

*Chemical Systematics of the
Bignoniaceae*

CHAPTER 2CHEMICAL SYSTEMATICS OF THE BIGNONIACEAE2:1 Introduction

The Bignoniaceae, a tropical family of 113 genera and 800 species (Gentry, 1979), with a few genera in warm temperate region; are particularly abundant in northern America. A few genera occur in tropical Africa and Madagascar, a few in Asia and only two (Catalpa, Camposia) have species in both the old and new world.

In India the family is widely distributed upto an altitude of 3000 feet (C.B. Clarke in Hooker, 1884); however, most of the genera are restricted to western peninsula or central provinces and extended upto Bengal. Genus Stereospermum is generally found throughout moister parts of India, so also the Oroxylum.

The family is economically important because of its predominantly woody members. Some of the members are also medicinally useful.

Members of the family Bignoniaceae are predominantly woody and include many large trees and climbers, rarely herbs (Incarvillea) or shrubs (Eccremocarpus). The climbers

include simple twiners (Tecomaria, Pandorea), root climbers (Campsis) and tendril twiners (Bignonia).

The leaves are characteristically compound in all the genera except Tecomella, Crescentia. They are opposite, deccusate, rarely alternate and exstipulate. Presence of intrafoliar spines in case of Parmentiera is a rare feature. The flowers are generally arranged in dichasial cyme, passing into monochasial cymes. Panicle in case of Jacaranda and pendent raceme in genus Kigelia are noted. They are produced on the old wood (cauliflorous condition), as in the Crescentia and Parmentiera. The bracts and bracteoles are present.

The flowers are bisexual, hypogynous, zygomorphic and showy. The calyx shows considerable variation in form, structure and the manner of opening. It is usually 5-lobed, cupular or truncate, spathe like in Spathodea and Dolichandrone.

The showy corolla is sympetalous with a conspicuous tube, comprising of five lobes. The shape is usually campanulate or funneliform with descending imbricate aestivation, rarely two lipped (Millingtonia, Amphilophium). In Crescentia, the corolla tube is constricted below the middle portion and swollen above into five curved toothed lobes.

Stamens are epipetalous, arising from the lower part of the corolla tube. They are typically 4 in number, didynamous with the posterior one represented by a staminode. In Catalpa, the fertile stamens are only 2 (with or without 3 staminodes). 5 fertile, perfect stamens are present in Oroxylum. The anthers are 2-celled. The cells are usually widely divergent, seemingly one above the other. The filaments are slender and dehiscence of anther lobe is longitudinal. The family is characterized by presence of nectariferous hypogynous disc.

Ovary is superior, bicarpellary, typically bilocular with axile placentation, however, unilocular with 2 parietal placentae in Kigelia, Crescentia, Eccremocarpus. The ovules are numerous, anatropous, usually erect with micropyle pointing downward. The style is simple and terminal with 2-lobed stigma.

Fruit is generally a 2-valved septicidal or loculicidal capsule or sometimes fleshy and indehiscent as in Parmentiera, Kigelia, and Crescentia. The seeds are many, large, flattened, with membranous wing and non-endospermic.

2:2 Taxonomy

Bentham and Hooker (1865) have assigned the family Bignoniaceae to personales along with families like

Scrophulariaceae, Lentibulariaceae, Pedaliaceae and Acanthaceae based mainly on the character of corolla, limited number of stamens and multiovulated condition of the ovary.

The family is considered allied to Scrophulariaceae due to didynamous stamens, multiovulated condition of the ovary and axile placentation. However, it differs from this family in habit and seed characters. The fruit is a capsule in both the families, but the seeds of the Scrophulariaceae are many, small and endospermic as against winged and non-endospermic of the Bignoniaceae. This family is considered to be homogeneous by many taxonomists although classified differently by systematists. The tribal division in the Bignoniaceae is largely based on fruit morphology. ^(FIG-1) Bentham and Hooker (1865) classified the family into four tribes; Bignonieae, Tecomeae, Jacarandae and Crescentieae on the basis of number of locules, nature of the capsule and its mode of dehiscence. (TABLE-3)

The tribe Bignonieae includes usually climbers or scandent shrubs, rarely trees with opposite, pinnately or palmately compound leaves. The ovary is bilocular with axile placentation. Tribe Bignonieae have capsules dehiscing parallel to the septum and a specialized replum. The important genera are Adenocalymma, Millingtonia, Oroxylum etc.

