# 12. Family RHAMNACEAE

The Rhamnaceae, chiefly distributed in tropic and temperate regions of the world, comprise of 40 genera and 550 species. Few of them are confined to the dry and arid zones. The family consists of armed (with thorns) or unarmed shrubs or woody vines. The leaves are simple, alternate and stipulate, the stipules sometimes modified into spines. Flowers are small, regular, bisexual or unisexual by abortion with persistant floral tube, occuring in axillary cymes. Perianth is tetra - or pentamerous, petals clawed enclosing the stamens or sometimes absent (**Zizyphus** Sp.). Stamens opposite to petals inserted on or at the margins of disk, dithecous and introrse. The disk is conspicuous, nectariferous and intrastaminal. Gynoecium syncarpous, 2/3 carpellary, peri - or epigynous having two to three locules usually incompletely septate. Ovules are solitary in each locule on subbasal or parietal placenta. Style bifid and stigma glandular. The fruit is a drupe with 2 or 3 indehiscent pyrenes or with indehiscent or dehiscent stones. Seeds are convex, smooth with lateral raphe and sometimes minutely arillate. Endosperm is copious or scanty.

**Anatomy :**

A tendency towards adnation between the members of adjacent whorls of floral members followed by the fusion of vascular supply is seen in flowers (Nair and Sarma, 1961). The stamens unite with the petals, and the cohesion of calyx, corolla and disk results in the formation of a floral tube or the hypanthium. The floral anatomical studies indicate that the flower is originally obdiplostemonous and the inner whorl of stamens alongwith the lower part of the perianth is modified into a disk. Tortosa (1982) does not support this view and according to him the peri- or epigynous condition is due to the cohesion and adhesion of the ovary with the disk. The placentation of the family is considered to be basal

by Bentham and Hooker (1862) and others, while Puri (1952) referred it as parietal. Nair and Sarma (1961) suggested that the nature of the vascular supply indicates that the basal condition is derived from parietal and therefore can be termed as subbasal. Another line of evolution, observed in the ovary, is the tendency towards unilocular condition. The ovary is incompletely partitioned and this is resulted by the receding of the placenta to the periphery, a condition similar to that seen in the Vitaceae.

The wood in the Rhamnaceae shows considerable variations. The growth rings are distinctly demarkated by thin lines of parenchyma. The vessels are small, numerous and evenly distributed. Vessel segments have simple perforations, tracheary elements are imperforate having simple pits, rays are heterocellular and wood parenchyma vary from mainly apotracheal to mainly paratracheal. The heartwood of **Sageratia** is exceedingly dense, hard and horn-like. The genus **Rhamnus** has flame-like arrangement of vessels and rays are of both moderately broad and fine nature while **Zizyphus** does not have flame-like arrangement and the rays are fine and invisible. The phloem has S-type of plastids.

**Embryology** :

The anther wall is five-layered, multinucleate and has secretory type of tapetum. The ovules are bitegmic, crassinucellate, anatropous and epitropous with downward directed micropyle. Only the outer integument takes part in the formation of micropyle. The archesporium is multicellular. Embryo sac development is Allium or Polygonum type. Bisporic embryo sacs are observed occasionally (Arora, 1953). Nucellar cap and hypostase are well-developed and the embryo development is Asterad type (Wang, 1983). The endosperm is nuclear.

**Palynology :**

The pollen are uniform in the family. They are small to medium sized, 3-colporate, suboblate to subprolate, with smooth to slightly reticulate exine, binucleate and triangular in polar view.

**Taxonomy :**

The family is divided into 4 tribes by Lawson (1875) : 1) Ventilagineae - disk filling the calyx tube, ovary superior or half superior, fruit dry one-seeded, exalbuminous (**Ventilago, Smithia**); 2) Zizipheae - disk filling the calyx tube, fruit a dry or fleshy drupe with a 3-celled stone (**Zizyphus, Berchama**); 3) Rhamneae - disk lining or filling the calyx tube, fruit superior or half superior, dry or fleshy of 3 pyrenes or cocci (**Rhamnus, Hovenia, Scutia, Sageratia, Colubrina**) and (4) Gouanieae - fruit inferior crowned with persistant calyx (**Apleron, Gounia, Helinus**).

Weberbauer (1897) divided the family into 6 tribes: (1) Maesopsideae (2) Ventilagineae (3)Zizypheae (4) Rhamneae (5) Colletieae and (6) Gouanieae.

