CHAPTER I

INTRODUCTION AND BACKGROUND

A knowledge of the biological and/or chemical constituents of plants is desirable, not only for the discovery of new therapeutic agents, but also because such information may be of value in the disclosing of new sources of such economically important materials as tannins, industrial oils and gums. They also may be precursors for the synthesis of complex chemical substances. In addition, a novel chemical structure which is isolated from plant sources often leads to the preparation of a series of synthetic analogs which may have medicinal or economical values. A knowledge of the chemical constituents of so-called "toxic" plants could place the treatment of plant poisonings of both humans and animals on a more rational and specific basis. A knowledge of the chemical constituents of a plant is also important for the study of plant chemotaxonomy (biochemical systematics) and plant biosynthesis, as well as deciphering the actual value of folkloric remedies.

The problems of the natural product investigators interested in biologically active compounds are complex and differ from those of organic chemists who synthesize or manipulate molecules using structure-activity relationships as their theoretical motivations to design. Natural product investigators must initially select their plants from a total number of available species that have been estimated to be as high as 750,000 excluding bacterias and fungi. When this selection has been made, whether it be on theoretical grounds or on the basis of preliminary experimentation, the problems of acquisition and the variability of plant materials become complicating factors. Also the natural product investigators must enlist the aid of a cooperative pharmacologist, or make other agreements to insure a suitably biological evaluation for the extracts and isolated compounds. The problems inherent in the biological evaluation of crude plant extracts are in themselves unique since those who are concerned with biological evaluation usually have little interest in crude plant extracts. In effect, priority is usually given to the biological evaluation of crystalline compounds. However, it should be remembered that in natural product studies, those pure compounds are realized only after initial biological test on crude extracts provide justification for a phytochemical investigation. The lack of interest in the biological evaluation of crude plant preparation will probably continue as the major block to progress in the study of natural products.

The importance of plant-derived compounds in modern medicine is often underestimated. A recent survey has pointed out that 47% of some 300 million new precriptions written by physicians in 1961 contained, as one more active ingredients, a drug of natural origin. Furthermore, between 1950 and 1960, precriptions containing drugs of natural origin increased by 7.7% (1,2).

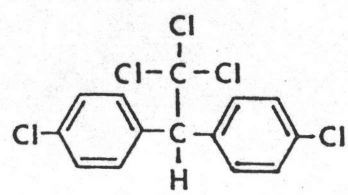
1.1 <u>Agricultural Chemistry</u> (3-6)

There are two major types of chemical substances widely used in agriculture, i.e., inorganic compounds and organic ones.

Inorganic substances, for instance, sulfur and copper as fungicides; inorganic arsenicals such as arsenic trioxide (As_2O_3), sodium arsenite ($NaAsO_2$ and Na_2HAsO_3) as herbicides and lead arsenate ($PbHAsO_4$) and fluorine compounds as inorganic insecticides, are used as broad-spectrum pesticides. Nevertheless, these compounds are well-known pesticides, they are found to cause poisoning effect not only to animals and plants, but also to human beings. The most appropriate ones, which are currently used, are the compounds obtained from organic sources, both synthetic and naturally occurring substances. Thus, organic chemicals have been interesting to be the key to this process. However, insecticides, fungicides and herbicides are poisonous and must be used with appropriate care.

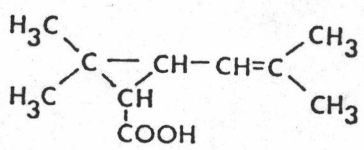
1.1.1 Insecticides

History does not tell very much about chemicals used against insects. The earliest records of insecticides pertain to the burning of "brimstone" (sulfur) as a fumigant. Even as recently as 1940, the insecticide supply was still limited to several arsenicals, petroleum oils, nicotine, pyrethrum, rotenone, sulfur, hydrogen cyanide gas and cryolite. After the World War II, the first synthetic organic insecticide, 1,1,1-trichloro-2,2'-bis-(p-chlorophenyl)ethane (DDT), was prepared successfully.

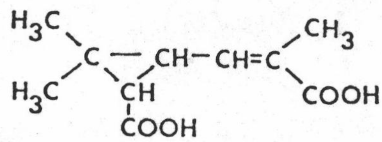


DDT

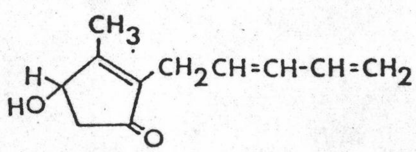
Nowadays, not only DDT and its related compounds, but also various sorts of synthetic chemicals such as organic phosphorus compounds, carbamates, organosulfurs, formamidines, thiocyanates and organotins are synthesized and employed as broad-spectrum insecticides. Besides the insecticides which are derived from synthetic organic substances, some powerful insecticides are synthesized by plant themselves. Pyrethrum is the oldest and still most widely used as a natural insecticide. It is obtained from the flower head of pyrethrum, Chrysanthemum cinerariaefolium, and it is the mixture of esters of chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid with the keto alcohols, pyrethrolene and cinerolene.



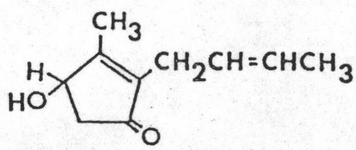
Chrysanthemum monocarboxylic acid



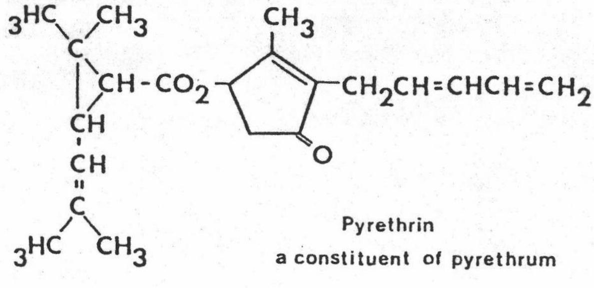
Chrysanthemum dicarboxylic acid



Pyrethrolene

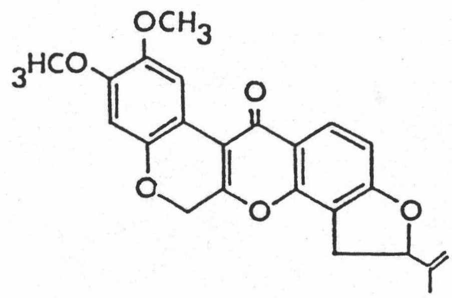


Cinnerolene



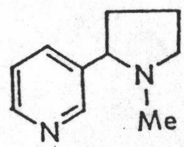
Pyrethrin
a constituent of pyrethrum

Extract from the tuba plant (<u>Derris elliptica</u>) was used by the Chinese as an insecticide at very early date and since before 1800 as a fish poison. The active ingredient is rotenone, which is effect as an insecticide against aphids, cabbage worm, Japanese beetle, rose chafer etc.