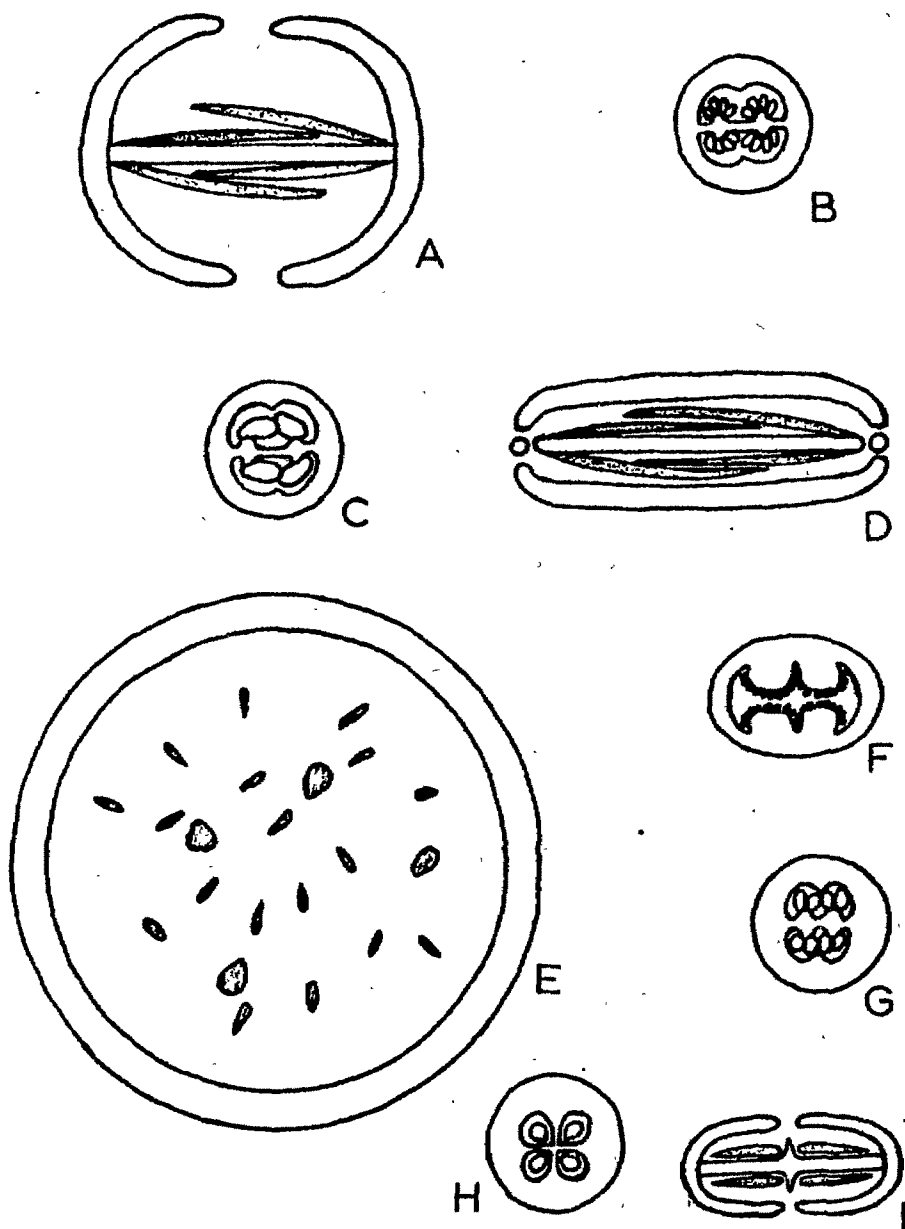


FIGURE 1. Fruit and ovary cross sections of Bignoniaceae (schematic).—A. Tecomeae fruit.—B. Tecomeae ovary.—C. Bignoniaceae ovary.—D. Bignoniaceae fruit.—E. Crescentieae fruit.—F-G. Crescentieae ovary.—H. Tourrettieae ovary.—I. Tourrettieae fruit.

**FROM: COEVOLUTIONARY PATTERNS IN CENTRAL
AMERICAN BIGNONIACEAE.**

A.H. GENTRY (1974) *Ann. Missouri Bot. Gard.*

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FIG.- 1

Table : 3. BIGNONIACEAE taxa screened and their arrangement in various schemes of classifications

Plant names	C L A S S I F I C A T I O N		S Y S T E M S	
	Bentham and Hooker (1865)	Schumann (1895)	Goldblatt and Gentry (1979)	
1. <u>Adenocalymma alliaceum</u> Miqers.				
2. <u>Amphilophium paniculatum</u> (L.) H.B.K.				
3. <u>Bignonia magnifica</u> Bult.				
4. <u>Bignonia capreolata</u> L.				
5. <u>Macfadyena unguis-cati</u> (L.) Gentry (= <u>Bignonia unguis Cati</u> L.)	1. <u>BIGNONIACEAE</u> [1-8]	3. <u>BIGNONIACEAE</u> [1-8]	3. <u>BIGNONIACEAE</u> [1-5]	TAXA
6. <u>Millingtonia hortensis</u> Linn. f.				
7. <u>Oroxylum indicum</u> (L.) Vent.				
8. <u>Pyrostegia venusta</u> (Ker.) Miers.				
9. <u>Campsis grandiflora</u> Loisel.				
10. <u>Dolichandrone atrovirens</u> (Heyne ex Roth.) Sprague.				
11. <u>D. falcata</u> Seem.	2. <u>TECOMNEAE</u> [9-13]	2. <u>TECOMNEAE</u> [9-13]	1. <u>TECOMNEAE</u> [9-13]	
12. <u>Haplophragma adenophyllum</u> (Wall. ex G. Don) Dop.				
13. <u>Heterophragma quadriloculare</u> (Roxb.) K. Schum. (Syn. <u>H. roxburghii</u> DC.)				
14. <u>Paulownia tomentosa</u> (Thunb.) Steudel.				
15. <u>Radermachera xylocarpa</u> (Roxb.) Schum.				
16. <u>Stereospermum personatum</u> (Hassk.) Chatter.				
17. <u>S. suaveolens</u> (Roxb.) DC.				
18. <u>S. bathodea campanulata</u> Beauv.				
19. <u>Tabernaemontana argentea</u> Benth.				
20. <u>T. pentaphylla</u> (L.) Hemsl.	2. <u>TECOMNEAE</u> [15-26]	2. <u>TECOMNEAE</u> [15-26]	1. <u>TECOMNEAE</u> [15-26]	
21. <u>T. rosea</u> (Bertol.) DC.				
22. <u>T. spectabilis</u> L.				
23. <u>Tecoma stans</u> (L.) Juss. ex H.B.K.				
24. <u>T. alata</u> DC.				
25. <u>Tecomella undulata</u> (Sm.) Seem.				
26. <u>Tecomaria capensis</u> (Thunb.) Spach.				
*A. <u>Tourrettia lappacea</u> Fougereux corr DC.				
*B. <u>Eccremocarpus scaber</u> Ruiz. and Pav.	4. <u>TOURRETTIACEAE</u> [15-26]	4. <u>TOURRETTIACEAE</u> [15-26]	6. <u>TOURRETTIACEAE</u> [15-26]	
27. <u>Jacaranda mimosifolia</u> D. Don	5. <u>ECCREMOCARPACEAE</u> [15-26]	5. <u>ECCREMOCARPACEAE</u> [15-26]	5. <u>ECCREMOCARPACEAE</u> [15-26]	
28. <u>Parmentiera cuneifera</u> Seem.	3. <u>JACARANDACEAE</u> [15-26]	3. <u>JACARANDACEAE</u> [15-26]	3. <u>JACARANDACEAE</u> [15-26]	
29. <u>Crecentaria cujeve</u> L.	2. <u>TECOMNEAE</u> [27]	2. <u>TECOMNEAE</u> [27]	1. <u>TECOMNEAE</u> [27]	
30. <u>Migelia pinnata</u> (Jacq.) LC.	4. <u>CRESCENTIACEAE</u> [28-31]	4. <u>CRESCENTIACEAE</u> [28-31]	5. <u>CRESCENTIACEAE</u> [28, 29]	
31. <u>Phyllanthron comorense</u> DC.			4. <u>COLEACEAE</u> [30, 31]	

*A/Not studied chemically under the present project.

Members of the tribe Tecomeae are mostly arborescent trees or scandent shrubs, having pinnately or digitately compound leaves. Another morphological difference lies in the loculicidal nature of the capsule. The capsule dehisces perpendicular to the septum. A number of genera, such as Dolichandrone, Heterophragma, Stereospermum, Spathodea and Tecoma belong to this tribe.

The tribe Jacarandae is generally distinguished from the rest of tribes by unilocular ovary and parietal placentation. It includes members like Eccremocarpus, Parmentiera and Jacaranda. All of them have dehiscent fruit and winged seeds.

The last tribe Crescentieae also show presence of distinct, unilocular ovary with two parietal placentae. However, the fruit is indehiscent capsule, a morphological characteristic feature of tribe Crescentieae. The various genera assigned to this tribe are Crescentia, Kigelia and Phyllarthron.

The difference in fruit morphology between tribe Crescentieae and the rest of the family are so pronounced that some authors (Lindley, 1847; Seemann, 1860) proposed their segregation as a separate family. However, an understanding of their mode of seed dispersal indicates that the

Crescentieae are closely related to Tecomeae. The indehiscent fruit of Crescentieae is derived from the dehiscent fruit of Tecomeae through coevolution with frugivorous mammals (Gentry, 1974).

Therefore, morphologically, tribe Tecomeae including Jacaranda of Bentham and Hooker forms the basic stock whereas tribe Bignonieae is more advanced and Crescentieae, the most advanced tribe within the family Bignoniaceae (Gentry, 1974).

