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Metabolites and bioactivities of Rhizophoraceae mangroves

Murukesh NEBULA,[a,*] H.S. HARISANKAR,[b] and N. CHANDRAMOHANAKUMAR[a,b]

[a]Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Fine Arts Avenue, Kochi 682016, Kerala, India

[b]Inter University Center for Development of Marine Biotechnology, School of Marine Sciences, Cochin University of Science and Technology, Fine Arts Avenue, Kochi 682016, Kerala, India

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Abstract: This review examines the chemical compositions and bioactivities of mangrove plants belonging to the Rhizophoraceae family. The Rhizophoraceae family of true mangrove plants is the most common and is also widely distributed species. It consists of 24 species across four genera. Of the 24 species, 12 species remain unexamined for their phytochemical constituents. There have been 268 metabolites reported from 16 species. The key phytochemical constituents identified across the family are the diterpenoids and triterpenoids. The major diterpenoids include pimaranes, beyeranes, kaurenes, dolabranes and labdanes whereas the significant triterpenoids are lupanes, dammaranes and oleananes. Disulphides, dolabranes and labdanes are considered to be the chemotaxonomic markers of the genera *Bruguiera, Ceriops* and *Rhizophora* respectively.

Keywords: Rhizophoraceae, *Bruguiera*, *Rhizophora*, terpenoids, *Ceriops*

Introduction

Mangrove plants are potential sources of biologically active chemicals that are discernible from their wide spread application in ethnopharmaceutical practices. There habitat exists under stressful conditions and serve as a bridging ecosystem between freshwater and marine systems. These plants have specially adapted their own morphological structures and physiological mechanisms to their harsh natural surroundings. Pneumatophores, stilt roots and buttresses, with salt-excreting glands found in their leaves, and viviparous propagules are some of the several highly specialized adaptations of this group. The path of photosynthesis in mangroves is different from other glycophytes. Furthermore, there are alterations in other physiological processes such as carbohydrate metabolism or polyphenol synthesis. These plants survive under extreme conditions of salinity, temperature gradients, tidal fluctuations and anoxic soil conditions, with these plants possessing many chemical compounds, which protect them from these destructive elements[1]. Even though extracts from mangroves and mangrove-dependent species possess therapeutic activity against humans, animal and plant pathogens, the specific metabolites responsible for these bioactivities remains to be elucidated.

*To whom correspondence should be addressed. E-mail: nebulamurukesh@gmail.com

1 Rhizophoraceae

The global mangrove plant have 84 species belonging to 24 genera and 16 families[2]. Among them, 70 species are true mangroves pertaining to sixteen genera and eleven families whereas fourteen species are semi mangroves belonging to eight genera and five families. According to Wu et. al, suggests the family Rhizophoraceae belongs to true mangrove family, which contains 21 species in four genera[2]. In contrast three more species; *Rhizophora annamalayana*[3], *Kandelia obovata*[4] and *Ceriops zeppeliana blume*[5] become 24 species in four genera in the Rhizophoraceae family of true mangroves. Thus the family Rhizophoraceae include: *Bruguiera* which contains seven species, *Ceriops* (five species), *Kandelia* (two species) and *Rhizophora* (ten species). The distribution of species in Rhizophoraceae family is detailed in Table 1. 54 studies can achieve the validity of ethnomedicines as well as apply the use of mangrove plants in the development of new drugs.

In this review, the compounds identified from this family were listed, and their reported biological activities were compiled. Also chemotaxonamy and importance of further phytochemical research is discussed.

2 Chemical Constituents

2.1 *Bruguiera*: The genus *Bruguiera* has six species and one hybrid species which are derived from *B. sexangula*, including *B. cylindrica*, *B. exarista*, *B. gymnorrhiza*, *B. hainessi*, *B. parviflora*, *B. sexangula* and *B. sexangula* var.

Table 1. Mangroves of Rhizophoraceae family of true mangroves

Bruguiera	*Ceriops*	*Kandelia*	*Rhizophora*
B. cylindrica	*C. decandra*	*K. candel*	*R. apiculata*
B. exarista	*C. tagal*	*K. obovata*	*R. harrisoni*
B. gymnorrhiza	*C. tagal* var. *australasica*		*R. lamarckii*
B. hainessi	*C. tagal* var. *typical*		*R. mangle*
B. parviflora	*C. zeppeliana blume*		*R. mucronata*
B. sexangula			*R. racemosa*
B. sexangula var. *rhynchopetala*			*R. samoesis*
			R. selala
			R. stylosa
			R. annamalayana

rhynchopetala. The metabolic pattern of this genus has been extensively characterised by a suite of diterpenes and triterpenes. In addition, these species also produce flavonoids, tropane derivatives and cyclic polysulphides. These include 22 metabolites from *B. cylindrica*, 54 metabolites from *B. gymnorrhiza*, nine metabolites from *B. exaristata*, six metabolites from *B. parviflora*, two metabolites from *B. sexangula* and 40 metabolites from *B. sexangula* var *rhynchopetala* were identified so far. A total of 114 metabolites have been reported form this genus including. A detailed list of chemical compounds identified from *Bruguiera* is recorded in Table 2.

Three sulphur compounds along with an alkaloid brugine were reported from the stem and bark of *B. cylindrica* by Japanese scientists of during 1975–1976. 20 years later, a number of oleananes and lupanes (triterpenoids) and one kaurane (diterpenoid) were reported. The first report on the chemical constituents of *B. gymnorrhiza* dates back to 1978 in which Sarkar and Ganguly reported a new triterpenoid called gymnorhizol (3-epi-δ-amyrin). Since then various triterpenoids (lupanes, oleananes, ursanes, dammaranes) and diterpenoids (kauranes, pimaranes, beyaranes) along with sulphur compounds, sterols and aromatic compounds were reported from this plant.

Only two reports are available regarding the chemical constituents of *B. exaristata*. As part of their investigation on tumor inhibitory plants, in 1969 Loder and Russell identified the presence of alkaloids (brugine, tropine and tropine esters of acetic, iosbutyric, iosvaleric, propionic, n-butyric and benzoic acids) in the bark extracts of *B. exaristata*[6] while a pronounced accumulation of 1-d-1-*O*-methyl-muco-inositiol in the young leaves of *B. exaristata* was reported later by Richter and his team[7].

In a continuing search for bioactive constituents from Thai medicinal plants, Chumkaew and his team isolated and elucidated a new triterpenoid ester 3-(*Z*)-caffeoyllupeol along with five other tritepenoids; lupeol caffeate, 3-(*Z*)-coumaroyllupeol, dioslupecin A, lupeol and lupenone from the fruits of *B. Parviflora*[8]. The earliest work regarding the chemical constituents of mangroves deals with the isolation and characterization of the tropine 1,2-dithiolane-3-carbonylate named as bruguine from the stem bark of *B. sexangula*[9]. Later the same team identified additional alkaloids from the same plant as part of their investigation on tumor inhibitory plants[6]. In a study focusing on the marine fauna and flora from Chinese coasts, Li and his coworkers collected samples of the mangrove *B. sexangula* from Hainan Province, China. On separation of an EtOAc-soluble fraction of a methanol extract of the title plant, they isolated a new triterpene, named sexangulic acid[10].

Investigation of Chinese mangrove plants led to the isolation and characterisation of 13 compounds; three new diterpenes; six known diterpenes, a new dithiobenzoquinone two cyclic disulfides and 2,6-dimethoxy-1,4-benzoquinone from the EtOH extract of the stem of *B. sexangula* var. *rhynchopetala*[11]. Further several triterpenoids and sterols were reported[12]. Recently, a continuous investigation for chemical diversity of *B. sexangula* var. *rhynchopetala* led to the isolation and characterization of six new phenolic constituents named rhyncosides A–F, together with twelve known compounds including two phenolic glycosides, four flavonoids, and six lignan derivatives[13].

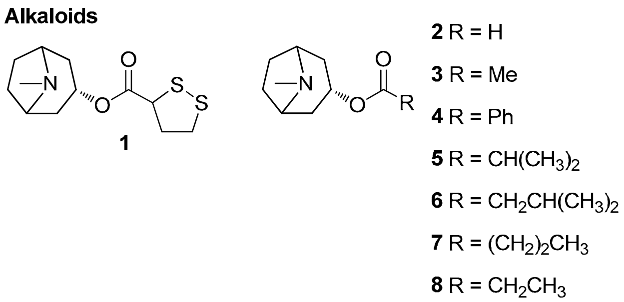


Figure 1. Alkaloids from Rhizophoraceae mangroves

2.2 ***Ceriops*****:** The genus of *Ceriops* has two species and two varieties, namely *C. tagal* (Perr.), *C. decandra*, *C. tagal* var. *australasica* and *C. tagal* var. typical. These plants are valued for their rich tannin content and are a rich source of pentacyclic triterpenoids[17]. To date, 30 metabolities from *C. decandra* and 72 metabolites from *C. tagal* are known. Thus a total of 92 metabolites including 45 diterpenoids (23 dolabranes, six dimeric diterpenoids, four beyeranes, five kauranes, and seven pimaranes) and 45 tritepenoids (35 lupanes, seven dammaranes, one oleanane, one ursane, and one abietane) along with two steroids have been reported so far from this genus.

On examination of the roots of *C. decandra* collected from the Kauvery estuary (Parangipettai coast), Anjaneyulu and his team isolated and characterised twelve diterpenoids[30,31,32]. Subsequently, two novel triterpene esters were isolated from the leaves of *C. decandra* in addition to 16 known triterpenes[33] by scientists from Thailand. Dolabranes (diterpenoids) are the marker metabolites of *C. tagal*. These compounds can be used as chemotaxonomic markers of this plant. Dimeric diterpenoids (tetraterpenoids) and triterpenoids of lupane, dammarane, pimarane groups are also found in this plant. One abietane and an oleanane triterpenoid were also isolated from the stems and twigs of *C. tagal*. The chemical constituents identified from *ceriops* are listed in Table 3.

Table 2. Chemical constituents from the genus *Bruguiera*

Compound Class and Name	Plant	Plant Part	References
Alkaloids			
brugine (**1**)	*B. cylindrica*	stem and bark	14
	B. exaristata	stem bark	6
tropine (**2**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
tropine acetate (**3**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
tropine benzoate (**4**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
tropine isobutyrate (**5**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
tropine isovalerate (**6**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
tropine n-butyrate (**7**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
tropine propionate (**8**)	*B. exaristata*	stem bark	6
	B. sexangula	stem bark	6
D-Friedooleananes (Triterpenoids)			
3*α*-taraxerol (**9**)	*B. cylindrica*	fruits	15
3*α*-*E*-caffeoyltaraxerol (**10**)	*B. cylindrica*	fruits and hypocotyls	16
3*α*-*E*-coumaroyltaraxerol (**11**)	*B. cylindrica*	fruits	15
3*α*-*E*-feruloyltaraxerol (**12**)	*B. cylindrica*	fruits	15
3*α*-*Z*-coumaroyltaraxerol (**13**)	*B. cylindrica*	fruits	15
3*α*-*Z*-feruloyltaraxerol (**14**)	*B. cylindrica*	fruits	15
3*β*-taraxerol (**26**)	*B. cylindrica*	fruits	15
3*β*-*E*-feruloyltaraxerol (**17**)	*B. cylindrica*	fruits	15
3*β*-*Z*-feruloyltaraxerol (**23**)	*B. cylindrica*	fruits	15
taraxerone (**25**)	*B. sexangula var. rhynchopetala*	stem	12
Lupanes (Triterpenoids)			
3*α*-lupenol (**32**)	*B. cylindrica*	fruits and hypocotyls	16
3*α*-*E*-coumaroyllupeol (**34**)	*B. cylindrica*	fruits and hypocotyls	16
3*α*-*Z*-coumaroyllupeol (**37**)	*B. cylindrica*	fruits and hypocotyls	16
3*β*-*E*-caffeoyllupeol B (**44**)	*B. cylindrica*	fruits and hypocotyls	16
3*β*-*Z*-caffeoyllupeol (**38**)	*B. parviflora*	fruits	8
3*β*-*E*-coumaroyllupeol (**45**)	*B. cylindrica*	fruits and hypocotyls	16
3*β*-*Z*-coumaroyllupeol (**55**)	*B. cylindrica*	fruits and hypocotyls	16
	B. parviflora	fruits	8
betulin (**57**)	*B. gymnorrhiza*	leaves	17
lupenone (**64**)	*B. cylindrica*	fruits and hypocotyls	16
	B. sexangula var. *rhynchopetala*	stem	12
	B. parviflora	fruits	8
lupeol (**65**)	*B. cylindrica*	fruits and hypocotyls	16
	B. gymnorrhiza	leaves	17
	B. sexangula var. *rhynchopetala*	stem	12
	B. parviflora	fruits	8
trans-hydroxy-cinnamoyl lupeol (**66**)	*B. sexangula* var. *rhynchopetala*	stem	12
dioslupecin A (**57**)	*B. parviflora*	fruits	8
Oleanane (Triterpenoids)			

oleanolic acid (**70**)	*B. gymnorrhiza*	leaves	17
β-amyrin (**71**)	*B. gymnorrhiza*	leaves	17
β-amyril palmitate (**72**)	*B. sexangula* var. *rhynchopetala*	stem	12
Ursanes (Triterpenoids)			
ursolic acid (**73**)	*B. gymnorrhiza*	leaves	17
α-amyrin (**74**)	*B. gymnorrhiza*	leaves	17
Dammaranes (Triterpenoids)			
bruguierin **A** (**75**)	*B. gymnorrhiza*	flowers	18
bruguierin B (**76**)	*B. gymnorrhiza*	flowers	18
bruguierin C (**77**)	*B. gymnorrhiza*	flowers	18
Triterpene alcohol			
gymnorhizol (3-*epi*-*δ*-amyrin) (**85**)	*B. gymnorrhiza*	leaves	19
Lanostanes (Triterpenoids)			
sexangulic acid (**86**)	*B. sexangula*	stem	10
squalene *(Triterpenoid)*			
squalene (**87**)	*B. sexangula* var. *rhynchopetala*	stem	12
Fatty acids			
linoleic acid (**88**)	*B. gymnorrhiza*	leaves	20
linolenic acid (**89**)	*B. gymnorrhiza*	leaves	20
palmitic acid (**90**)	*B. gymnorrhiza*	leaves	20
Steroids			
3-*O*-*α*-L-rhamnopyranosyl-(+)-catechin-(4*α*→2)phloroglucinol (**91**)	*B. gymnorrhiza*	bark	21
campesterol (**92**)	*B. gymnorrhiza*	leaves	17
cholesterol (**93**)	*B. gymnorrhiza*	leaves	17
daucosterol (**94**)	*B. sexangula* var. *rhynchopetala*	stem	12
β-sitosterol (**96**)	*B. sexangula* var. *rhynchopetala*	stem	12
	B. gymnorrhiza	leaves	17
stigmaste-7-en-3*β*-ol (**98**)	*B. gymnorrhiza*	leaves	17
stigmasterol (**99**)	*B. gymnorrhiza*	leaves	17
α-hydroxy-sitosterol (**100**)	*B. sexangula* var. *rhynchopetala*	stem	12
Kauranes (Diterpenoids)			
(16*R*)-13,17-epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-al (**101**)	*B. sexangula var. rhynchopetala*	stem	11
13,16,17-trihydroxy-*ent*-9(11)-kaurene-19-oic acid (**102**)	*B. gymnorrhiza*	stem	22
13-hydroxy-16-ent-kauren-19-al (**103**)	*B. gymnorrhiza*	stem	22
	B. gymnorrhiza	bark	23
16,17-dihy-droxy-ent-9(11)-kaurene-19-al (**107**)	*B. gymnorrhiza*	stem	22
	B. sexangula var. *rhynchopetala*	stem	11
16,17-dihydroxy-*ent*-9(11)-kauren-19-oic acid (**108**)	*B. gymnorrhiza*	stem	22
16,17-dihydroxy-19-nor-*ent*-kaur-9(11)-en-3-one (**109**)	*B. sexangula* var. *rhynchopetala*	stem	11
16-*ent*-kaurene-13,19-diol **(115)**	*B. gymnorrhiza*	stem	22
	B. gymnorrhiza	bark	23
	B. cylindrica	roots	24
16-*ent*-kauren-19-ol (**110**)	*B. gymnorrhiza*	stem	22
16*H*-17,19-*ent*-kauranediol (**104**)	*B. gymnorrhiza*	stem	22
16*H*-17-hydroxy-*ent*-kauran-19-oic acid (**105**)	*B. gymnorrhiza*	stem	22
16,17-dihydroxy-*ent*-kauran-19-al (**106**)	*B. gymnorrhiza*	stem	22
17-chloro-13,16-dihydroxy-*ent*-kauran-19-al (**111**)	*B. gymnorrhiza*	stem	22
ceriopsin F (**113**)	*B. sexangula* var. *rhynchopetala*	stem	11
steviol (**120**)	*B. gymnorrhiza*	bark	23

