3. Family SAPINDACEAE

The Sapindaceae (including Aceraceae, Hippocastanaceae, Melianthaceae and Staphyleaceae) consist of woody trees, shrubs or rarely tendril climbers. The family has stipulate or exstipulate, alternate usually pinnately or palmately compound or simple leaves. Plants are polygamo- or andromonoecious or dioecious with their flowers arranged in panicles. The flowers are usually small, irregular or regular, unisexual by abortion or occasionally bisexual. Sepals are 4-5, free, unequal and imbricate. Petals 4-5, free, clawed with appendages on the inner surface and imbricate. Nectariferous disk is extrastaminal or intrastaminal, continuous, unilateral or oblique. Stamens often 8, sometimes 6-9, united or free, inserted on or within the disk, dorsifixed or versatile and introrse. Gynoecium is syncarpous, usually tricarpellary, rarely 2-4 or 6; ovary 3-locular sometimes deeply lobed; ovules usually 1-2 or rarely numerous in each locule on axile placentation. The ovules are apotropous, bitegmic, crassinucellate and anatropous. Fruit is a drupe, berry, capsule or schizocarp often unilocular and one-seeded by abortion, many times with inflated fruit wall. The seedcoat coriacious, crustaceous and the seeds mostly winged. Endosperm scanty. The family characteristically contains unicellular or multicellular hairs, mucilage cells and secretory cells on the epidermis of the leaves.

Hiern (1875) divided the family into five tribes i.e. 1) Sapindeae (stamens inserted inside the disk, seeds exalbuminous, leaves exstipulate alternate), 2) Acerineae (flowers regular, stamens inserted outside the disk, lobes of the fruit indehiscent., seeds exalbuminous, leaves opposite, exstipulate), 3) Dodonaeeae (flowers regular, stamens outside the disk, seeds exalbuminous, leaves alternate, exstipulate), 4) Melliantheae (flowers irregular, stamens inserted inside the disk, seeds albuminous, leaves alternate, stipulate) and 5) Staphyleae - (flowers regular, stamens inserted outside the disk, seeds albuminous, leaves alternate, stipulate). All these tribes except Dodonaeeae have been elevated to separate families by Radlkofer (1934). He separated **Aesculus** and **Billia** of the tribe Sapindeae into a new family, the Hippocastanaceae.

The family Sapindaceae sensu stricto is characterised by alternate pinnate leaves, polygamodioecious flowers, scale/gland-appendaged petals, unilateral extrastaminal disk, tricarpellary ovary and arillate seeds. Flowers are regular in **Litchi**, **Filicium** and **Dodonea** while in **Allophylus**, **Cardiospermum** and **Sapindus**, they are irregular. Aril occurs only in a few members of the family i.e. **Allophylus**, **Harpullia**, **Nephelium** and **Schleichera**. Ovules are usually apotropous except in **Filicium** which has epitropous ovules. Hemianatropous condition of ovules occursin **Allophylus**.

The Aceraceae are distinguished from the closely related Sapindaceae by the opposite mostly simple leaves, regular flowers often with intrastaminal nectariferous disk, regular bicarpellate gynoecium and schizocarpic fruit. The family consists of two genera **Acer** (150 species) and **Dipteronia** (2 species). The Aceraceae exhibit a lot of variations in the floral morphology within. The disk varies from extrastaminal to intrastaminal. There exist varying degrees of cohesion between members of the different whorls. There is also a tendency towards reduction in number of whorls. Tetramerous condition is seen in **Acer negundo**. The suppression of one of the sex in bisexual flowers leads to the polygamodioecious nature found in a number of species. A gradual evolution of the inflorescence from panicle to umbel through spike and raceme is also met with in this family (Hall, 1954).

The Hippocastanaceae include two genera **Aesculus** and **Billia** which are distributed in North America, Europe and Asia,. This family is characterised by palmately compound leaves and leathery capsules enclosing large solitary seeds. The inflorescence of the family, termed as 'thyrsus' by Radlkofer (1934), is a condensed panicle (Hardin, 1956).

The Melianthaceae are distinguished from the Sapindaceae by typically four basally connate anthers, irregular flowers, numerous seeds with copious endosperm and the pedicel twisting by 180° at the time of anthesis. **Melianthus** and **Bersama** are the two genera included in this family and both these taxa are endemic to Southern Africa. The latter genus is sometimes kept in a separate family Bersamaceae. The Staphyleaceae, consisting of five genera and 60 species, are confined mostly to the Northern Hemisphere of America, Asia and Europe and have cup like intrastaminal disk, usually perfect flowers, numerous ovules in each locule and abundant endosperm. The family shows a tendency towards basal connation of floral parts developing into a hypanthium.

Anatomy :

The Sapindaceae, Aceraceae, Hippocastanaceae, Melianthaceae and Staphylaceae share a number of characters. The wood in the Sapindaceae is differentiated to sapwood and heartwood and is medium to fine-textured with fairly straight or slightly wavy grains. The vessels in the Sapindaceae are small sized usually short (except in **Dodonea** where they tend to become longer and clustered) and possess simple perforations. The rays are exclusively uniseriate and the fibers are typically septate with simple pits. Though the family exhibits uniformity in vessel and ray characters, the component taxa differ in the nature of parenchyma. Wood parenchyma are either apotracheal, paratracheal or in some cases combining both.

The Aceraceae are distinct from the Sapindaceae in having larger intervessel pitting, fusiform parenchyma, broader rays and in not having septate fibers. The vessels in the Hippocastanaceae are angular and contain simple or scalariform pitting and large intervessel pits whereas the fibres are non-septate with simple or bordered pits. The rays are uniseriate here. The Melianthaceae have styloids (elongated prismatic crystals) in most of the cells, small vessels with simple pits, paratracheal parenchyma and 3-9 celled wide rays and non-septate simple pitted fibers. The Staphylaceae are characterised by numerous uniseriate rays, frequent scalariform perforation and non-septate fibers containing bordered pits. The parenchyma are scanty and the rings are not clearly distinct as in the other families.

Embryology :

The Sapindaceae exhibit a uniform pattern of embryogeny. The embryo sac is Polygonum type, but is broader towards the micropyle and narrower towards the chalaza. The micropyle is formed by both the integuments or only of inner integument. (Singh and Shiam, 1977). The formation of the obturator and hypostase is a constant feature of the family. However, the nature of the obturator varies from placental (**Litchi, Dodonea, Allophylus, Cardiospermum**) to funicular (**Sapindus**). Synergids are ephemerals except in **Cardiospermum** (Nair and Joseph, 1960) where they become multinucleate. The endosperm is nuclear and the wall formation starts only at the later stages of embryo development, leading to the formation of one or two layered cells. Haustoria occur frequently. Development of embryo is Asterad or Onagrad type with unequal cotyledons. Adventitive polyembryony is observed in **Allophylus** (Mathur and Gulati, 1980) and parthenocarpy in **Dodonea** (Joshi, 1938). The embryogenesis of the Aceraceae, Hippocastanaceae (List and Steward 1965), Melianthaceae and Staphyleaceae is similar to that of the Sapindaceae.