Schumann (1895) assigned the family Bignoniaceae to the order Tubiflorae and sub-order Solanineae, after Scrophulariaceae. He recognised five tribes in Bignoniaceae. viz., Bignonieae, Tecomeae, Eccremocarpeae, Crescentieae and Tourrettieae on the basis of fruit morphology and seed character.

The tribes suggested by Schumann almost coincide with those of Bentham and Hooker except the tribe Eccremocarpeae and Tourrettieae. The sole genus Eccremocarpus of Eccremocarpeae was earlier placed along with Jacaranda, Parmentiera and Colea in Bentham and Hooker's tribe Jacarandaeae. The tribe Eccremocarpeae shows unilocular ovary. The capsule splits from bottom and extends upward. Also, the genus Eccremocarpus possesses tendril which is not found in

the remaining genera of Jacarandaeae of Bentham and Hooker. The other genus Tourrettia was also raised to tribe Tourrettieae.

Thus Schumann recognised tribe Bignonieae, Tecomeae and Crescentieae but disbanded tribe Jacarandaeae in either Tecomeae or Crescentieae. In addition to these 3 tribes, he erected monogeneric tribes Eccremocarpeae and Tourrettieae. In the latest edition of Engler's "Syllabus der Pflanzenfamilien" (ed. Melchior, 1964), the earlier classification is maintained. Tubiflorae, encompasses Bignoniaceae under "untereche Solanineae". Goldblatt and Gentry (1979) proposed the classification of Bignoniaceae, based on the cytological studies. They recognised 8 tribes. According to them, Bignoniaceae are probably fairly close to the basal stock of Tubiflorae, especially if woody habit is accepted as an important criterion of primitiveness. The fossil record of Bignoniaceae supports the family's claim to antiquity, going back to the upper cretaceous (Darrah, 1939) and with well preserved flowers and fruits of Catalpa, one of the most advanced genera of the family on account of reduction of its androecium to two stamens.

The 8 tribes recognised by Goldblatt and Gentry (1979) are Tecomeae, Oroxyleae, Bignonieae, Coleeae, Crescentieae, Tourrettieae, Schlegelieae and an unnamed tribe to accomodate

Paulownia tomentosa whose family position according to them is uncertain. Tribe Tecomeae is exactly in accordance with that of Schumann and forms the basal group of family. The tribe Bignoniaceae of Bentham and Hooker, Schumann, is split into two separate tribes. They are tribe Bignoniaceae and tribe Oroxyleae. Tribe Oroxyleae includes Millingtonia and Oroxylum. The separation of these two genera and their subsequent elevation to separate tribe level is done due to the similar chromosome number $2n = 30$. Therefore, both these genera do not find a place with other Bignoniaceae members which possess basic chromosome number, $2n = 40$.

Goldblatt and Gentry follow Schumann's generic transfer of genus Jacaranda to their tribe Tecomeae and Parmentiera to Crescentiaceae. Therefore, Parmentiera and Crescentia form a separate tribe Crescentiaceae on the basis of cytological similarities. At the same time, they regrouped Kigelia and Phyllarthron under a new tribe Coleaceae. The genus Eccremocarpus surprisingly is not included by Goldblatt and Gentry in their cytological studies.

Hallier (1912) also placed the Bignoniaceae under the order Tubiflorae and considered it, to be derived from the Scrophulariaceae. Bessey (1915) grouped this family in Scrophulariales, which comprised the Bignoniaceae, Scrophulariaceae, Pedaliaceae, Martyniaceae, Orobanchaceae,

Gesneriaceae, Collumeliaceae, Lentibulariaceae, Globulariaceae and Acanthaceae. Bignoniaceae was placed next to Scrophulariaceae.

According to Bessey, the Scrophulariaceae with zygomorphic flowers might have arisen from the polemoniales, wherein the flowers are actinomorphic. In contrast to this along the second line of evolution Lamiales show further reduction in the number of ovule and therefore, occupies the highest position in the phylogeny. Therefore, Bessey's order Scrophulariales slightly differs from the Tubiflorae of Engler in placement of the families. However, in both the systems Bignoniaceae has been grouped along with Scrophulariaceae and Orobanchaceae.

Rendle (1938) in his classification of sympetalae retained Bignoniaceae in order Tubiflorae and agreed with Hallier's placement of the family.

Almost all botanists include the Bignoniaceae in Tubiflorae (or its equivalent). Thus we have Tubiflorae : Wernham (1911-12), Hallier (1912), Wettstein (1935), Rendle (1938), Pulle (1952), Skottsberg (1940) and Melchior (1964).

The family is usually kept in order Scrophulariales (personales or equiv.) : Bentham and Hooker (1865), Bessey

(1915), Gates (1940), Soo (1953), Boivin (1956), Benson (1957), Crete (1959), Cronquist (1968), Takhtajan (1969). However, Gundersen (1950) has assigned it to polemoniales.

In Hutchinson's (1959, 1973) system of classification, the status of Bignoniaceae has been raised to the rank of order Bignoniales, under the division Lignosae. Order Bignoniales include 4 families - Cobaeaceae, Bignoniaceae, Pedaliaceae and Martyniaceae. The order is considered as one of the most highly evolved group of sympetalous families occupying a very advanced position. It includes many climbers and ends in two herbaceous families - Pedaliaceae and Martyniaceae.

Within the family, the position of genus Paulownia is controversial. According to Cronquist (1968), "The Bignoniaceae are related to Scrophulariaceae and the genus Paulownia has been shifted back and forth between the two. Its arborescent habit and winged seeds are anomalous in the Scrophulariaceae but its copious endosperm is anomalous in Bignoniaceae".

Campbell (1930) in his studies noticed that Catalpa speciosa warder was almost equally conspicuous and immediately invited comparison with Paulownia tomentosa (Thunb.) Steudel, which in habit is extraordinarily like Catalpa, as it is in

the form of flower and inflorescence. The fruit differs in shape from that of Catalpa but closely resembles that of some other Bignoniaceae, as do the winged seeds. On referring to manuals and such authoritative work as *Natürlichen Pflanzenfamilien* of Engler and Prantl, he found that Paulownia was assigned to Scrophulariaceae, instead of the Bignoniaceae - where he expected to find it. Apparently the only point in which it differs from the typical Bignoniaceae is the presence of endosperm in the seeds, a condition which is characteristic of the Scrophulariaceae. This single character, according to him, was not sufficient for removing Paulownia from its obvious position within the Bignoniaceae.

Originally named as Bignonia tomentosa by Thunberg (1784), who evidently regarded it as a member of Bignoniaceae, the name Paulownia was given by Siebold and Zuccharini (1835), who called it P. imperialis. It was Endlicher (1839) who transferred it to the Scrophulariaceae and defended the change on the basis of presence of endosperm in the seed. Since that time most authoritative manuals have included Paulownia in the Scrophulariaceae. Britton (1920) in his paper has expressed the view that Paulownia should be replaced in the Bignoniaceae and the same was supported by Pennell.

Campbell (1930) on examining the seeds of Paulownia,

arrived at a conclusion that though some endosperm is present, nevertheless the embryo is much larger than in any of the Scrophulariaceae, at the same time since the endosperm in Paulownia is much lesser abundant than in Scrophulariaceae, and in as much as in all other essential characters it agrees with the typical Bignoniaceae. It is much more likely that Paulownia should be regarded as a slightly aberrant member of Bignoniaceae rather than an extremely isolated genus of the Scrophulariaceae. It is only because no other member of later showing any evidence of a near relationship with Paulownia.

