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Natural products chemistry of the mangrove species *Avicennia* spp. - Review and new data

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ABSTRACT

The genus *Avicennia* is one of the major plant components of mangrove ecosystems being present worldwide. This review of natural products chemistry of the genus summarises the presently available information on *n*-alkanes, *n*-alcohols, fatty acids, terpenoids, steroids, lignans, phenylpropanoids and phenolic compounds. Furthermore, compounds involved in salt tolerance are considered. New data for an Avicennia alba specimen from E Sumatra, Indonesia, are included.

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KEYWORDS

Mangrove;
Avicennia spp.;
Natural product chemistry;
Review.

INTRODUCTION

The genus *Avicennia* is one of the major plant components of mangrove ecosystems. There is, however, no general agreement among specialists on its taxonomy. While some authors consider it as a member of the Verbenaceae family (e.g.[1]) others[2] put it in the family Avicenniaceae. Duke[3] distinguishes 11 species (TABLE 1). Moldenke[2a-c] proposed a distinction between *A. africana* from West Africa and *A. germinans* from the Atlantic and Pacific coasts of America, which, however, has not been accepted by other authors[3,4]. From isozyme analysis, Duke[3] subdivided *A. marina* into three varieties (*A. marina* var. *australasica*, *A. marina* var. *marina* and *A. marina* var. *eucalyptifolia*) while Everett[5] raised these varieties to the status of subspecies (*A. marina* ssp. *australasica*, *A. marina* ssp. e*ucalyptifolia* and *A. marina* ssp. m*arina*.

Especially the geographically more widely distributed species *A. germinans* and *A. marina* have evoked controversy. Dodd et al.[7] noted that

TABLE 1 : Taxonomy of *Avicennia* species[3]

Genus: *Avicenni* L., Family: Acanthaceae, subfamily Avicennioideae
A. alba
A. caseolaris
A. germinans
A. integra[6]
A. marina (Synonyms: *A. eucalyptifolia*[2d], *A. balanophora*[4a], *A. intermedia* Griffith, *A. mindanaense* Elmer, *A. sphaerocarpa* Stapf ex Ridley
A. maxima
A. nitida
A. officinalis
A. rumphiana (syn. *A. lanata)*
A. schaueriana
A. tomentosa

considerable variations do exist between populations of *A. germinans* growing in the Old and the New Worlds. Based on data from a detailed field survey in Australia Duke[4a] showed that the morphological variations in *A. marina* can be correlated with environmental factors such as air temperature, rainfall, intertidal position and upriver location. Major differences were also observed within individuals, as e.g. in sun and shade leaves. These observations suggest that a number of morphological attributes, especially those of leaves, are controlled by environmental factors, thus demonstrating their unsuitability in earlier systematic considerations.

Chemotaxonomy has so far not been applied to the genus in a consequent way and only iridoids have been considered so far. In general, this compound class represents an important taxonomic character of dicotyledons[8]. In *A. marina* several iridoids have been reported (see below). König and Rimpler[9] pointed out that the presence of iridoids in this species suggests a close relationship between the genus *Avicennia* and the family Verbenaceae.

MATERIAL AND METHODS

Avicennia alba leaf was collected in March 2005 in the Siak River Estuary, E Sumatra. Leaves were rinsed with tap water and air dried. After return to the home laboratory they were lyophilised and then ground in an agate ball mill at 160 rpm.

Extracts were prepared by ultrasonic extraction using solvent systems of sequentially increasing polarity: 1. *n*-hexane, 2. *n*-hexane/dichloromethane (50:50 v/v), 3-5. dichloromethane/methanol (90:10 v/v) corresponding in polarity to hydrocarbons, alcohols and polar N,S,O compounds, respectively. The combined lipid extracts were rotary-evaporated to dryness and a mixture of squalane, 5α-androstanol, 5α-androstanone and erucic acid was added as internal standards. The *n*-alkanes were separated from the total extracts using a 1.0 * 20 cm glass chromatography column packed with activated silica gel (100-200 mesh). On top of the silica gel, about 10 mm anhydrous Na_2SO_4 was added to retain remaining water. After adding an aliquot of the redissolved total lipid extract to the column, *n*-alkanes were eluted with 15 ml of hexane while polar compounds were eluted with a mixture of 40 ml dichloromethane/methanol (9:1 v/v):.

