

11. Family CELASTRACEAE

The Celastraceae (including the Hippocrateaceae), consisting of 50 genera and 200 species, have a worldwide distribution. Only 13 genera of this family are located in India. The family consists of trees, erect or scandent shrubs, with stem sometimes producing rootlets (*Euonymus*). Leaves are simple, alternate or opposite with caducous stipules. Flowers are small, green, bisexual or rarely unisexual having pentamerous persistent perianth and 4-5 stamens which alternate with petals arising from below or above the nectariferous disk. Ovary tri- or pentacarpellary, partially or completely sunken in the disk, stigma simple or lobed, ovary with two or more ovules per locule in axile placentation. Fruit is a loculicidal capsule or with 3 divergent separate or laterally connate follicles or drupaceous. The seeds, sometimes winged, are covered with brightly colored aril.

Anatomy :

The floral anatomical studies indicate that the disk represents the reduced stamens and the cup like structure of the flower is formed of fused floral parts. The aril of the Celastraceae is a false aril. They are formed by the dilation and expansion of the edges of the exostome. The leaves and stem have latex sacs and canals which contain guttapercha. The wood is fine textured and diffuse-porous. A tendency towards ring-porous also occurs in the family. Vessels are medium sized, with tyloses wanting. The rays are fine to very fine and closely packed. According to Heimsch (1942) the family is peculiar in possessing both primitive and derived features. The primitive features are fibre tracheids, scalariform perforation plates, radial multiple pores, wood parenchyma are in multiseriate bands and in long wings of multiseriate rays. The advanced features are libriform fibres, simple perforation plates, solitary pores, wood parenchyma sparse and shortwings of multiseriate rays.

Embryology :

The ovule is apotropous, anatropous, bitegmic, tenuinucellate or rarely crassinucellate. The embryo sac ontogeny is Polygonum type and during the development it absorbs the nucellus leaving a pedestal at the chalazal end (Copeland, 1966). Adventitive embryos are found in a few members of the family. These develop from nucellus (Berkeley, 1953). The development of the embryo sac is Solanad type.

Palynology :

The Pollen structure within the family is uniform. They are tricolporate, suboblate and binucleate. The size of the lumen decreases towards colpi. Sexine is thicker than nexine with usually reticulate exine.

Classification Of The Family :

Lawson (1875) divided the family into two tribes, (1) Celastrieae-containing taxa with 4 or 5 stamens or rarely more, which are inserted on or beneath the disk; filaments subulate and seeds albuminous and (2) Hippocrateae - with 3 stamens, rarely 2, 4 or 5, inserted on the face of the disk, filaments flatten before anthesis making the stamens extrorse and seeds exalbuminous (Hippocratea and Salacia). The Celastrieae are further divided into 3 subtribes, a) Celastreae-leaves alternate, two erect ovules in each cell, and dehiscent fruits (Celastrus, Gymnosporia); b) Euonymeae - leaves opposite, fruit dehiscent (Euonymus, Lophopetalum, Catha), and c) Elaeodendreae - leaves opposite or subopposite, fruit dry or pulpy (Elaeodendron).

Lösener (1897), Wettstein (1935) and Hutchinson

(1969) elevated the tribe Hippocrateae to a family Hippocrateaceae while Takhtajan (1980), Thorne (1981) and Dahlgren (1980) keep it as a subfamily within the Celastraceae. The data from pollen morphology (Erdtman, 1952) and wood anatomy (Metcalfe and Chalk, 1950) indicate the close affinity of these taxa with other genera of the family; thus are in favour of inclusion of these genera in the Celastraceae. Smith and Bailey (1941) taking into consideration the overall characters and their similarities, state that the separation is purely artificial while Adatia and Gavde (1962) agree in separating the family.