The Bignoniaceae, with very few exceptions, are woody plants - some of them trees of large size like Paulownia and Catalpa. They are mostly tropical or subtropical. The Scrophulariaceae are predominantly herbaceous and have their maximum distribution in temperate zones. The only truly arborescent form is Veronica.

Wettstein (1835), discussing the relationships of Scrophulariaceae, indicated that "They have points in common with several families, notably Bignoniaceae. It is conceivable that the two families may have been derived from a common stock but which is the older it is impossible to decide".

Considering all these facts Westfall (1949) in his cytological and embryological studies established that the chromosome number of Paulownia tomentosa is $2n = 40$, which agrees with number previously reported from woody genera of Bignoniaceae as Tecoma, Campsis, Kigelia, Bignonia and Catalpa. Members of the Scrophulariaceae with the exception of those in tropical genus Scoparia and the shrubby New Zealand taxon Hebe, do not as a rule, possess $2n = 40$ chromosomes. Further studies of chromosome morphology, anatomy and critical stages in embryology in supplement to previous one, indicate that Paulownia should be assigned to Bignoniaceae.

The occurrence of chromosome number $n = 20$ in Paulownia supports its placement in Bignoniaceae with a remark "family position uncertain" (Goldblatt and Gentry, 1979).

2:3 Review of previous chemical works

The known chemical data (Tables 4a, 4b, 4c, 4d, and 4e) of various Bignoniaceae members include flavonoids, quinones, iridoids, alkaloids and steroidal saponins.

The chemical information of the family is too inadequate and scattered; and thus, useless for any taxonomic considerations. Not a single taxa has been chemically screened fully so as to enable taxonomists to assess the interrelationship

EARLIER CHEMICAL WORK
FLAVONOIDS

Table : 4 a.

Plant	Organ	Compound	Author
<u>Adenocalymma diaceum</u>	Fls. Lvs.	Apigenin-7-glucoside Apigenin-7-glucuronide Scutellarein-7-glucuronide	Apparao, M. and Rao, E.V. (1978).
<u>Adenocalymma aliaceum</u>	Fls. Lvs.	Diallyl-di-,tri-,tetra sulphide	Apparao, M. et al. (1978).
<u>Anemopaegma chamberlaynii</u>	Fls. Lvs.	Carotenoids Flavonoids absent	Harborne, J.B., (1967).
<u>Arrabidaea chica</u>	Lvs.	Carajuron and Carajurin	Chapman, E., Perkin, A.G., and Robinson, R. (1927)
<u>Bignonia gracilis</u>	Lvs.	Quercetin-3-rutinoside	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972).
<u>Bignonia magnifica</u>	Lvs.	Rutin	Subramanian, S.S., Ramesh, P. (1973).
<u>Bignonia megapotamica</u>	Lvs.	Quercetin-3-rutinoside Quercetin-3-galactoside	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972).
<u>Campsis radicans</u>	Fls. Lvs.	Cyanidin-3-rutinoside Luteolin-7-glucoside	Harborne, J.B. (1967).
<u>Catalpa bignonioides</u>	Fls. Lvs.	Cyanidin-3-rutinoside Lutcolir-7-glucoside	"
<u>Catalpa bungei</u>	Fls. Lvs.	Absent 6-CH.luteolin, Luteolin	"
<u>Catalpa speciosa</u>	Fls. Lvs.	Absent Luteolin	"
<u>Chilopsis saligna</u>	Fls. Lvs.	Absent Luteolin and Apigenin	"
<u>Clytostoma callistigiodes</u>	Fls. Lvs.	Carotenoid Methylated flavones	"
<u>Cydista aequinoctialis</u>	Lvs.	Quercetin	"

Contd...

Table : 4 a. Contd.

Plant	Org n	Compound	Author
<u>Delichandrone falcata</u>	Lvs.	Chrysin-7-rutinoside Chrysin-7-glucoside Chrysin	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972).
<u>Ecuremocarpus scaber</u>	Fls. Lvs.	Cyanidin-3-rutinoside Flavonoid Absent	Harborne, J.B. 1967
<u>Incarvillea mairei</u>	Fls.	Cyanidin-3-rutinoside Kaempferol and Flavones	Harborne, J.B. 1967
<u>Jacaranda mimosaeifolia</u>	Lvs.	Scutellarein-7-glucuronide	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972)
<u>Kigelia pinnata</u>	Root	6-methoxy mellein (8-OH, 6-Ome-3 methyl-3,4,di- hydro-isocoumarin)	Govindachari, T.R., Patankar, S.J. and Viswanathan, N. (1971)
<u>Kigelia pinnata</u>	Bark	Kigelin (8-OH-3 methyl 3,4, di-hydro-isocoumarin)	Iyer, A. and Joshi, B.C. (1974).
<u>Millingtonia hortensis</u>	Fruit	Mellilotic acid	Sharma, R.C., Zaman, A. and Kidwai, A.R. (1968)
<u>Millingtonia hortensis</u>	Fls.	Scutellarein-5-galactoside Scutellarein	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1971)
<u>Millingtonia hortensis</u>	Lvs.	Scutellarein 6-Ome, 5,7,4 tri OH flavone (Danatin = Hispidulin)	
	Fruit	Hispidulin	
	Fls.	Scutellarein Hispidulin Glucuronic acid	
<u>Oroxylum indicum</u>	Lvs.	Scutellarein Baicalin-glucuronide	Subramanian, S.S., Nair, A.G.R. (1972)
<u>Oroxylum indicum</u>	Bark	Chrysin, Oroxylidin (6-Ome baicalin)	Bose, P.K., Bhattacharya, S.N. (1933)

Contd...

Table : 4 a. Contd.

Plant	Organ	Compound	Author
<u>Pajanelia longifolia</u>	Lvs.	Quercetin Kampferol-3- Sphoroside Dihydro kampferol-7-glucoside	Subramanian, S.S., Nair, A.G.R. (1972)
<u>Pajanelia longifolia</u>	Stem Root	Pajanelin p-OH Cinnamic acid	Kameshwaramma, A., Seshadri, T.R. (1947) (Ref.. Subramanian, S.S., Nair, A.G.R. (1972)
<u>Phyllanthron madagascariense</u>	Lvs.	5-OH, 5, 7, 4'-tri Ome flavone	Tillequin, F., Melle, E. and Paris, R.R. (1977)
<u>Podranea ricusollian</u>	Fls. Lvs.	Flavonoid absent Flavones Luteolin 6-OH luteolin	Harborne, J.B. (1967)
<u>Pyrostegia venusta</u>	Fls. Lvs.	Carotenoids Flavonoid absent	Harborne, J.B. (1967)
<u>Stereospermum chelonoides</u>	Lvs.	Dinatin-7-glucuronide Diosmetin-7-glucuronide	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972)
<u>Stereospermum xylocarrum</u>	Lvs.	Dinatin and its glucoside	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972)
<u>Soathodea campanulata</u>	Lvs.	Quercetin	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972)
<u>Tabebuia</u> sp.	Lvs.	Quercetin-3-diglucoside	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1972)
<u>Tabebuia</u> sp. (<u>Tabebuia impetiginosa</u>), <u>T. avellaneda</u> var. <u>pauillensis</u> , <u>T. heptaphylla</u>)		Flavonoids Coumarins Saponin	Wasicky, R., Akisue, M.K. and Saito, T. (1967).
<u>Tecoma standleyi</u>	Call. Tissue	Chlorogenic, Caffeic, Ferulic, Vanillic, O-Coumaric, Sinapic acid	Dohnall Barbara (1977)
<u>Tecoma garrocha</u>	Fls. Lvs.	Cyanidin-3-rutinoside Luteolin	Harborne, J.B. (1967)

Contd....