Rotenone

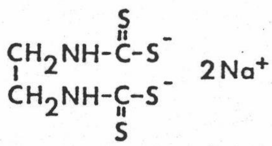
Another well known insecticide is an alkaloid, nicotine, which could be obtained from either solvent extraction or steam distillation of tobacco.



Nicotine

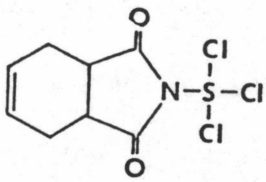
1.1.2 <u>Fungicides</u>

Fungicides have a disastrous effect on many crops, and their control has been a major concern of organic chemists and agricultural experts. Dithiocarbamates, phenol compounds and quinone substances are the most important organic fungicides. The manganese (Maneb), sodium (Nabam) and zinc (Zineb) salts of ethylene-bis-dithiocarbamate, chloranil, dichlone, dithianon, 2,4,6-trichloro-phenol and pentachlorophenol are also broad-spectrum fungicides. In recent years, two other materials, Captan, Folpet and pentachloro-nitrobenzene (PCNB), alone or combination with other fungicides such as Captan have been employed widely as fungicides.

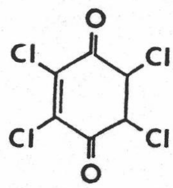


Nabam

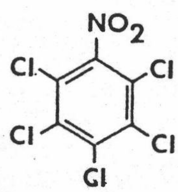
(For Meneb, the cation is Mn^{2+}, for Zineb, Zn^{2+})



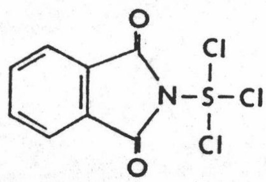
Captan



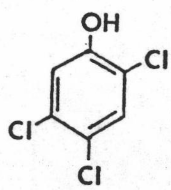
Chloranil



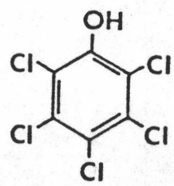
PCNB



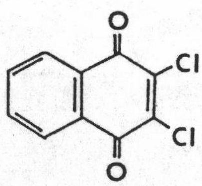
Folpet



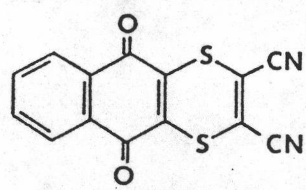
2,4,5-Tri-chlorophenol



Pentachlorophenol



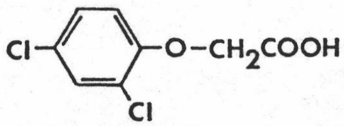
Dichlone



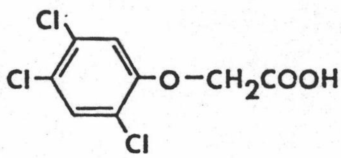
Dithianon

1.1.3 Herbicides

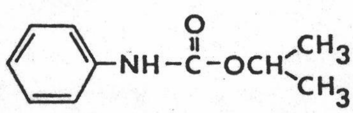
Herbicides are presently account for about one-quarter of the agricultural chemicals used. The discovery of selective herbicidal activity of 2,4-dichlorophenoxyacetic acid (2,4-D) launched the modern era of weed control. A closely substance, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), has also derivable herbicidal properties. Carbamates, petroleum oils, organic arsenicals, aliphatic acids, arylaliphatic acids and some phenol derivatives are the examples of herbicides that are presently used.



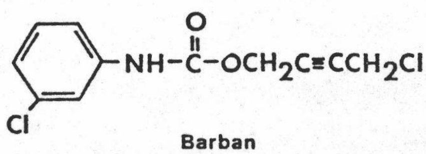
2,4-D



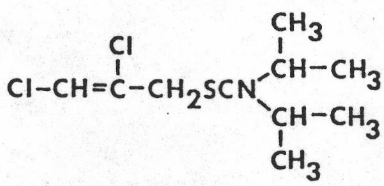
2,4-T



IPC



Barban



Avadex

However, there is a great need for new biodegradable agrochemicals which can be compatible with the environment. Plants from the tropical regions of the world such as Thailand offer particularly intriguing possibilities in this regard, since they are subject to serve disease and insect pressure. This is espectially true for mangrove and salt marsh plants because of their proximity to water. Hence, the mangrove and salt marsh plants are ideal conditions for providing novel agrochemicals which can eventually be produced through synthetic process.

1.2 Chemistry of Mangroves

The mangrove forest covers the areas where sea water can flood, or in another case, it means the area where sea water and river water join together. Mangrove area is usually muddy and full of organic substances as well as mineral elements which are useful for plants and animals living in this environment. Therefore, the mangrove areas are important as natural resources in case of forestry, fisheries and preserving the ecosystems. Moreover, the mangrove areas are known to be used as coastline stabilizers, retainers and builders of land, buffers against waves and storms, and reserviors in the tertiary assimilation of wastes, and in the global cycle of carbon dioxide, nitrogen and sulfur (7).

The total mangrove area in the world is approximately 15,429,000 ha. distributing among many countries, while the area in Thailand is just only 278,308 ha. This figure is a small number as compared with the land forest area in Thailand or the mangrove areas which belong to other Asian countries (8). Thai mangrove areas distribute in the southern and southeastern parts of the country and also the upper part of the Gulf of Thailand. There are more than 60 species (approximately 27 genera or 13 families) that have distributed in Thai mangrove areas. The community structure of Thai mangrove areas is varying from the edge of the estuary to inland sites, with Rhizophora apiculata, R. mucronata and the palm, Nypa fruticans, the dominant species along estuary and chemical edge. Avicennia and Bruguiera associated Rhizophora formed a more distrinct zone further inland. On areas adjacent to the Avicennia and Bruguiera zone which have drier soils and loss to tidal in undation, Xylocarpus and Excaecaria become the dominant species (9).

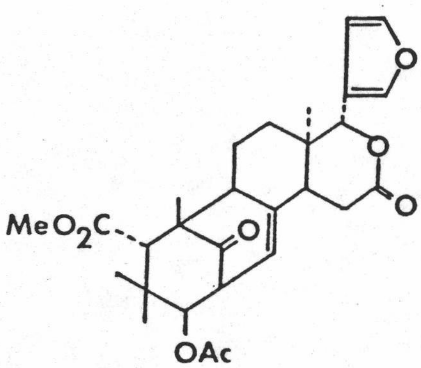
In the past, most of the mangrove plants were used for many purposes. For instance, they were used as firewood, charcoal, fish stakes, piles, pit props and animal food, including other minor products. Besides, some plants were used as drugs for curing diseases followed ancient believes. Many commercially important fishes, crabs and prawns use the mangrove as a nursery ground and shelter during their juvenile stages. The potential of mangrove and marsh areas for aquaculture is gaining attention, particularly in Thailand due to the increasing demand for protein food sources. Nowadays, they have still been used as mentioned above. Moreover, many mangrove areas in Thailand have been destroyed in many ways such as constructing houses, building factories and mines as well as shrimp and fish farms. In order to preserve the mangrove areas, while at the same time maximizing the benefits from an economic and agricultural point of view, scientists should consider the study of the utilization of mangrove plants more than they had in the past.