Polar compounds were analysed using an Agilent 5973 GC-MS System operating at 70 eV with a mass range of m/z 50-650 in the scan modus. The GC was equipped with a fused silica capillary column of the same specifications as described above. The carrier gas was helium. The same temperature program as above was used. Before measurement the polar compounds were derivatised to trimethylsilyl ethers by adding 50 µl of N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA) to each sample. Components were identified by comparison of their mass spectra and retention times with synthetic standards or published data. The different internal standards added prior to the sample extraction were used for quantification.

Salt tolerance

Adrian-Romero et al.[10] report the presence of glycinebetaine in the aerial parts of *A. marina* with a relatively high content of 2.03 % dry weight (dw). Among the 63 flowering plant species examined by the authors only *Salicornia europaea* (Chenopodiaceae, 3.52 %), *Spartina* x *townsendii* (Gramineae, 2.52 %) and *Atriplex hastata* (Chenopodiaceae, 2.08 %) exceeded this level. This high content of a compatible osmolyte is in accordance with the role these species play as pioneer plants in mangroves and salt marshes.

A. marina accumulates glycine betaine, asparagine and stachyose according to Ashihara et al.[11].

Hanson and Gage[12] report choline-*O*-sulphate in *A. germinans* to be 8 µmol g^{-1} dw while *Limonium* spp. and *Armeria maritima* accumulated >100 µmol g^{-1} DW. Apparently choline-*O*-sulfate does not play a dominant role in salt tolerance in *Avicennia* species.

Proline which has been found in *A. marina* and *A. officinalis*[13] is a known osmoregulator in halophytes (e.g.[14]). Popp et al.[15], on the other hand, failed to find significant quantities of proline in *A. marina* from northern Queensland, Australia, and reported accumulation of methylated quaternary ammonium compounds instead.

Based on the assumption that the plant-cell membrane itself is a barrier to a number of external stress factors such as varying salinity Oku et al.[16] assumed that the lipids in these membranes may also play an

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important role in the adaptation of plants to environmental stress factors. Although no Avicennia species was investigated in detail the relative contents of free triterpenoids increased with ambient salinity in Kandelia candel (leaves and roots) and Bruguiera gymnorrhiza (roots only). No salt-dependent changes were noted in the phospholipid and fatty acid compositions for both species. These results suggest that salt stress may specifically act on the terpenoid contents in mangroves.

CHEMICAL COMPOSITION

Hydrocarbons

Hydrocarbons from epicuticular waxes have been reported by a number of authors[17]. While Mohan et al.[17f] did not give quantitative data all other studies (exception see below) indicate a dominance of odd-numbered compounds in the C_{29} to C_{33} range (Figure 1).

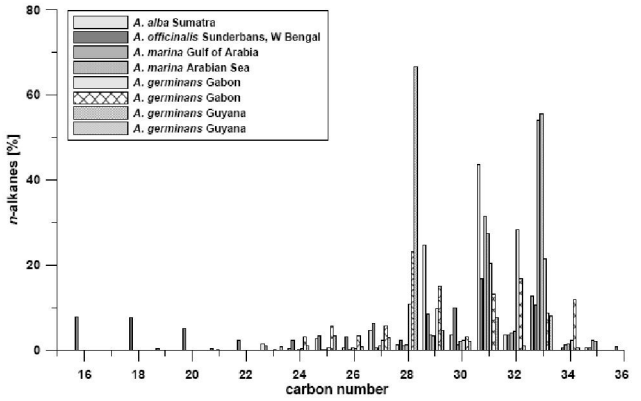


Figure 1 : *n*-Alkane distribution patterns in leaf waxes of *Avicennia* spp. Data from Misra et al. ([17b,18] – Sunderbans), Rafii et al. ([17e] – Gabon and Guyana) and Dodd et al. ([17g] – Gulf of Arabia and Arabian Sea). Sumatra data are own unpublished results.

Raffii et al.[17e] found the C_{28} alkane to be dominant in *A. germinans* both from Gabon and Guyana (Figure 1). This is highly unusual and contradictory to findings for terrestrial plants in general where odd-numbered alkanes clearly dominate the distribution patterns[19].

Triacontane was reported to be present in the bark in minor amounts[20]. Mohan et al.[17f] reported the presence of the branched alkanes 2-methyl-C_{28}, 3-methyl-C_{29}, 2-methyl-C_{30} and 3-methyl-C_{31} from GC/MS data. In addition to the latter three compounds Dodd et al.[17g] found 2-methyl-C_{31} and 3-methyl-C_{33}. The 3-methyl-C_{29}, 2-methyl-C_{30} and 3-methyl-C_{31} hydrocarbons accounted for 4.16. 1.81 and 6.76 %, respectively, of the hydrocarbon fraction while the other branched compounds contributed less than 1 %. An uncharacterised alkene ($C_{28}H_{56}$) was found by Mohan et al.[17f] while Wannigama et al.[17a] found trace amounts of $C_{28:1}$, $C_{30:1}$ and $C_{32:1}$. In pneumatophores of *A. marina* Wannigama et al.[17a] found hydrocarbons from *n*-C_{17} to *n*-C_{29} with the C_{23} and C_{25} compounds representing 29.6 and 35.0 % of the total fraction, respectively.