Table : 4 a. Contd.

Plant	Organ	Compound	Author
<u>Tecoma sp.</u>	Lvs.	Flavones	Harborne, J.B. (1967)
<u>Tecoma stans</u>	Lvs.	Quercetin and Kaempferol	Harborne, J.B. (1967)
<u>Tecoma stans</u>	Fls.	Luteolin	Jaurez, B.E., Peter, S. (1978)
<u>T. fabrisi</u>	Fls.	Quercetin, Luteolin-arabinosyl-glucoside	
<u>T. garrocha</u>	Fls.	Luteolin, a methylated flavone	
<u>T. tenuiflora</u>	Fls.	Quercetin, Quercetin 3-O monoglucoside	
<u>Tecomella undulata</u>	Fls.	Rutin Quercetin Luteolin-7-glucoside	Taneja, S.C., Bhatnagar, R.P. and Tiwari, H.P. (1975)
<u>Tecomella undulata</u>	Stem bark	2-Methyl, 5,7-di-hydro chromone 7-O-B-D-glucopyranoside (chromone glucoside)	Gujral, V.K., Gupta, S.R. and Varma, K.S. (1979)
<u>Zeyhera tuberculosa</u>	Lvs.	5,6,7 tri-Ome and 5,6,7,8-tetra Ome flavone	Kutney, J.P. Hansen, H.W. (1971)
<u>Zeyhera digitalis</u>	Stem wood	Vanillic acid Zeyherol (dillagnol)	Silveira, D.A., et al. (1975)

QUINONES

Table : 4 b.

Plants	Organ	Compounds	Author
<u>Catalpa ovata</u>	Stem wood	Catalpanone Deoxylapachol	Inoue, K. et al., (1979)
<u>Catalpa bignonioides</u>		Catalpol	Plouvier, V. (1971)
<u>Haplophragma adenophyllum</u>	Ht. wood	Dehydro- -lapachone, Lapachol, Dehydroiso- -lapachone, Dehydro- tectol, Tectol	Joshi, K.C. et al., (1979)
<u>Heterophragma adenophyllum</u>	Ht. wood	Lapachol	Singh, P., Prakash, L. and Joshi, K.C. (1972)
<u>Jacaranda mimosaeifolia</u>	Lvs.	Hydroquinone	Subramanian, S.S., Nagarajan, S. and Sulochana, N. (1973)
<u>J. mimosaeifolia</u>	Ht. wood	Lupenone	Joshi, K.C. et al., (1975)
<u>Kigelia pinnata</u>	Root/Bark	Lapachol	Govindachari, T.R., Patanker, S. and Viswanathan, N. (1971)
<u>Markhamia stipulata</u>	Ht. wood	Dehydro- -lapachone, lapachol, Dehydroiso- -lapachone, -lapachone, Tectol, Paulownin.	Joshi, K.C., Singh, B. and Pardisani, R.T. (1973)
<u>Oroxylum indicum</u>	Lvs.	Alloe-emodin	Dey, A.K. et al., (1978)
<u>O. indicum</u>	Ht. wood	Prunellin	Joshi, K.C., Prakash, L. and Shah Ramakant, (1977)
<u>Paulownia tomentosa</u>		Catalpol	Plouvier, V. (1971)
<u>Phyllanthron comoreuse</u>	Ht. wood	Lapachol, dehydrotectol, dehydro- lapachone, p-lapachone, Tectol, paulownin, paulownin-methanolate	Joshi, K.C., Prakash, L. and Singh, P. (1973)
<u>P. comoreuse</u>	Stem bark	Lapachol, dehydrotectol	Joshi, K.C. et al., (1975)
<u>P. comoreuse</u>	Root	Lapachol, dehydrotectol, dehydro- lapachone Paulownin	Joshi, K.C., Singh, P. and Singh, J. (1976)

Contd...

Table : 4 b. contd.

Plants	Organ	Compounds	Author
<u>Tabebuia rosea</u>	Ht. wood	Lapachol dehydrotectol, dehydro- lapachone, dehydro-iso -lapachone	Joshi, K.C., Prakash, L. and Singh, P. 1973.
<u>Tabebuia rosea</u>		Dehydro- -lapachone	Joshi et al., 1973.
		Dehydro-iso- -lapachone	
<u>T. rosea</u>	Root	Lapachol, dehydrotectol, dehydro- -lapachone, dehydro iso lapachone	Joshi, K.C., Prakash, L. and Shah, R. 1977.
<u>T. rosea</u>	St. Bark	Lapachol, lupenone	Joshi, K.C., Singh, P. and Singh, G. 1976.
<u>Tabebuia sp.</u>	Pith	Desoxy lapachol	Dietrichs, H.H. 1964.
<u>Tabebuia guayacana</u>	Ht. wood	Tectol, guayacanol (NQ)	Manner's G.D., et al., 1975.
<u>T. guayacana</u>		Lapachol, dehydro- -lapachone, -lapachone, -lapachone	Warner's G.D., Jurd, L. 1976.
<u>T. avellonedae</u>	Wood	-lapachone and dehydro-lapachone	Cosinovi, C.G. et al., 1963.
<u>Tecoma undulata</u>	Ht. wood	Lapachol	Gupta, S.R., Malik, K.K. and Seshadri, T.R. 1969.
<u>Tecomella undulata</u>	St. Bark	Verotrycol, -glucoside (Tecomol)	Pandey, V.B., Dasgupta, B. 1971.
<u>T. undulata</u>	Root	Lapachol, dehydrotectol, dehydro- lapachone	Joshi, K.C., Singh, P. and Pardasani, R.T. 1977.
		6-O-veratroyl catalposide and veratric acid	
<u>T. undulata</u>	Bark	Lapachol, Veratric acid, dehydrotectol	Singh, P., Prakash, L. and Joshi, K.C. 1972.
<u>T. undulata</u>	Ht. wood	Tecomelloside	Joshi et al. (Ref.: Maneja, S.C., Bhatnagar, R.P. and Tiwari, H.P. 1975).
<u>Zeyhera digitalis</u>	St. wood	Lapachol Veratric acid	Silveira, D.A. et al., 1975.