Lösener (1897) classified the Celastraceae into 4 sub-families: Celastroideae (with 2 tribes), Tripterygioidae, Cassinoideae and Goupioideae. Takhtajan (1980) excludes Goupioideae but keeps Hippocrateoideae and Campylostemonoideae within. Thorne's (1981) treatment of the family is similar to that of Takhtajan but he creates another unigeneric subfamily Siphondontoideae. Cronquist (1968) relates the Celastrales to Rosales, Santalales, Rhamnales, Euphorbiales and Sapindales. Gornall *et al.* (1979) find Celastraceae closer to Sapindales (seed wall, aril and similar disk) but exhibiting some relationships with the Fabales and Geraniales.

Economic Importance :

Though the Celastraceae were once considered not of great economic importance, of late, a number of medicinally important principles have been isolated from many members of the family. The taxa of this family produce a variety of alkaloids which have a wide range of pharmacological properties. Among them, maytansinoids and their esters, isolated from *Maytenus* and *Putterlickia*, form the most important group of alkaloids. They possess antileukemic and antitumor proper-

ties and inhibit Helva-229 cervical cancer cells and murine sarco virus (Remillard et al., 1975; Wolpert - Delifilipes et al., 1975). These Compounds are under extensive clinical trial. Phenylalkylamines of *Catha edulis* are hallucinogenic and are used for this purpose. Ester alkaloids such as celapanin, cathedulin-2, maytenin (*Catha*, *Maytenus* and *Celastrus*) are sedatives while wilfordine (*Tripterygium* and *Euonymus*) is insecticidal. A group of modified triterpenes - quinone-methides-are hypoglycaemic and used in the treatment of skin cancer. The cardiac glycosides - cardiotonic compounds-are located in *Euonymus*, *Lophopetalum* and *Elaeodendron*. The family thus is a reservoir of a wide range of pharmacologically active compounds and trials to exploit them in large scale are in progress.

The wood of the Celastraceae are economically not important. However the wood with a fine structure form an ideal material for carving, engraving and turnery articles. The wood of *Elaeodendron* is used for house building. Some of the *Euonymus* sp. are grown as ornamentals.

Previous Chemical Reports :

The Celastraceae produce highly characteristic complex and unique compounds. A review of the literature of the chemistry of the family is available (Brüning and Wagner, 1978). The family exhibits a great diversity in the structure of terpenoids and alkaloids. The triterpenes here can be grouped into 3: 1) Cardiac glycosides, 2) Modified triterpenes and 3) Quinone-methides. Cardiac glycosides based on digitoxigenin are located in *Euonymus*, *Celastrus* and *Lophopetalum*. But those of *Elaeodendron* are unique in that they possess an octacyclic skeleton. Modification occurs mostly in the pentacyclic triterpenoids while the tetracyclic triterpenoids

are relatively undifferentiated. The variety includes lupanes (lupeol, lupeon and betulin) from *Celastrus*, *Euonymus*, and *Maytenus*, friedelans (friedelin and its derivatives) and taraxerans (taraxerol) from *Euonymus*. The modified triterpenes - the quinone methides-are present in almost all the taxa. The compounds reported are pristimerin, tigenon and its hydroxy derivatives, dispermoquinone and iguesterin. Ferrugion type of diterpenes are found in the family. They are maytenon, dispersinol and dispermon. From *Tripterygium* diterpene triepoxides such as triptolide, triptidiolide and triptonide are isolated. All these compounds are found to be antileukemic. Sesquiterpenes also are frequent in the family. They are basically of dihydro- - agarofuran type with a maximum of 9 hydroxyl groups. These polyhydric alcohols are usually stored in the seed oil and as a result the saponification value of the oil goes very high. The sesquiterpenes also enter into ester combination with alkaloids forming sesquiterpene ester alkaloids, which are characteristic to the family.

The alkaloids of the Celastraceae also exhibit unique chemical structures. Maytansinoids, the antitumor compounds, possess 19-membered amide ring arranged ansa-like on chlorine substituted benzene ring. On the macroring there is a cyclic carbamate grouping with carbinolamide arrangement at C-9; and N-derived glycine at C-3, bound in an ester linkage. These are isolated from *Maytenus* and *Putterlickia*. Xanthine alkaloids of purine base (caffeine and theobromine) also are present in *Maytenus*. Alkaloids with phenylalkylamines such as D-nor-pseudoephedrine and canthinone are the principles of the hallucinogenic beverage khat (*Catha edulis*). Peptide alkaloids similar to those of the Rhamnaceae are known from *Euonymus*. Spermidine alkaloids having triazacyclotridecene-system are present in *Maytenus*, *Pleurostylis* and *Peripterygium*.