Fatty acids

Fatty acids in wax esters from *A. officinalis* were dominated by C_{16} and $C_{18:1}$ followed by $C_{18:2}$ with minor amounts of C_{12}, C_{14}, C_{18} and C_{20}[21]. This is similar to our free fatty acid data for *A. alba* from Sumatra (Figure 2) although Misra et al.[17b] did not report compounds with chain lengths >20. Rajendran and Kathiresan[22] found a comparable predominance pattern in leaf fatty acids of *A. marina* from Pichavaram, southeast cost of India, but found in addition the C_9, 2-OH-C_{10} and 2-OH-*i*-C_{15} acids. Again, compounds with chain lengths >20 were not reported.

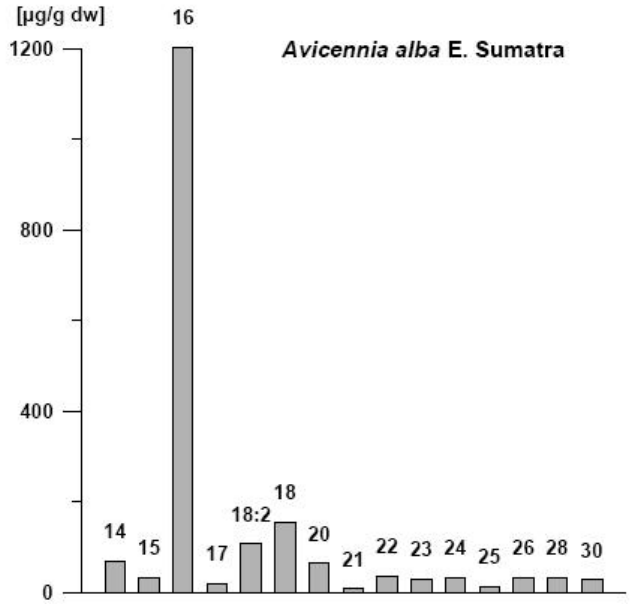


Figure 2 : Composition of free fatty acids in *Avicennia alba* leaves from Sumatra. Numbers refer to chain length.

In *A. marina* from North Sinai, Egypt, Ramadan et al.[23] noted the presence of the 18:2, 18:3, 20:2 and 24:1 unsaturated acids. Here the C_{16} compound was also dominant followed by $C_{18:1}$.

Both in sterol esters and triglycerides a more

homogenous fatty acid distribution was found[21]. In these fractions the $C_{18:3}$ and $C_{22:1}$ acids were additionally found.

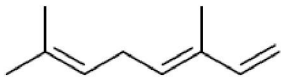
Norman et al.[24] in an investigation on chilling sensitivity found the phosphatidylglycerol (PG) fraction of *A. germinans* from both Harbor Island, Texas, and Belize to contain 16:0, 16:1, 18:0, 18:1,18:2 and 18:3 fatty acids with hexadecanoic acid accounting for 48 and 42 %, respectively, of the PG fraction. The hexadecenoic acid was present as the *trans n-13* isomer. This isomer occurs only in PG compounds of photosynthetic membranes. As this fatty acid is absent from etiolated tissue, it has been inferred that it has a specific role associated with the light reactions of photosynthesis[25]. Markedly higher contributions from the unsaturated C18 fatty acids was found in the phosphatidylcholine fraction[24].

Alcohols

In *A. officinalis* Misra et al. (1986) found a series of saturated and unsaturated *n*-alcohols in the wax ester fraction with chain lengths from 14 to 30 in submerged leaves and from 14 to 34 in normal leaves. In both cases the C_{24} compound was the dominant one accounting for 39 and 48 %, respectively. Our own data for free *n*-alcohols show only the C_{18}, C_{26}, C_{28} and C_{30} compounds to be present with 4.1, 54.3, 76.8 and 52.0 µg/g DW, respectively.

Terpenoids

Azuma et al.[26] identified from the floral scent of Taiwan samples α-farnesene, cis-β-ocimene ((3Z)-3,7-dimethylocta-1,3,6-triene) and trans-β-ocimene ((3E)-3,7-dimethylocta-1,3,6-triene; **(1)**). Both compounds were also found in the headspace sample.