Palynology :

The pollen of all the 4 families are more or less similar. The pollen of the Sapindaceae are eurypalynous, 3-colporate and pororate. They are usually peroblate, oblate or suboblate. Amb is circular or triangular with 3 radiating structures (Berg, 1978; Muller, 1979). **Lepisanthes** has very short and narrow endoaperature which is wider than ektoaperature. Exine has annulate or reticulate sculpture. **Allophylus** pollen is oblate with striate ornamentation which becomes concentric around the aperature. Cruze et al. (1984) recognised 4 groups with regard to the aperature and symmetry of the pollen grains. They are, 1) 3-porate, 2) 3-colporate, 3) heteropolar and 4) 3-parasynacolporate.

Pollen of the Aceraceae and Hippocastanaceae are 3-colpate, peroblate or prolate with usually suboblate reticulate to striate pattern. The colpi in the latter family are membraneous glandular. In both these families the sexine is thicker than nexine. The Melianthaceae have pollen 3-colporate, subprolate distinctly reticulate with ora crassimarginate and lalongate. Staphyleaceae have tricolporate suboblate subprolate pollen in which the sexine is equally thick as nexine. The pollen of the Staphyleaceae resemble that of the Celastraceae. (Dickson, 1987).

Taxonomy :

The families Aceraceae, Hippocastanaceae, Melianthaceae, Sapindaceae and Staphyleaceae, conventionally, are included in the order Sapindales. Robert et al. (1975) consider the differences existing between Sapindaceae, especially **Ungandia**, and the Hippocastanaceae to be meagre and do not warrant a separate family status for the latter taxon. Müller and Leenhouts (1976) opine that in pollen characters the Aceraceae and Hippocastanaceae are similar to the Sapindaceae and therefore, should be retained as separate tribes in the Sapindaceae. Bessey (1915), Rendle (1950) and Wettstein (1935), grouped the staphyleaceae within the Celastrales while Thorne (1981), Whitmore (1972) and Hallier (1912) related them to the Cunoniales. Cronquist (1981) considers the Staphyleaceae to be anamolous in the Celastrales because of their compound leaves. He places this family in his Sapindales keeping it as a connecting link between the Cunoniales and Sapindales. Dickson (1986) concluded that the family has the closest affinity with the Cunoniales in both floral and palynological characters.

The family Sapindaceae **sensu stricto** is classified into two subfamilies by Radlkofer (1934); (1) Eusapindaceae (Sapindoideae)- one erect ovule in each locule and downward directed micropyle and (2) Dyssapindaceae (Dodoneaoideae) having two to several ovules in each locule with upward directed micropyle. The subfamily Sapindoideae is subdivided into 2 tribes Nomophyllae (leaves usually imparipinnate and disk oblique) and Anomophyllae (leaves usally paripinnate and disk annular). Takhtajan (1980) accepts this classification but Thorne (1981) includes 2 more subfamilies Stylobasioideae and Emblingioideae.

The Staphyleaceae also are divided into two subfamilies : (1) Staphyleoideae (stipulate opposite leaves, distinct disk, free sepals, partially fused carpels and numerous ovules), (2) Taspiscoideae (stipulate alternate leaves, gamosepalous condition, disk minute or absent, totally fused carpels and 1 or 2 ovules per pistil). The Aceraceae, Hippocastanaceae and Melianthaceae being uni/bi-generic families are not divided further.

The taxonomic position of **Filicium decipiens** Thw. remained always controversial. Hiern (1875) and Hutchinson

(1973) included this plant in the Burseraceae while Wight (c.f. Hooker, 1875) kept it in his Anacardiaceae. Radlkofer (1934) transfered **Filicium** to the Sapindaceae. Gulati and Mathur (1977) based on embryological evidences consider that **Filicium** differs from the Sapindaceae in a few exomorphic characters such as presence of superior micropyle and ovules attached to the apex of the ovary only, but it shares a number of features such as micropyle formed from both the integuments, campylotropous ovules, Asterad type of embryogeny and unequal cotyledons with the Sapindaceae and justifies its placement in the Sapindaceae. Surandakar and Vaikos (1988) support this placement on the basis of nodal anatomical characters. The status of **Litchi chinensis** Sonn. which was included in the genus **Nephelium** as **N. litchi** Camb. (Hiern, 1875) is also debated often. This plant, at times, is placed in a new genus **Litchi** as **L. chinensis** Sonn. (Benthal, 1933). There exists ambiguity in the names of **Sapindus trifoliatus** and **S. emarginatus.** It was Hiern (1875) who recognised two different forms of **S. trifoliatus** L., one with acuminate glabrous leaves and the other with emarginate leaves and pubescent beneath. Vahl (1974) raised these two forms to distinct species **S. laurifolius** and **S. emarginatus.** This concept was accepted by a number of authors. Radlkofer (1956) considered **S. laurifolius** as a synonym to **S. trifoliatus** and reduced **S. emarginatus** to a variety of **S. trifoliatus** as **S. trifoliatus** var. **emarginatus.**

In a similar way **Acer negundo** of the family Aceraceae, was elevated to a genus **Negundo** as **N. aceroides** Moensch by Endlicher (1836). This was accepted by Bentham and Hooker (1862) and latter by Hutchinson (1926). Pax (1885) opposed the idea of establishment of the genus **Negundo** commenting that the characters do not sharply demarkate the two taxa to warrent a generic status. The idea is supported by Heimsch (1942) on wood characters.

Economic Importance :