Table 4.c. IRIDOIDS AND ALKALOIDS

Plant	Organ	Compound	Author
<u>Tecoma capensis</u>	Leaf	Iridoid glycoside trans-p-methoxy cinnamic acid.	Hammouda Y. and Khalafallah, N. (1971)
<u>Tecomella undulata</u>	Ht. wood	6-O veratryl catalposide	Joshi, K.C., Prakash, L. and Singh, L.B. (1975)
<u>Tecoma stans</u>		Tecostanin	Hammouda, Y., Michel, P. and Jeaur, L. (1963)
<u>Tecoma stans</u>		Tecomanine	Dickinson, E.M. and Jones, G. (1969)
		4-noractinidine	Pyridine
		N-normethylskytanthin	alkaloids
		Boschniakine	
<u>Tecoma stans</u>		5-dehydrostytyanthin	Gross, D., Berg, W.W. and Schuette, H.R. (1973)
		-skytanthin	

Table: 4 d.
SAPONINS (STEROIDAL SAPONINS)

Plant	Organ	Compound	Author
<u>Adenocalymna alliacea</u>	Fls. Lvs.	-amyrin, -sitosterol	Apparao, M., Rao, E.V. (1978)
<u>Heterophragma adenophyllum</u>	Ht. wood	Sitosterol	Singh, P., Prakash, L. and Joshi, K.C. (1972)
<u>Heterophragma adenophyllum</u>	fruit	-amyrin, -sitosterol	Rizvi, S.A.I., and Sultana T. (1973)
<u>Haplophragma adenophyllum</u>	Lvs.	-sitosterol, -amyrin	Joshi, K.C. et al., (1979)
	Ht. wood	-sitosterol	Zirvi, K.A. and Falmida, A. (1973)
<u>Jacaranda acutifolia</u>	Leaf	-sitosterol	Joshi, K.C. et al., (1975)
<u>Jacaranda mimosaefolia</u>	Ht. wood	-sitosterol	Govindachari, T.R., Patanker, S.J., Viswanathan, N. (1971)
<u>Kigelia pinnata</u>	Root/Bark	-sitosterol	Joshi, K.C., Singh, B. and Pardasani, R.T. (1978)
<u>Markhamia stipulata</u>	St. wood	-sitosterol	Singh, P., Prakash, L. and Joshi, K.C. (1972)
<u>Millingtonia hortensis</u>	Ht. wood	Sitosterol	Joshi, K.C., Prakash, L. and Shah, R. (1977)
<u>Oroxylum indicum</u>	Ht. wood	-sitosterol	Joshi, K.C., Prakash, L. and Singh, P. (1973)
<u>Phyllanthron comorense</u>	Ht. wood	Sitosterol	Joshi, K.C. et al., (1975)
<u>P. comorense</u>	St. bark	-Sitosterol, Hendriacontanol	Joshi, K.C., Singh, P. and Singh, G. (1976)
<u>P. comorense</u>	Root	-sitosterol	Joshi, K.C., Prakash, L. and Singh, P. (1973)
<u>Tabebuia rosea</u>	Ht. wood	Sitosterol	Joshi, K.C., Singh, P. and Singh, G. (1976)
<u>T. rosea</u>	St. bark	-sitosterol	Joshi, K.C., Prakash, L. and Shah, R. (1977)
<u>T. rosea</u>	Root	-sitosterol	Pandey, V.B., Dasgupta, B. (1971)
<u>Tecomella undulata</u>	Bark	-sitosterol	Singh, P., Prakash, L. and Joshi, K.C. (1972)
<u>T. undulata</u>	Bark	Sitosterol	Joshi, K.C., Prakash, L. and Singh, P. (1973)
<u>T. undulata</u>	Ht. wood	n-hendriacontanol	Taneja, S.C., Bhatnagar, R.P., and Tiwari, H.P. (1975)
<u>T. undulata</u>	Fls.	-sitosterol	Joshi, K.C., Singh, P. and Pardasani, R.T. (1977)
<u>T. undulata</u>	Root	-sitosterol	Dohal Barbara, (1977)
<u>Tecoma stans</u>	Callus tissue	-sitosterol	
<u>Tecoma stans</u>	Fruit	-sitosterol	Maheshwari, J.P. and Banerjee, S.K. (1970)

of various tribes and the evolutionary trends within the family Bignoniaceae.

In the present work, 31 Bignoniaceae members have been screened for leaf phenolics and various other chemical markers. The leaf phenolics have been characterised and data have been used to understand the intrafamilial classification and the interrelationships of the Bignoniaceae with allied taxa. Data on various other chemical markers have a corroborative role in the general discussion on the taxonomic position of the Bignoniaceae.

2:4 Materials and Methods

The plants were collected from some of the well known botanical gardens in the states of Gujarat and Maharashtra. Plant collections were also done from Dangs forest in Gujarat. The dry specimens of Paulownia tomentosa were made available by Dr. C. R. Parks, University of North Carolina, at Chappel Hill. All the voucher specimens have been deposited in the herbarium of the M.S. University of Baroda, Baroda.

The plants were properly identified. Leaves were chosen for analysis of phenolics and other chemical markers. The leaves were air dried in an oven at 55-60°C for 2-3 days.

About 5 gms of the powdered material was used for extraction of flavonoids and phenolic acids. The methods of detection, isolation, identification and analysis of phenolic compounds are based on the polarity of the hydroxyl group attached to an aromatic ring as well as chemical composition of the biological source.

The material was thoroughly extracted in a soxhlet apparatus using methanol (MeOH) as the solvent. The extraction was continued for 48 hrs till the MeOH in the extractor becomes^a colourless. After the completion of extraction, the methanolic extract was concentrated to dryness in a waterbath by distillation method. To this dry, viscous residue, which remained in the flask, 25-30 ml of water was added. The water soluble phenolic glycosides were filtered out. The filtrate was hydrolysed in a waterbath using 7% HCl acid for half an hour. The aglycones separated were extracted in di-ethyl ether (Fraction A) and the hydrolysis was continued for another 10 hrs, so as to ensure that all the O-glycosides were completely hydrolysed. The aglycones were once again precipitated using di-ethyl ether (Fraction B). The residual aqueous fraction was neutralized, evapo^arated and chromatographed for glycoflavones.

The two ether fractions A and B, collected after $\frac{1}{2}$ an hr

and 10 hrs hydrolysis were combined and analysed for aglycones and phenolic acids using standard procedures (Harborne, 1967; 1973; Mabry, 1970). The concentrated extract was loaded on Whatman No. 1 paper for chromatography along with the reference sample - Quercetin. The solvent systems employed were Forestal (Conc. HCl : Acetic acid : Water 3:30:10) or 30% glacial Acetic acid or chromatographic paper prewashed with 15% glacial acetic acid and then run in 30% acetic acid in ascending direction.

The chromatograms were dried and the separated compounds were visualized by their visible colour in UV light, reaction with NH_3 vapours and by spraying Na_2CO_3 solution. The Rfs were calculated for various separated compounds, however, they are unreliable for proper identification. Since, they vary according to the temperature fluctuations and concentration of solute. The compounds separated on the chromatogram were eluted in spectroscopic methanol and their absorption maxima in UV and visible range were recorded using VSU 2P spectrophotometer. The subsequent bathochromic or hypsochromic shifts were also recorded after adding various reagents like NaOMe, AlCl_3 , $\text{AlCl}_3 + \text{HCl}$, NaOAc etc. The characterisation of the various flavonoid compounds was carried out on the basis of colour reaction in visible and UV light, with Na_2CO_3 and spectroscopic

analysis followed by co-chromatography using authentic sample.