(1)

Various more common triterpenoids have been reported in different *Avicennia* species and plant parts (TABLE 2).

TABLE 2 : Triterpenoid compounds in *Avicennia* species

Compound	Plant part	Species	Reference
betulic acid, taraxerol, taraxerone	bark	*A. marina*	[20]
betulinic acid, lupeol, lupenone, ursolic acid	leaf	*A. officinalis*	[27]
β-amyrin, betulin, betulinic acid, taraxerol, taraxerone,	bark, leaf	*A. officinalis* *A. alba* *A. tomentosa*	[28]
α-amyrin, β-amyrin, friedeoolean-3β-ol, lupeol, 1 unidentified alcohol	leaf	*A. marina*	[17a]
α-amyrin, β-amyrin*, lupeol, oleanolic acid, taraxerol, ursolic acid * *not in submerged leaves*	leaf	*A. officinalis*	Misra et al., 1985a
betulinic acid, betulin, lupeol, ursolic acid	leaf	*A. officinalis*	[29]
lupeol	leaf epicuticular wax	*A. marina*	[17f]
α-amyrin, β-amyrin, friedoolean-8-en-3-one, friedoolean-14-en-3-one, germanicol, lupeol, taraxerol, taraxasterol,	leaf epicuticular wax	*A. germinans*	[30]
betulin, betulinic acid, betulin aldehyde, lupeol	root	*A. officinalis*	[31]
lupeol, taraxerol, betulinic acid	pneumatophores	*A. marina*	[32]
α-amyrin, β-amyrin, betulin, betulinaldehyde, betulinic acid, lupeol, oleanolic acid, ursolic acid	leaf	*A. alba*	own results

Dodd et al[30] found marked differences between *A. marina* foliar waxes in samples from West Africa and South America, the latter showing only taraxerol and taraxasterol to be present while in the West Africa sample all terpenoid compounds given in TABLE 1 were present.

Oleanolic acid, a major component pentacyclic triterpene in the leaves of *A. officinalis* was found to be oxidized to oleanonic acid **(2)** in the natural environment of the Sunderban mangrove forest. (Misra et al., 1985b).

Oku et al.[16] suggested a group of unknown compounds in A. marina separated by high performance thin layer chromatography to be triterpenoids derived

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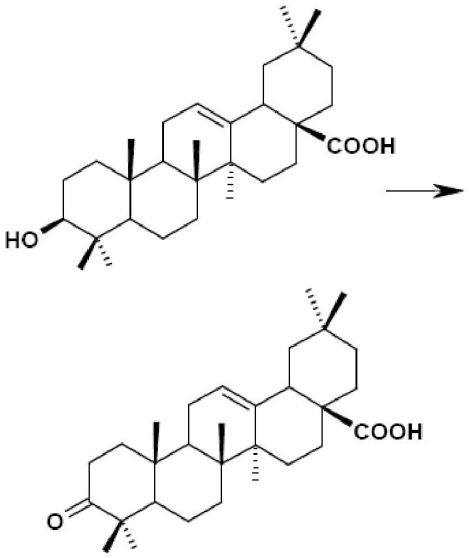
from the dammarane cation. No further identification was, however, attempted for the A. marina sample.



(2)

Steroids

The spectrum of free sterols in *A. marina* and *A. marina* var. *resinifera* is dominated by stigmasterol (24-ethylcholesta-5,22-dien-3β-ol) and sitosterol (24-ethylcholest-5-en-3β-ol), the latter compound accounting for 61.8 to 70.2 %. Other sterols such as cholesterol, campesterol (24-methylcholest-5-en-3β-ol) and 28-isofucosterol ((24E)-stigmasta-5,24(28)-dien-3β-ol or Δ5-avenasterol) were present in minor quantities[17a,33]. In addition, up to 6.5 % unidentified sterols were present. In an *A. marina* specimen from North Sinai, Egypt, Ramadan et al.[23] identified campesterol as the major steroid accounting for 80 % of the identified sterols. In addition to the compounds mentioned above Δ7-avenasterol was found while cholesterol was absent.

Steryl esters of submerged leaves showed the same dominance pattern in *A. officinalis* while for "normal" leaves stigmasterol was replaced by 28-isofucosterol[17b]. In addition, in the steryl ester fraction stigmast-7-en-3*β*-ol was present as minor component.

Total contents showed considerable variations (TABLE 3). It is also evident that the majority of sterols in *Avicennia* species is present in an esterified form.