Some of the processes which need more study are the extraction of tannins from the bark of mangrove plants and the production of methanol, acetic acid and coal tar from the wood. Another form of utilization is to investigate the chemicals which are present in the plants and how they can be used. Thus, the natural product chemistry of mangrove plants is very important because the possible use of each chemical can be explored.

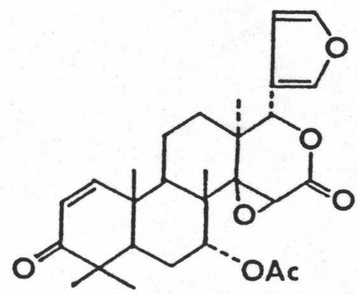
Two basis reasons are used to justify the constituents of mangrove plants. The first one is that the plants in mangrove areas are under stressful conditions such as violent environments, high concentration of moisture, the low and high tides of water and the abundant living organisms such as microorganisms and insects which exist in this environment. Hence, the plants that can survive in this area may have compounds which protect them from destruction. The second reason for investigating mangrove plants is that numerous mangrove plants have been used as folklore medicinal plants. *Acanthus* spp. and *Xylocarpus* spp. are two examples.

Although the chemistry of natural product of mangrove plants is poorly known (10), there were some examples in recent years to support the two hypotheses that are established. Various plants in this area have been selected for investigation of their chemical constituents. Several substances were identified as novel compounds, and also lots of known compounds were isolated again and proved to be biologically active substances. For instance, J.W. Loder and G.B. Russel in 1967 (11) isolated a new alkaloid "brugine" as well as tropine and the tropine esters of acetic, propionic, n-butylic, α-methylbutylic or isovaleric and benzoic acids from the tumor inhibitory plants, Bruguiera sexangula and B. exaristata (Family: Rhizophoraceae). These alkaloids whose structures are shown in Fig. 5 were reported to be toxic against the tumor cells.

In 1970, D.A. Okorie and D.A.H. Taylor (12), studied the seeds and the timbers of Xylocarpus granatum (Family: Meliaceae). Xylocarpin (I) was identified as the new compound, methyl-3 β-acetoxy-8 α,30 α-epoxy-1-oxomeliacate. The antifungal substance, gedunin (II), was also isolated from this plant (13).

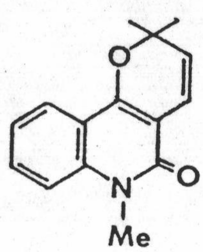


Xylocarpin (I)



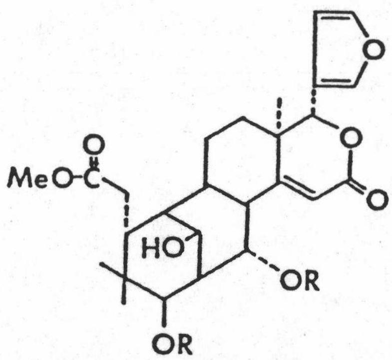
Gedunin (II)

F.Y. Chou and co-workers (1977) (14) isolated an insect antifeedant N-methylflindersine (III) from X. granatum.



N-methylflindersine (III)

J.D. Connolly et al. (1976) (15) reported the structure of the new compounds, xyloccensins A,B,D and F (IV-VII) from X. moluccensis seeds and timbers. These compounds are derivatives of methyl meliacate and contain a 1,8-hemiacetal group. Xyloccensin E (VIII) is pharmalintriacetate.



R = CO-iso Pr or iso-Bu

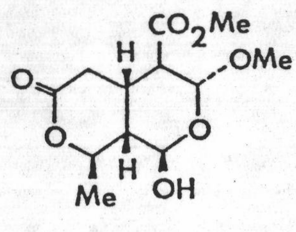
Xyloccensin B (V) is 14,15-dihydro (IV)

Xyloccensin D (VI) is 2-hydroxy (IV)

Xyloccensin F (VII) is 2-hydroxy (V)

Xyloccensin A (IV)

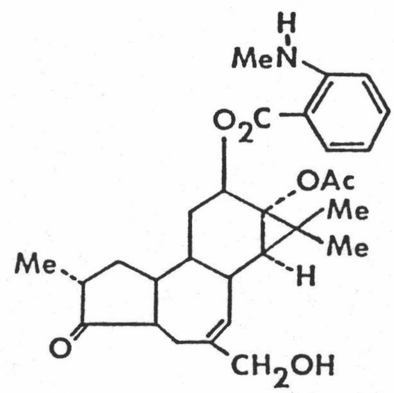
In the same year, 1976, J. Kubo and colleagues (16) isolated an antifeedant, xylomollin (IX), from the unripe fruits of African tree X. moluccensis. This compound is an antifeedant against the African army worm Spodaptera exempta.



Xylomollin (IX)

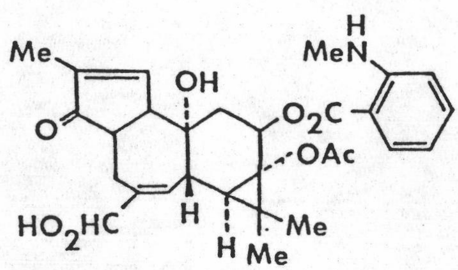
In 1977, G.A. Miana and co-workers (17) isolated a non-irritant diterpene ester, 4 α-sapinine (X), from Sapium indicum.

(Family: Euphorbiaceae) which was identified as 13-O-acetyl-4-deoxy-O-(N-methylanthraniloyl)-4α-phorbol.



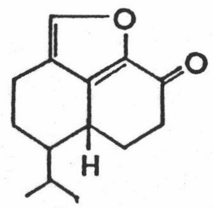
4α-sapinine (X)

In 1981, S.E. Taylor and co-workers (18) isolated a new biologically active sapintoxin (XI) from the unripe fruits of S. indicum. This compound was an irritant and confirmed as 12-O-[N-methyl aminobenzyl]-13-O-acetyl-4-deoxyphorbol.

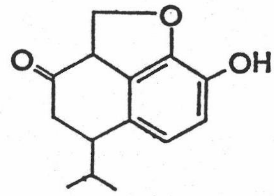


Sapintoxin (XI)

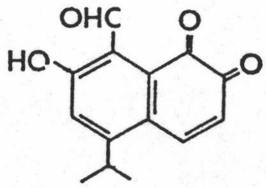
S. Ali et al. (1980) (19) isolated the new sesquiterpenoid quinone and related compounds from the heartwoods of Hibiscus tiliaceus (Family: Malvaceae). These compounds were identified as hibiscones A, D (XII-XIII) and hibisco quinone A, D (XIV-XV).