The family is usually associated with the Vitaceae and placed in a separate order Rhamnales. This order is considered closely related to the Celastrales by Rendle (1950), Cronquist (1968) and Takhtajan (1980), orginating from a common obdiplostemonous ancestor Rutales or Saxifragales in two parallel lines i.e. stamens alternate in the Celastrales and stamens opposite to petals in the Rhamnales. Bessey included the Rhamnaceae in Celastrales. Thorne (1981) included the Rhamnaceae and Elaeaginaceae in Rhamnales and separated the Vitaceae while Dahlgren (1980) keeps only Rhamnaceae. Both the authors group the Rhamnales in Malviflorae taking into consideration

their affinity with the Euphorbiaceae. The characters these 2 families share are the mucilage cells, S-type of plastids in phloem, peptide alkaloids, O-methyl anthocyanins, 7,3',4'-trimethoxy or 5'-methoxy flavonoids and biflavones (Gornall et al., 1979).

**Economic Importance :**

The family is known for their medicinal properties. The wellknown laxative "cascara sagrade" is the product of **Rhamnus purshiana.** It is used to relieve chronic constipation. **R.Wightii,** and **R. frangula** also yield drugs similar to cascara. The active principles are the anthraquinones. The saponins of **Zizyphus jujuba** seeds, jujuboside A and B, are found to have sedative and tranquilizing action (Watanbe et al., 1973). In China they are used for strengthening nervous system and for insomnia. The fruits of **Zizyphus** have emollient and pectoral properties and are prescribed for scabies and throat treatments. The leaves are antidotes to aconitine poisoning. The neo-lignans isolated from the leaves are found to be a potent natural inhibitor of platelets aggregation and a vasodilator. The roots of **Ceanothus americanus,** containing alkaloid ceanothin, are used in the treatment of syphilis. The leaves of **Zizyphus jujuba** contain a saponin, ziziphin, which is a taste modifier.

Some of the plants yield important dye-stuffs. Yellow and green dyes are obtained from **Rhamnus** and orange and red dyes from roots of **Ventilago.** These are used for coloring cotton, wool and silk. The tannins of **Zizyphus** are employed in leather industry. The stem of **Ventilago** yields cordage and fibre.

Though the Rhamnaceae are not very significant from the view point of timber, it is of interest because it produces

the hardest and heaviest wood in the world - the 'black iron wood' from **Krugiodendron ferreum. Zizyphus chloroxylon** produces a lesser important wood, the 'jamaican cog wood' best for cogs and rollers.

**Previous chemical reports** :

The Rhamnaceae are noted for their ability to produce cyclopeptide alkaloids having marked pharmacological activities (Hindenlang et al., 1980). These compounds are essentially macrocyclic conjugated peptides in which the non-amino acid component is pyrocoll. These alkaloids are reported from the genera **Ceanothus** (Tschesche et al., 1968; Lagarias et al., 1979), **Phylica** (Arndt and Baarschers, 1964) and **Scutia** (Merkuza et al., 1974; Sierra et al., 1974, Shah et al., 1989; Dwivedi et al., 1987).

Another group of compounds prominent in the family is the quinones, especially the anthraquinones. **Rhamnus** contains emodin, chrysophanol, physcion and anthranols (Turhan, 1977; Demuth et al., 1978; Tripati et al., 1979; Chaor et al., 1980). Similar type of quinones are reported from **Ventilago** (Cooke et al., 1980; Rao et al., 1984; Misra and Chandhok, 1981) also. Saponins based on ebelin (Shibata, 1977) ceanothic acid (Merkuza et al., 1971), jujubogenin (Kawai et al., 1974) manogenin, taxifolin (Srivastava and Chauhan, 1977) ziziphin and zizynumin (Sharma and Kumar, 1983) are isolated from **Zizyphus, Colletia, Discaria** and **Ceanothus.**

The reports on phenolics, though very few, include 3,8- coumaranonyl flavanone from **Phyllogeiton zeyheri** (Volsteedt and Roux, 1971), spinosin, a C-glycoside of apigenin (Woo et al., 1979); acylated flavone from seeds of **Z.jujuba** (Woo et. al., 1980) and quercetin, rutin, hyperin and quercitrin (Nawwar et al., 1984). The only neo-lignan reported occurs

in the leaves of **Z.jujuba** (Fukuyama et al., 1986).

In the present work leaves of 9 plants belonging to five genera of the family Rhamnaceae are subjected to chemical analysis for their plant products.

**Materials and Methods:**

Mature leaves of the 9 plants used for the analysis were collected from various regions of India. **Ventilago** and **Zizyphus rugosa** were collected from Waghai garden, Gujarat; **Colletia, Pommaderis** and **Rhamnus** from Ooty and **Zizyphus** from Baroda, Gujarat. The standard procedures (Chapter 2) are followed for the extraction, isolation and identification of various phenolics and other natural products.

