¹³C-DEPT spectra of compound SB4 (in CDCl₃)



Figure 26b. The 125 MHz ¹³C-DEPT spectra of compound SB4 (expanded)



Figure 27a. The 500 MHz ¹H-¹³C HMQC NMR spectrum of compound SB4 (in CDCl₃)



Figure 27b. The 500 MHz ¹H-¹³C HMQC NMR spectrum of compound SB4 (expanded)



Figure 28a. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB4 (in CDCl₃)



Figure 28b. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB4 (expanded)



Figure 28c. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB4 (expanded)



Figure 29. UV Spectrum of compound SB5 (in DMSO)



Figure 30. IR spectrum of compound SB5



Figure 31. EIMS of compound SB5



Figure 32. The 500 MHz ¹H-NMR spectrum of compound SB5 (in DMSO-*d*₆)



Figure 33a. The 500 MHz ¹H-¹H COSY spectrum of compound SB5 (in DMSO-*d*₆)



Figure 33b. The 500 MHz ¹H-¹H COSY spectrum of compound SB5 (expanded)



Figure 34. The 125 MHz ¹³C-NMR spectrum of compound SB5 (in DMSO-*d*₆)



Figure 35. The 125 MHz ¹³C-DEPT spectra of compound SB5 (in DMSO-*d*₆)



Figure 36. The 500 MHz ¹H-¹³C HMQC NMR spectrum of compound SB5 (in DMSO-*d*₆)



Figure 37a. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB5 (in DMSO-*d*₆)



Figure 37b. The 500 MHz ¹H-¹³C HMBC NMR spectrum of compound SB5 (expanded)

VITA

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