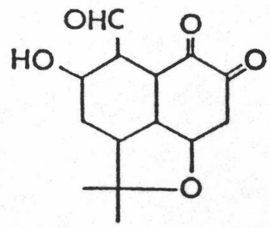
Hibiscone A (XII)



Hibiscone D (XIII)



Hibiscoquinone A (XIV)

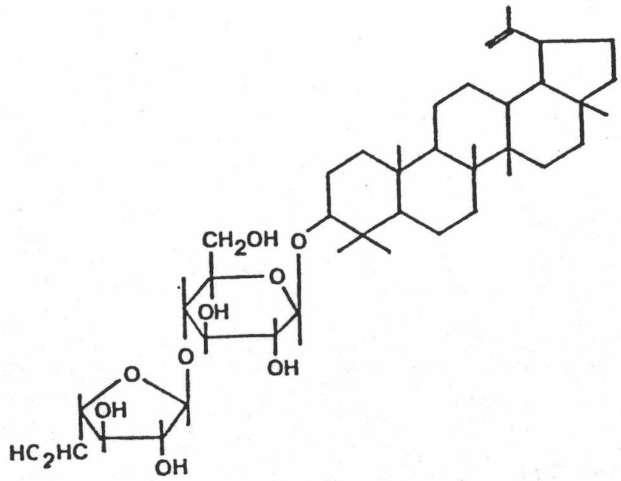


Hibiscoquinone D (XV)

In 1983, S. Rodkird (20) isolated a new substance from the leaves of Pluchea indica (Family: Compositae) which was 3-(2', 3'-diacetoxy-2'-methyl butyryl)-cuauhtemone (XVI).

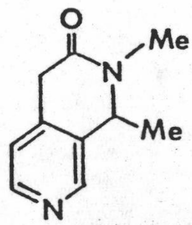
(XVI)

N.R. Bhosale et al. (1978) (21) found a new triterpenoidal saponin in the roots of Acanthus illicifolius (Family: Acanthaceae) which was identified as α-L-arabinofuranasyl-(1-4)- α-D-glucopyranosyl-(1,3)-β-hydroxylup-20(29)-ene (XVII).



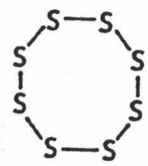
(XVII)

K.P. Tiwari and co-workers, in 1980, (22) isolated, identified and reported many known substances from A. illicifolius and a new alkaloid, acanthicifolin (XVIII).

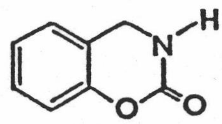


Acanthicifolin (XVIII)

In 1983, U. Kokpol, V. Chittawong and D.H. Miles (23) reported that 9 pure compounds were isolated from the roots of A. illcifolius. Two of which were S_8 (XIX) and benzoxazolin-2-one (XX) which had been reported to have pharmacological activity.



S_8 (XIX)



Benzoxazolin-2-one (XX)

Up to now, not only novel compounds, but also biologically active substances have been isolated from mangrove plants. Therefore, the utilization of them is worth considering. This justifies a study on the chemical constituents of the mangroves.

In this research, Rhizophora apiculata Bl., one of the dominant Thai mangrove plants in Rhizophoraceae family, was selected to examine for chemical constituents.

Rhizophora apiculata Bl., or Kong Kang in Thai, belongs to Rhizophora genus in Rhizophoraceae family. There are approximately 7 species in this genus (24), but only 2 species, i.e., Rhizophora apiculata Bl. (Kong Kang bai lek) and R. mucronata Poir. (Kong Kang bai yai) are found in Thailand (25,26). In this country, these two species have been distributed to every province on the seashores, lagoons and along the rivers at level between low and high tides such as Ranong, Samutsakorn, Samutsongkram and Petchaburi, etc.

The Flora of Thailand (25) stated that these two species, R. apiculata and R. mucronata, possesses close character. However, there are some distinctions to separate these two plants from each other. The descriptions of the character of Rhizophora apiculata and _R. mucronata_ were given below and the pictures of these two species were shown in Fig.1 and Fig.2, respectively.

Rhizophora apiculata: Tree up to 30 m. or more, 50 cm. diam. Leaves elliptic-oblong to sublanceolate, 7-18 by 3-8 cm.; apex acute to apiculate; base cuneate; petiole 1.5-3 cm. Stipules 4-8 cm. long. Flowers sessile. Calyx lobes ovate, concave, acute, 10-14 mm. long. Peatles lanceolate, 8-11 mm. long, membranous, flat, glabrous. Stamens mostly 12:4 epipetalous and 4 pairs episepalous, 6-7.5 mm. long. Free part of the ovary 1.5-2.5 mm. high, enclosed by the disk; hypocotyl cylindrical-clavate, blunt, up to 38 cm. by 12 mm. before falling.

Rhizophora mucronata: Tree up to 27 m., rarely over 30 m. by 70 cm. Leaves broad-elliptic to oblong, 11-18 by 5-10.5 cm.; apex, blunt, acute, base cuneate; petiole 2.5-5.5 cm. Stipules 5.5-8.5 cm. long. Flowers pedicellate (4-8 mm.). Calyx lobes ovate, 13-15 mm. long, Petals lanceolate, 9 mm. long, freshy, involute, margins villose. Stamens 8:4 epipetalous and 4 episepalous, 6-8 mm. long. Free part of the ovary 2.5-3 mm. high, in anthesis already emerging far beyond the disk; hypocotyl cylindrical, 36-64 by 1.8 cm..