TABLE 3 : Steroid contents of *Avicennia* spp.

A. marina		A. marina	A. alba	A. officinalis	A. officinalis *var.* resinifera
fresh leaves	dead leaves	fresh leaves	fresh leaves	fresh leaves	fresh leaves
free sterols				steryl esters	
1.900 µg/g dw	1.640 µg/g dw	320 µg/g fw	651 µg/g dw	13.991 µg/g fw (3790)*	4399 µg/g fw (1000)*
				* free sterols	
				no compositional data given	
Australia	Australia	Australia cultured specimen	Sumatra	Sunderbans, India	
[17a]		[33]	own data	[17b]	

In roots of *A. officinalis* Anjayneyulu et al. (2003) identified β-sitosterol as the only steroid compound present in samples from the Indian coasts. In *A. officinalis* 26,27-di(nor)-cholest-5,7,23-trien-22-ol,3-methoxy was identified by Ganesh and Venilla[34].

Flavonoids

Feng et al. (2006) isolated four flavonoid compounds **(3a-d)** from *A. marina*. Velutin **(3a)** was also isolated from defatted leaves of *A. officinalis*[29,35]. Sharaf et al.[36] reported on the presence of isorhamnetin 3-O-rutinoside **(4)**, chryoseriol 7-*O*-glucoside **(3e)**, luteolin 7-*O*-methylether **(3f)** and the 3'-*O*-β-D-glucoside and 3'-*O*-β-D-galactoside derivatives of **(3f)**.

Iridoids

The iridoid compounds geniposidic acid **(5a)**, geniposide **(5b)**, 10-*O*-(5-phenyl-2,4-pentadienoyl)-geniposide **(5c)** been isolated[10]. Compounds **(5b)** and **(5a)** had been described previously from other plant sources. Shaker et al.[37] further identified compounds **(5d-f)** in *A. marina* from Egypt.

A number of mussaenosidic acid **(6a)** derivatives have been found in *Avicennia* species: mussaenoside **(6b)**, 2'-cinnamoyl-mussaenoside **(6c)** and 7-O-(5-phenyl-2,4-pentadienoyl)-8-epiloganin **(6d)**[10].

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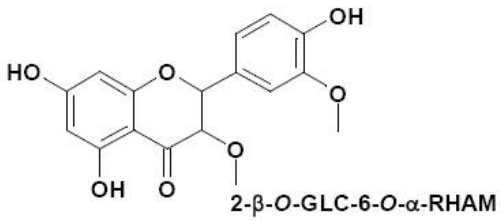
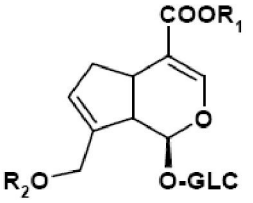
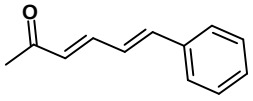
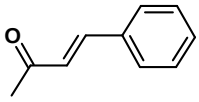
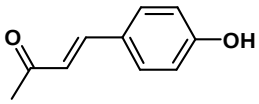
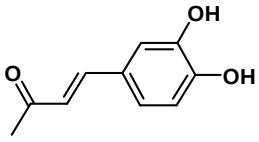


(4)

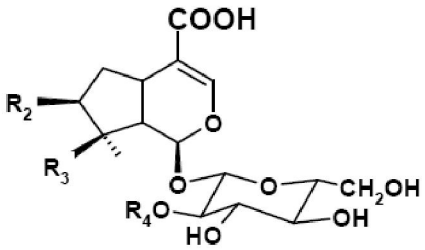
R1	*R2*	*R3*	
OCH_3	H	OCH_3	3a
OCH_3	OCH_3	OCH_3	3b
OH	H	H	3c
OCH_3	H	OH	3d
OH	OCH_3	H	3e
OCH_3	OH	H	3f



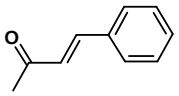
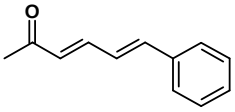
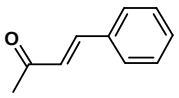
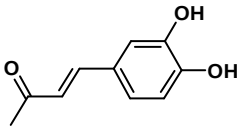
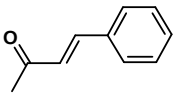
(5)