The Sapindaceae include a number of important plants. Some of the delicious fruits which are highly prized desserts are obtained from this family. The best known among them are 'litchi' produced by **Nephelium litchi** and the 'rambutan' from **N.lappaceum**. The fruits of the former plant have stomachic, antihelmintic and astringent properties. The 'akee apple' (the vegetable marrow) is produced by **Blighia sapida** which are eaten after par-boiling or frying. The young fruits of this plant contain toxic compounds hypoglycin -A (β -methylene cyclopropyl-L-α-amino propionic acid) and hypoglycin -B (a depside of hypoglycine-A and glutamic acid). These compounds produce acute hypoglycaemia which results in vomiting and sometimes to death (Milner and Wirdnam, 1977; Melville and Addae, 1988). Hypoglycine is used effectively to reduce sugar levels in the blood. The fruits of **Sapindus laurifolius** and **S. emarginatus** contain 15% of saponins and are used in soaps and in preparation of detergents. These fruits are found to cure rheumatic arthritis (Dev, 1972) also. Guarana is the product of **Paullinia cupana** which is one of the most stimulating of all the caffiene beverages and contains 3 times as much caffiene as in coffee. This beverage, prepared from the roasted seeds, is primarily used in Africa (Hill, 1952). The unroasted seeds are used in the preparation of bread. The family possesses astringent, tonic, toxic (especially to fishes) and narcotic properties. The leaves of **N. litchi** and **Dodonea viscosa** are chewed for their narcotic effects. The toxicity to fish is due to the saponins located in a number of plants. The plaster produced from the fruits of **S. laurifolius** with vineager is said to be efficacious for the reptile bites and scrofulous swellings whereas the juices of the bark are applied to the nose for lock jaw. **Scheichera trijuga** (Kusum) is best known for the high quality lac with finest colour-shellac. The seed oil of this plant, 'macassar oil' is said to be a stimulant for hair growth and is used to cure rheumatism. The alkaloids and volatile oils of **Cardiospermum** show antibacterial and antispasmodic properties (Shukla et al. 1973). An embrocation of tender leaves of **Dodonea** is applied to sprains and bruises and also used for treating wounds, swelling and burns. The leaves of **Dodonea** are known febrifuges, antipyretics and are also used against sore throat (Rao, 1962). The family produces dense, hard and heavy wood but not many of them are used as timbers except for some of the Australian species, such as **Harpullia pendula** (tulip wood), **Nephelium semiglaucum** (wild quince) and **Schleichera oleosa** (Kusum). **Pometia** species (Kasan) and **Filicium decipiens** produce lesser important woods, which are preferred for cabinet and carving purposes. The wood of **Dodonea** is ideal for turnery and engraving.

Aesculus of Hippocastanaceae is an ornamental tree. It's fruits show antiinflammatory activity (Shibata, 1977; Ikram and Gilani, 1986; Singh et al., 1986) due to a sapogenin aescin. Another sapogenin, 21,22-diangeloyl-barringtol, is active against P_{388} lymphocytic leukemia and human epidermal carcinoma of nasopharynx (Sati and Rana, 1987). The sprouts and young seeds contain a hydroxycoumarin, aesculin, which is toxic. The commercial timbers of the Hippocastanaceae include buck-eye (**A. octandra** and **A. glabra**) of horsechestnut (**A. hippocastanum**) and Indian horsechestnut, (**A. indica**). They are used for buildings, packing cases and water troughs. These are some of the timbers used for better class mathematical instruments such as set squares, T-squares and rulers. Straight grain timbers are employed in making household wooden utensils, tooth picks, brushbacks etc.

The genus **Acer** is much in demand for its maple syrup and wood. The sap of **A. nigrum** (black maple) and **A. Saccharum** (sugar maple) produces commercial sugars. These two plants also produce woods, hard maples, and are considered among the hard woods in America. They are used for flooring, furnitures, boxes, tooth picks and crates, wood distillation and wood pulp (Guha, et al. 1965; Karnik and Misra,, 1964). Hard maple with fiddle-back figures is in demand for violin and those with bird eye figures for ornamental veneers. The leaves of **A.saccharum** contain an antitumor compound, methylgallate (Bailey and Aspluno, 1986), triterpenes such as acerotin, acerocin (Kupchan et al. 1971) and acetogenin (Narayana, et al. 1973).

The Staphyleaceae are not of much known economic value. The seed oil of **Staphylea** is used as an illuminant and in medicines. **Staphylea** and **Melianthus** are grown as ornamentals.

Previous chemical reports. :

The Sapindaceae are unique among the angiosperms in their ability to synthesise both cyanolipids and cyanogenic glycosides. Cyanogenic lipids occur frequently among the Sapindaceae. They yield hydrogen cyanide on mild hydrolysis. Four cyanolipids designated as I,II,III and IV are isolated, all of which possess acyl moieties consisting of oleic acid and saturated and unsaturated C_{20} fatty acids (Mikoljizak, 1978). All these 4 compounds are mutually exclusive. Compound I is found in **Allophylus, Cardiospermum, and Paullinia,** while compound II is present in **Nephelium** and **Sapindus**. Compound III & IV are located in **Stocksia** and **Ungandia** respectively (Siegler et al. 1987; Siegler and Butterfield, 1976; Siegler and Kennard, 1977; Mikoljczak and Weisleder, 1978; Stephen, 1980). Another interesting group of compounds reported from the family are the non-protein amino acids (Fowden and Smith, 1969; Bell, 1980). They are leucine derived neutral aliphatic unsaturated cyclopropane amino acids. **Blighia** produces hypoglycin - A, which is 3-(methylene cyclopropyl) alanine, and hypoglycine

B, which is a depside of hypoglycine A and glutamic acid (Hassall and Reyle, 1955). **Litchi chinensis** contains 2-(methylene cyclopropyl) glycine (Gray and Fowden, 1962). Three acetylenic amino acids possessing 7 carbon atoms have been located from **Euphoria longana** (Fowden et al., 1970). Very few reports on the flavonoid data are available. **Dodonea** produces prenylated flavonoids (santin, aliarin, penduletin, viscocol) and a number of highly hydroxylated flavones (Sachdev and Kulshreshtha, 1983, 1986). The other flavonoids common in the family are kaempferol, quercetin, isorhamnetin and their glycosides (Nair and Subramanian, 1975) Coumarins are rare and scopoletin is the only hydroxycoumarin identified (Murraya et al., 1981). Naphthoquinones occur in **Sapindus** (Gibbs, 1974). Triterpenoid saponins are accumulated in fruits of **Sapindus, Dodonea, Koelreuteria** and **Filicium.** The sapogenins isolated are hederagenin derivatives, (the glycosides being mukuroside and emargino - side) in **Sapindus** (Biswas, 1948; Row and Rukmini, 1966; Kasai et al., 1988; Linde, 1979) and steroidal sapogenins, dodonin and dodogenin in **Dodonea** (Rao, 1962). Cascarillin group of diterpenes such as hautriwaic acid, acetoxyhydroxy acids are the monocarbocyclic compounds isolated from **Dodonea** (Jefferies and Payne, 1967; Payne and Jefferies, 1973). **Cardiospermum** has the ability to produce peculiar sulphur compounds nitrosulphone (Adinarayana, 1987) and cardiospermin sulphate (Hubel and Nahrsted, 1979).

The family Aceraceae is well-known for the sugarmaple which is an important commercial source of sucrose. The sugar syrup contains a number of neutral arabinogalactans. They also contain acerosides I to IV (diarylheptanoid glycosides) and apiosylepirhododendrin (Masayoshi et al., 1983; Nagai et al., 1983). The tannins obtained from the leaves and wood of **Acer** are both of hydrolysable and condensed types (Haslam, 1965; Bate-Smith, 1978). The proanthocyanidins are based on cyanidin and delphinidin. Gallic and ellagic acids constitute the hydrolysable tannins. The other phenolic compounds reported from **Acer** include the flavonoids such as luteolin, quercetin and kaempferol. The family contains amyrin, β-sitosterol, campesterol, stigmasterol (Inoue et al., 1978) and acergenin (Narayana et al., 1973, Kupchan et al., 1971). Another constituent accumulated is isoamylamine, a lower aliphatic monoamine (Smith, 1980). **A. negundo** produces a quaternary alkaloid (Fong et al., 1972).