**Results :**

**The table** - 12.1 shows the distribution of the compounds obtained. All the 9 plants screened contained flavonols. Flavones (7-OMe apigenin) and glycoflavones are restricted to the genus **Colletia**. Among the various flavonols screened, quercetin is present in all the plants while kaempferol is less frequent (3/9). Myricetin is found in **Z.nummularia** and **Z.rugosa**; 3'4'diOMe gossypetin in **Colletia** and 3'4'- diOMe querectin in most of the species of **Ziziphus**. Quinones are located in all the plants screened and proanthocyanidins in seven taxa. 12 phenolic acids are identified of which gentisic, p-hydroxybenzoic, vanillic, syringic and protocatechuic acids are the benzoic acids and **cis** and **trans** p- coumaric and **cis** and **trans** - ferulic acids are the cinnamic acids. **Rhamnus** is the only taxon containing protocatechuic acid. Saponins are present in all the plants; tannins and alkaloids in 6 plants each.

**Table : 12.1 The Distribution of Chemical Characters Among 9 Members of the Rhamnaceae.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. **Colletia ferox** Gill.et. Hook | + | | | + | | | | | | + | + | | + | + | + | + | + | + | | + | + | | + | + |
| 2. **Pomaderris apetalus** Labill. | | | + | + | | + | | | | | + | + | | + | + | + | + | + | | + | + | + | + | |
| 3. **Rhamnus wigntii** W & A | | | + | + | + | | | | | | + | + | | + | + | | | | + | + | + | | + | |
| 4. **Ventilago maderaspatana** Gaertn. | | | | + | | + | | | | | + | + | + | + | + | + | + | + | | + | + | | + | |
| 5. **Ziziphus jujuba** Lam. | | + | | + | + | + | + | | | | + | + | | | + | | | | | | | + | + | + |
| 6. **Z. nummularia** W & A | | | + | + | | | + | + | + | | + | + | | | + | | | | | | | + | + | + |
| 7. **Z. oenoplia** Mill. | | | | | + | | + | | | | + | + | | | + | | | | | | | + | + | + |
| 8. **Z. rugosa** Lam. | | | | + | + | | | + | | | + | | + | + | | + | + | + | | + | + | + | + | + |
| 9. **Z. xylopyra** Willd. | | | | + | + | | + | | + | | + | + | + | + | + | | + | + | | + | + | + | + | + |

1) 7-OMe Apigenin 2) Glycoflavone 3) Kaempferol 4) Quercetin 5) Rhamnetin 6) 3'-OMe Quercetin 7) 3',4'-DiOMe Quercetin 8) 7,3',4'-TriOMe Quercetin 9) Myricetin 10) 3',4'-DiOMe Gossypetin 11) Quinones 12) Proantnocyanidins 13) Gentisic acid 14) p - Hydroxybenzoic acid 15) Vanillic 16) Syringic acid 17) **cis** p- Coumaric acid 18) **trans**-p-Coumaric acid 19) Protocatecnuic acid 20) **cis**-Ferulic 21) **trans**-Ferulic acid 22) Tannins 23) Saponins 24) Alkaloids.

**Discussion :**

The flavonoid chemistry of the family is more or less homogeneous. The characteristic features include the uniform distribution of flavonols (especially querectin), quinones and proanthocyanidins. In addition, the family is also peculiar in having cinnamic acids in both **cis** and **trans** forms. The occurence of peptide alkoloids in most of the Rhamnaceae plants, which are otherwise rare in plant kingdom, forms a significant chemical marker. Therefore, there is apparently no doubt about the homogeneity of the Rhamnaceae. However, **Colletia** is distinct in producing flavones and 6-hydroxy flavonols. This may be explained in terms of its xerophytic adaptation. In an oxidative environment of the desert, it would be definitely advantageous for the plant to produce such stable polyphenols which may serve as effective anti-oxidants. The elimination of tannins from this plant is also noteworthy. So the specilization achieved by **Colletia** may not warrant a distinct taxonomic status when considered in terms of its environment. More data are to be made available before some valid taxonomic conclusions are made. **Zizyphus** is characterised by tannins, methoxylated flavonols (3',4'-diOMe quercetin) and myricetin and so this genus combines both primitive and advanced features. Comments on the intrafamilial classification are reserved because of the poor representation of the tribes.

The chemical characters do not support the proposed amalgamation of the Vitaceae and Rhamnaceae. The distinguishing features of the Rhamnaceae, quinones and peptide alkaloids, are not even located in traces in the Vitaceae (incl. Leeaceae).