R1	R2	
H	H	5a
CH_3	H	5b
CH_3		5c
H		5d
H		5e
H		5f

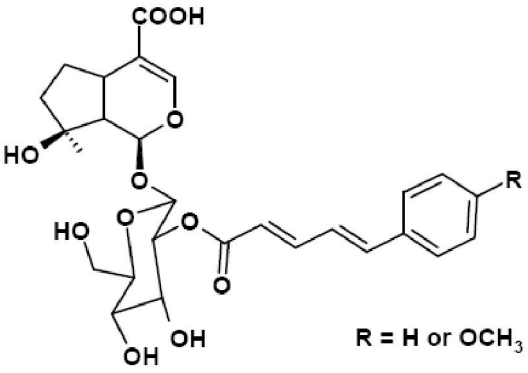
Bousquet Mélou and Fauvel[38] reported the mussaenosidic acid derivatives 2'-cinnamoyl mussaenosidic acid **(6e)** and 2'-caffeoyl mussaenosidic acid **(6f)** in *A. bicolor, A. germinans, A. marina, A. officinalis and A. schaueriana.* The caffeoyl derivative was originally reported for *A. germinans*[39]. Feng et al.[40] isolated 2'-*O*-[(2*E*,4*E*)-5-phenylpenta-2,4-dienoyl] mussaenosidic acid, 2'-*O*-(4-methoxycinnamoyl) mussaenosidic acid and 2'-O-coumaroyl mussaenosidic acid from *A. marina*. The latter compound has been shown by NMR analysis to occur in two isomeric forms[41]. The 4''-hydroxycinnamoyl compound was found by Fauvel et al. (1997) in *A. germinans*. König et al.[42] characterised 7-cinnamoyl-8-epiloganic acid **(6f)** in addition to **(5a)** and **(6e)** from *A. officinalis*.



(6)

R1	R2	R3	R4	
H	H	OH	H	6a
CH_3	H	OH	H	6b
CH_3	H	OH		6c
CH_3		H	H	6c
H	H	OH		6d
H	H	OH		6e
H		H	H	6f

Feng et al.[40] isolated the two iridoid glycosides **(7)** from a Chinese specimen of *A. marina*.



(7)

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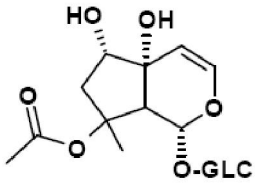
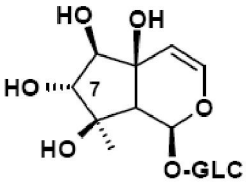
8-*O*-Acetylharpagide **(8)** was identified in the ethyl acetate fraction of *A. officinalis*[29,43].



(8)

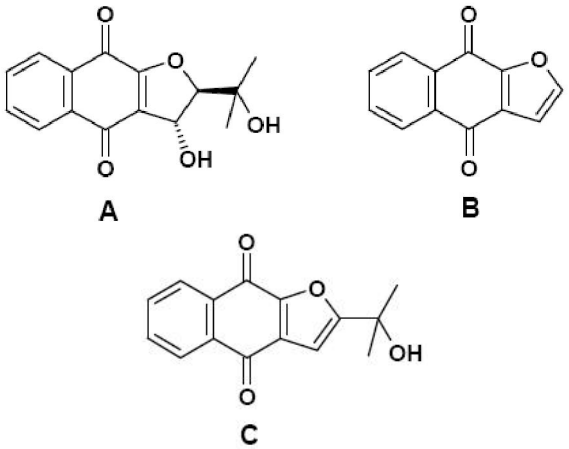
Avicennioside **(9)** was isolated from *A.officinalis* by König et al.[42]. Nass and Rimpler[44] revised this structure after additional mass spectral analysis. The suggested correct structure of **(9)** bears a 7-chlorine instead of the 7-hydroxy group. This compound, originally isolated from *Linaria japonica*, a plant used in Japanese folk medicine as a laxative and diuretic, by Kitagawa et al.[45] is named linarioside. It was isolated from *A. officinalis* also[46].



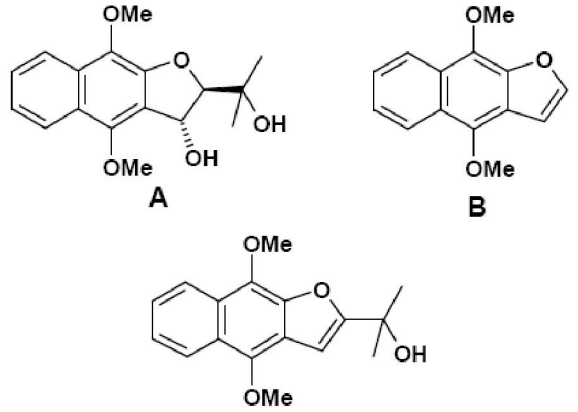
(9)

Quinones

Three new naphthoquinones and their hydroquinone analogues, named avicequinones A, B, C **(10)** and avicenols A, B and C **(11)** were isolated from the stem bark of *A. alba* collected in Singapore[47]. Structural elucidation was by ^{13}C NMR. Avicenol C has also been found in *A. officinalis*[31]. Synthesis of avicequinone B has been described[48].