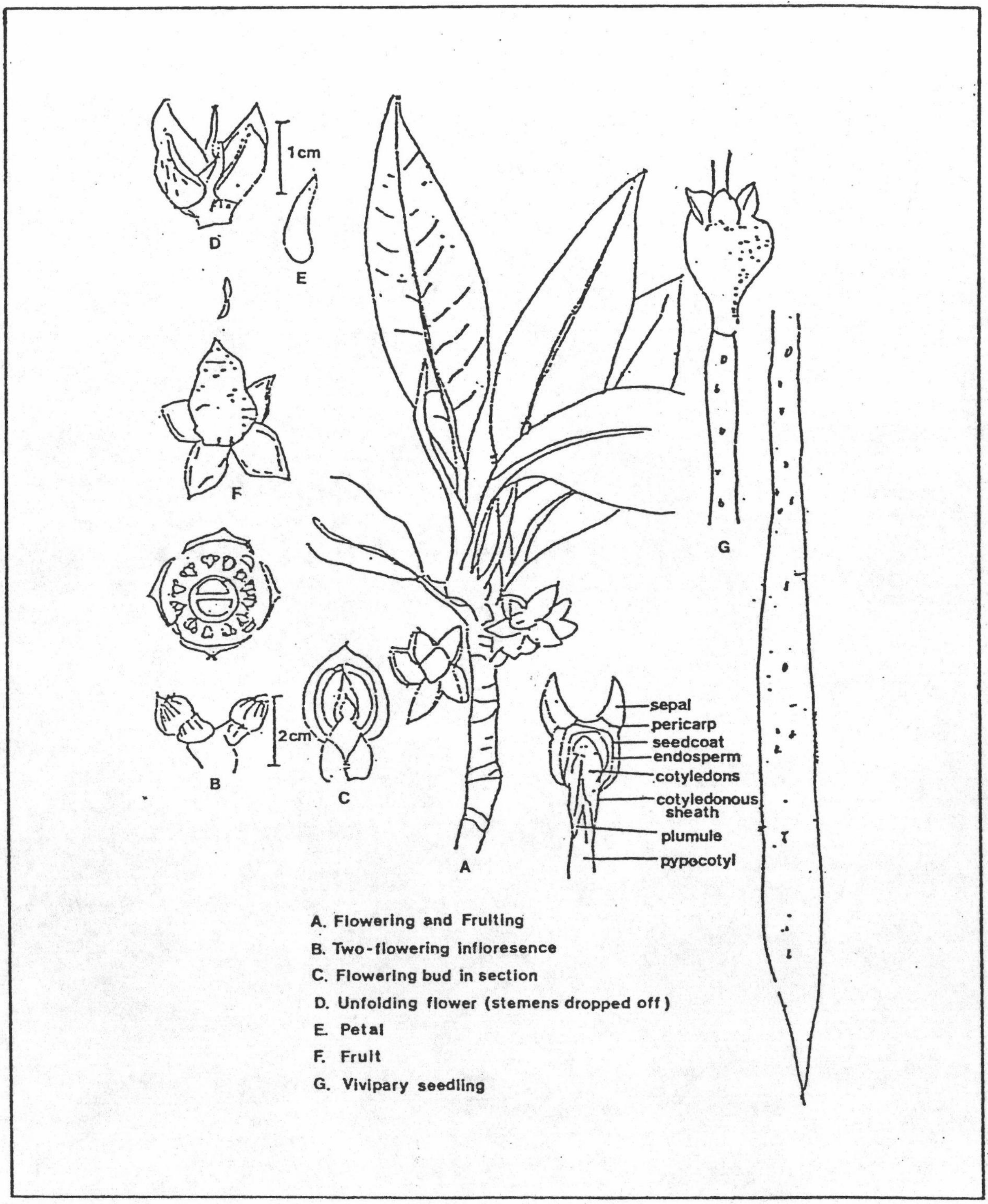


Figure 1 *Rhizophora apiculata* Bl.

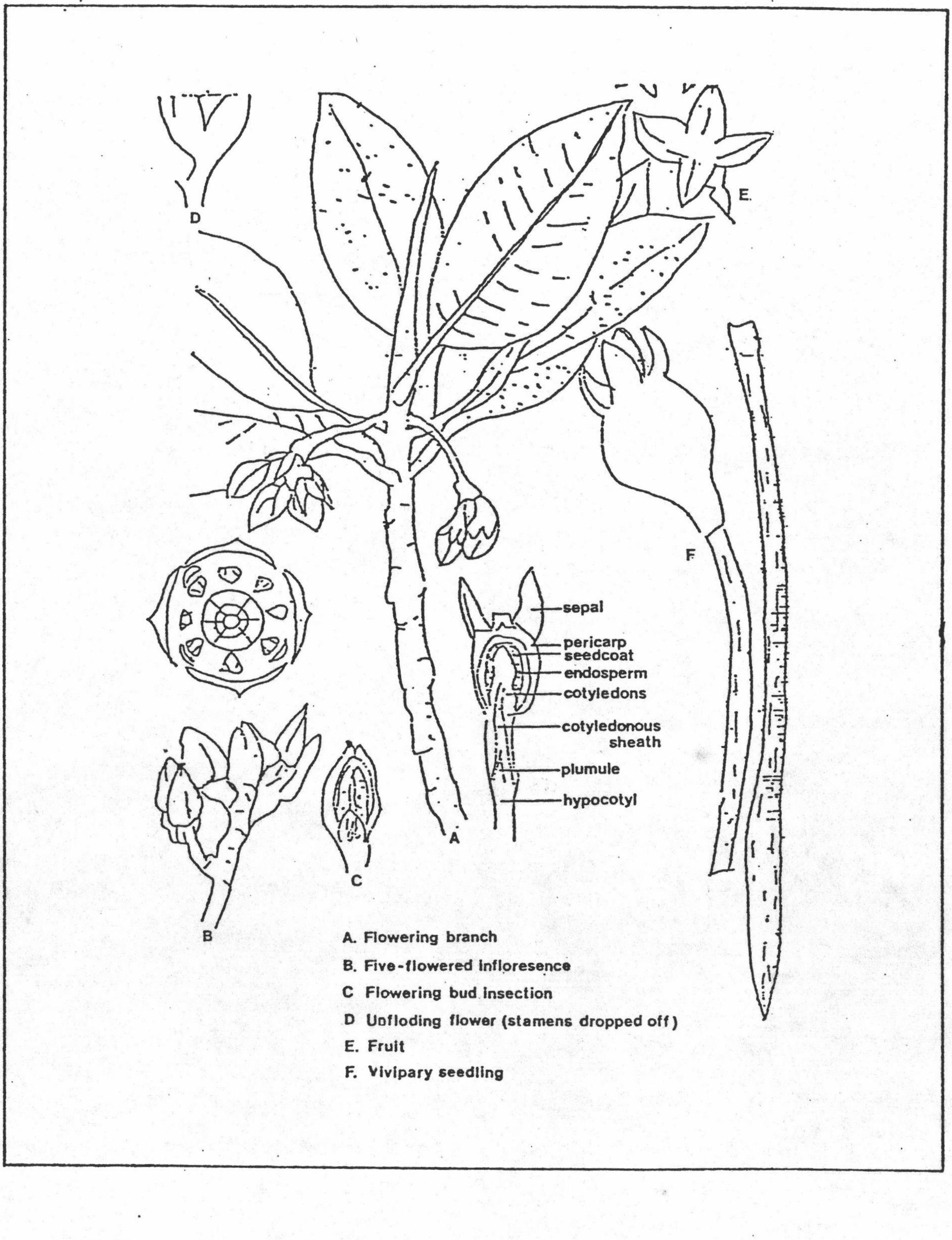


Figure 2 Rhizophora mucronata Poir

"Kong Kang" is an economically important plant and is found to occur in the greatest abundance, 90% of mangrove plants, in Thai mangrove area (8). In the past, as for other mangrove plants, it was used for firewood, house construction, fishing gears, animal food and making charcoal. The Kong Kang charcoal is excellent because of high caloric value and long-burning character. People who lived in mangrove areas always use this plant as dyestuffs and folkloric medicine (27). Following primitive believes, the boiled water of its bark was used as astrigent for diarrhea, nausea vomiting, antiseptic, stop bleeding in fresh wound and chronic typhoid fever. Other well-known utilizations of Kong Kang are as a good source of tannin (28,29), espectially in its bark, the production of methanol, acetic acid, and coal tar (30). In the Phillipines, this plant has been exported for utilization in the textile industry (31).