The Hippocastanaceae possess a number of non-protein aminoacids similar to those of the Sapindaceae. The various non-protein aminoacids identified are β-(methylene cyclopropyl) β-methylalanines, cis α-(carboxycyclopropyl) β -glycine and **α-trans** (carboxycyclopropyl) - glycine (Fowden and Smith, 1969). The triterpenes identified in this family are aescin, aesculosides A, B, G-A to G.E., protoaescigenin (Wulff and Tschesche, 1969; Ikram et al., 1978; Bhattacharya et al., 1981; Auradha et al., 1984; Stankovii et al. 1985; Singh et al. 1987; Sati and Rana, 1987; Soulelens and Vayas, 1986). The flavonoids reported are myricetin, 7,3',4'-trimethoxy myricetin, quercetin, kaempferol and their derivatives (Wollen and Egger, 1970; Corcilius, 1955; Mukherjee and Bhattacharya, 1983). Coumarins such as aesculin, aesculetin, fraxin, fraxalin and scopoletin are frequent in the family (Gorecki and Mscisz, 1985).

Except for some stray reports of amides (isoamylalanine, isobutylamine and 2-methylbutylamine) the chemistry of **Staphylea** is not much known. The Melianthaceae contain hydrolysable tannins.

Materials and Methods :

Mature leaves of the plants analysed are collected from Kashmir (**Staphylea, Acer, Aesculus**), Ooty (**Acer acuminata, Melian-**

thus) TBGRI, Trivandrum (**Allophylus, Nephelium,**), BSI, Calcutta (**Blighia, Erioglossum, Lepisanthes**) FRI, Dehra Dun (**Cupania, Koelreuteria**) and Baroda (**sapindus, Dodonea, Cardiospermum**). Standard procedures explained in Chapter 2 are followed for the isolation and identification of various compounds. Data from morphology and chemistry are employed for the cladistic analysis of these taxa. Characters selected are presented in Table 3.2 and their distribution in Table 3.3.

Choice of the Characters :

Character-1 : Habit Trees = 0, Shrubs/climbers = 1.

Since the most primitive angiosperms are woody trees and the herbaceous and climbing habit are secondary, the latter habit is considered advanced.

Character-2 : Stipulate leaves = 0, Exstipulate leaves = 1.

Stipules are common in less advanced angiosperms and they commonly accompany the woody habit. The reduction in size or the total loss of the stipules is an advanced character.

Character-3 : Alternate phyllotaxy = 0, Opposite phyllotaxy=1

Most of the primitive dicot families show a spiral phyllotaxy. In course of evolution, this has given rise to an alternate arrangement and finally to the opposite phyllotaxy.

Character-4 : Simple leaves = 0, Compound leaves = 1.

Fossil leaves of Cretaceous and Tertiary period

TABLE : 3.2 Characters selected for the cladistic analysis of the Sapindaceae

	Plesiomorphic state	Apomorphic State
1. Habit	Trees	Shrubs/climbers.
2. Leaves	Stipulate	Exstipulate
3. "	Alternate	Opposite
4. "	Simple	Compound
5. Compound leaves	Pinnately	Palmately
6. Inforescence	Diffuse	Condensed
7. Flowers	Bracteate	Ebracteate
8. "	Regular	Irregular
9. "	Bisexual	Polygamous
10. "	Monoecious	Dioecious
11. Sepals	Five	Four
12. Corolla	Present	Absent
13. Stamens	Eight	Less than eight
14. Stigma	Trifid	Simple
15. Ovary	Three celled	Two celled
16. Number of ovules	Two per locule	One per locule
17. Fruit	Not inflated	Inflated
18. "	Dehiscent	Indehiscent
19. Aril	Absent	Present
20. Samara	Absent	Present
21. Flavonoids	Flavonols	Flavones
22. Methoxy flavonols	Absent	Present
23. Methoxy flavones	Absent	Present

Table 3.2 (Contd.)

	Plesiomorphic state	Apomorphic State
24. 3-OMe flavonols	Absent	Present
25. Prenylated flavonoids	Absent	Present
26. Coumarins	Absent	Present
27. Glycoflavones	Absent	Present
28. Proanthocyanidins	Present	Absent
29. Syringic acid	Present	Absent
30. Gallic acid	Absent	Present
31. Tannins	Present	Absent
32. Diterpenes	Absent	Present
33. Triterpenoids	Absent	Present
34. Saponins	Absent	Present
35. Alkaloids	Absent	Present
36. Cyanolipids	Absent	Present
37. Cyanogenic glycosides	Absent	Present
38.Fructosyl glycosides	Absent	Present
39. Tetrasaccharides	Absent	Present
40. Non-protein aminoacids	Absent	Present

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	28	29	30	31	32	33	34	35	36	37	38	39	40	AD (I
0	1	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	1	0	1	0	0	0	0	1	0	1	1	0	0	0	0	0	0	0	1	0	1	9
0	1	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	1	1	1	1	1	0	0	1	0	1	1	0	0	0	0	0	0	0	1	0	1	12
0	1	0	0	0	1	0	0	1	1	1	1	0	0	1	0	0	0	0	1	0	1	0	1	0	0	0	0	1	1	0	0	0	0	1	0	0	1	1	0	15
0	1	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	1	1	1	1	1	0	0	0	0	1	1	0	0	0	0	0	0	0	1	0	1	12
0	1	1	1	1	1	1	1	1	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	1	1	1	15
0	1	1	1	0	1	1	1	1	0	0	0	1	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	1	1	1	15
0	1	1	1	0	0	0	1	1	1	1	0	0	0	1	1	0	0	1	0	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	14
0	1	0	1	0	0	0	0	1	0	0	0	0	0	0	1	0	1	1	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	10
1	1	1	1	0	1	0	1	1	1	1	0	0	0	0	1	1	1	1	0	1	1	1	0	0	0	1	1	1	0	0	0	0	1	0	1	1	0	0	1	22
1	1	1	1	0	1	0	1	1	1	1	0	0	0	0	1	1	1	1	0	1	1	1	0	0	0	1	1	1	0	0	0	0	1	0	1	1	0	0	1	22
1	1	1	0	0	1	1	0	1	1	1	1	0	0	0	0	1	1	0	0	0	1	0	0	1	0	0	0	0	0	0	1	0	1	1	0	0	0	0	0	17
0	1	1	1	0	0	0	1	1	1	0	0	0	0	0	1	0	0	1	0	0	1	0	0	0	0	0	0	0	1	1	0	1	1	0	0	0	0	0	0	13
0	1	1	1	0	0	0	0	1	0	0	0	1	1	1	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	11
0	1	1	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	7
0	1	0	1	0	0	0	1	1	0	0	1	1	0	0	0	1	1	0	0	0	1	0	0	0	0	1	0	1	0	0	0	0	1	0	1	0	0	0	0	12
0	1	1	1	0	1	0	0	1	1	1	0	0	1	0	1	0	0	0	0	1	1	1	0	0	1	0	0	0	0	1	0	0	1	1	0	0	0	0	0	16
0	1	1	1	0	0	0	0	1	0	1	1	0	0	0	1	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	11
1	0	1	1	0	0	1	1	0	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	1	0	0	10
0	1	1	1	0	0	0	0	0	0	1	1	0	0	0	1	0	0	1	0	0	1	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	1	11
0	1	1	1	0	0	0	0	0	0	1	1	0	0	0	1	0	0	1	0	0	1	0	0	0	0	0	0	0	1	1	0	0	1	1	0	0	0	0	0	12
0	1	1	1	1	0	0	0	0	1	0	1	0	0	0	1	1	0	0	1	0	1	1	1	0	0	1	0	0	0	0	1	0	1	1	1	1	0	0	0	18
0	1	1	1	0	0	0	0	1	0	1	0	0	0	0	1	0	0	1	0	1	0	1	0	0	1	0	0	0	0	1	1	1	1	0	1	0	0	0	0	15
0	1	1	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	1	0	1	1	1	0	0	1	0	0	0	0	0	0	1	1	0	1	0	0	0	0	13
0	1	1	1	0	0	0	0	1	0	1	0	0	0	0	1	0	0	1	0	0	0	0	0	0	1	0	0	0	0	1	0	1	1	0	1	0	0	0	0	13
0	1	1	0	1	0	0	0	1	1	0	1	1	1	0	1	0	0	1	0	1	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	13
0	0	1	1	0	0	0	1	0	0	0	0	1	0	0	0	1	1	0	0	0	1	0	0	0	0	1	1	1	0	1	0	0	0	0	0	0	0	0	0	11