methyl(16*R*)-13,17-epoxy-16-hydroxy-*ent*-kaur-9(11)-en-19-oate (**119**)	*B. sexangula* var. *rhynchopetala*	stem	11
	B. gymnorrhiza	bark	23
methyl-16*α*,17-dihydroxy-*ent*-kaur-9(11)-en-19-oate (**116**)	*B. sexangula* var. *rhynchopetala*	stem	11
	B. gymnorrhiza	stem	22
methyl-16,17-dihydroxy-*ent*-kauran-19-oate (**117**)	*B. gymnorrhiza*	stem	22
Pimaranes (Diterpenoids)			
15(*S*)-isopimar-7-en-15,16-diol (**123**)	*B. gymnorrhiza*	stem	25
	B. gymnorrhiza	root bark	23
ent-8(14)-pimarene-15*R*,16-diol (**128**)	*B. gymnorrhiza*	stem	25
ent-8(14)-pimarene-1*α*,15*R*,16-triol (**129**)	*B. gymnorrhiza*	Stem, root bark	25, 23
isopimar-7-ene-1β,15R,16-triol **(130)**	*B. gymnorrhiza*	stem	25
(5*R*,9*S*,10*R*,13*S*,15*S*)*ent*-8(14)-pimarene-1-oxo-15*R*,16-diol (**122**)	*B. gymnorrhiza*	stem	25
(1*α*H,15*R*)-ent-pimar-8(14)-ene-1,15,16-triol (**121**)	*B. sexangula* var. *rhynchopetala*	stem	11
Beyeranes (Diterpenoids)			
(4*R*,5*S*,8*R*,9*R*,10*S*,13*S*)-*ent*-17-hydroxy-16-oxobeyeran-19-al (**135**)	*B. gymnorrhiza*	stem	22
ent-17-hydroxy-16-oxobeyer-9(11)-en-19-al (**136**)	*B. sexangula* var. *rhynchopetala*	stem	11
Sulphur compounds			
4-hydroxy-1,2-dithiolane (**144**)	*B. cylindrica*	stem and bark	14
brugierol (**145**)	*B. cylindrica*	stem and bark	14
	B. gymnorrhiza	flowers, leaves and stem	26, 27
	B. sexangula var. *rhynchopetala*	stem	11
bruguiesulfurol (**146**)	*B. gymnorrhiza*	Flowers, leaves and stem	26, 27
cis-3,30-dihydroxy-1,5,10,50-tetrathiacyclodecane (**147**)	*B. gymnorrhiza*	leaves and stem	27
gymnorrhizol (**148**)	*B. gymnorrhiza*	leaves and stem	27
isobrugierol **(149)**	*B. cylindrica*	stem and bark	14
	B. gymnorrhiza	flowers, leaves and stem	26, 27
	B. sexangula var. rhynchopetala	stem	11
neogymnorrhizol (**150**)	*B. gymnorrhiza*	leaves and stem	27
trans-3,30-dihydroxy-1,5,10,50-tetrathiacyclodecane (**151**)	*B. gymnorrhiza*	leaves and stem	27
(–)-3,4-dihydro-3-hydroxy-7-methoxy-2*H*-1,5-benzodithiepine-6,9-dione (**152**)	*B. sexangula* var. *rhynchopetala*	stem	11
Aromatic compounds			
1-(3-hydroxyphenyl)-hexane-2,5-diol (**153**)	*B. gymnorrhiza*	stem	28
2,3-dimethoxy-5-propylphenol (**154**)	*B. gymnorrhiza*	branch	29
3-(3-hydroxybutyl)-1,1-dimethylisochroman-6,8-diol (**155**)	*B. gymnorrhiza*	stem	28
bruguierol A (**156**)	*B. gymnorrhiza*	stem	28
bruguierol B (**157**)	*B. gymnorrhiza*	stem	28
bruguierol C (**158**)	*B. gymnorrhiza*	stem	28
bruguierol D (**159**)	*B. gymnorrhiza*	branch	29
Carbohydrates			
1-d-1-*O*-methyl muco inositiol (**161**)	*B. exaristata*	leaves	7
Benzoquinone			
2,6-dimethoxy-1,4-benzoquinone (**162**)	*B. sexangula* var. *rhynchopetala*	stem	11
Phenolic glycosides			

1-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]-3,4,5-trimethoxybenzene (**163**)	*B. sexangula* var. *rhynchopetala*	stem	13
3,4,5-trimethoxyphenyl-β-D-glucopyranoside (**164**)	*B. sexangula* var. *rhynchopetala*	stem	13
rhyncoside A (**168**)	*B. sexangula* var. *rhynchopetala*	stem	13
rhyncoside B (**169**)	*B. sexangula* var. *rhynchopetala*	stem	13
rhyncoside C (**170**)	*B. sexangula* var. *rhynchopetala*	stem	13
rhyncoside D (**171**)	*B. sexangula* var. *rhynchopetala*	stem	13
Flavonoids			
myricetin-3-*O*-rutinoside (**199**)	*B. sexangula* var. *rhynchopetala*	stem	13
nicotiflorin (**200**)	*B. sexangula* var. *rhynchopetala*	stem	13
rutin (**205**)	*B. sexangula* var. *rhynchopetala*	stem	13
tricin (**206**)	*B. sexangula* var. *rhynchopetala*	stem	13
Lignans			
(+)-5′-methoxyisolariciresinol-9′-β-D-xylopyranoside (**207**)	*B. sexangula* var. *rhynchopetala*	stem	13
(+)-lyoniresinol-3α-*O*-α-L-rhamnopyranoside (**208**)	*B. sexangula* var. *rhynchopetala*	stem	13
brugunin A (**209**)	*B. gymnorrhiza*	branch	29
hedyotisols A (**210**)	*B. sexangula* var. *rhynchopetala*	stem	13
hedyotisols B (**211**)	*B. sexangula* var. *rhynchopetala*	stem	13
hedyotisols C (**212**)	*B. sexangula* var. *rhynchopetala*	stem	13
lyoniside (**213**)	*B. sexangula* var. *rhynchopetala*	stem	13
rhynocoside E (**214**)	*B. sexangula* var. *rhynchopetala*	stem	13
rhynocoside F (**215**)	*B. sexangula* var. *rhynchopetala*	stem	13

Table 3. Chemical constituents of *Ceriops*

Compound Class and Name	Plant	Plant Part	References
Dolabranes (Diterpenoids)			
tagalsin A (**223**)	*Ceriops tagal*	stem and twigs	34
		aerial parts	35
tagalsin B (**224**)	*C. tagal*	stem and twigs	34
		aerial parts	35
tagalsin C (**225**)	*C. tagal*	stem and twigs	34
		aerial parts	35
		roots	36
tagalsin D (**226**)	*C. tagal*	stem and twigs	34
tagalsin E (**227**)	*C. tagal*	stem and twigs	34
		aerial parts	35
tagalsin F (**228**)	*C. tagal*	stem and twigs	34
		aerial parts	35
		roots	37, 38
tagalsin G (**229**)	*C. tagal*	stem and twigs	34
		aerial parts	35
tagalsin H (**230**)	*C. tagal*	stem and twigs	34
tagalsin O (**231**)	*C. tagal*	aerial part	35
tagalsin P (**232**)	*C. tagal*	stems and twigs	38
tagalsin Q (**233**)	*C. tagal*	stems and twigs	38
tagalsin R (**234**)	*C. tagal*	stems and twigs	38
tagalsin S (**235**)	*C. tagal*	stems and twigs	38
tagalsin T (**236**)	*C. tagal*	stems and twigs	38
tagalsin U (**237**)	*C. tagal*	stems and twigs	38
(5*S**,8*S**,9*S**,10*R**,13*S**)-3-hydroxy-16-nor-2-oxodolabr-3-en-15-oic acid (**219**)	*C. tagal*	stems and twigs	38
(5*S**,8*S**,9*S**,10*R**,13*S**)-3,16-dihydroxydolabar-3-ene-2,15-dione (**218**)	*C. tagal*	stems and twigs	38

(5*S**,8*S**,9*S**,10*,13*S**)-2-hydroxy-16-nor-3-oxodolabr-1,4(18)dien-15-oic acid (**217**)	*C. tagal*	stems and twigs	38
(5*S**,8*S**,9*S**,1*R**,13*S**)-dolabr-3-ene-15-,16-diol (**220**)	*C. tagal*	stems and twigs	38
(5*S**,8*S**,9*S**,10*R**,13*S**)-dolabr-4(18)-ene-15,16-diol (**216**)	*C. tagal*	stems and twigs	38
erythroxydiol Y (**222**)	*C. tagal*	stems and twigs	38
dolabr-4(17),15(16)-dien-3-one (**238**)	*C. tagal*	roots	39
7-glycoloyl-2-hydroxy-1,4b,7,10a-tetramethyl-4a,4b,5,6,7,8,8a,9,10,10a-decahydrohenanthren-3(4*H*)-one (**239**)	*C. tagal*	roots	40
Dimeri diterpenoids			
tagalsns I (**244**)	*C. tagal*	stems and twigs	41
	C. tagal	roots	36
tagalsins J (**245**)	*C. tagal*	stems and twigs	41
tagalsin L (**241**)	*C. tagal*	roots	42
tagalsin M (**242**)	*C. tagal*	roots	42
tagalsin N (**243**)	*C. tagal*	roots	42
8(14)-enyl-pimar-2'(3')-en-4'(18')-en-15'(16')endolabr-16,15,2',3'-oxoan-16-one (**240**)	*C. tagal*	roots	36
Beyranes (Diterpenoids)			
ceropsin A (**137**)	*C. tagal*	roots	30
ceiopsin B (**138**)	*C. tagal*	roots	30
criopsin G (**139**)	*C. tagal*	roots	31
isosteviol (**140**)	*C. tagal*	roots	31
Auranes (Diterpenoids)			
cerioprin E (**112**)	*C. tagal*	roots	32
ceriopsin F (**113**)	*C. tagal*	roots	31
steviol (**120**)	*C. tagal*	roots	31
methyl-ent-16*β*,17-dihydroxy-9(11)-kauren-19-oate (**118**)	*C. tagal*	roots	31
ent-16*β*,17-dihydroxy-9(11)-kauren-19-oic acid (**114**)	*C. decandra*	roots	31
Dammarane (Triterpenoids)			
cereotagalol A (**78**)	*C. tagal*	hypocotyls and fruits	43
cereotagalol B (**79**)	*C. tagal*	hypocotyls and fruits	43
cereotagaloperoxide (**80**)	*C. tagal*	hypocotyls and fruits	43
dammarenediol II (**81**)	*C. tagal*	hypocotyls and fruits	43
fouquierol (**82**)	*C. tagal*	hypocotyls and fruits	43
isofouquierol (**83**)	*C. tagal*	hypocotyls and fruits	43
ocotillol II (**84**)	*C. tagal*	hypocotyls and fruits	43
Oleananes (Triterpenoids)			
oleanolic acid (**70**)	*C. tagal*	hypocotyls and fruits	43
ursane (Triterpenoid)			
ursolic acid (**73**)	*C. decandra*	leaves	33
Lupanes (Triterpenoids)			
28-hydroxylup-20(29)-en-3-one (**27**)	*C. tagal*	aerial parts	44
	C. tagal	roots	36
3-*epi*-betulin (**28**)	*C. tagal*	aerial parts	44
30-nor-lup-3*β*-ol-2-one (**29**)	*C. decandra*	leaves	33
3-*epi*-betulinic acid (**30**)	*C. tagal*	aerial parts	44
3-oxo-lup-20(29)-en-28-oic acid (**31**)	*C. tagal*	roots	36
3*α*-betulinic acid (**33**)	*C. tagal*	hypocotyls and fruits	43
	C. decandra	leaves	33
3*α*-*O*-*trans*-coumaroylbetulinic acid (**35**)	*C. tagal*	aerial parts	44

3α-*O*-*trans*-feruloylbetulinic acid (**36**)	*C. tagal*	aerial parts	44
3β-*E*-caffeoyllupeol (**44**)	*C. decandra*	leaves	33
3β-*O*-*cis*-coumaroylbetulin (**39**)	*C. tagal*	aerial parts	44
3β,20-dihydroxylupane (**40**)	*C. decandra*	leaves	33
3β-acetylbetulinic acid (**41**)	*C. tagal*	hypocotyls and fruits	43
3β-*E*-caffeoylbetulin (**42**)	*C. tagal*	hypocotyls and fruits	43
3β-*E*-caffeoylbetulinic acid (**43**)	*C. tagal*	hypocotyls and fruits	43
3β-*E*-coumaroyllupeol (**45**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
3β-*E*-feruloylbetulin (**46**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
3β-*E*-feruloylbetulinic acid (**47**)	*C. tagal*	hypocotyls and fruits	43
3β-*E*-feruloyllupeol (**48**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
3β-hydroxylupan-29-oic acid (**49**)	*C. decandra*	leaves	33
3β-*O*-*cis*-coumaroylbetulinic acid (**50**)	*C. tagal*	aerial parts	44
3β-*O*-*trans*-feruloylbetulin (**51**)	*C. tagal*	aerial parts	44
3β-*O*-*cis*-feruloylbetulin (**52**)	*C. tagal*	aerial parts	44
3β-*O*-*trans*-coumaroylbetulinic acid (**53**)	*C. tagal*	aerial parts	44
3β-*O*-*trans*-coumaroylbetulin (**54**)	*C. tagal*	aerial parts	44
3β-*Z*-coumaroyllupeol (**55**)	*C. decandra*	leaves	33
3β-*Z*-feruloyllupeol (**56**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
betulin (**57**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
	C. tagal	aerial parts	44
betulinaldehyde (**58**)	*C. decandra*	leaves	33
betulinic acid (**59**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
betulonic acid (**60**)	*C. tagal*	hypocotyls and fruits	43
lup-20(29)-en-3β,28-diol (**61**)	*C. tagal*	roots	39
	C. tagal	roots	36
lup-20(29)-en-3β,30-diol (**62**)	*C. decandra*	leaves	33
lup-20(29)-en-3β-hydroxy-28-oic (**63**)	*C. tagal*	roots	39
lupenone (**64**)	*C. decandra*	leaves	33
lupeol (**65**)	*C. decandra*	leaves	33
	C. tagal	hypocotyls and fruits	43
	C. tagal	aerial parts	44
	C. tagal	roots	39
Pimaranes (Diterpenoids)			
8,15-repoxypimaran-16-ol (**125**)	*C. decandra*	roots	31
ceriopsin C (**126**)	*C. decandra*	roots	30
ceriopsin D (**127**)	*C. decandra*	roots	30
ent-8(14)-pimarene-15*R*,16-diol (**128**)	*C. tagal*	roots	45
	C. tagal	stems and twigs	38
isopimar-8(14)-en-15,16-diol (**131**)	*C. tagal*	roots	39
isopimar-8(14)-en-16-hydroxy-15-one (**132**)	*C. tagal*	roots	39
methoxy-ent-8(14)-pimarenely-15-one (**133**)	*C. tagal*	roots	45
Abietane (Triterpenoid)			
abieta-8,11,13-trien-18-oic acid (**246**)	*C. tagal*	stems and twigs	38
Steroids			
stigmasterol (**99**)	*C. tagal*	roots	45
β-sitosterol (**96**)	*C. tagal*	roots	45