The phenolic acids present in the ether extract were separated using two-dimensional ascending chromatography (Ibrahim and Towers, 1960). Paper chromatography is the most efficient method for separating and identifying the mixture of natural products into their constituents and has been widely applied to phenolics (Block, et al., 1958). The choice of a particular solvent and the exact proportion of the components depends in part on the resolving power of solvent. The solvent system used in the first direction was benzene : acetic acid : water (6:7:3) organic layer and sodium formate : formic acid : water (10:1:200) in second direction. The developed chromatograms after drying were sprayed using diazotized, (1) p-nitro-aniline and (2) sulphanilic acid, with an overspray of 10% Na_2CO_3 solution. The colour reactions of the phenolic acids with these reagents being specific, they are used as the main criteria for identification.

The aqueous fraction, from which the aglycones were separated out, was then neutralized by addition of Na_2CO_3 and concentrated to dryness. The alcoholic extract of glycoflavone residue on unidirectional chromatographic

analysis gets separated into various glycoflavones or C-glycosidic compounds using water as the solvent system (Wagner, 1966). Further analysis and identification was carried out using spectroscopic methods.

Leucoanthocyanins

The presence of leucoanthocyanins were tested by the following method. Glass-stoppered test tubes were marked at 5 ml and 10 ml levels. About 5 gms of finely chopped material was taken in the test tube and then covered by 5 ml (approximately) 2N HCl. The test tube was placed in a boiling waterbath for 20-30 minutes. It was then cooled and decanted, and then shaken with amyl alcohol. On separation of two layers, the upper isoamyl layer, may be red or carmine colour, denotes a positive reaction for leucoanthocyanins. Sometimes some other colour, like greenish-yellow indicates a negative reaction (Gibbs, 1974).

Iridoids

Iridoids were detected following Weifferring (1966) procedure, using Trim-Hill reagent (Trim and Hill, 1951). Fresh leaf material (about 1 gm) was cut into small pieces and placed in a test tube containing 5 ml of 1% aqueous hydrochloric acid. After 3-6 hrs, 0.1 ml of the macerate

was decanted into another test tube containing 1 ml of the Trim-Hill reagent (10 ml of glacial acetic acid, 1 ml 2% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water and 5 ml of conc. HCl). When the test tube was heated for a short time in a flame, a colour was produced (Blue or Green or Red, Harborne, 1973), if certain iridoids are present.

Saponin (steroidal saponin) and Tannin

Dried and powdered plant material was used for analysing the presence of Tannin and Saponin. About 5 gm of the powder was boiled with water (10-15 ml) for about half an hour. After cooling, half of the extract was taken in a test tube and shaken vigorously for a minute or two to froth and then was allowed to stand for a few minutes. The saponin content was grouped on the basis of following criteria.

No froth = -ve; A persistent froth of about 1 cm high = weakly +ve, and > 2 cm = strongly + ve (Hungund, et al., 1971).

To the aqueous solution 2%, freshly prepared gelatin solution was added. The formation of a white or milky precipitate shows the presence of tannin in the plant material (Hungund, et al., 1971).

Alkaloid Test :

About 5 gms of dried, powdered plant material was extracted with 5% ammoniacal ethanol for 48 hrs. The extract was then filtered and concentrated to dryness by distillation. The residue was treated with 10 ml of 0.1 N H_2SO_4 and then centrifuged. The sulphuric acid soluble fraction was tested with Mayer's reagent, with which it forms a white precipitate (Amarsingham, et al., 1964).

20 gms of the powdered plant material was extracted with 5% ammoniacal ethanol for 48 hrs. After filtration and concentration of the crude extract, around 50-100 ml of 0.1 N $\text{H}_2\text{SO}_4/\text{HCl}$ were added and filtered once again. The filtrate was then neutralized by adding conc. NH_4OH solution drop by drop till the alkaloids get precipitated. The precipitate was dissolved in chloroform and this aliquot was chromatographed on Whatman No. 1 paper. The papers were run in Butanol-aq. citric acid (435 ml : 2.4 gm of citric acid in 65 ml of water) as solvent system and developed by spraying Dragendroff reagent (Raffauf, 1970) and various colours were noted down. The chromatographs were also observed under UV light after keeping them for some time in Iodine chamber.

Quinones

For extraction of quinone type of phenolic compounds, approximately 5-10 gm of dried, powdered, leaf material was exhaustively extracted with hot benzene for 3x12 hrs and then concentrated to dry residue. The residue was dissolved in solvent ether and segregated into acidic and neutral fractions by repeatedly shaking with 2N Na_2CO_3 solution.

The Na_2CO_3 soluble fraction was acidified with ice cold 2N HCl drop wise till precipitates settled down. The acidified solution in turn, was extracted with diethyl ether and separated again into two layers. The lower layer was discarded, while upper acidic fraction was chromatographed over TLC silica gel G plates using light petroleum ether - benzene as the solvent (9:1) as the solvent system (Joshi, et al., 1973).

The neutral fraction was also chromatographed over silica gel TLC plates using the same solvent system. The various quinone compounds (Anthra-, Benzo-, Naphthaquinones) were visualized by their colour in visible, UV light and colour reaction after spraying Mg-acetate or aqueous NaOH. The separated compounds (purple/pink/orange yellow) were analysed spectroscopically for a wide range from 220-450 nm.



The quinones are grouped into 3 broad categories - Benzo-Naphtha-, and anthraquinone depending upon the spectral maxima or number of peaks. The benzoquinones show one strong peak between 260-290 nm and the other peak with less intensity in the range of 375-410. As against this naphthaquinone shows 3-4 spectral maxima (one or two below 300 nm, one at 330-340 and other one above 400 nm). The anthraquinone in their ethanol spectrum exhibit 4-5 maxima, out of which 3 fall between 215-300 nm span and another one above 430 nm.

2:5 Results

The distribution of various flavonoids viz., flavones, flavonols, glycoflavones, leucoanthocyanins and phenolic acids along with alkaloids, iridoids, saponin, tannin and quinones in leaves of members of the Bignoniaceae is presented in Tables 5, 6a, 6b, 6c, 7 and 8. The plants are arranged following Bentham and Hooker (1865).