1.3 Chemical Constituent Studies on Rhizophoraceae Family

Literature surveys of plants belonging to Rhizophoraceae family found that there are 9 genera in this family (22) from which many organic compounds have been isolated. The various types of organic substances are shown in Tables 1.1-1.4 and the structures of some of these compounds are exhibited in Figs. 3-6.

Table 1.1 Steroids found in Rhizophoraceae family

Scientific names (Common names)	Plant parts	Steroids	Ref.
Bruguiera gymnorhiza Linn.	leave	β-sitosterol	32
= B. conjugata Merr.	leave	β-sitosterol, chloresterol	33
= Rhizophora gymnorhiza		campesterol, stigmasterol,	
Linn.		28-isofucosterol	
(พังกาหัวสุม,พังกาหัวสุมดอกแดง	fresh	chloresterol, campesterol	34
โกงกางหัวสุม,ประสัก,พลัก)*	leave	β-sitosterol, stigmasterol	
		28-isofucosterol	
	-	β-sitosterol	35
Ceriops decandra Griff.	leave	β-sitosterol	32
= C. roxburghiana Arn.	fresh	cholesterol, campesterol,	34
= Bruguiera decandra Griff.	leave	β-sitosterol, stigmasterol	
(โปรงขาว,กะปูโลง,ปูโลง,		stigmast-7-en-3β-ol	
ปรงขาว,โปรงหนู*,แหม่,แสม,			
แสมมาเนาะ)			
Kandelia candel Linn.	leave	β-sitosterol	32
= K. rheedei Linn.			
= Rhizophora candel Linn.			
(รังกะแท้,ลุ่ย,ถั่วนางช้อย)*			

Table 1.1 (Cont.)

Scientific names (Common names)	Plant parts	Steroids	Ref.
Rhizophora apiculata Bl. = R. candelaria D.C. = R. conjugata Kurz. (โกงกางใบเล็ก,โกงกาง, พังกาใบเล็ก,พังกาทราย)*	leave	β-sitosterol	32
Rhizophora mucronata Poir. (โกงกางใบใหญ่,พังกาใบใหญ่, โกงกางนอก,ลาน,กางเกง)*	leave	β-sitosterol,chloresterol, campesterol,stigmasterol, stigmast-7-en-3β-ol, 28-isofucosterol	33
	fresh leave	β-sitosterol,chloresterol campesterol,stigmasterol stigmast-7-en-3β-ol	34

* (7,27)

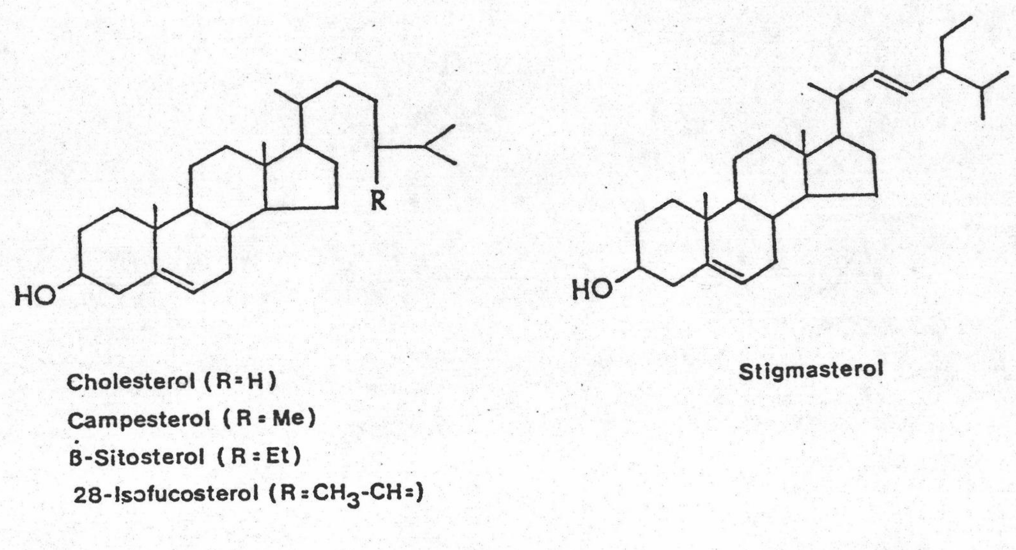
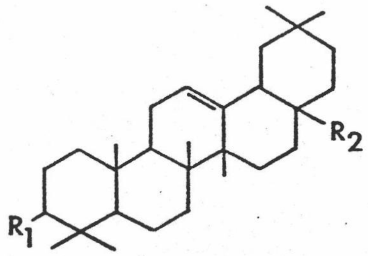


Figure 3 Steroids found in Rhizophoraceae family

Table 1.2 Triterpenoids found in Rhizophoraceae family

Scientific names (Common names)	Plant parts	Triterpenoids	Ref.
Bruguiera gymnorhiza Linn. (พังกาหัวสุม)*	leave	β-amyrin,taraxerol	32
	-	gymnorhizol	35
	fresh leave	α-amyrin,β-amyrin,lupeol oleanolic acid,ursolic acid	34
Bruguiera sexangula = B. eriopetala W&A ex Arn. = Rhizophora sexangula Lour. (ประสัก,พังกาหัวสุมดอกขาว, โกงกางหัวสุม,ขลัก)*	-	betulin,betulinic acid	36
Ceriops decandra Griff. (โปรงขาว)*	leave	β-amyrin,taraxerol,betulin, betulinic acid	32
	fresh leave	β-amyrin,lupeol,oleanolic acid,ursolic acid	34
Kandelia candel Linn. (รังกะแท้)*	leave	β-amyrin,taraxerol,friedelin	32
Rhizophora apiculata Bl. (โกงกางใบเล็ก)*	leave	β-amyrin, β-amyrone,taraxerol	32
Rhizophora mucronata Poir. (โกงกางใบใหญ่)*	fresh leave	α-amyrin, β-amyrin,lupeol,betulin oleanolic acid,ursolic acid	34

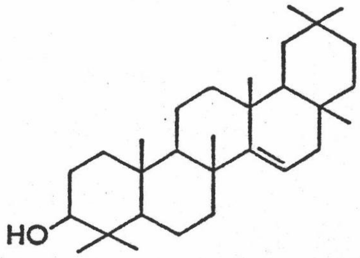
* (7,27)