Table 4. Chemical constituents of the bark of *Kandelia candel*

Compound Class	Compound Name
Propelargonidin dimers	afzelechin-(4α→8)- afzelechin (**180**) afzelechin-(4α→8)- catechin (**181**) afzelechin-(4α→8)- epicatechin (**182**)
Procyanidin trimers	epicatechin-(4β→6)-epicatechin-(4β→6)-epicatechin (**188**) epicatechin-(4β→6)-epicatechin-(4β→8)-catechin (**189**) epicatechin-(4β→6)-epicatechin-(4β→8)-epicatechin (**190**)
Proanthocynadins	cinchonain Ia (**184**) cinchonain Ib (**185**) cinchonain IIa (**186**) cinchonain IIb (**187**) kandelins A-1, A-2, B-1, B-2, B-3, B-4 (**193–198**) proanthicyanidin B-1, B-2, C-1 (**201–203**) proanthicyanidin trimer (**204**)
Flavan-3-ols	(–)-epicatechin (**172**) (+)-afzeleczhin (**173**) (+)-catechin (**174**) (+)-gallocatechin (**176**)

Table 5. Chemical constituents of the genus *Rhizophora*

Compound Class and Name	Plant	Plant Part	References
D-Friedooleananes (Triterpenoids)			
3β-*O*-*E*-coumaroyl-taraxerol (**15**)	*R. stylosa*	stems and twigs	48
3β-*E*-caffeoyltaraxerol (**16**)	*R. mucronata*	fruits	49
3β-*O*-*Z*)coumaroyl-taraxerol (**19**)	*R. stylosa*	stems and twigs	48
3β-taraxerol acetate (**20**)	*R. stylosa*	stems and twigs	48
3β-taraxerol formate (**21**)	*R. stylosa*	stems and twigs	48
3β-*Z*-caffeoyltaraxerol (**22**)	*R. mucronata*	fruits	49
3β-*Z*-*p*-coumaroyltaraxerol (**24**)	*R. mucronata*	fruits	49
3β-*E*-*p*-coumaroyltaraxerol (**18**)	*R. mucronata*	fruits	49
careaborin-(3β-*E*-*p*-coumaroyltaraxerol) (**18**)	*R. apiculata*	leaves	47
	R. stylosa	leaves	50
	R. stylosa	leaves	50
taraxerol (**28**)	*R. apiculata*	leaves	47
	R. mangle	leaves and stems	51
	R. stylosa	leaves	50
	R. stylosa	stems and twigs	48
	R. mucronata	fruits	49
taraxerone (**26**)	*R. stylosa*	leaves	50
taraxeryl-*cis*-*p*-hydroxycinnamate (**24**)	*R. apiculata*	leaves	47
Lupanes (Triterpenoids)			
trans-hydroxycinnamoyllupeol (**66**)	*R. mangle*	leaves and stems	51
lupeol (**65**)	*R. apiculata*	stem	52
	R. mucronata	leaves	17
	R. mucronata	stem bark	53
Oleananes (Triterpenoids)			
15α-hydroxy-β-amyrin (**67**)	*R. stylosa*	stems and twigs	48
3β-*O*-(*E*)-(4-methoxy)-cinnamoyl-15α-hydroxyl-β-amyrin (**68**)	*R. mucronata*	stem bark	53
3β-*O*-(*E*)-coumaroyl-15α-hydroxy-β-amyrin (**69**)	*R. stylosa*	stems and twigs	48
oleanolic acid (**70**)	*R. mucronata*	leaves	17
β-amyrin (**71**)	*R. mucronata*	root bark	54
	R. mucronata	leaves	17
Ursanes (Triterpenoids)			

ursolic acid (**73**)	*R. mucronata*	leaves	17
α-amyrin (**74**)	*R. mucronata*	root bark	54
Aliphatic alcohols			
dotriacontanol (**247**)	*R. apiculata*	heartwood	55
hentriacontanol (**248**)	*R. apiculata*	heartwood	55
nonacosanol (**249**)	*R. apiculata*	heartwood	55
octacosanol (**250**)	*R. apiculata*	heartwood	55
triacontanol (**251**)	*R. apiculata*	heartwood	55
Aliphatic saturated carboxylic acids			
doicosanoic (**252**)	*R. apiculata*	heartwood	55
henicosanoic (**253**)	*R. apiculata*	heartwood	55
hentriacontanoic (**254**)	*R. apiculata*	heartwood	55
heptacosanoic (**255**)	*R. apiculata*	heartwood	55
hexatriacontanoic (**256**)	*R. apiculata*	heartwood	55
octacosanoic (**257**)	*R. apiculata*	heartwood	55
pentacosanoic (**258**)	*R.a apiculata*	heartwood	55
tetracosanoic (**259**)	*R. apiculata*	heartwood	55
tetratriacontanoic (**260**)	*R. apiculata*	heartwood	55
triacontanoic (**261**)	*R. apiculata*	heartwood	55
tritriacontanoic (**262**)	*R. apiculata*	heartwood	55
Steroids			
campesterol (**92**)	*R. apiculata*	heartwood	55
daucosterol (**94**)	*R. mucronata*	root bark	54
	R. stylosa	leaves	50
ergosta-7,22-dien-3*β*-ol (**95**)	*R. apiculata*	stem	52
sitosterol (**96**)	*R. apiculata*	heartwood	55
	R. mucronata	root bark	54
	R. stylosa	leaves	50
sitosteryl-3-glucoside (**97**)	*R. apiculata*	heartwood	55
stigmasterol (**99**)	*R. apiculata*	heartwood	55
Aromatic compound			
syringaldehyde (**160**)	*R. apiculata*	heartwood	55
Benzoquinone			
2,6-dimethoxy-*p*-benzoquinone (**162**)	*R. apiculata*	heartwood	55
Labdanes(Diterpenoids)			
apiculol (**263**)	*R. apiculata*	roots	56
rhizophorin A (**264**)	*R. mucronata*	roots	57
	R. mucronata	roots	58
Beyeranes (Diterpenoids)			
rhizophorin B (**141**)	*R. mucronata*	roots	58
rhizophorin C (**142**)	*R. mucronata*	roots	58
rhizophorin D (**143**)	*R. mucronata*	roots	58
Pimaranes (Diterpenoids)			
15(*S*)-isopimar-7-en-1-oxo-15,16-diol (**124**)	*R. apiculata*	stem	52
rhizophorin E (**134**)	*R. mucronata*	roots	58
Kauranes (Diterpenoids)			
13,16*α*,17-trihydroxy-*ent*-9(11)-kauren-19-oic acid (**102**)	*R. apiculata*	stem	52
16*R*-13,17-epoxy-16-hydroxy-ent-kaur-9(11)-en-19-al (**101**)	*R. apiculata*	stem	52
ent-12,17-epoxy-16*β*-hydroxy-9(11)-kauren-19-oate (**112**)	*R. apiculata*	stem	52
methyl-*ent*-16*β*,17-dihydroxy-9(11)-kauren-19-oate (**118**)	*R. apiculata*	stem	52
methyl-ent-kaur-9(11)-*ent*-13,17-expoxy-16-hydroxy-19-oate (**119**)	*R. apiculata*	stem	52
Sesquiterpene			

mucronatone (**265**)	*R. mucronata*	fruits	49
Carbohydrate			
1-d-*O*-methyl-muco-inositol (**161**)	*R. mucronata*	roots	7
Hopanoid			
adian-5-en-3-ol (**266**)	*R. mucronata*	stem bark	53
Phenolic compounds			
atranorin (**165**)	*R. mucronata*	root bark	54
protocatechuic acid (**167**)	*R. stylosa*	leaves	50
isovanillic acid (**166**)	*R. stylosa*	leaves	50
Xanthone(aromatic ketone)			
lichixanthone (**267**)	*R. mucronata*	root bark	54
Aliphatic ketone			
palmitone (**268**)	*R. mucronata*	root bark	54
Flavonoids			
rutin (**205**)	*R. stylosa*	leaves	50
astilbin (**183**)	*R. stylosa*	leaves	50
(–)-3,7-*O*-diacetyl-epicatechin (**178**)	*R. stylosa*	stems and twigs	59
(–)-epicatechin (**172**)	*R. stylosa*	stems and twigs	59
	R. stylosa	stems	60
(–)-3-O-acetyl-epicatechin (**179**)	*R. stylosa*	stems and twigs	59
(–)-3,3′,4′,5,7-O- pentaacetyl-epicatechin (**177**)	*R. stylosa*	stems and twigs	59
(+)-afzelechin (**173**)	*R. stylosa*	stems and twigs	59
(+)-catechin (**174**)	*R. stylosa*	stems and twigs	59
	R. stylosa	stems	60
proanthocyanidin B2 (**202**)	*R. stylosa*	stems and twigs	59
glabraoside A (**191**)	*R. stylosa*	stems	60
glabraoside B (**192**)	*R. stylosa*	stems	60
cinchonain IIa (**186**)	*R. stylosa*	stems	60
cinchonain IIb (**187**)	*R. stylosa*	stems	60
(+)-catechin-3-*O*-α-L-rhamnoside (**175**)	*R. stylosa*	stems	60
cinchonain Ia (**186**)	*R. stylosa*	stems	60
	R. stylosa	stems	60
cinchonain Ib (**185**)	*R. stylosa*	stems and twigs	59
	R. stylosa	stems	60

2.3 *Kandelia*: There are two species in the mangrove genus *Kandelia*: *K. candel* and *K. obovata*. Only one report is available regarding the chemical constituents of plants of this genus. A few tannin compounds have been reported from *K. candel*. Investigation of *K. obovata* for its chemical constituents remains to be observed. 24 phenolic compounds including three propelargonidin dimmers, three procyanidin trimers, fourteen proanthocyanidins and four flavan-3-ols have been isolated from the bark of *K. candel Druce*[46].

2.4 *Rhizhophora*: The mangrove genus *Rhizophora* has ten species: *R. apiculata*, *R. harrisonii*, *R. lamarckii*, *R. mangle*, *R. mucronata*, *R. racemosa*, *R. samoesis*, *R. selala*, *R. stylosa* and *R. annamalayana*. Of these ten species, chemical constituents have only been reported in *R. apiculata*, *R. mangle*, *R. mucronata*, and *R. stylosa*. These reports reveal a total of 34 metabolites from *R. apiculata*, two metabolites from *R. mangle*, 23 metabolites from *R. mucronata* and 25 metabolites from *R. stylosa*, thus a total of 81 different metabolites from the genera *Rhizophora*, with details shown in Table 5.

The chemical investigation carried out by Majumdar and Patra in 1976 resulted in the isolation of β-amyrin, β-amyrone, taraxerol, β-sitosterol, and triacantanol from *R. apiculata*[47]. Later in early nineties Kokpol and his team had identified three terpenoids, five long chain aliphatic alcohols, eleven long chain aliphatic saturated carboxylic acids, three steroids, 2,6-dimethoxy-*p*-benzoquinone, syringaldehyde and sitosteryl 3-glucoside from this plant species. Also, five kauranes, one labdane and one pimarane diterpenoids and one lupane triterpenoid are reported so far from *R. apiculata*.

The study conducted by Williams et. al[51] reported the isolation and chemical characterisation of taraxerol and cinnamoyllupeol, two triterpenoids from the leaves and stems of *Rhizophora mangle* L. A variety of steroids, diterpenoids and triterpenoids were reported from the leaves and bark of *R. mucronata.* A few beyeranes (diterpenoids) were identified from this plant, and are unique to this species. Only triterpenoids of the classes oleananes and D-friedooleananes from *R. stylosa* are reported to date.

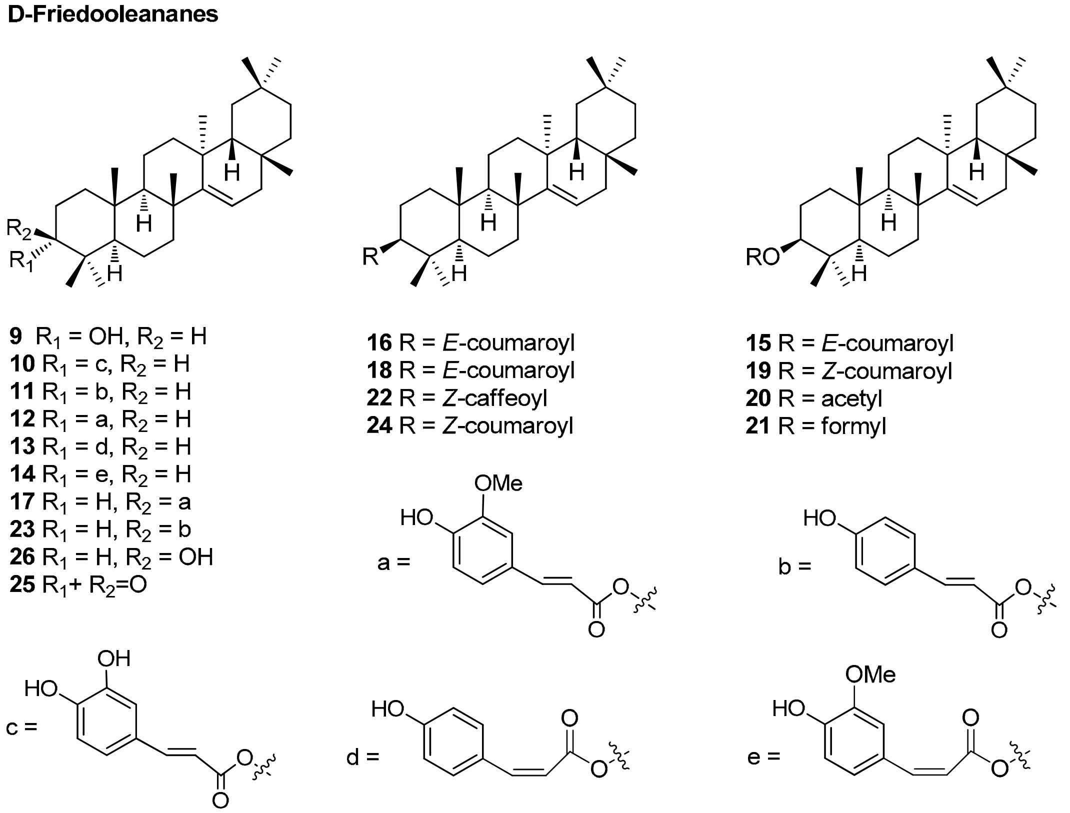


Figure 2. D-friedooleananes (triterpenoids) from Rhizophoraceae mangroves

3 Bioactivities

3.1 Bioactivities of Compounds Identified: With stably transfected HepG2 cells, three new dammarane triterpenes; bruguierins A–C and a new cyclic 4-hydroxy-dithiosulfonate-bruguiesulfurol as well as two known 4-hydroxydithiolane-1-oxides; brugierol and isobrugierol, were isolated from the flowers of *Bruguiera gymnorrhiza*. These phytochemicals activated an antioxidant response element (ARE luciferase activation) with EC_{50} values of 7.8, 9.4, 15.7, 56.7, 3.7 and 1.8 µM, respectively. Furthermore, bruguierin A, brugierol and isobrugierol also inhibited phorbol ester-induced NFκB (nuclear factor-κB) luciferase activation with an IC_{50} value of 1.4, 85.0 and 14.5 µM respectively, while bruguierin A and brugierol selectively inhibited cyclooxygenase-2 (COX-2) activity with an IC_{50} value of 0.37 and 6.1 µM respectively[18,26].

The compounds 16*α*-17,19-*ent*-kauranediol; 13-hydroxy-16-*ent*-kaurene-19-ol and 16-*ent*-kaurene-19-ol showed promising activity against K-562 (human chronic myeloid leukemia) and L-929 (mouse fibroblasts) of which 16-*ent*-kaurene-19-ol showed the greatest selectivity for K-562 (IC_{50} 6.8 µg/mL)[22]. (5*R*,9*S*,10*R*,13*S*,15*S*)*ent*-8(14)-pimarene-1-oxo-15,16-diol showed moderate cytotoxic activities against L-929[25].

The 15 membered macrocyclic polysulfide, gymnorrhizol, possesses an novel carbon skeleton which was isolated from *B. gymnorrhiza* and exhibited potent inhibitory activity against protein tyrosine phosphatase 1B (PTP1B). PTP1B is an enzyme involved in the regulation of insulin signaling and which is regarded as a key for treatment of type III diabetes and obesity[27]. One of the aromatic compounds extracted from the stem of *B. gymnorrhiza*, bruguierol C showed moderate activity against gram-positive and gram-negative bacteria including mycobacteria and resistant strains (MICs 12.5 µg/mL)[28].