Table 11.1

The Recent Chemical Reports from the Celastraceae.

Plant name	Compound	Reference
1. <i>Catha edulis</i>	Dihydromyricetin 3-O-rhamnoside Alkaloids having mono and bismacrolide bridge	Gellert <i>et al.</i> , 1980 Baxter <i>et al.</i> , 1976; Crombie, 1980
	Cathedulins	Crombie <i>et al.</i> , 1978.
	Quinone - methides	Baxter <i>et al.</i> , 1979
2. <i>Catha cassionoides</i>	Terpenoids	Betancor <i>et al.</i> , 1980
3. <i>Elaeodendron glaucum</i>	Elaeodendrol and elaeodendradiol	Anjaneyulu & Rao, 1980
4. <i>Emmenospermum pancheriarum</i>	Triterpenes	Vernon <i>et al.</i> , 1980
5. <i>Euonymus sieboldiana</i>	Euonymine & Neo- euonymine	Yamada <i>et al.</i> , 1977
6. <i>E. pendulus</i>	Terpenes	Krishna <i>et al.</i> , 1978
7. <i>E. alatus</i>	Alatamine & Wilfordine	Ishiwata <i>et al.</i> , 1983 Yamada <i>et al.</i> , 1978
8. <i>E. europaeus</i>	Sesquiterpene esters	Röemer <i>et al.</i> , 1981
9. <i>Maytenus emarginatus</i>	O-Oxolup-20(29)en-30-ol	Wijeratne <i>et al.</i> , 1981

...2..

Table 11.1 (Contd.)

Plant name	Compound	Reference
10. <i>M.horrida</i>	Triterpenes	Gonzalez <u>et al.</u> , 1987
11. <i>M.heterophylla</i>	Spermidine alkaloids	Wagner & Burghat, 1977
12. <i>Tripterygium wilfordii</i>	Sesquiterpene alkaloids	Deng <u>et al.</u> , 1987
13. <i>Salacia macrosperma</i>	Quinone - methides	Viswanathan <u>et al.</u> , 1979
14. <i>Pleurostyliia africana</i>	Spermidine alkaloids	Wagner & Burghat, 1981
15. <i>P. opposita</i>	Triterpenes	Muthukuda & Balasubramanian, 1983; Uvias and Sultanbawa, 1981.

The flavonols from the Celastraceae are principally mono-, di- and bisglycosides of kaempferol and quercetin. Myricetin is located only in *Catha*. Proanthocyanidins and anthocyanins are frequent. Mangiferin, the xanthone C-glycoside, is seen in *Salacia prinoidea*. The Celastraceae are also well-known for their accumulation of dulcitol, a hexitol which has a restricted occurrence in plant kingdom. Guttapercha, the *-trans* polyisoprene, is found in the latex sacs and ducts of these plants. The most recent chemical reports from the family are given in Table 11.1

In the present work leaves of 14 plants belonging to seven genera have been analysed for their constituents.

Materials & Methods

Euonymus, *Catha* and *Elaeodendron* were collected from Kashmir, *Salacia* and *Lophopetalum* from TBGRI, Trivandrum and *Gymnosporia* and *Celastrus* from Baroda. The methodology followed is already explained (Chapter 2).

Results :

The results obtained are presented in Table 11.2. Flavonols, flavones and glycoflavones are the various flavonoids located in the family. Myricetin, quercetin and kaempferol and their methoxylated derivatives are the flavonols encountered. Flavonols form the dominant phenolics of the family. Kaempferol, quercetin and their derivatives are widespread. Myricetin is rare, found in two genera *Catha* and *Salacia*. Flavones are located in *Gymnosporia*. They are luteolin, 3'-OMe luteolin, 7,3'-diOMe luteolin and 3'4' - diOMe luteolin. Glycoflavones are seen only in *Elaeodendron*. Proanthocyanidins based on procyanidin and prodelfinidin were common, having been located in 10/14 plants. Seven phenolic

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27

E CELASTRIEAE

-tribe Euonymeeae

Euonymus hamiltonianus wall.