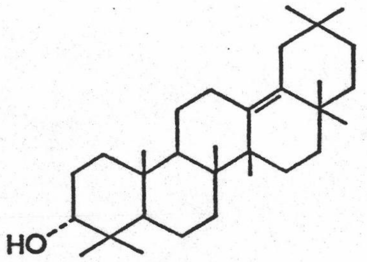
β-Amyrin (R_1=OH(H), R_2=CH_3)

β-Amyrone (R_1=O, R_2=CH_3)

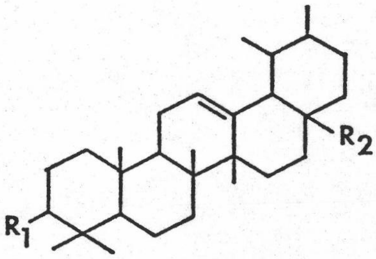
Oleanolic acid (R_1=OH(H), R_2=CO_2H)



Taraxerol

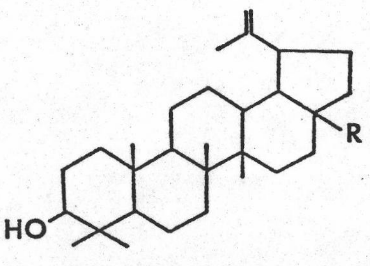


Gymnorhizol



α-Amyrin (R_1=OH(H), R_2=CH_3)

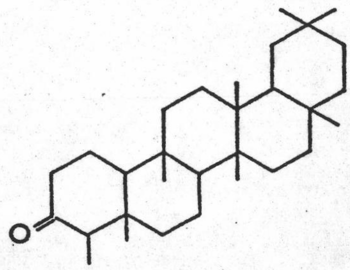
Ursolic acid (R_1=OH(H), R_2=CO_2H)



Lupeol (R = CH_3)

Betulin (R = CH_2OH)

Betulinic acid (R = CO_2H)



Friedelin

<u>Figure 4</u> Triterpenoids found in Rhizophoraceae family

Table 1.3 Alkaloids found in Rhizophoraceae family

Scientific names (Common names)	Plant parts	Alkaloids	Ref.
Bruguiera cyllndrica Bl. = B. caryophylloides Bl. = Rhizophora cyllndrica Linn. = R. caryophylloides Burmf. (รุ่ย,ถั่วคำ,โปรง,บรุ้ย)*	stem and bark	brugine	37,38
Bruguiera exeristata (-)	stem and bark	brugine,tropine,tropine ester**	11,39
Brruguiera sexangula Poir. (ประสัก)*	stem and bark	brugine,tropine,tropine ester**	11,39
Carrallia brachiata Merr. (-)	leave	(+)-hygroline	40
Cassipourea gummiflua (-)	twigs and leave	cassipourine	41,42

* (7,27)

** Tropine ester of acetic,propinoic (a new natural ester), n-butyric acid (a new natural ester),isobutyric,α-methylbutyric or isovaleric and benzoic acid.

Table 1.3 (Cont.)

Scientific names (Common names)	Plant parts	Alkaloids	Ref.
Cassipourea gerrardii (-)	twigs and leave	gerrardine.,gerradamine, gerradoline	41,42
Ceriops decandra Griff. (โปรงขาว)*	-	brugine,brugine ester	36
Gynotroches axillaris Bl. (-)	bark	(+)-hygroline	44
Rhizophora mucronata Poir. (โกงกางใบใหญ่)*	leave	rhizophorine	45

* (7,27)