predominantly are simple. The primitive living flowering plants also have simple, pinnately nerved coriaceous leaves. A comparative study in the Vitaceae showed many series leading from simple through increasing dissection to compound leaves. Therefore the latter character is derived (apomorphic state) and a score 1 is given.

Character-5 : Compound leaves. Pinnate = 0, Palmate = 1.

Since the palmate venation is evolved from pinnate venation it is logical to assume that the pinnate compound leaves precede the palmately compound leaves.

Character-6 : Diffuse inflorescence = 0, Condensed infloresence = 1.

In the evolutionary modification of inflorescence reduction and condensation have played a major part (Eames, 1961). Therefore a condensed inflorescence is considered apomorphic.

Character-7 : Flowers bracteate = 0, Flowers ebracteate = 1.

In the formation of a condensed inflorescence a number of reduction processes are taking place which involve a reduction in bracts also. Therefore the ebracteate flowers are considered advanced.

Character-8 : Flowers regular = 0, Flowers irregular = 1.

An advancement from a regular to an irregular flower facilitate the specificity of an insect visitor (for pollination) to any flower. This guarantees that the pollinator which has an access to a particular flower will only visit a similar flower. Therefore the zygomorphic flowers are advanced.

Character 9 & 10 : Bisexual flowers = 0 Polygamous flowers=1.
Plant monoecious = 0, Plant dioecious = 1.

The primitive flowers are bisexual with numerous stamens and carpels. The unisexual flowers are derived from the bisexual flowers and this is evidenced by the presence of remnants of the lost parts. So polygamous flowers are considered advanced traits. Further reduction eliminates one of sex from the plants and this results in dioecioius condition. Therefore the latter character is given the score 1.

Character-11 : Sepals five = 0, Sepals less than five = 1.

In the process of specialisation of the flowers a reduction in the floral parts takes place. These reduction processes resulting in overall economy of the floral parts are always considered advanced.

Character-12 : Corolla present = 0, Corolla absent = 1.

In angiosperms the apetalous condition has been shown to represent a high stage in perianth specialization and therefore a derived one.

Character-13 : Ten fertile stamens = 0, Less than 10 fertile stamens = 1.

The evolutionary tendency is towards reduction of the floral parts, as seen in sepals and petals. The reduction in the number of stamens by the loss of some, is evidenced by the presence of vestigeal traces.

Character-14 : Stigma trifid = 0, Stigma simple = 1.

The derivation of syncarpous ovary from an apocarpous ovary is by the connation and fusion. This connation may be partial or complete. The fusion of the ovaries and styles alone leads to the formation of syncarpous ovary with free stigmatic surfaces. A complete fusion of the carpels results in a single syncarpous ovary with simple stigma.

Character-15 & 16 : Ovary three celled = 0, Ovary one celled = 1.

Two ovules per locule = 0, One ovule per locule = 1.

These also represent the reduction processes operative in flowers.

Character-18 : Fruit dehiscent = 0, Fruit indehiscent = 1.

The most primitive and basic fruit type consists of many distinct follicles. According to Hutchinson the capsule precedes the berry or drupe. Generalising these factors it is considered that the indehiscent fruit is advanced.

Character-19 : Aril absent = 0, Aril present = 1.

Though the aril is considered to be a primitive feature, according to Eames (1961) it is a specialisation of the ovule for the dissemination by animals and also occurs in taxa scattered throughout.

Character-20 : Samara absent = 0, Samara present = 1.

The fruit samara is winged and therefore helps in a better dispersal of the fruit. The winged fruits being an adapted or acquired character is considered as an apomorphic state.

Character-21 : Flavonols present = 0, Flavones present = 1.

According to Harborne (1977) flavonols are more frequent in the primitive families and the flavones are prevalent in the advanced dicots. The replacement of flavonols by flavones is observed in many families.

Character-22 & 23 : Methoxy flavonols absent = 0, Methoxy flavonols present = 1.
Methoxy flavones absent = 0, Methoxy Flavones present = 1.

The studies of the biosynthetic pathways of flavonoids indicate that the O-methylation is a late step (Crawford 1978). Harborne (1977) concludes that the compounds occuring earlier in the biosynthetic pathways need fewer enzymes therefore are simpler (primitive) while the compounds occuring at later steps need more enzymes so they become complex and more advanced.,

Character-24 : Prenylated flavones absent = 0, Present = 1.

Prenylation in flavonoids introduces lipophilic properties into compounds which are otherwise highly polar in character. In this way it reduces the reactivity and increases the stability and therefore is similar to methylation.

Character-25 : Coumarins absent = 0, Coumarins present = 1.

Coumarins are antimicrobial compounds and have very restricted distribution. The phylogeny of this character is judged by an outgroup comparision. Since these compounds are not synthesized by sister groups it is considered apomorphic.

Character-26 : Glycoflavones absent = 0, Glycoflavone present =1.

The presence of glycoflavones in advanced woody plants and primitive herbaceous plants of dicots tempted Harborne (1967) to consider it primitive to flavones. Due to the flavone skeleton glycoflavones are advanced over the flavonols. The C-glycosylation precedes O-glycosylation in the biosynthetic pathways (Swain 1975) and therefore, glycoflavones are considered intermediate between the flavonols and the flavones. The presence of glycoflavones in a flavonol-rich family is an apomorphic character.

