Chapter 7

Chemotaxonomical studies on some members of the Rhizophoraceae

The family Rhizophoraceae consists of about 14 genera and a hundred species widely distributed in the tropical regions. The four mangrove genera included in the tribe Rhizophoreae contain 17 spp. The majority of genera are not mangroves and are found on land. The plants are trees or shrubs mostly with unicellular hairs, tanniniferous (or at least with vertically elongate tanniniferous cells) with no internal phloem and producing pneumatophores by the mangrove genera. Leaves are simple, opposite (but not decussate) with well-developed but caducous interpetiolar stipules, these sheathing the terminal bud and at least sometimes with colleters on the inner surface at the base. Flowers are solitary and axillary, perfect or seldom some of them unisexual, regular-4-5 merous, hypogynous to epigynous, the hypanthium in epigynous flowers sometimes prolonged beyond the ovary. Sepals are 4-5, thick, fleshy or leathery. Petals also are 4-5 distinct, commonly fleshy. Stamens are twice as many as sepals or petals or more, often in pairs opposite the petals. Filaments are distinct or connate at the base, attached to or around the base of a perigynous nectary disc. Gynoecium of 2-5 syncarpous carpels, 2-5 loculed or ovary unilocular by failure of the partitions. Ovules 2 in each locule in apical axile placentation. Fruit is baccate 1- seeded or with 1 seed per locule or seldom capsular. Seeds often green, sometimes arillate, in the mangrove genera, viviparous and with an enlarged hypocotyle.

Almost all the mangroves contain abundant tannin in the bark. *Rhizophora mangle*, a native of tropical swamps, is the major source of tannin in Africa and South and Central America. The bark contains 34-46 % tannin. The leaves of this plant also are used as a source of tannin.

Anatomical Characters

Nodes are always trilacunar, vessel segments with scalariform and simple perforations; imperforate tracheary elements with simple or bordered pits; wood-rays nearly always heterocellular, usually mixed uniseriate and pluriseriate with short ends, the latter sometimes as much as 10-15 cells wide. Solitary or clustered crystals of calcium oxalate often present in some of the cells of the parenchymatous cells. No internal phloem present.

Previous Chemical Reports

Stem of *Bruguiera gymnorrhiza* was found to contain five new aromatic compounds (1-5), of which bruguierols A-C (1-3) represented a new structural skeleton in natural product chemistry (Ha *et al.*, 2005). A new lupane caffeoyl ester (1), 3-(Z), caffeoyllupeol alongwith 5 known triterpenoids lupeol caffeate (2), 3-(Z)-coumaroyllupeol (3), dioslupecin A (4), lupeol (5) and lupenone were isolated from fruits of *Bruguiera parviflora* (Chumkaew, 2005).

Taxonomy

According to Cronquist (1981), the proper taxonomic disposition of this family presented a difficult problem. It was traditionally kept in the Myrtales. Cronquist (1957) took away Rhizophoraceae from Myrtales because of the following reasons. The Myrtales nearly always have internal phloem, no well developed stipules, seeds with little or no endosperm, vessels with simple perforations and alkaloids, whereas the Rhizophoraceae are wanting internal phloem and have large interpetiolar stipules, seeds with well developed endosperm, vessels with scalariform perforations and alkaloids of groups unknown in the Myrtales. But there exists a similarity between Rhizophoraceae and Combretaceae (Myrtales) in having some mangrove genera in both families. Therefore in 1957 Cronquist placed Rhizophoraceae in the order Cornales. But Cornales are a rather diverse group and do not possess certain characters of the Rhizophoraceae such as stipulate leaves, perigynous flowers, convolute or infolded petals, two or more ovules per carpel, bitegmic ovules, capsular fruits and different alkaloids. In addition, iridoid compounds are widespread in Cornales are unreported from the Rhizophoraceae. Furthermore the fruits of most Cornales are drupaceous. Therefore in 1981 Cronquist treated the Rhizophoraceae as a distinct unifamilial order Rhizophorales.

Another place suggested for the Rhizophoraceae is in the order Rosales. But the Rhizophoraceae do not appear to be closely allied to any family of Rosales, and they have none of the primitive features which mark that order.