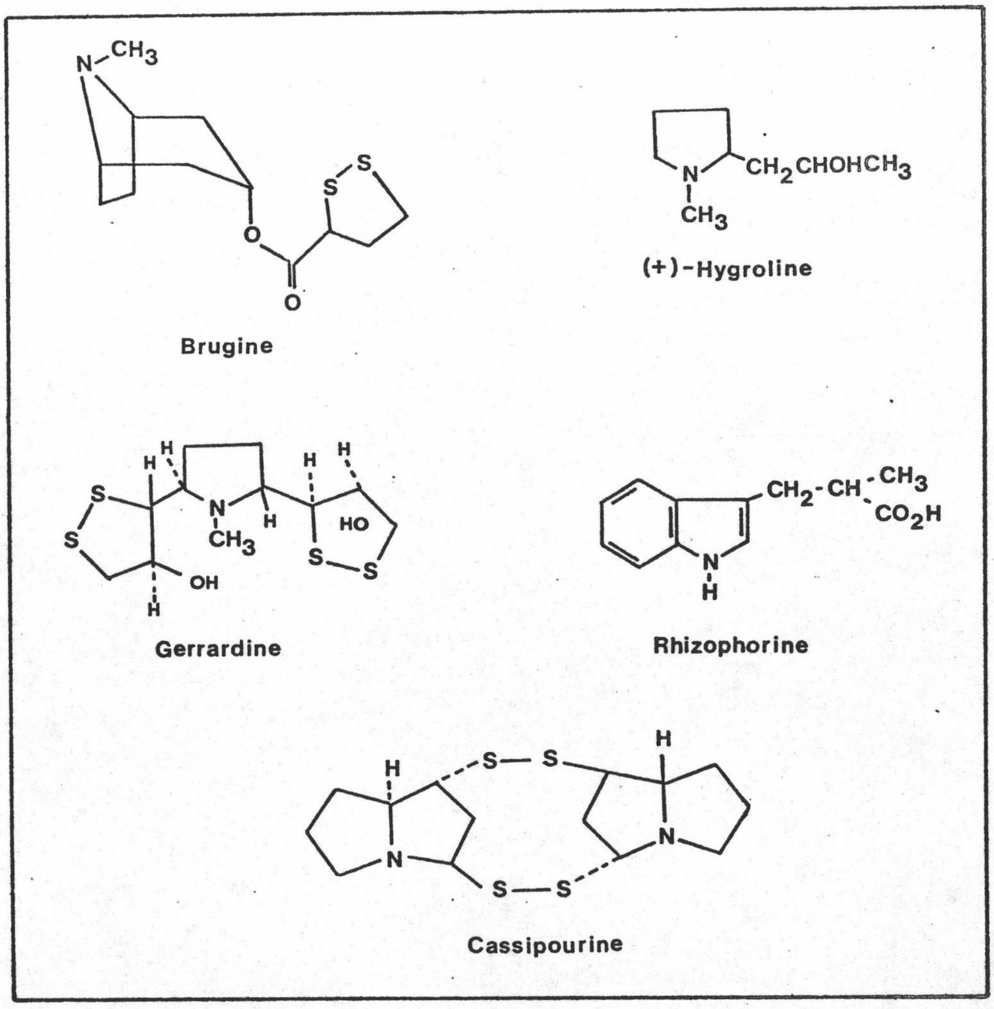


Figure 5 Alkaloids found in Rhizophoraceae family

Table 1.4 Other organic compounds found in Rhizophoraceae family

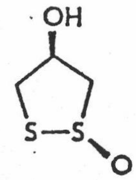
Scientific names (Common names)	Plant parts	Other compounds	Ref.
Bruguiera gymnorhiza Linn. (พังกาหัวสุม)*	stem and bark	brugierol,isobrugierol	46
	leave	triacontanol	33
	bark	leucocyanidin	47
	fruit	gibberellins A_3,A_4,A_7	48
Bruguiera cylindrica Linn. (รุ่ย)*	stem and bark	brugierol,isobrugierol 4-hydroxy-1,2-dithiolane	37
Bruguiera parviflora Roxb. = Rhizophora parviflora Roxb. (ถั่วขาว,รังกะแท้,ถั่วทะเล, ลังกะไต,หนังกะไต)*	bark	leucocyanidin	47
Ceriops decantra Griff. (โปรงขาว)*	leave	triacontanol	32
	-	cyanidin chloride,α-catechin leucoanthocyanin,procyanidin	36
Kandelia candel Linn. (รังกะแท้)*	-	2,6-dihydroxy-p-benzoquinone, 2,6-dimethoxy-p-benzoquinone	49 50

* (7,27)

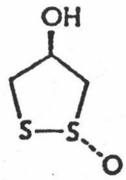
Table 1.4 (Cont.)

Scientific names (Common names)	Plant parts	Other compounds	Ref.
Rhizophora apiculata Bl. (โกงกางใบเล็ก)*	leave	triacontanol	32
Rhizophora mucronata Poir. (โกงกางใบหญ่)*	leave	gibberellin A_3, A_5, A_9	48

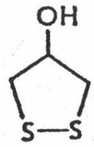
* (7,27)



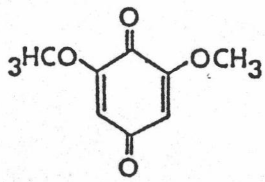
brugierol



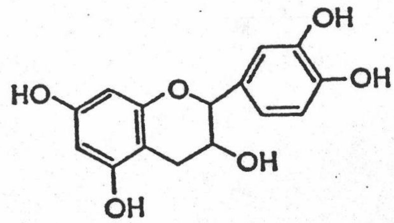
Isobrugierol



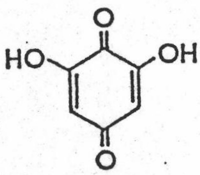
4-hydroxy-1,2-dithiolane



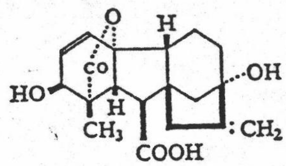
2,6-dimethoxy-p-benzoquinone



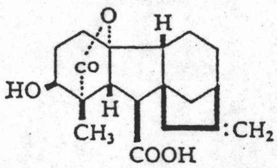
α -catechin



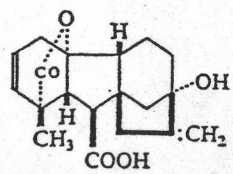
2,6-dihydroxy-p-benzoquinone



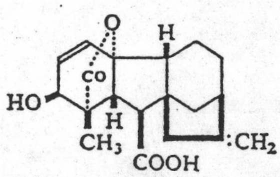
Gibberellin A_3



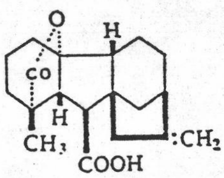
Gibberellin A_4



Gibberellin A_5



Gibberellin A_7



Gibberellin A_9

Figure 6 Other compounds found in Rhizophoraceae family

1.3.1 Chemical Constituent Studies of Rhizophora Genus

There are approximately 7 species that belong to Rhizophora genus, however, only two species are found in Thailand, i.e., R. apiculata Bl. (Kong Kang bai lek) and R. mucronata Poir. (Kong Kang bai yai).

Literature surveys on this genus found that there was only one report which was concerned with the chemical constituents of R. apiculata. There was, nevertheless, several publications that reported the isolation of compounds from R. mucronata as well as other Rhizophora species.

The only report on R. apiculata was by S.G. Majumdar and G. Patra (1976) (32). They reported that 5 pure compounds had been isolated from petroleum ether extract of the leaves. These compounds were identified as β-amyrin, β-amyrone, taraxerol, β-sitosterol and triacontanol.

B.T. Sokoloff et al. (51) reported, in 1949, the presence of thiamine, riboflavin, folic acid and pantothonic acid in the leaves of R. mucronata in such a large amount that they can be used as chicken food in order to provide vitamin A.

S.N. Ganguly and S.M. Sirger reported in 1974 (48) that they could isolate gibberellins A_3, A_5 and A_9 from the leaves of R. mucronata.

In 1976, N.G. Bhosale et al. (52) found that carbohydrate, protein and lipid were existed in high concentrations in the leaves of R. mucronata and could therefore be used as an animal food.

P.K. Saha et al. (45) in 1978 isolated a new alkaloid, m.p. 168-170 °C, called "Rhizophorine" from the methanolic extract of the leaves of R. mucronata.

From the leaves of R. mucronata; Co, Mn, Mo, Cu and Zn were found to be trace elements and L.J. Bhosale (1979) (53) also reported that Mn was the greatest amount while Co was the least.

W.G. Untawale and co-workers reported in 1980 (54) that the largest amount of the heavy metals found in monsoon season in Goa were Fe and Ni. The Ni was found to occur in the largest quantity in the leaves of R. mucronata.

In 1984, S. Misra et al. (33) reported the presence of β-sitosterol, chloresterol, campesterol, stigmasterol, 28-isofucosterol and stigmast-7-en-3β-ol in the leaves of R. mucronata.

In 1985, A. Ghosh et al. (34) found that there were 11 compounds, namely, cholesterol, campesterol, stigmasterol, β-sitosterol, stigmast-7-en-3 β-ol, α-amyrin, β-amyrin, lupeol, betulin, oleanolic acid and ursolic acid in the fresh leaves of R. mucronata.

1.4 The Goal of this Research

From a preliminary study involving cooperative research between the department of chemistry, Chulalongkorn University and the chemistry department at Mississippi State University, U.S.A. in searching for biodegradable agrichemicals from Thai mangrove plants showed that the ethanolic extract of the leaves of R. apiculata gave a high level of inhibition against the fungus Helminthosporium teres. The dichloromethane extract of the heartwoods of this plant showed high antifungal activity against *Pythium ultimum* and *Rhizoctonia solani* as well as antibacterial activity against *Xanthramonas campestrous*.

The goal of this research can be summarized as follows:

1. Preliminary phytochemical screening tests of various parts of *R. apiculata*.

2. To extract and isolate the organic constituents from the leaves and the heartwoods of *R. apiculata*.

3. To elucidate the structural formulae of the isolated substances from these two parts.

4. To search for the bioactive ingredients that can be used in agriculture and/or otherwise from the two parts of *R. apiculata* by using bioassay results as a guide.