Character-27 : Proanthocyanidins present = 0, Proanthocyanidins absent = 1.

Bate-smith (1962) inferred that the presence of proanthocyanidins and flavonols (especially myricetin) is characteristic of woody families. Correlation studies proved that these primitive chemical characters co-occur with 13 primitive morphological characters. The tendency to eliminate these compounds are seen in the advanced taxa.

Character-28 : Syringic acid present = 0, Syringic acid absent = 1.

The phenolic acids, vanillic and syringic acids, are the components of lignin which is abundant in woody plants. The advanced herbaceous angiosperms possess more of hemicelluloses and less lignin. So the absence of syringic acid which indicate lesser quantity of lignin is an advanced character.

Character-29 : Gallic acid absent = 0, Gallic acid present = 1.

Tannins (plesiomorphic character) are of two types condensed and hydrolysable. The condensed tannins, principally containing proanthocyanidin, occur in primitive woody plants. These are replaced by hydrolysable tannins, made up of gallic acid and ellagic acid, in the advanced woody plants. Therefore the presence of gallic acid in tanniferous woody families is considered apomorphic.

Character-30 : Tannins present = 0, Tannins absent = 1.

Tannins also are a group of compounds associated with woodiness indicating that the presence of these compounds denotes the early stages of evolution.

Character - 31 -39 :

All these compounds are the end products of specialised biosynthetic pathways and reflect the biochemical virtuosity of the plants in which they are present. Therefore these characters which represent the chemical advancements are given a score 1.

Results :

The results ob tained are tabulated in Table 3.1 . Flavonoids are located in all the plants screened except **Glennia zeylanica.** Flavones, glycoflavones, flavonols and proanthocyanidins are the various flavonoids obtained. The Sapindaceae are rich in flavonols such as kaempferol, 4'-OMe kaempferol, quercertin, 3'-OMe quercetin, 7,3',4'-triOMe quercetin, 7-OMe quercetin, 3,3',4'- triOMe quercetin and santin. Flavones such as apigenin and luteolin and their derivatives are of common occurence. Glycoflavones are present in 8 plants of the Sapindaceae. Derivatives of vitexin are more frequent than that of orientin. Proanthocyanidins which

Table 3.1 (Contd.)

	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	28	29	30	31
STPHYLEACEAE																														+	+
27. **Staphylea emodi** Wall.																														+	+

1. Apigenin 2. Acacetin 3. 7-OMe Apigenin 4. 7,4'-OMe apigenin 5. Luteolir 6. 4'-OMe Luteolin 7. 3',4'-DiOMe Luteolin 8. 4
DiOMe Vitexin 10. Orientin 11. 7-OMe Orientin 12. Kaempferol 13. 4'-OMe Kaempferol 14. 3-OMe Kaempferol 15. 6-OMe Kaempfero
OMe Quercetin 18. 3'-OMe Quercetin 19. 7-OMe Quercetin 20. 3,3'-DiOMe quercetin 21. 3',4'-DiOMe Quercetin 22. 3,3',4'-TriOMe
4'-TriOMe Quercetin 24. Santin 25. Propelargonidin 26. Procyanidin 27. Propeonidin 28. Prodelphinidin 29. Promalvidin 30.
31. Vanillic acid 32. Syringic acid 33. Melilotic acid 34. Gallic acid 35. p-Coumaric acid 36. Ferulic acid 37. Tannins 38.

are uniformily distributed are predominantly based on cyanidin and deliphinidin. Vanillic, syringic, p-hydroxybenzoic, ferulic and p-coumaric acids are the phenolic acids identified.

The Aceraceae also have flavonols as dominant pigments accompanied by flavones and proanthocyanidins. 3-OMe Kaempferol and 3-OMe quercetin are confined to the family. The flavones identified are apigenin and acacetin. Glycoflavones are absent. Hippocastanaceae show the absence of flavones in their leaves. Flavonols and proanthocyanidins are present. The Melianthaceae do not contain flavones and methoxylated flavonols. Among the various phenolic acids isolated, syringic acid is restricted to **Aesculus** and **Melianthus**, while gallic acid to the latter taxon and all the species of **Acer** except **A. negundo. Staphylea** contains kaempferol and 4'-OMe kaempferol. Saponins are restricted to the genus **Aesculus.**

Discussion :

The members of the family Sapindaceae (including the Aceraceae, Hippocastanaceae, Melianthaceae and Staphyleaceae) appear to form a homogeneous taxon in possessing similar flavonoid profiles. The other characters shared by these plants are the presence of proanthocyanidins such as procyanidin, prodelphinidin, and propeonidin and phenolic acids-p-hydroxybenzoic, vanillic, syringic, gallic and p-coumaric. **Aesculus** is not distinct from other genera since it contains the very same flavonoids kaempferol, quercetin, 3',4'-diOMe quercetin, procyanidin and prodelphinidin which are prevalent in the Sapindaceae. In addition, this genus also has sapogenins based on hederagenin and a number of non-protein aminoacids common in the Sapindaceae. Thus the chemical data negate the possibility of having a separate Hippocastanaceae. The data from other disciplines such as morphology and palynology are also in favour of this concept and therefore **Aesculus** should be kept only as a separate tribe within the Sapindaceae. Similarly **Acer** also contains the same flavones, flavonols and proanthocyanidins as that of the Sapindaceae. The two taxa have longchain fattyacids in common. However **Acer** differs from the rest of the Sapindaceae in producing 3-OMe kaempferol, 3-OMe quercetin, ellagitannins and in accumulating certain carbohydrates (Acerosides I-IV). These differences are not just enough to warrant a distinct family status for the genus **Acer** and so it may be included in the Sapindaceae as a separate tribe.

Melianthus and **Staphylea** which are treated as two separate families differ from the rest of the genera in not containing proanthocyanidins, methoxylated flavones and flavonols which are frequent in the Sapindaceae. These characters uphold the chemical identity of these taxa. The occurence of ellagitannins in the Melianthaceae is suggestive of their affinity with **Acer.** The evidences from chemistry and other disciplines clearly indicate that the Melianthaceae are an independant taxon and justifies the family status accorded to it. Though **Staphylea** is distinct chemically, it is premature to conclude because of the single species screened and therefore further comments are reserved till data from more plants are available.

In addition to the chemical characters mentioned in the beginning it is interesting to note that some of the genera of the Sapindaceae have the ability to synthesise cyanolipids and store them in seeds. Within Sapindaceae the grouping done by Radlkofer (1931) is favoured on the chemical grounds. The two subfamilies Sapindoideae and Dodoneaoideae may be distinguished from each other in that the former subfamily has a fairly high frequency of flavones and glycoflavones than the latter. The two tribes within the Sapindoideae also are chemically distinct in that the Anomophylleae contain glycoflavones and delphinidin whereas the Nomophyllieae are devoid of them.