The lupane caffeoyl ester, 3-(*Z*)-caffeoyllupeol extracted from *B. parviflora* exhibited antimalarial activity with an EC_{50} value of 8.6 µg/mL[8]. Sexangulic acid obtained from *B. sexangula* showed moderate *in vitro* cytotoxicity against human lung cancer (A-549) and human luekaemic (H-L60) cell lines at a concentration of 5 µg/ml[10]. Tagalsin C found in *C. tagal* was found to exhibit moderate cytotoxicity against HeLa human cervical carcinoma cell lines[35]. The dimeric diterpenoid, 8(14)-enyl-pimar-2'(3')-en-4'(18')-en-15'(16')-endolabr-16,15,2',3'-oxoan-16-one and the other terpenoids; tagalsin C, tagalsin I, lup-20(29)-ene-3*β*,28-diol , 3-oxolup-20(29)-en-28-oic acid and 28-hydroxy-lup-20(29)-en-3-one isolated from the roots of the mangrove plant *Ceriops tagal* exhibited antifouling activity against cyprid larvae of the barnacle without significant toxicity[36]. The other nontoxic antifouling compounds identified were ethoxy-*ent*-8(14)-pimarenely-15-one, *ent*-8(14)-pimarene-15*R*,16-diol, stigmasterol and *β*-sitosterol[45]. Tagalsins Q, R and U showed moderate antifeedant activity against the third instar larvae of

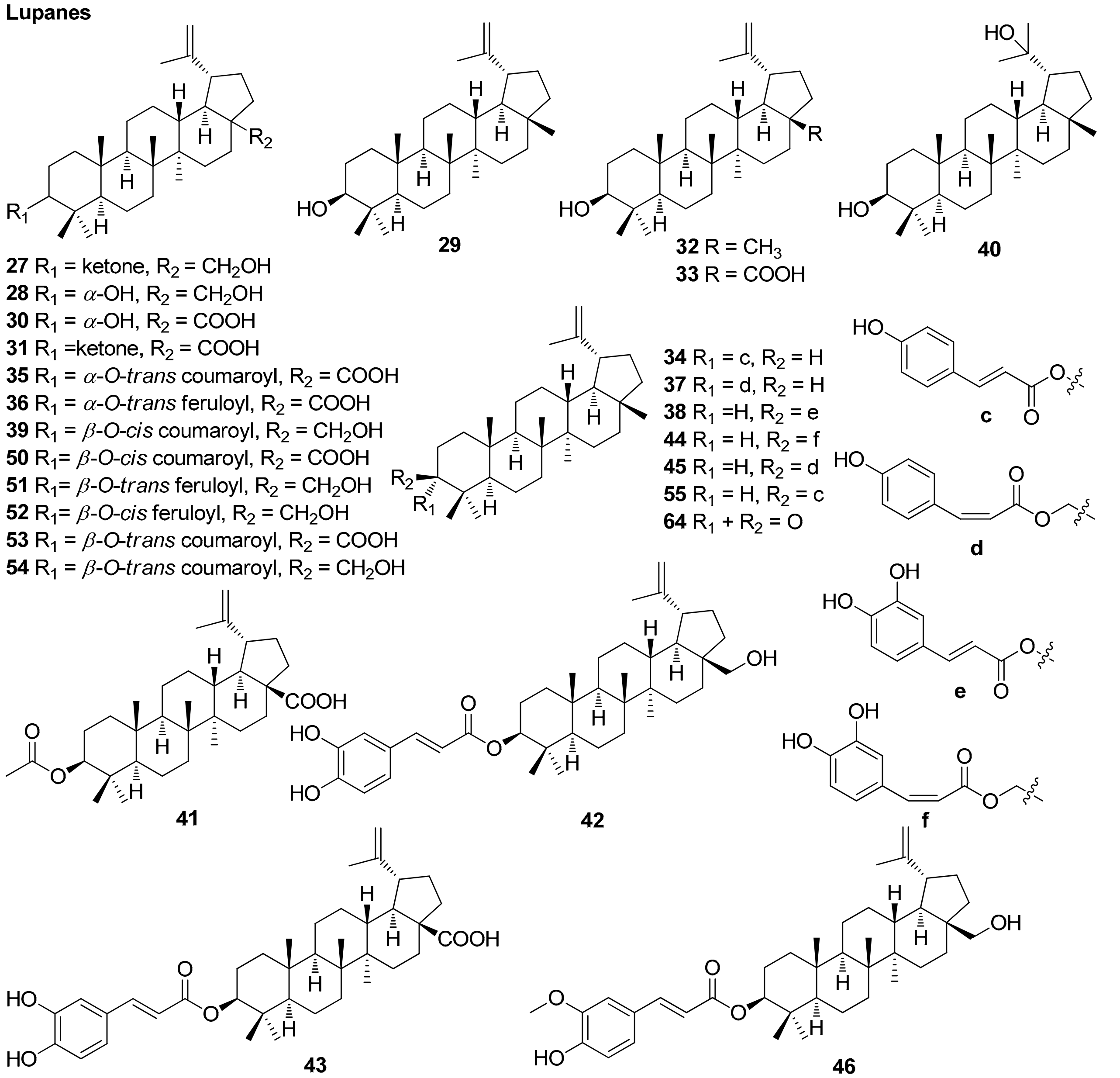


Figure 3-1. Lupanes from Rhizophoraceae mangroves

Brontispa longissima at a concentration of 1 mg/mL[38]. Dolabr-4(17),15(16)-dien-3-one, isopimar-8(14)-en-15,16-diol, isopimar-8(14)-en-16-hydroxy-15-one, lupeol, lup-20(29)-en-3*β*,28-diol and lup-20(29)-en-3*β*-hydroxy-28-oic acid were isolated from the roots of marine mangrove *C. tagal* which were evaluated for the activation of caspase-3 enzyme using caspase-3 colourimetric assay. Caspase-3 enzyme was activated by all compounds in cleaving *p*NA from Ac-DEVD-*p*NA in the presence of caspase-3-inhibitor; Ac-DEVD-CHO[39].

2,6-dimethoxy-*p*-benzoquinone isolated from *R. apiculata* was identified as an active constituent component against fungi, bacteria and boll weevils[55]. Taraxerol and cinnamoyllupeol, are two triterpenoids derived from the leaves and stems of *Rhizophora mangle* L, were found exhibit insecticidal activity towards *Cylas formicarius*: one of the most destructive pests of the sweet potato[51].

Among the compounds isolated from the leaves of *Rhizophora stylosa*, taraxerol has been confirmed to have growth inhibitory effects of Hela and BGC-823 with IC_{50} of 73.4 μmol/L and 73.3 μmol/L, respectively, while *cis*-careaborin may inhibit the growth of BGC-823 and MCF-7 with IC_{50} of 45.9 μmol/L and 116.0 μmol/L, respectively. Furthermore, the presence of astilbin and rutin were initially reported to stimulate the proliferation of mice splenic lymphocytes markedly in a dose-dependent manner[50]. The

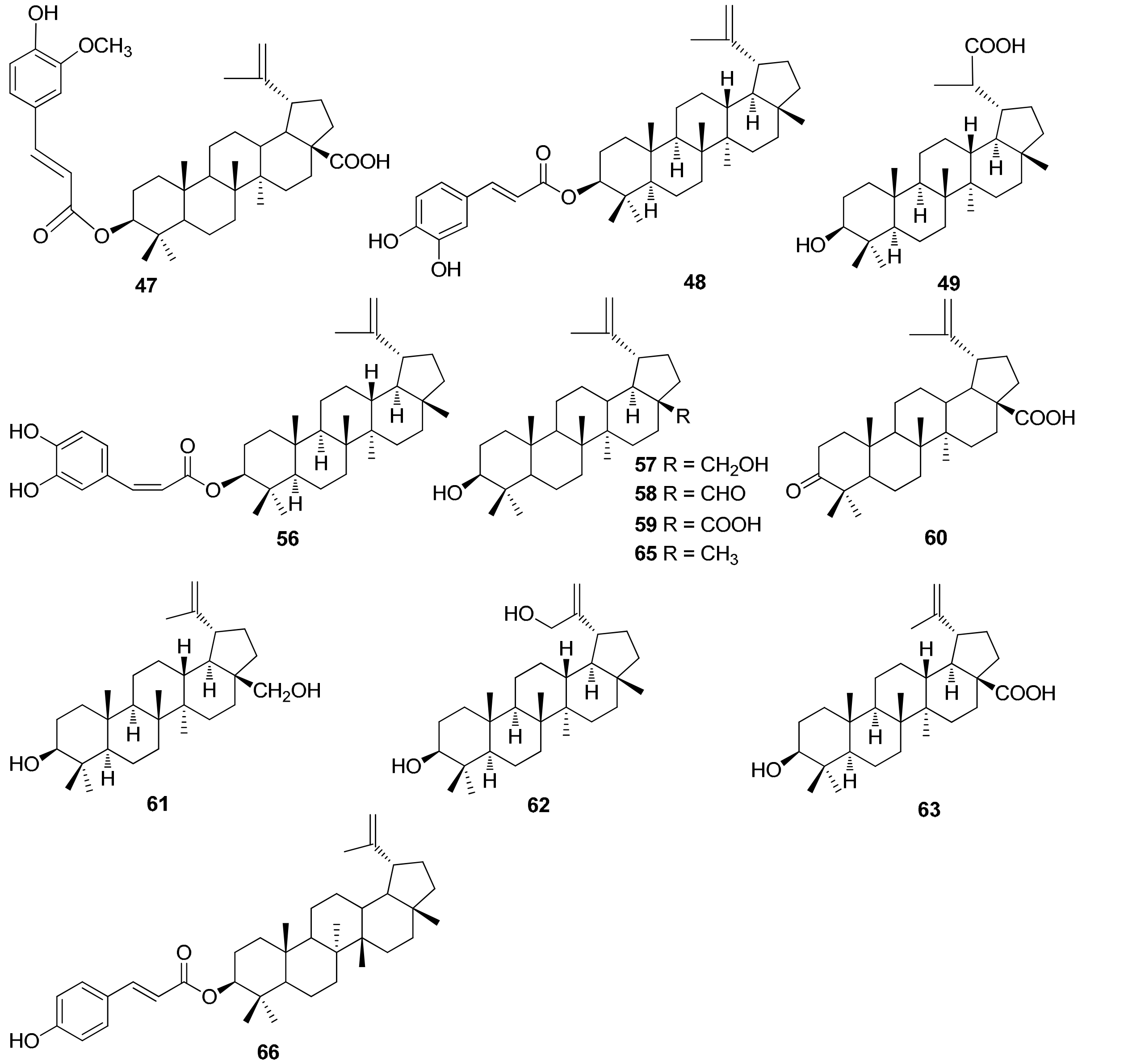
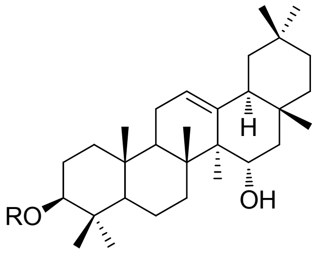


Figure 3-2. Lupanes from Rhizophoraceae mangroves

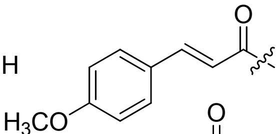
compounds, (–)-epicatechin, (–)-catechin, 3-O-acetyl-(–)-epicatechin, 3,7-O-acetyl-(–)-epicatechin, (+)-afzelechin, cinchonain 1b and proanthocyanidin B2 were isolated from the same plant displayed DPPH radical scavenging activity which were comparable to that of the positive control butylated hydroxytoluene (BHT). Proanthocyaninidin B2 showed the strongest activity with IC_{50} 4.3 μg/mL, being four fold greater than the positive control, BHT (IC_{50} 18.0 μg/mL). The antioxidant flavan-3-ol glycosides from *R. stylosa* showed an increase in their radical scavenging activities with increase in number of catechol moieties present in the molecules[60].

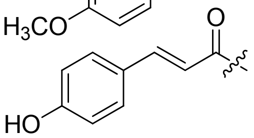
3.2 Bioactivities of Mangrove Extracts: Various publications have reported the biological activities of mangrove extracts. The components of crude alkaloid mixtures from *B. sexangula* and *B. exarista* were identified as tumor inhibitors[6]. A polysaccharide extracted from the leaves of *B. cylindrica*, *R. apiculata* and *R. mucronata* of Rhizophoraceae along with some other mangrove plants exhibited positive activity against human immunodefiency viruses (HIV)[61]. All parts of *Ceriops decandra* have proven antiviral activity[61]. It also possess promising antibacterial[62], antiinflammatory[63], and antidiabetic activity[64]. The leaves and bark extract of *C. tagal* shows antibacterial activity[65]. Phenolics are important components of the leaf extract and hypocotyls of *K. candel* and show excellent antioxidant activities[66,67]. Therefore, *K. candel* can be a good candidate for further development as an antioxidant medicine. During the study on the antibacterial activities of mangrove extracts against two antibiotic resistant

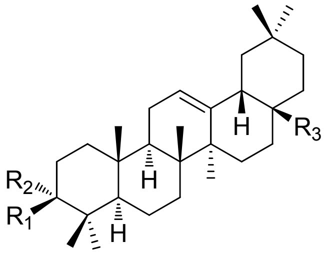
Oleananes and Ursanes



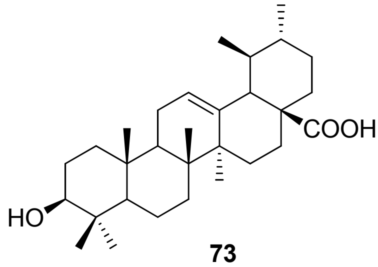
67 R = H

68 R = 

69 R = 



70 R_1 = OH, R_2 = H, R_3 = COOH
71 R_1 = OH, R_2 = H, R_3 = CH_3
74 R_1 = H, R_2 = OH, R_3 = CH_3



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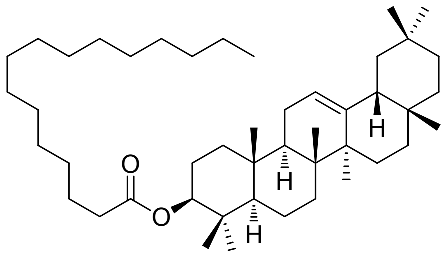

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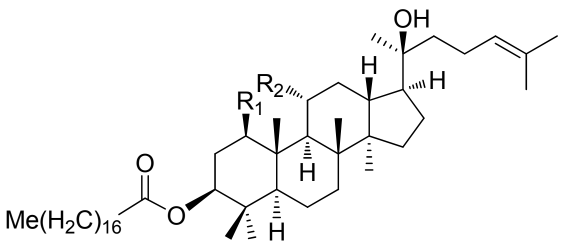
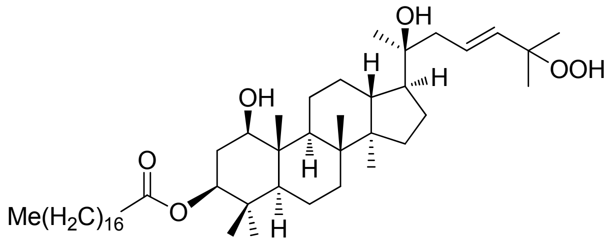
Dammaranes



75 R_1 = OH, R_2 = H
76 R_1 = H, R_2 = OH



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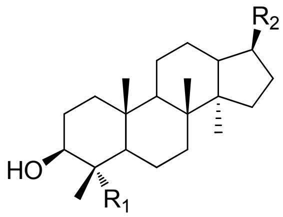
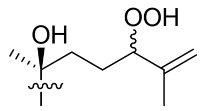


78 R_1 = CH_2OH, R_2 = B
79 R_1 = CH_2OH, R_2 = C
80 R_1 = CH_3, R_2 = A
81 R_1 = CH_3, R_2 = D
82 R_1 = CH_3, R_2 = B
83 R_1 = CH_3, R_2 = C
84 R_1 = CH_3, R_2 = E



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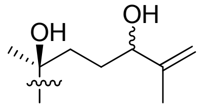

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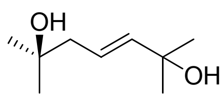