E. fimbriatus Wall.

E. japonicus Tounb.

Lophopetalum wightianum Arn.

b tribe Celastreae

Celastrus paniculatus Willd.

C. stylosa Wall.

Catha edulis Forsk.

Gymnosporia montana Bartn.

G. emarginata Roth.

tribe Elaeodendreae

Elaeodendron glaucum pers.

E. orientale Jacq.

B HIPPOCRATEAE

Salacia bedddomi Gamble

S. reticulata Wight

S. oblonga Wall

Luteolin 2) 7-Ome Luteolin, 3) 7,3'-DiOme Luteolin 4) 3',4'-DiOme Luteolin 5) Vitexin 6) 3-Ome Orientin 7) Myricetin 8) Kaempferol, 10) 7',4'-DiOme Kaempferol 11) Quercetin 12) 3'-Ome Quercetin 13) 3',4'-DiOme Quercetin 14) 7,3',4' TriOme Quercetin 15) Gosypetin 17) Quinones 18) Proanthocyanidins 19) p - Hydroxybenzoic acid 20) Gentisic acid 21) Vanillic acid 22) Syringic acid 24) Protocatecnic acid 25) p-Coumaric acid 26) Ferulic acid 27) Saponins 28) Tannins and 29) Alkaloids.

acids are identified, of which vanillic, syringic, p-hydroxybenzoic, and gentisic acids are present in all the plants whereas p-coumaric acid is found in 5, protocatechuic in 3 and ferulic in one. Tannins of the condensed type are frequent (9/14) and alkaloids are present in all the plants except *Elaeodendron*.

Discussion :

The Celastraceae are chemically a very homogeneous family. The homogeneity is expressed by the near uniform presence of flavonols, proanthocyanidins, tannins and alkaloids and in the near absence of flavones/glycoflavones. The presence of unique compounds such as dulcitol, guttapercha, quinone-methides and ester alkaloids are some other chemical characters exemplifying the close affinity existing among the members of this family.

The absence of any distinct chemical feature in *Salacia* casts doubt on the validity of the Hippocrateaceae. This genus snugs comfortably among the genera of the Celastraceae. The tribes and subtribes envisaged by the different taxonomists also do not get any backing from the chemical evidences. However, certain genera stand out from among the rest. Prominent among them are *Euonymus* and *Gymnosporia*. *Euonymus* produces 8-hydroxy flavonol (gossypetin), peptide alkaloids and cardiac glycosides and eliminates proanthocyanidins and tannins from its leaves. *Gymnosporia* also exhibits a plethora of chemical diversity. The magnitude of variations exhibiting in maytansinoids and in elaborating flavones is otherwise unheard in the family.

Evidently the Celastraceae do not occupy an elevated position in the evolutionary hierarchy if only flavonoids

are taken into consideration. But the complex modifications and diversity achieved in the chemistry of terpenoids and alkaloids of this family lifts it to a higher evolutionary level and keep it as a specialized line. It is to be noted that the ability to modify the triterpenoids does occur in the Sapindaceae s.l. This may bring the Celastrales and Sapindales closer as two parallel lines specialized in terpenoid biosynthesis. The 5-deoxy flavonoids reported from the Celastraceae are common in Sapindales also (Gornall et al., 1979). Peptide alkaloids (characteristic of the Rhamnaceae) in *Euonymus* bring the Rhamnaceae closer to this genus in the Celastraceae.

The genus *Gymnosporia*, producing flavones and most of the highly modified terpenes/terpene-quinoids and alkaloids, is the most evolved taxon of the family. *Euonymus*, though retains a few primitive features such as gossypetin, is also rich in chemical characters usually associated with advanced forms (absence of proanthocyanidins and presence of methoxylated flavonols). The myricetin-containing genera *Catha* and *Salacia* are the primitive members of the family.