The elaboration of prenylated flavonoids indicates a new biosynthetic pathway of flavonoids operative in **Dodonea** and this character makes it distinct from the remaining genera of the family Sapindaceae. In addition, **Dodonea** has diterpenes of cascarillin group and a steroidal sapogenin which are not seen in any other member of the Sapindaceae. This genus was kept in a separate tribe **Dodoneeae** (Bentham and Hooker 1862). These overwhelming features which make this genus distinct from the other Sapindaceae, warrant the elevation of this taxon to a higher level in hierarchy i.e. to a subfamily. It is to be recalled that Bentham and Hooker (1862) treated Dodoneeae equal in status to the Acerinae (the Aceraceae **Sensu lato**). Therefore, it is proposed to elevate the tribe Dodoneeae to a subfamily Dodoneoideae. In possessing only condensed tannins and 3'-OMe quercetin **Litchi** differs from **Nephelium** and so the status of L. **chinensis** away from **Nephelium** is chemically valid and is being upheld. The distinct chemical identities of **Sapindus laurifolius** and **S. emarginatus** have been chemically established. The former possesses 4'-OMe apigenin, 7,4'-OMe vitexin against apigenin, 3',4'-OMe apigenin, 4'-OMe Vitexin and coumarin of latter. These differences in flavonoids evidently indicate that **S. laurifolius** and **S. emarginatus** are two chemical identities and the evidences corroborate the existing morphological differences and justify the specific status accorded to both the plants by Vahl (1974). They also differ in the epidermal structures (Farooqui and Subramanian 1986). **Sapindus mukorossi** Gaertn., having only flavonols, also is distinct from the other flavone-containing species of **Sapindus**. But status of this taxon is to be revised only after acquiring more data. In containing flavonols and proanthocyanidins, **Filicium decipiens** Thw. a controversial taxon, is similar to both the Sapindaceae and Burseraceae. But it is different from the latter family in not producing any of the mono- and diterpenes which are characteristic of the Burseraceae and therefore finds a better place in the Sapindaceae. This view is supported by embryological (Gulati and Mathur, 1977), nodal anatomical (Surandkar and Vaikos, 1988) and chemical evidences (Hopkins et al., 1968; Venkataramaiah and Rao, 1986). **Acer negundo,** which sometimes is treated as a new genus **Negundo (N. aceroides** Moech; Bentham and Hooker 1862, Airyshaw, 1973), is different from the remaining species of **Acer** studied here in its flavonoid chemistry. This plant contains 6-OMe kaempferol, 3-OMe quercetin, 7-OMe quercetin and alkaloids which are not located in **Acer.** The vanillic/syringic ratio of **Negundo** is calculated to be 0.5 to 0.6 as against the radically different value of 2 of **Acer** (Brown, 1965). These evidences validate the generic status of **Negundo.**

The family Sapindaceae has a number of advanced chemical features such as flavones, methylated and prenylated flavonols and hydrolysable tannins. This correlates well with the morphological advancement (unisexual irregular flowers, dioecious plants, reduction in floral parts and specialized fruits i.e. winged fruits and seeds) the family has reached. Therefore, the Sapindaceae occupy a higher level in the evolutionary ladder. The Melianthaceae, though evolved in their morphological features such as saccate calyx, didynamous stamens, twisting of flower by 180° before anthesis, retain primitive characters such as the prevalence of flavonols and tannins and are unable to produce advanced flavones and thus may be considered evolved as an offshoot from a pro-sapindalean group.

Cardiospermum, in synthesising flavones, alkaloids and sulphur compounds and in eliminating proanthocyanidins, is the most advanced genus which is in par with the evolved habit and flower. **Dodonea** is another evolved taxon with elaborate enzyme systems for prenylation of flavonoids and synthesis of cascarillan group of diterpenes. **Aesculus, Litchi, Nephelium, Sapindus mukurossi, Filicium** and **Koelreuteria** with flavonols as principal flavonoid compounds form the primitive members while **Acer** having 3-OMe flavonols, a step towards production of flavones, forms an intermediate taxon.

Cladistic Analysis :

The cladogram is presented in the Fig. 3.1. **Melianthus** and **Staphylea** form a separate branch from the first node HTU3 and **Glennia** from the second node HTUI. An unequal dichotomy occurs at the node HTU2. Of the two branches, the smaller one carries all the four species of **Acer**. The larger branch divides at HTU5 with **Litchi, Nephelium** and **Sapindus** on one clade and the other branch dividing at HTU12. **Erioglossum, Lepisanthes, Schleichera, Allophylus** and **Cardiospermum** form one branch and **Filicium, Koelreuteria, Dodonea** and **Aesculus** the other.

The AD (I) values of various taxa are high, ranging from 7 (**Glennia**) to 22 (**Cardiospermum**).

Discussion :

The validity of keeping **Melianthus** and **Staphylea** separate from the Sapindaceae is established by their earlier divergence from ancestor (ANC) and their high minimal distances with the other genera. The genus **Acer** forms a separate group within the Sapindaceae. The distinguishing characters are enough to place it in a separate tribe in the Sapindaceae. **Glennia** also occupies a similar position. **Aesculus** fits very well among the **Dodonea - Koelreuteria** group and therefore its placement as a separate tribe or a family is not favoured.