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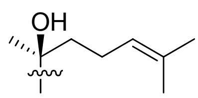

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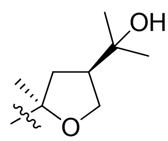


E

Figure 4. Oleananes, ursanes and dammaranes from Rhizophoraceae mangroves

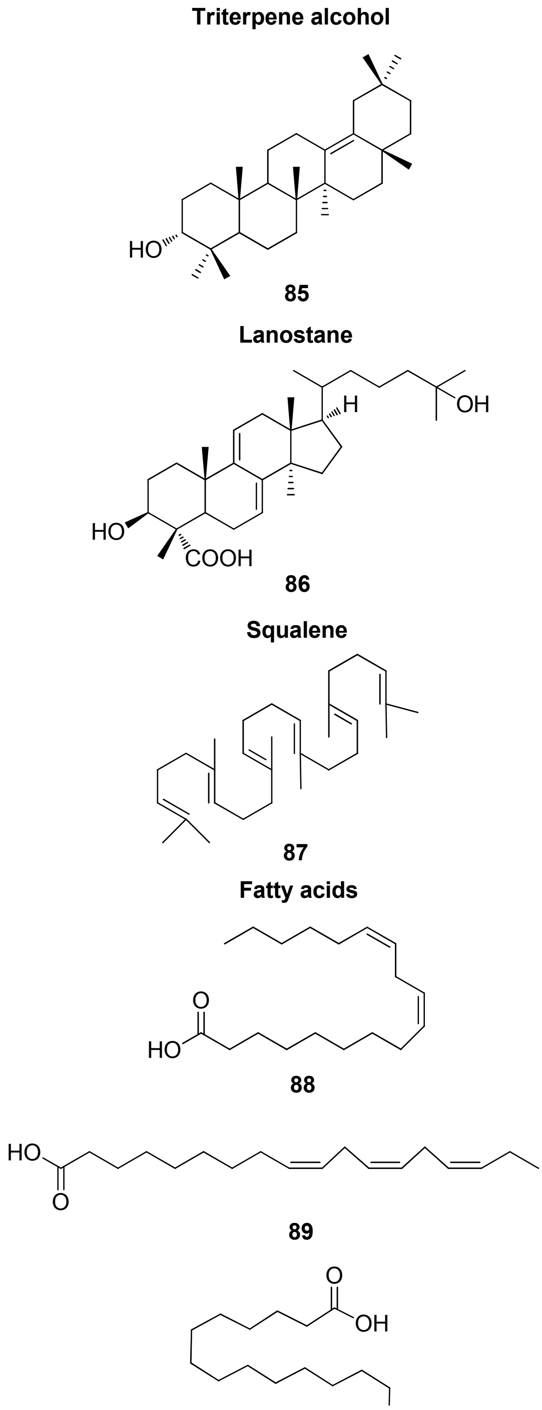


Figure 5. Triterpene alcohol, lanostane, squalene and fatty acids from Rhizophoraceae mangroves

pathogenic bacteria *Staphylococcus aureus* and *Proteus* sp., it was observed that the ethyl acetate extract of *B. Sexangula* and *R. apiculata* also possessed promising antibacterial activity[68]. This antibacterial activity was also reported in a study showing that gallic acid was extracted from hydrolysable tannin from the barks of *R. apiculata*. The gallic acid possessed a significant antiyeast (anticandidal) activity towards some yeast species of medical importance. It is anticipated that gallic acid from *R. apiculata* is a novel antiyeast agent which may be useful in the treatment of candidiasis[69]. Alcoholic extract of the leaves of *Rhizophora apiculata* from the mangrove forest of Sunderbans, West Bengal, India were prepared and displayed manglycemic/anti-hyperglycemic activity in streptozotocin induced diabetic rats fed a glucose bolus. The results of this study revealed that this plant extract had potential hypoglycemic action[70]. The cholinesterase inhibition activity of *R. lamarckii* was established by Natarajan et. al 2009. The antihyperglycaemic effect of *R. mangle* was studied[71]. The leaf extracts of three mangrove plants of Rhizophoraceae family; *Rhizophora mucronata*, *R. apiculata* and *R. annamalayana* were found to have potential anti-diabetic capacity due to the presence of an insulin-like protein[72]. The various studies mentioned, provide scientific support for the use of the mangroves in folklore medicine for the treatment of diabetes.

Various mangrove plants were tested for their antioxidant capacity[65,73]. It was found that the Rhizophoraceae mangroves showed comparatively higher antioxidant capacity which can be attributed to their higher phenolic content. Additionally, the mangrove plants of Rhizophoraceae family are the source of potent antiviral substances[61].

4 Chemotaxonomy

The chemical constituents of mangrove plants of the three true mangrove genera (Rhizophoraceae); *Bruguiera*, *Ceriops* and *Rhizophora*, are the diterpenoid class kauranes exist in the genera *Bruguiera* and *Ceriops*, however kauranes are absent in the genus *Rhizophora*. The genus *Bruguiera* is characterised by the presence of disulphides and polydisulphides which are unique to the genus. Thus they can be considered as significant chemotaxonamic markers of this genus. Also, it was observed that *ent*-pimarane coexists with isopimarane in the genus *Bruguiera*. Interestingly, dolabranes only exist in the genus *Ceriops* making it a significant chemotaxonomic marker. Similarly, labdane was found only in the genus *Rhizophora*, making it a significant chemotaxonomic marker of that specific genus.

Furthermore, extensive investigation is needed to identify and classify the chemical constituents of mangrove plants to construct a thorough basis for the chemotaxonamic studies of these versatile plants.

5 Conclusions

In this review, the chemistry and bioactivities of mangroves plants of Rhizophoraceae family have been summarised. Two types of diterpenoids; beyerane and pimarane, and three types of triterpenoids; lupane, oleanane and dammarane, are common chemical constituents ubiquitously found in this family, including 268 metabolites. To date, the chemical constituents from all the mangrove plants of this family have not been investigated. It is clear that mangrove plants can provide a new

Steroids

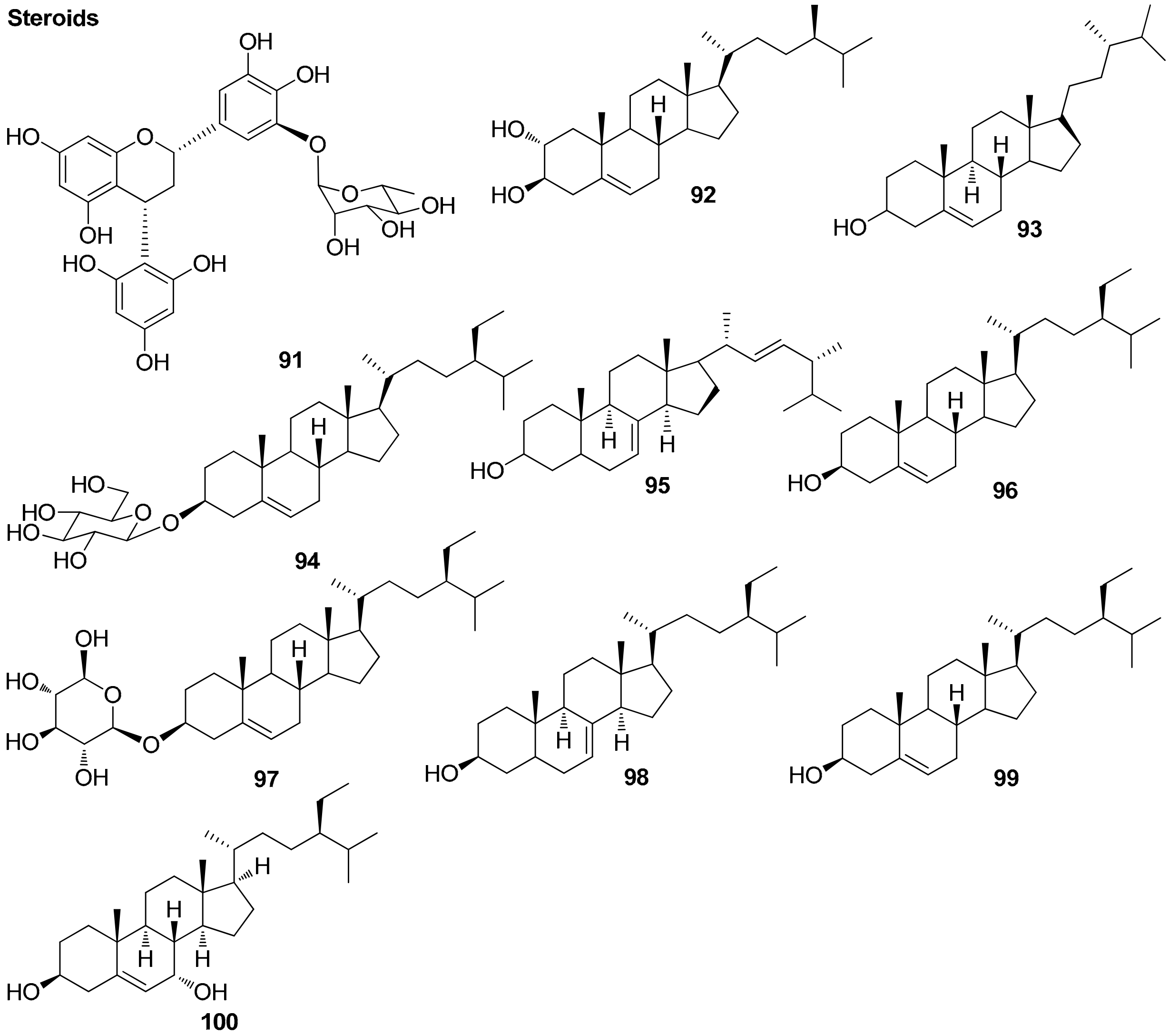
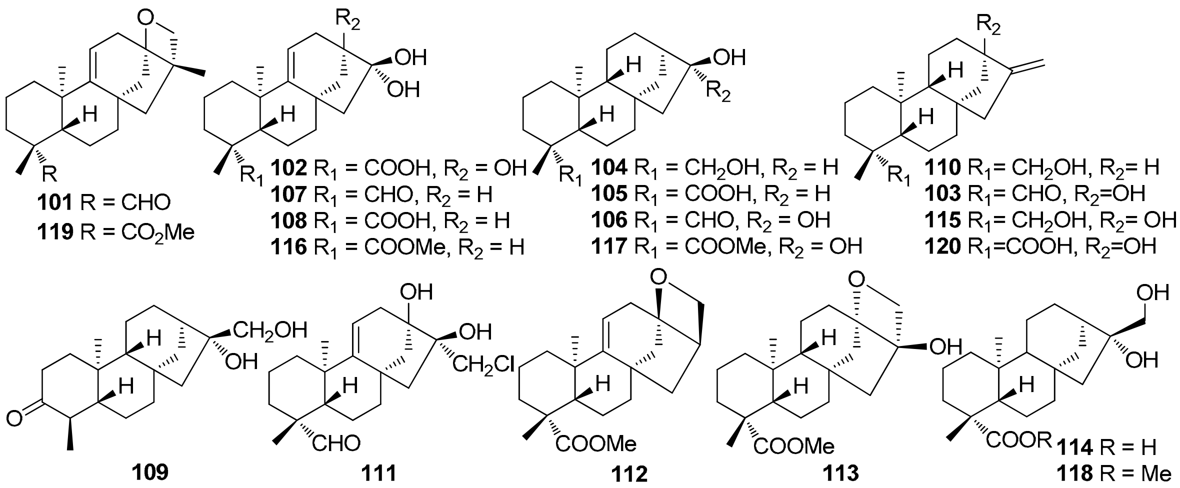
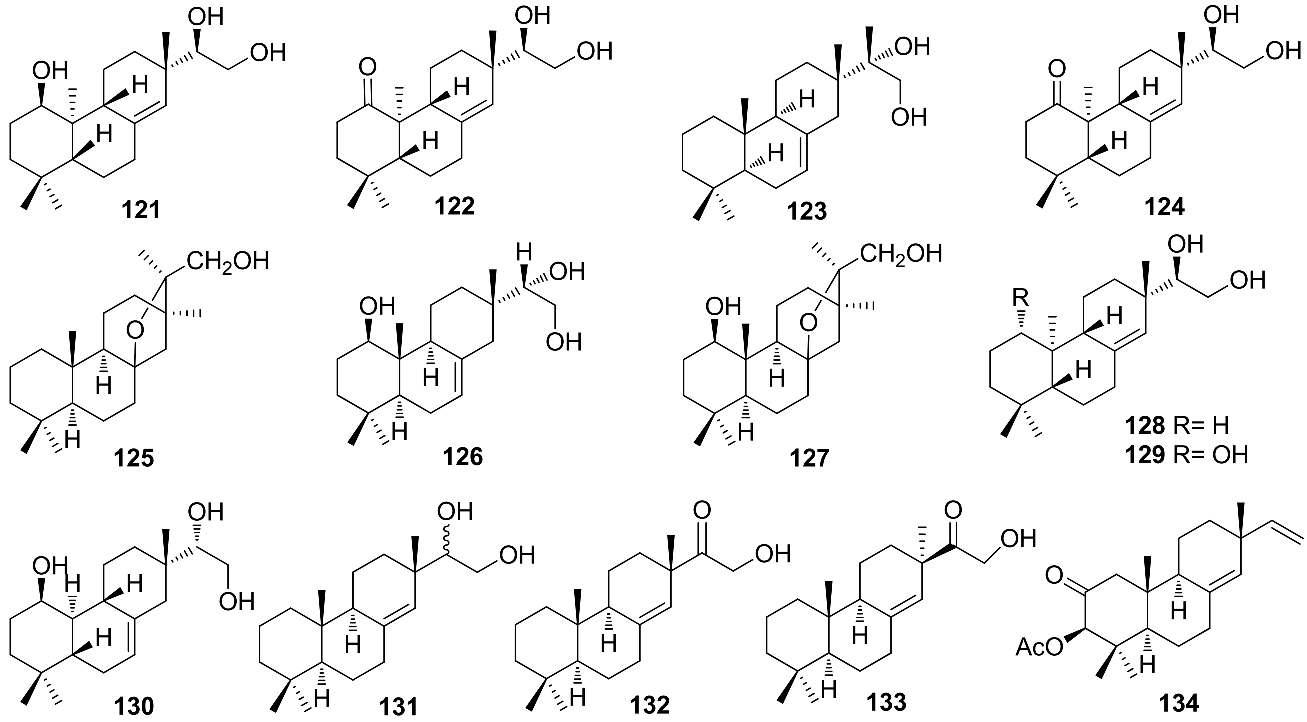