Based on the data on ultra structure of sieve element plastids of Myrtales and allied groups (Behnke, 1984, 1988), serology (Dahlgren, 1988) and vascular organization (Tomlinson, 1986), Thorne (2000) shifted the Rhizophoraceae to the order Geraniales alongwith families like Zygophyllaceae, Geraniaceae, Linaceae, etc

In the present work, three plants *Rhizophora mucronata*, *Bruguiera gymnorhiza* and *Carallia integerrima* belonging to this family have been screened for their phytochemicals to find out the relationships of this family with other families.

Materials and Methods

Rhizophora mucronata was collected from Saurashtra coasts where as *Bruguiera gymnorhiza* and *Carallia integerrima* were procured from Bombay coasts and Castle Rock respectively. Standard methods described in Chapter 2 were followed for the screening of the stem and leaves of these plants for their phytochemicals.

Results

The distribution of various flavonoids and phenolic acids in three members of the Rhizophoraceae are presented in Table **5**. All the three plants screened contained various flavonoids in leaves and stem. The flavonoids observed were both flavonols and flavones. The various flavonols were quercetin and its 4'-OMe and 3', 4'-diOMe derivatives. The flavones identified were apigenin and luteolin along with their 4'-OMe derivatives. 3', 4'-diOMe quercetin was common to all. *Bruguiera* and *Rhizophora* were very similar in flavonoids containing quercetin, 4'-OMe quercetin and 3', 4'-diOMe quercetin. *Carallia* had an entirely different flavonoid profile in having flavones

Table 5. The distribution of various chemical markers in some members of the Rhizophoraceae

Sr. No	Name	Apigenin	4' - OMe Apigenin	Luteolin	4' - OMe Luteolin	Quercetin	4' - OMe Quercetin	3', 4' - diOMe Quercetin	Vanillic acid	Syringic acid	Gallic acid	Ferulic acid
1	*Rhizophora mucronata* Lam.(leaves)					+	+	+	+	+		+
	———"——— (stem)							+	+	+		+
2	*Bruguiera gymnorhiza* Lam.(leaves)					+	+	+	+	+	+	
	———"——— (stem)						+	+	+	+	+	
3	*Carallia integerrima* DC(leaves)	+	+	+	+			+	+	+		+
	———"——— (stem)		+		+			+	+	+		

apigenin and luteolin with their 4'-OMe derivatives. It was similar to the other two plants in having 3', 4'-diOMe quercetin.

The phenolic acid profile gave a different picture. The various phenolic acids observed were vanillic, syringic, ferulic and gallic acids. Vanillic and syringic acids were omnipresent. But ferulic acid was present both in *Carallia* and *Rhizophora. Bruguiera* was very distinct in having gallic acid confined to it and in not possessing ferulic acid common in other two species.

Discussion

The flavonoid profile indicates the taxonomic position of the Rhizophoraceae very clearly. The distinct flavonols of the Myrtales, the gossypetin and its methoxy derivatives are visibly absent here. Therefore this family may not be at home with the other families of the Myrtales such as Myrtaceae, Combretaceae, etc. The absence of the isoquinoline alkaloids of the Cornales and iridoids keeps this family away from the Cornales also. The Rhizophoraceae are similar to the members of Rosales in having flavonols as the dominant pigments. But the absence of sorbitol (a characteristic compound of the Rosales), apocarpous pistil and numerous stamens do no favour the inclusion of this family in the Rosales either. The presence of flavones along with flavonols in *Carallia* brings this family closer to the Combretaceae and other families of the Myrtales. Therefore the phenolic profile favour the treatment of Rhizophoraceae in a unifamilial order Rhizophorales closer to the Myrtales.

The shifting of this family to the Geraniales as practiced by Thorne (2000) does not get any chemical support because tannins are unheard in any of the member families of the Geraniales. Most of the plants in the Geraniales are herbs characterized by lignans (Linaceae), volatile oils (Geraniaceae) or saponins (Zygophyllaceae) and all these compounds are not synthesized by any member of the Rhizophoraceae.

Within the family, *Rhizophora and Bruguiera* are the primitive members due to the presence of flavonols in them. The synthesis of flavones keeps *Carallia* as the advanced genus here.