(10)

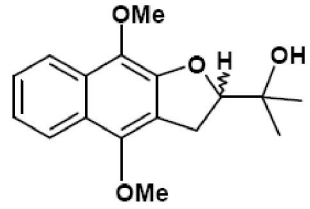


(11)

Sutton et al.[49] have proposed that the structures of the new phytoalexins extracted from the fungus *Phytophora* sp. isolated from *A. marina* are naphtha[1,2-*b*]furan-4,5-dione derivatives. Reappraisal of the spectral data and synthesis of the compounds in question[47] suggests that these compounds are indeed avicequinones A and B.

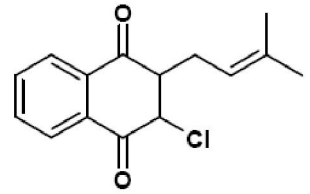
The napthtoquinones and their hydroquinone derivatives described above have been investigated for their activity against Epstein-Barr virus early antigen activation induced by 12-*O*-tetradecanoylphorbol-13-acetate in Raji cells[50].

Anjaneyulu et al.[31] characterised the hydroquinone compound **(12)** from roots of *A. officinalis*. Based on its spectral characteristics they suggest it to be the enantiomer of avicenol C.



(12)

3-Chlorodeoxy-lapachol **(13)**, a naphthoquinone derivative isolated from *A. germinans*, exhibited activity against a range of human cancer cell lines[51].



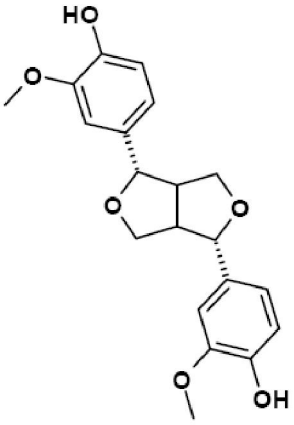
(13)

Review

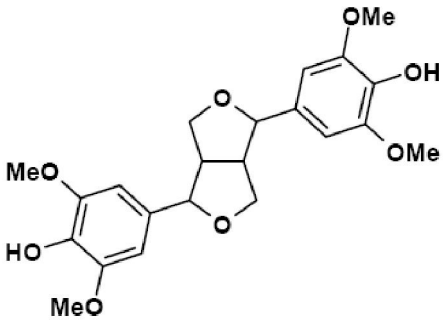
According to Hussain et al.[52] the parent compound lapachol occurs in *A. tomentosa* and *A. officinalis*[53] and is also active against various cancer types. De Almeida et al.[54] showed it to also be active as anti-inflammatory agent. Matsui et al.[55] isolated it from the acetone extract of the stem bark of *A. rumphiana* Hall. f. and found significant inhibition of the *in vitro* proliferation of hypertrophic scar fibroblasts, On the other hand, lapachol is a known elicitor of contact dermatitis[56].

Lignans

Pinoresinol **(14)** and syringaresinol **(15)** have been isolated from *A. germinans*[57]. This appears to the first report on the occurrence of lignans in Avicenniaceae. In view of the taxonomically complicated situation of *A. germinans* the authors suggest that the presence of lignans although otherwise widespread in the plant kingdom[58] might be of use in chemotaxonomy.



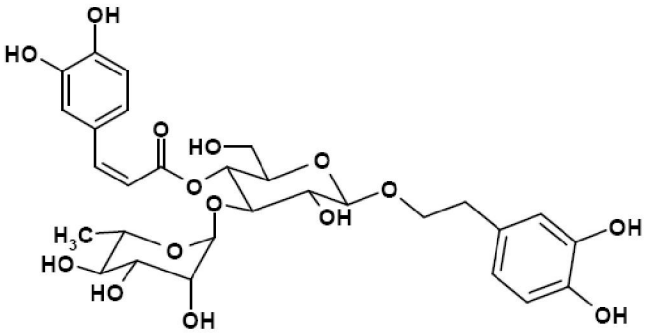
(14)



(15)

Phenylpropanoid glycosides

The caffeic acid glycosides verbascoside **(16)**, isoverbascoside, and rhamnosylverbascoside have been isolated by Fauvel et al.[39,59]. Mmatli et al.[60] suggest that these compounds are able to complex nickel, copper and iron (only verbascoside). These compounds also have antibacterial, antifungal, antiviral and antioxidant activities and are selective inhibitors of aldose reductase, 5-lipoxygenase and protein kinase C (cf.[61]).