Figure 6. Steroids from Rhizophoraceae mangroves

Kauranes



Pimaranes



Beyeranes

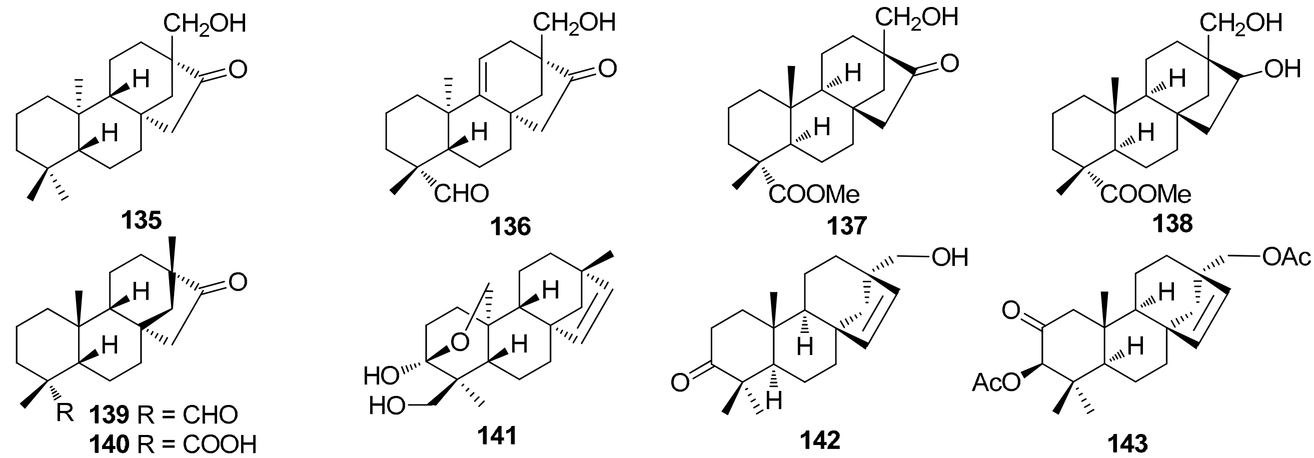
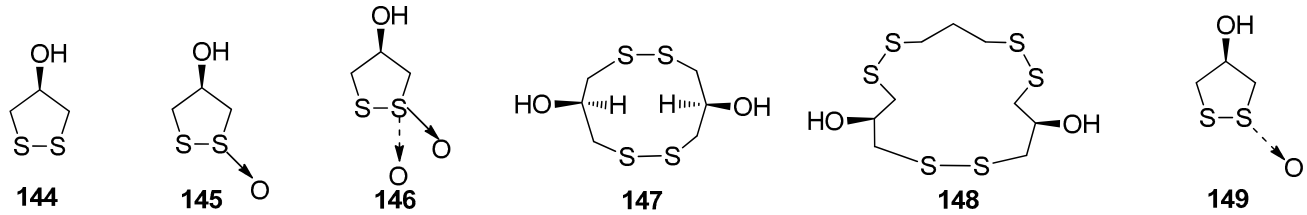
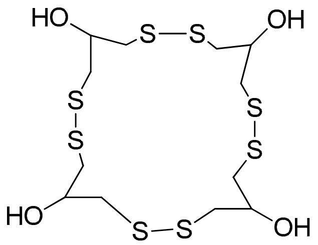


Figure 7. Kauranes, pimaranes and beyeranes (diterpenoids) from Rhizophoraceae mangroves

Sulphur compounds

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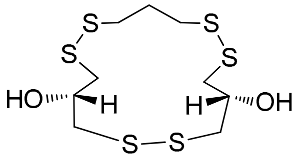
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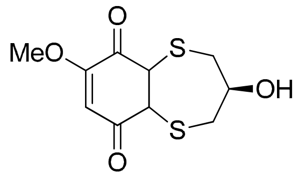
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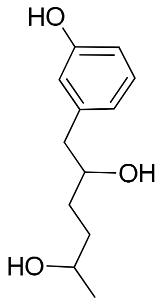
Figure 8. Sulphur compounds from Rhizophoraceae mangroves

Aromatic compounds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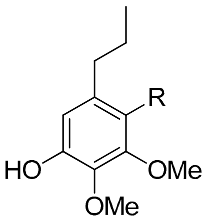
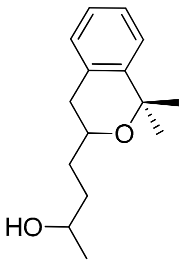

154 R = H
159 R = OMe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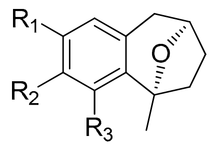
156 R_1 = OH, R_2 = H, R_3 = H
157 R_1 = OH, R_2 =OH, R_3 = H
158 R_1 = OH, R_2 = H, R_3 = OH

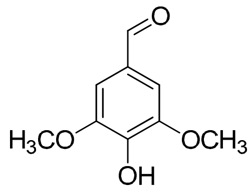
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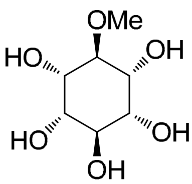
Figure 9. Sulphur compounds from Rhizophoraceae mangroves

Carbohydrate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Benzoquinone

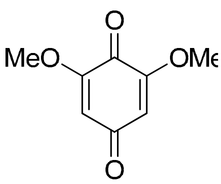
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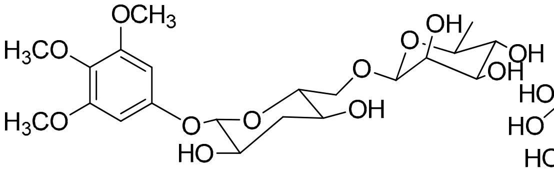
Figure 10. Carbohydrate and benzoquione identified from Rhizophoraceae mangroves

Phenolic compounds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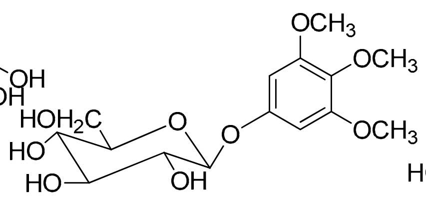
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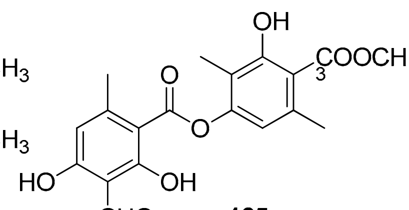
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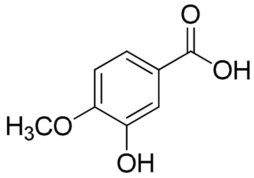

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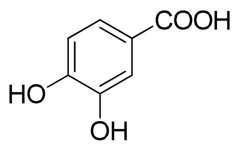

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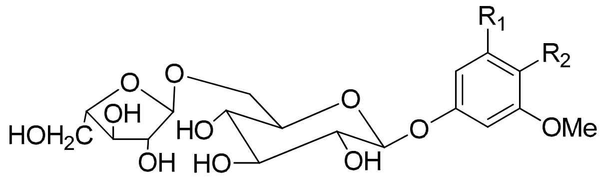

168 R_1 = H, R_2 = OH
169 R_1 = OMe, R_2 = OH
170 R_1 = OMe, R_2 = OMe

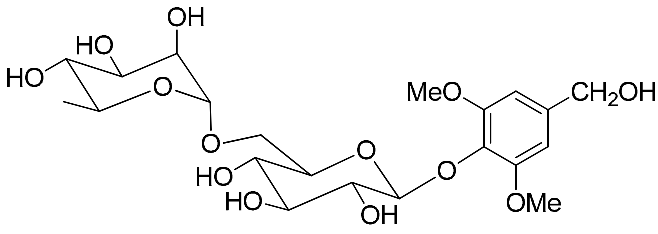

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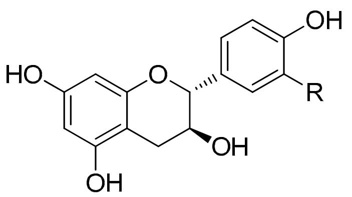
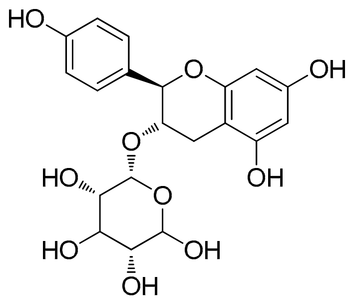
Figure 11. Phenolic compounds from Rhizophoraceae mangroves

Flavonoids



173 R = H
174 R = OH



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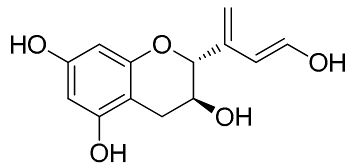

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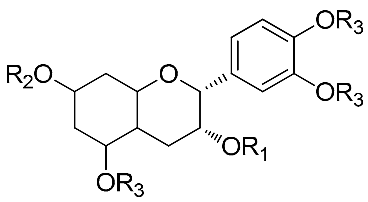
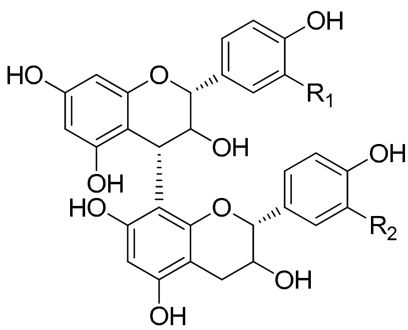
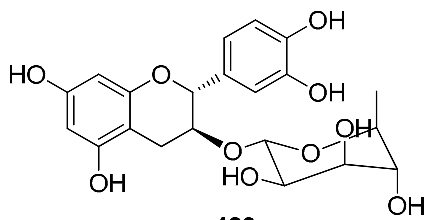


172 R_1 = H, R_2 = H, R_3 = H
177 R_1 = Ac, R_2 = Ac, R_3 = Ac
178 R_1 = Ac, R_2 = Ac , R_3 = H
179 R_1 = Ac, R_2 = H, R_3 = H



180 R_1 = H, R_2 = H
181 R_1 = H, R_2 = OH



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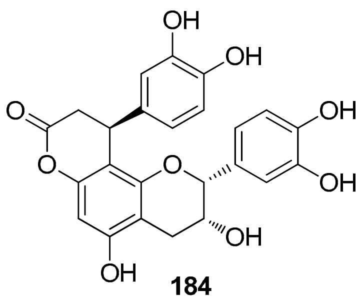

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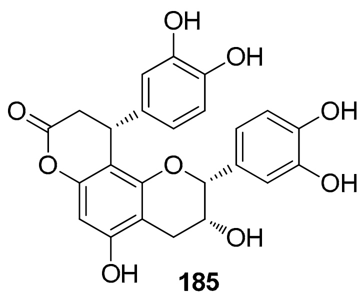

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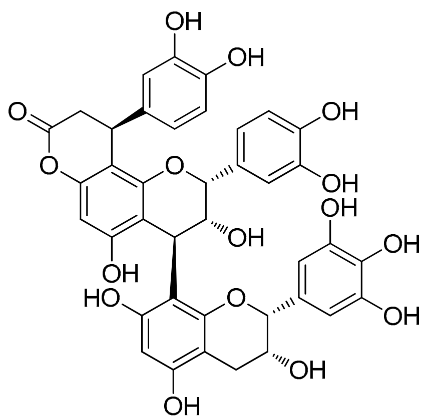

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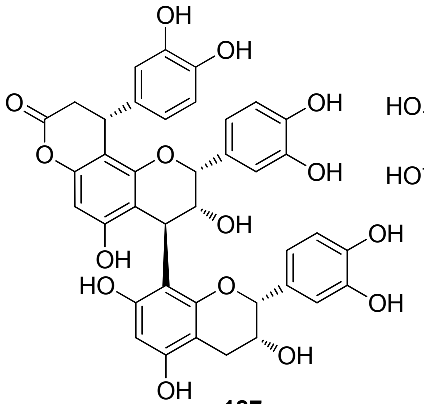

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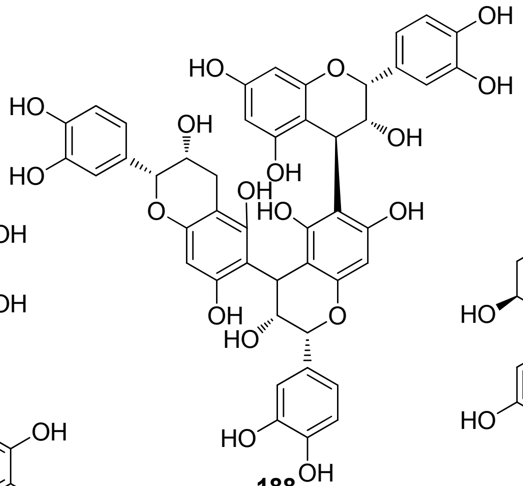

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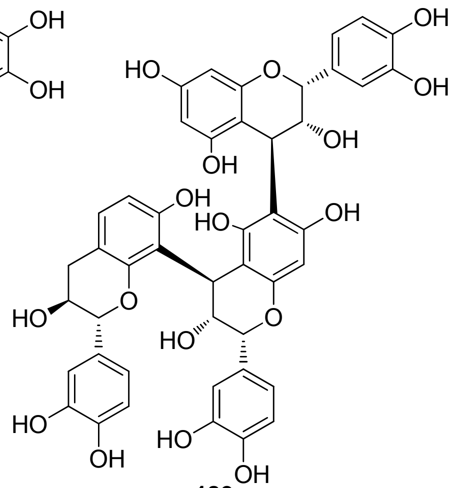

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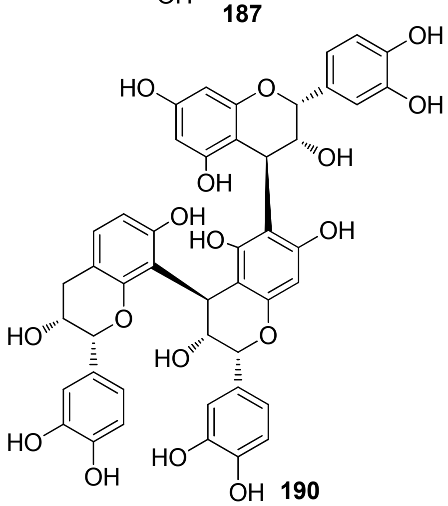

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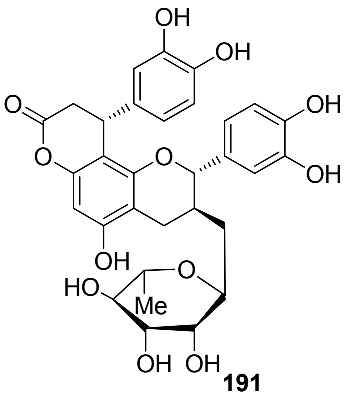

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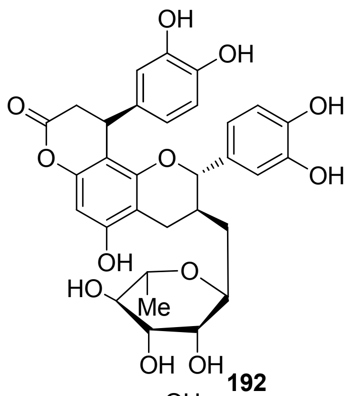

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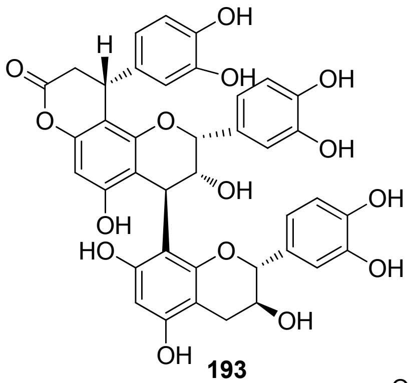

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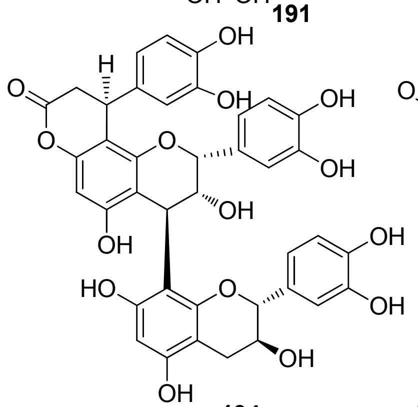

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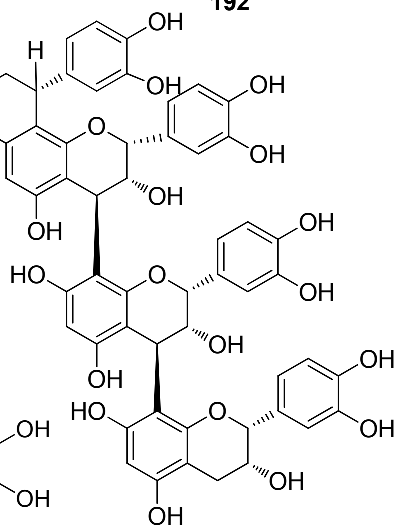

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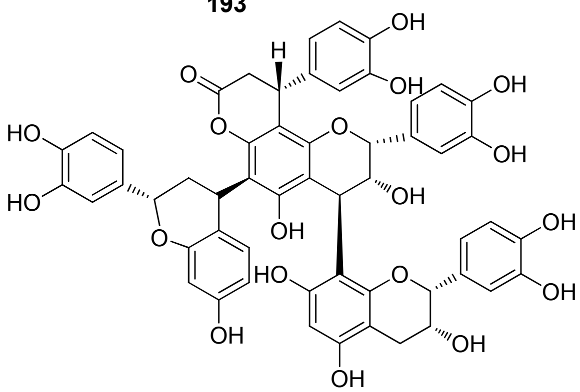