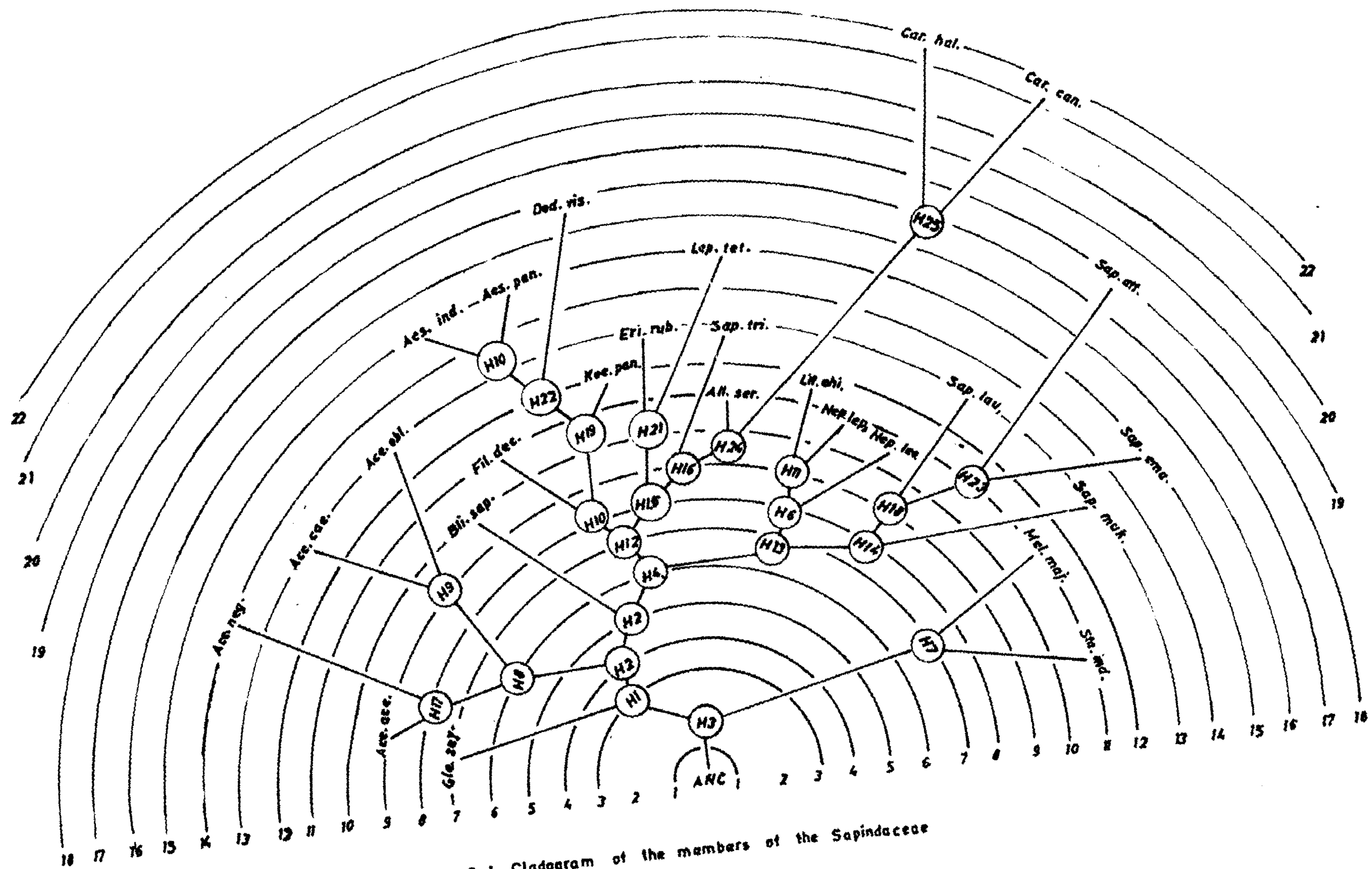

Fig. 3.1 Cladogram of the members of the Sapindaceae

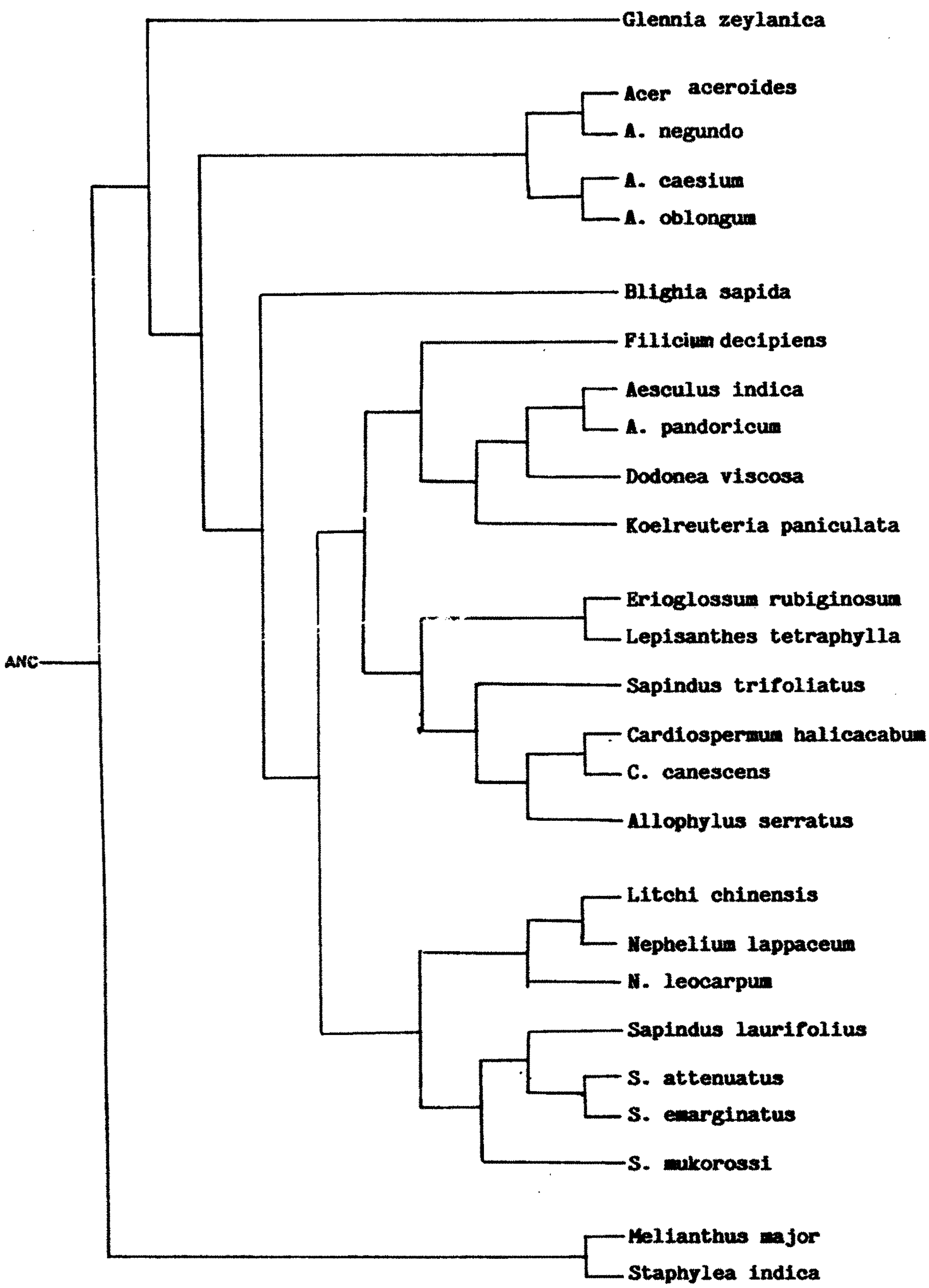

Fig. 3.2 Dendrogram of some members of the Sapindaceae

The various groups (excluding **Melianthus** and **Staphylea**) emerging from the cladistic treatment are represented in Fig 3.2. They are :-:

Group - I - **Acer**
Group - II - **Filicium, Koeltreuteria, Dodonea** and **Aesculus.**
Group - III - **Erioglossum, Lepisanthes, Schleichera, Allophylus** and **Cardiospermum.**
Group - IV - **Nephelium, Litchi** and **Sapindus.**

These groups may be given in the status of separate tribes.

The family may be considered evolved with the AD (I) values of most of the OTUs above 12. All the four groups occupy almost the same level in the evolutionary circle because of their similar AD (I) values. Therefore, the Sapindaceae may be considered morphologically and chemically an advanced family.