(16)

Phenolic constituents

A number of investigations deal with the determination of total phenols (TABLE 4). Earlier reports are largely concerned with the role of tannins in dyeing and tanning (e.g.[62]).

Ravi and Kathiresan[65] noted considerable seasonal variation in tannin content. For most mangrove species investigated the highest contents were found from October to December during the monsoon saison. Tannins are apparently used by plants as investigated for *A. marina* and *A. officinalis* to control bacterial colonisation of leaves[70].

Other compounds

Azuma et al.[26] identified 2,3-butanediol, 3-OH-2-butanone, hexenyl-2-methylbutanoate, and 2-phenylethanol in the floral scent. The long-chain aldehyde triacontanal was isolated by Majumdar and Patra[28]. Ganesh and Venilla[34] identified octahydro-3a,6-methano-3ah-inden-5-ol by GC/MS in *A. officinalis*.

δ-Tocopherol was reported by Ramadan et al.[23] to be present in *A. marina* while the α- and γ-isomers could not be detected. Ascorbic acid contents ranged from 140 to 160 mg/100 g DW in four species of *Avicennia* from Andra Pradesh, India[71].

DISCUSSION

The wide range of compounds found in the family

Review

TABLE 4 : Phenols in *Avicennia* species

Species	Tannin	Polyphenol	Phenolic acid	Unit	Reference
A. officinalis		22,43		g/100 g DW	[13a]
A. marina		13,04			
A.schaueriana		27.8* 24.8*		units of optical density/g DW	[63]
A. officinalis	18.02 ± 1.60		0.56 ± 0.046		[64]
A. marina	17.81 ± 1.5		0.56 ± 0.045		
A. officinalis	0.016 – 0.597**			mg/g DW	[65]
A. marina	0.125 – 0.786*				
A. officinalis	14.18	11.39		% in extract of 100 g FW	[66] [67]
A. officinalis	5.56			mg/g DW	[68]
A. marina	5.54				
A. alba leaf		11.73 ± 0.69*			
bark		4.4 ± 0.31*		mg gallic acid equivalents/g DW	[69]
root		4.79 ± 0.48*			

***total phenols, ** gallotannins**

Avicennia explains the wide spread traditional usage (cf.[72]). However, the data presented above also show that there is considerable inter- and intraspecific variation in natural products composition.

Furthermore, compositional changes may occur in different stages of development. Thus, Untawale et al.[73] report a decrease in total lipids and carbohydrates and an increase in total protein for five stages, i.e. from leaf buds to freshly fallen matures leaves. Seasonal variations in major constituents (carbohydrates, lipids, proteins) have been reported[74]. Similar changes for tannins and gallotannis were also observed[65,75].

Kotmire and Bhosale[13a] also point to the possible effect of soil physicochemical conditions, i.e. salinity, pH or grain size composition, on the composition of hydrophilic constituents such as carbohydrates, proteins and polyphenols. The effects of submergence on wax esters have already been mentioned[17b,18,21,76]. Further factors potentially controlling the presence or absence of secondary metabolites include e.g. oxidative stress, shading or insect herbivory have not been considered in greater detail. The role of the later may have been underestimated in its quantitative effects[77]. De Lacerda et al.[63] found that herbivory was higher in plants with high total phenolic compounds although the correlation between these two parameterswas not significant. On the other hand, Kathiresan[68] noted a higher incidence of leaf damage for *A. marina* and *A. officinalis* with low tannin content compared to other mangrove species. Turner[67] also found lower tannin content in four *Avicennia* species compared to a.o. *Bruguiera*, *Ceriops* or *Rhizophora* species, a fact which Saur et al.[78] used, together with their own data, to speculate on the role of tannins in mangrove defence against leaf herbivores. As Gilbert et al.[79] noted that *A. germinans* may use its salt excretion mechanism to prevent fungal colonisation defence mechanisms other than chemical ones should also be taken into consideration.

Phytochemical responses to oxidative stress are ascertained by the presence of δ-tocopherol or ascorbic acid (see above). In addition, antioxidant enzymes have been reported in *Avicennia* although most investigations deal with the effect of heavy metal exposure (cf.[80]).

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