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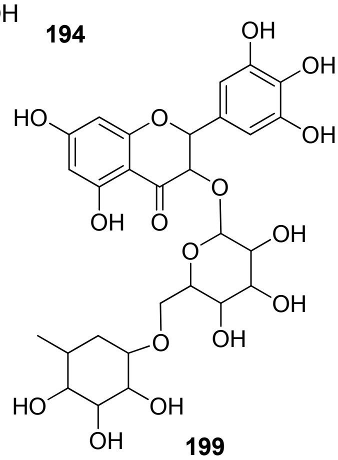

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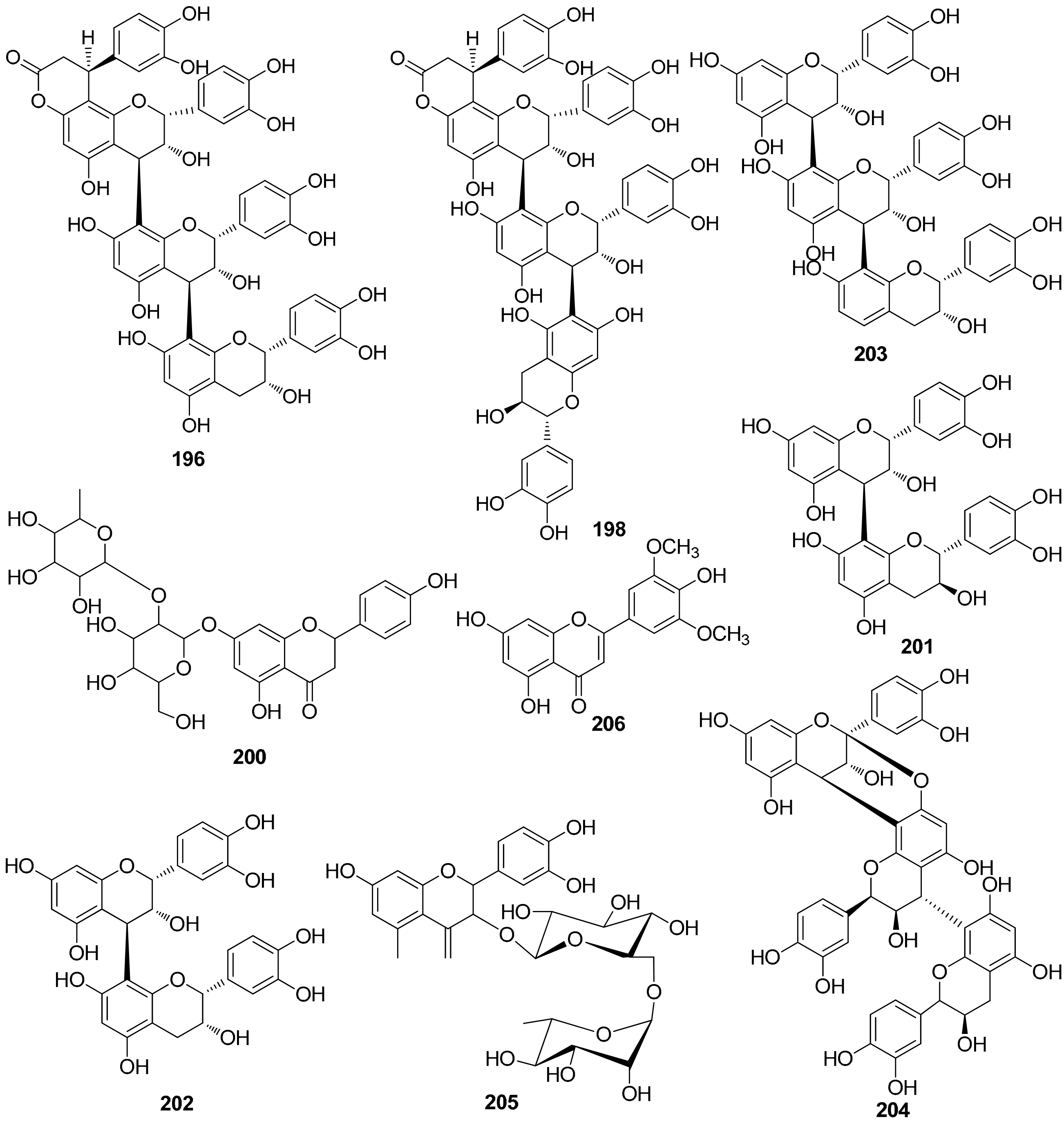
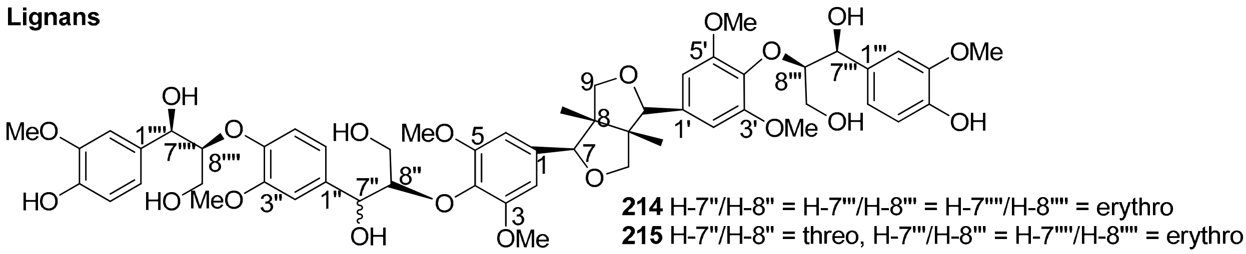
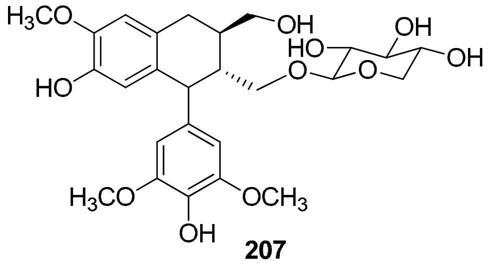


Figure 12. Flavonoids from Rhizophoraceae mangroves

Lignans



214 H-7''/H-8'' = H-7'''/H-8''' = H-7''''/H-8'''' = erythro
215 H-7''/H-8'' = threo, H-7'''/H-8''' = H-7''''/H-8'''' = erythro



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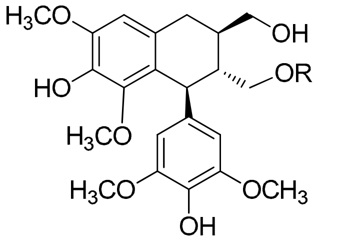
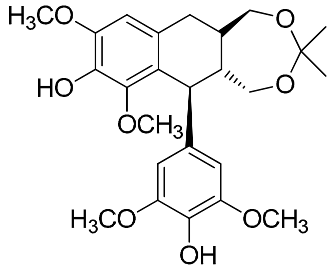
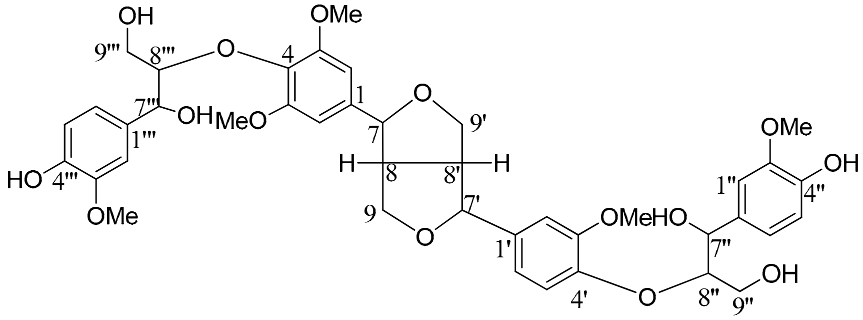


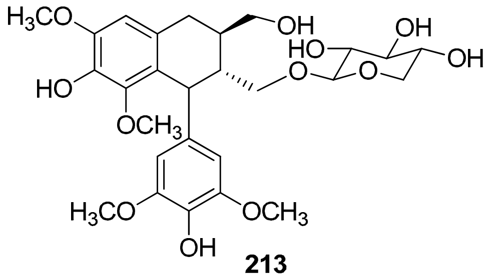
208 R = Rhamnosyl



209



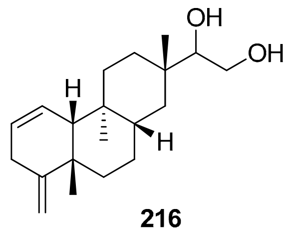
210 7",8" = 7"',8"' = erythro
211 7",8" = erythro, 7"',8"' = threo
212 7",8" = 7"',8"' = threo



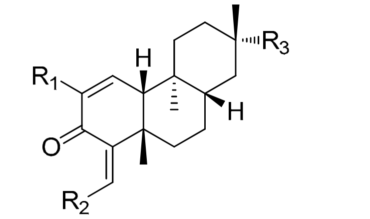
213

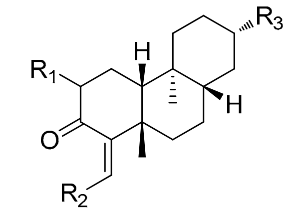
Figure 13. Lignans from Rhizophoraceae mangroves

Dolabranes



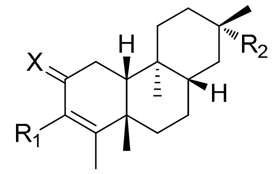
216



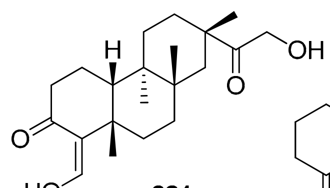


217 R_1 = OH, R_2 = H, R_3 = COOH
225 R_1 = OH, R_2= H, R_3 = CH_2=CH
231 R_1 = H, R_2 = H, R_3 = CH_2=CH
233 R_1 = H, R_2 = H, R_3 = OH

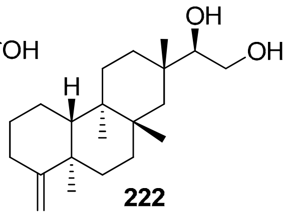
227 R_1 =H, R_2 = H, R_3 = H_2C=CH
228 R_1 = H, R_2 = OH, R_3 = H_2C=CH
234 R_1 = H, R_2 = OH, R_3 = COOH
235 R_1 = H, R_2 = OH, R_3 = HO−CH_2C(O)
236 R_1 = H, R_2 = OH, R_3 = HO−CH_2C(O)
237 R_1 = H, R_2 = OH, R_3 = HO−CH_2C(OH)



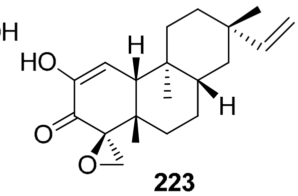
218 X = O, R_1 = OH, R_2 = HO−CH_2C(O)
219 X = O, R_1 = OH, R_2 = COOH
220 X = H_2, R_1 =H, R_2 = HO−CH_2C(OH)
229 X = O, R_1 = OH, R_2 = H_2C=CH
232 X = O, R_1 = OH, R_2 = OH



221



222



223

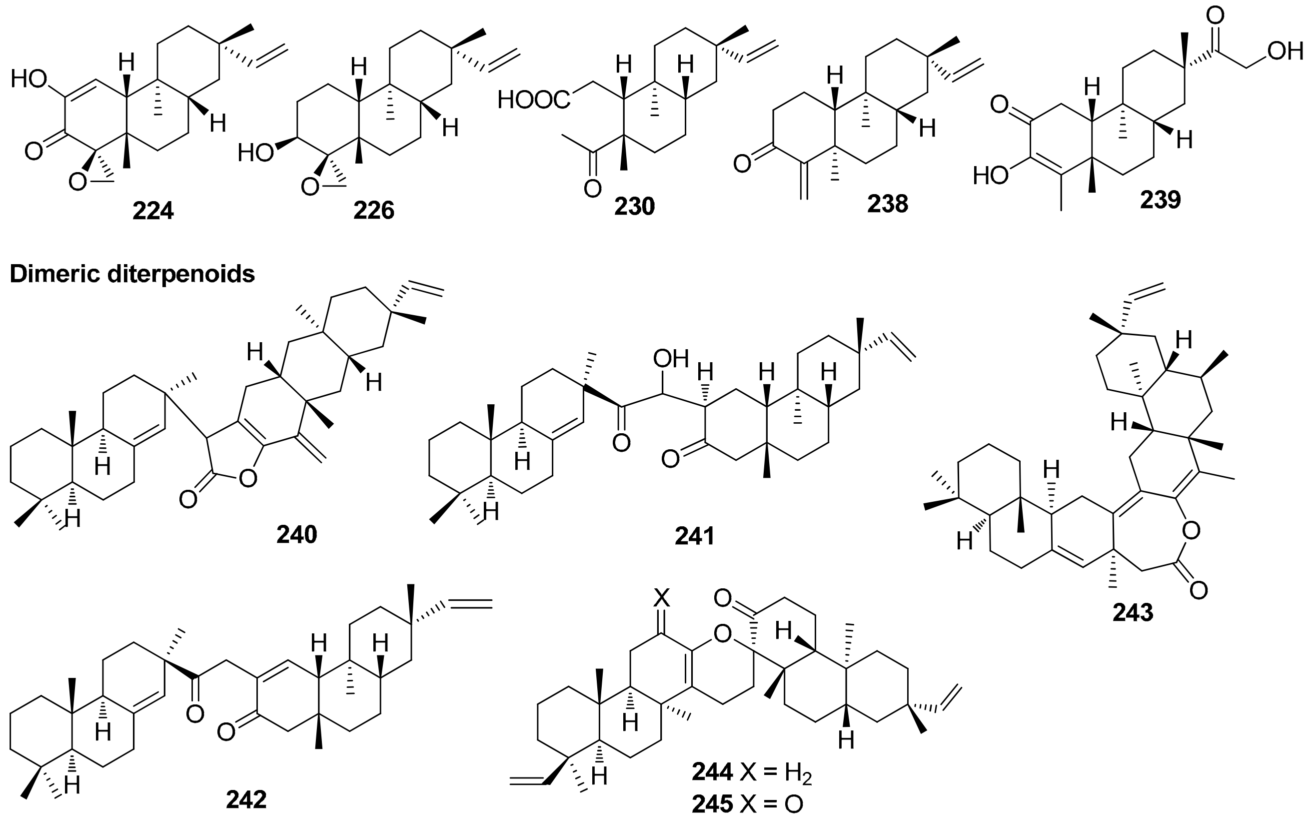


Figure 14. Dolabranes and dimeric diterpenoids from Rhizophoraceae mangroves

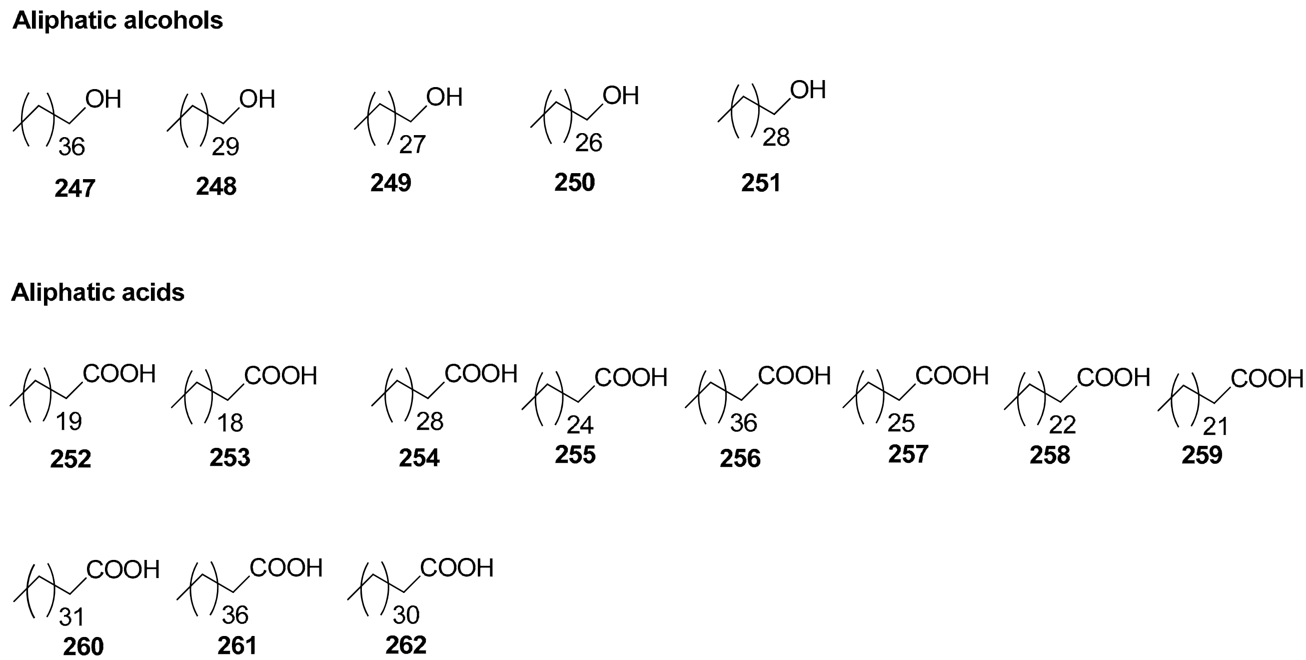


Figure 15. Aliphatic alcohols and acids in Rhizophoraceae mangroves

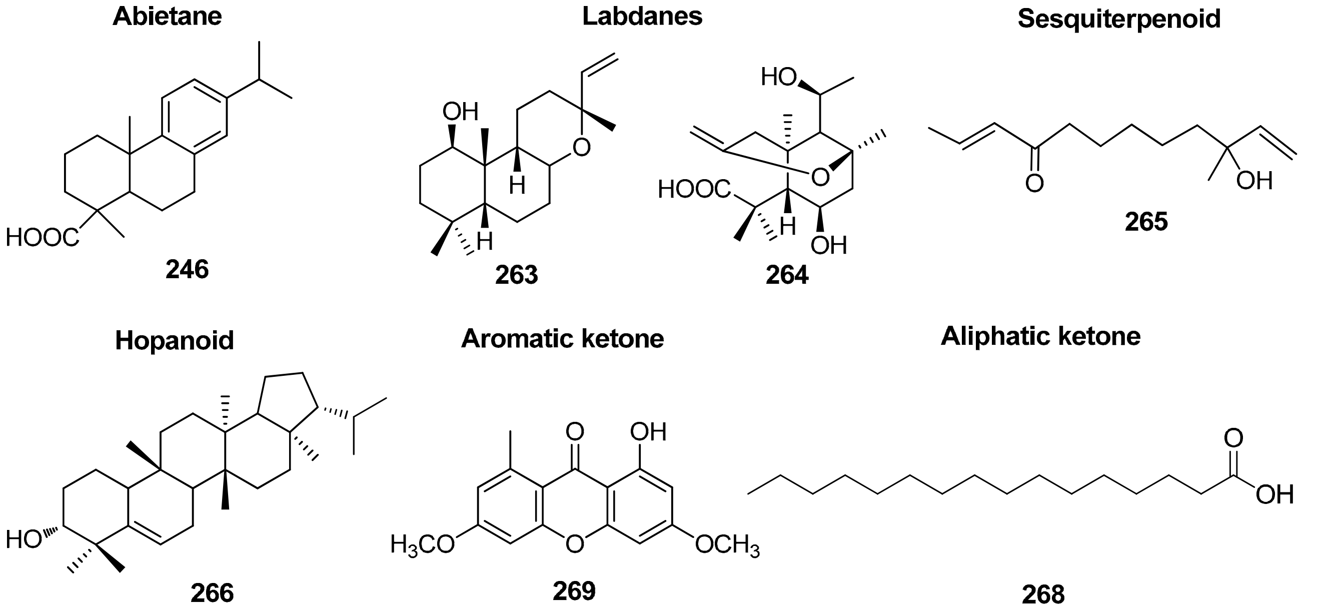


Figure 16. Terpenoids, abietane, labdanes, hopanoid, a sesquitepenoid, aromatic and aliphatic ketones in Rhizophoraceae mangroves

bank of phytochemical substances that are biologically active substances, with novel structures. It is essential to systematically conserve the biodiversity in the mangrove ecosystem and for the proper of this ecosystem for the future use of humanity.

References

[1] Bandaranayake, W. M. *Wetl. Ecol. Manag.* **2002**, *10*, 421–452.
[2] Wu, J.; Xiao, Q.; Xu, J.; Li, M. Y.; Pan, J. Y.; Yang, M. H. *Nat. prod. Rep.* **2008**, *25*, 955–981.
[3] Kathiresan, K. *Environ. Ecol.* **1995**, *13*, 240–241.
[4] Sheue, C.; Liu, H.; Yong, J. W. H. *Taxon* **2003**, *52*, 287–294.
[5] Sheue, C.; Rashid, S. M. A.; Yong, J. W. H.; Yang, Y. *Taiwania* **2010**, *55*, 72–77.
[6] Loder, J. W.; Russell, G. B. *Aust. J. Chem.* **1969**, *22*, 1271–1275.
[7] Richter, A.; Thonke, B.; Popp, M. *Phytochemistry* **1990**, *29*, 1785–1786.
[8] Chumkaew, P.; Kato, S.; Chantrapromma, K. *Chem. Pharm. Bull.* **2005**, *53*, 95–96.
[9] Loder, J. W.; Russell, G. B.; *Tetrahedron Lett.* **1966**, *51*, 6527–6529.
[10] Li, L.; Huang, C. G.; Wang, C. Y.; Guo, Y. W. *Nat. Prod. Res.* **2010**, *24*, 1044–1049.
[11] Bao, S.; Deng, Z.; Fu, H.; Proksch, P.; Lin, W. *Helv. Chim. Acta* **2005**, *88*, 2757–2763 .
[12] SY, B.; Lin, W. *Zhongguo Zhong Yao Za Zhi* **2006**, *31*, 1168–1171.
[13] Bao, S.; Ding, Y.; Deng, Z., Proksch, P.; Lin, W. *Chem. Pharm. Bull.* **2007**, *55*, 1175–1180.
[14] Katu, A.; Takahashi, J. *Phytochemistry* **1975**, *5*, 220–221.
[15] Laphookhieo, S.; Karalai, C.; Ponglimanont, C.; Chantrapromma, K. *J. Nat. Prod.* **2004**, *67*, 886–888.
[16] Karalai, C.; Laphookhieo, S. *Aust. J. Chem.* **2005**, *58*, 556–559.
[17] Ghosh, A.; Misra, S.; Dutta, A. K.; Choudary, A. *Phytochemistry* **1985**, *24*, 1725–1727.
[18] Homhual, S.; Bunyapraphatsara, N.; Kondratyuk, T.; Herunsalee, A.; Chaukul, W.; Pezzuto, J. M.; Fong, H. H. S.; Zhang, H. J. *J. Nat. Prod.* **2006**, *69*, 421–424
[19] Ganguly, S. N.; Sarkar, A. *Indian J. Chem. B.* **1978**, *16*, 742–744.
[20] Hogg, R. W.; Gillan, F. T. *Phytochemistry* **1984**, *23*, 93–97.
[21] Achamadi, S.; Syahbirin, G.; Choong, E. T.; Hemingway, W. R. *Phytochemistry* **1994**, *35*, 217–219.
[22] Han, L.; Huang, X.; Sattler, I.; Dahse, H. M.; Fu, H.; Lin, W.; Grabley, S. *J. Nat. Prod.* **2004**, *67*, 1620–1623.
[23] Subrahmanyam, C.; Rao, B. V.; Ward, R. S.; Hursthouse, M. B.; Hibbs, D. E. *Phytochemistry* **1999**, *83*, 83–90.
[24] Salae, A. W.; Chantrapromma, S.; Fun, H. K.; Ponglimanont, C. *Acta Crystallogr. E.* **2007**, *63*, 1899–1901.
[25] Han, L.; Huang, X.; Sattler, I.; Dahse, H. M.; Fu, H.; Grabley, S.; Lin, W. *Pharmazie* **2005**, *60*, 705–707
[26] Homhual, S.; Zhang, H. J.; Bunyapraphatsara, N.; Kondratyuk, T.; Santarsiero, B. D.; Mesecar, A. D.; Herunsalee, A.; Chaukul, W.; Pezzuto, J. M.; Fong, H. H. *Planta Med.* **2006**, *72*, 255–260.
[27] Huang, X. Y.; Wang, Q.; Liu, H. L.; Zhang, Y.; Xin, G. R.; Shen, X.; Dong, M. L.; Guo, Y. W. *Phytochemistry* **2009**, *70*, 2096–100.
[28] Han, L.; Huang, X.; Sattler, I.; Moellmann, U.; Fu, H.; Lin, W.; Grabley, S.; *Planta Med.* **2005**, 71, 160–164.
[29] Han, L.; Huang, X.; Sattler, I.; Moellmann, U.; Fu, H.; Lin, W.; Grabley, S. *J. Asian Nat. Prod. Res.* **2007**, 9, 327–331.
[30] Anjaneyulu, A. S. R.; Rao, V. L. *Phytochemistry* **2002**, 60, 777–782.
[31] Anjaneyulu, A. S. R.; Rao, V. L. *Phytochemistry* **2003**, 62, 1207–1211.
[32] Anjaneyulu, A. S. R.; Rao, V. L.; Lobkovsky, E.; Clardy, J. *J. Nat. Prod.* **2002**, *65*, 592–594.
[33] Ponglimanont, C.; Thongdeeying, P. *Aust. J. Chem.* **2005**, *58*, 615–618.
[34] Zhang, Y.; Deng, Z.; Gao, T., Proksch, P.; Lin, W. *Phytochemistry* **2005**, *66*, 1465–1471.
[35] Ouyang, X. W.; Wang, X. C.; Yue, Q. X.; Hu, L. H. *Nat. Prod. Commun.* **2010**, *5*, 9–12 .
[36] Chen, J. D.; Yi, R. Z.; Lin, Y. M.; Feng, D. Q.; Zhou, H. C.;

Wang, Z. C. *Int. J. Mol. Sci.* **2011**, *12*, 6517–6528.
[37] Fun, H. K.; Pakhathirathien, C.; Chantrapromma, S.; Karalai, C.; Chantrapromma, K. *Acta Crystallogr. E.* **2006**, *62*, 5539–5541.
[38] Hu, W. M.; Li, M. Y.; Li, J.; Xiao, Q.; Feng, G.; Wu, J. *J. Nat. Prod.* **2010**, *73*, 1701–1705.
[39] Chacha, M. *Int. J. Biol. Chem. Sci.* **2011**, 5, 402–409.
[40] Chantrapromma, S.; Fun, H. K.; Pakhathirathien, C.; Karalai, C.; Chantrapromma, K. *Acta Crystallogr. E.* **2007**, *63*, 459–461.
[41] Zhang, Y.; Lu, Y.; Mao, L.; Proksch, P.; Lin, W. *Org. Lett.* **2005**, *7*, 3037–3040.
[42] Chen, J. D.; Qiu, Y.; Yang, Z. W.; Lin, P.; Lin, Y. M. *Helv. Chim. Acta* **2008**, *91*, 2292–2298.
[43] Pakhathirathien, C.; Karalai, C.; Ponglimanont, C.; Subhadhirasakul, S.; Chantrapromma, K. *J. Nat. Prod.* **2005**, *68*, 1787–1789.
[44] Wang, X. C.; Ouyang, X. W.; Hu, L. H. *J. Asian Nat. Prod. Res.* **2010**, *12*, 576–581.
[45] Chen, J. D.; Feng, D. Q.; Yang, Z. W.; Wang, Z. C.; Qiu, Y.; Lin, Y. M. *Molecules* **2008**, *13*, 212–219.
[46] Hsu, F. L.; Nonaka, G. I.; Nishioka, I. *Chem. Pharm. Bull.* **1985**, *33*, 3142–3152.
[47] Kokpol, U.; Chavasiri, W. *J. Nat. Prod.* **1990**, *53*, 953–955.
[48] Li, D. L.; Li, X. M.; Wang, B. G. *Nat. Prod. Res.* **2008**, *22*, 808–813.
[49] Laphookhieo, S.; Karalai, C.; Ponglimanont, C. *Chem. Pharm. Bull.* **2004**, *52*, 883–885.
[50] Yang, X. H.; Li, H. B.; Chen, H.; Li, P.; Ye, B. P. *Yao Xue Xue Bao* **2008**, *43*, 974–978.
[51] Williams, L. *Die Naturwissenschaften* **1999**, *86*, 450–452.
[52] Gao, M. Z.; Yuan, X. Y.; Cheng, M. C.; Xiao, H. B.; Bao, S. X. *J. Asian Nat. Prod. Res.* **2011**, *13*, 776–779.
[53] Rohini, R. M.; Das, A. K. *Nat. Prod. Res.* **2010**, *24*, 197–202.
[54] Rao, B. V.; Rao, C. V.; Subrahmanyam, C.; Jairaj, M. A. *J. Indian Chem. Soc.* **2005**, *82*, 155–157.
[55] Kokpol, U.; Chavasiri, W.; Chittawong, V.; Bruce, M.; Cunningham, G. N.; Miles, D. H. *Phytochemistry* **1993**, *33*, 1129–1131.
[56] Saxena, E.; Garg, H. S. *Nat. Product Lett.* **1994**, *4*, 149–154.
[57] Anjaneyulu, A. S. R.; Rao, V. L. *Nat. Product Lett.* **2001**, *15*, 13–19.
[58] Anjaneyulu, A. S. R.; Anjaneyulu, V.; Rao, V. L. *J. Asian Nat. Prod. Res.* **2002**, *4*, 53–61.
[59] Li, D. L.; Li, X. M.; Peng, Z. Y.; Wang, B. G. *Molecules* **2007**, *12*, 1163–1169.
[60] Takara, K.; Kuniyoshi, A.; Wada, K.; Kinjyo, K.; Iwasaki, H. *Biosci. Biotech. Biochem.* **2008**, *72*, 2191–2194.
[61] Premanathan, M.; Kathiresan, K.; Nakashima, H. *South Pacific Study* **1999**, *19*, 49–57.
[62] Chandrasekaran, M.; Kannathasan, K.; Venkatesalu, V.; Prabhakar, K. *World J. Microb. Biotech.* **2008**, *25*, 155–160.
[63] Hossain, H.; Moniruzzaman, Sk.; Nimmi, I.; Kawsar, H.; Hossain, A.; Islam, A.; Jahan, I. A. *Oriental Pharm. Exp. Med.* **2011**, *11*, 215–220.
[64] Nabeel, M. A.; Kathiresan, K.; Manivannan, S. *J. Diabetes* **2010**, *2*, 97–103.
[65] Arivuselvan, N.; Silambarasan, D.; Govindan, T.; Kathiresan, K. *Adv. Biol. Res.* **2011**, *5*, 251–254.
[66] Zhang, L. L.; Lin, Y. M.; Zhou, H. C.; Wei, S. D.; Chen, J. H.; *Molecules* **2010**, *15*, 420–31.
[67] Wei, S. D.; Zhou, H. C.; Lin, Y. M. *Int. J. Mol. Sci.* **2010**, *11*, 4080–4093.
[68] Abeysinghe, P. D. *Indian J. Pharm. Sci.* **2010**, *72*, 167–172.
[69] Hong, L. S.; Ibrahim, D.; Kassim, J.; Sulaiman, S. *J. Appl. Pharm. Sci.* **2011**, *1*, 75–79.
[70] Sur, T. K.; Seal, T.; Pandit, S.; Bhattacharya, D. *Nat. Prod. Sci.* **2004**, *10*, 11–15.
[71] Alarcon-Aguilara, F. J.; Roman-Ramos, R.; Perez-Gutierrez, S.; Aguilar-Contreras, A.; Contreras-Weber, C. C.; Flores-Saenz, J. L. *J. Ethnopharmacol.* **1998**, *61*, 101–110.
[72] Nabeel, A. M.; Kathiresan, K.; Chinthamani, M.; Manivannan, S. *Nat. Prod. Res*. **2012**, *26*, 1161–1166.
[73] Agoramoorthy, G.; Chen, F. A.; Venkatesalu, V.; Kuo, D. H.; Shea, P. C. *Asian J. Chem.* **2008**, *20*, 1311–1322.