Flavonoids :

In the group of flavonoids, flavones, flavonols, glycoflavones and leucoanthocyanins were looked into. 31 plants yielded 26 flavonoid compounds, which have been

Table : 5. DISTRIBUTION OF FLAVONOIDS IN THE BIGNONIACEAE

Sr. No.	NAME OF THE PLANT	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
TRIBE I. BIGNONIEAE																											
1.	<u>Adenocalymma aliaceum</u> Miers.						+	+	+																		+
2.	<u>Amphilophium paniculatum</u> (L.) H.B.K.	+											+														
3.	<u>Bignonia magnifica</u> Bull.		+											+													+
4.	<u>B. capreolata</u> L.	+											+														
5.	<u>Macfadyena unguis-cati</u> (L.) Gentry																										
6.	<u>Pyrostegia venusta</u> (Ker.) Miers.																+										
TRIBE II. OROXYLAE																											
7.	<u>Hillingtonia hortensis</u> Lam. f.					+	+	+		+											+						+
8.	<u>Oroxylum indicum</u> (L.) Vent.		+		+		+																+				
TRIBE III. TECOMNEAE																											
9.	<u>Campsis grandiflora</u> Boiss.							+																			
10.	<u>Dolichandrone atrovirens</u> (Heyne ex Roth.) Sprague																										
11.	<u>D. falcata</u> Seem.																										
12.	<u>Haplophragma adenophyllum</u> (Wall. ex C. Don) Dop.											+															+
13.	<u>Heterophragma ueddioloculare</u> (Roxb.) Schum. (Syn. <u>H. roxburghii</u> DC.)													+													+
14.	<u>Paulownia tomentosa</u> (Thunb.) Steud l.		+										+														
15.	<u>Radermachera xylocarpa</u> (Roxb.) Schum																+										
16.	<u>Stereospermum persor</u> Tur (Hassk.) (natt.																										
17.	<u>Stereospermum suaveolens</u> (Roxb.) DC.																										
18.	<u>Spathodea campanulata</u> Beauv.																										

Table : 5. Contd.

Sr. No.	NAME OF THE PLANT																										
		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
19.	<u>Tabebuia argentea</u> Britt.														+										+		
20.	<u>T. pentaphylla</u> (L.) Hensl.																								+		
21.	<u>T. rosea</u> (Bertol.) DC.																								+		
22.	<u>T. spectabilis</u> L.																										
23.	<u>Tecoma stans</u> (L.) Jusé. ex H.B.K.																										
24.	<u>T. alata</u> DC.																										
25.	<u>Tecomella undulata</u> (Sm.) Seem.															+	+										
26.	<u>Tecomaria capensis</u> (Thunb.) Spach.																										
TRIBE IV. JACARANDEAE																											
27.	<u>Jacaranda mimosifolia</u> D. Don																+										+
28.	<u>Parmentiera cereifera</u> Seem.																	+									+
TRIBE V. CRESCENTACEAE																											
29.	<u>Crescentia cujete</u> L.																										
30.	<u>Kigelia pinnata</u> (Jacq.) DC.																										
31.	<u>Phyllanthron comorense</u> D.																										+

FLAVONES

1. Apigenin
2. 4'-Ome Apigenin (Acacetin)
3. 7-Ome Apigenin (Genkwanin)
4. 7,4' di-Ome Apigenin
5. 7,8 di-Ome Apigenin
6. Scutellarein
7. 4'-Ome Scutellarein
8. 6-Ome Scutellarein
9. 6',di-Ome Scutellarein
10. 5,7,4' tri-Ome Scutellarein
11. Luteolin
12. 3'-Ome Luteolin
13. 4'-Ome Luteolin
14. 3',4'-di-Ome Luteolin
15. 8-OH,3',4'-di-Ome Luteolin.

FLAVONOLS

16. Kaempferol
17. 4'-Ome kaempferol
18. 5-OH,3',4'-di Ome kaempferol
19. Quercetin
20. Myricetin

GLYCOPFLAVONES

21. Vitexin
22. 8-glucosyl acacetin
23. GF-7-Ome Apigenin
24. 3'-Ome Orientin
25. GF-7-Ome Orientin
26. GF-4'-Ome Luteolin

characterised fully. 20 members are found to contain flavones/flavonols. Flavones are found in 12 members. 5 members show flavonols and 3 show both flavones and flavonols.

In tribe Bignonieae, where 8 plants have been screened for the presence of flavones/flavonols, flavones are found to be predominant. The 6 members with flavones are Adenocalymma aliaceum, Bignonia magnifica, Amphilophium paniculatum, Bignonia capreolata, Millingtonia hortensis, and Oroxylum indicum. Only one plant belonging to this tribe, Pyrostegia venusta is found to contain flavonols. The genus Macfadyena is found to be totally devoid of any flavone or flavonol type of compounds.

The various flavones encountered in 6 members of this tribe are mostly methylated or hydroxylated derivatives of Apigenin, Scutellarein and Luteolin. Apigenin itself is detected from two members. They are Amphilophium paniculatum and Bignonia capreolata. Oroxylum indicum shows presence of 4'-Ome apigenin (acacetin), 7,4'-di Ome apigenin and scutellarein. Acacetin is also located in Bignonia magnifica. The presence of Baicalein (4'-OH Scutellarein) reported by Subramanian and Nair (1972) from leaves of Oroxylum indicum could not be detected.

Millingtonia hortensis shows presence of 6,7-diOme

Scutellarein and 7,8-diOme apigenin in addition to Scutellarein reported by previous workers (Subramanian, et al., 1971).

6-methoxy Scutellarein is found only in Adenocalymma aliaceum. Scutellarein, an aglycone reported by Apparao and Rao (1978) from Adenocalymma aliaceum is found to co-occur with its 4 and 6-methoxy derivatives. Three luteolin derivatives have been detected in three members of this tribe. They are 3'-methoxy luteolin from Bignonia capreolata, 4'-methoxy luteolin from Amphilophium paniculatum and 3',4'-dimethoxy luteolin from Bignonia magnifica.

Pyrostegia venusta, which was not worked out by Harborne (1967), show presence of kaempferol and quercetin as flavonols.

In second tribe Tecomeae, where 18 members have been screened, 10 plants show presence of flavones/flavonols. Of these 6 plants show only flavones and their various derivatives. 2 show presence of flavonols and 2 show both flavones and flavonols. Thus from the distribution of various flavones and flavonols, it is clear that though both type of compounds are present in this tribe, the incidence of flavones is higher than that of flavonols.

Totally 10 flavone compounds have been identified in

the tribe Tecomeae. Apigenin is encountered from only one member - Dolichandrone falcata. It does not show presence of chrysin as reported earlier by Subramanian, et al. (1972). 7,4' di-methoxy apigenin is identified from Radermachera xylocarpa, similarly Scutellarein from Campsis grandiflora, 5,7,4' -tri-methoxy Scutellarein from Haplophragma adenophyllum and 8-hydroxy, 3'-4' -di-methoxy luteolin from Tecomella undulata.

Acacetin is found to be present in Dolichandrone falcata and Paulownia tomentosa, while Genkwanin (7-methoxy apigenin) from Haplophragma adenophyllum and Radermachera xylocarpa.

Luteolin methylated at either 3' or 4' position is encountered in Campsis grandiflora, Paulownia tomentosa, and Heterophragma roxburghii. However, luteolin methylated at both these positions is located in Heterophragma roxburghii, Tecomella undulata and Tabebuia argentea.

In all 5 flavonols have been identified from this tribe. Spathodea campanulata and Tabebuia pentaphylla are the only members from tribe Tecomeae, which show presence of flavonols. In Spathodea campanulata along with Quercetin reported earlier, by Subramanian et al. (1972), kaempferol and its 4' -methoxy derivative have also been detected from

leaves. Tabebuia pentaphylla shows presence of Quercetin and Myricetin. The other two taxa, Tabebuia argentea and Tecomella undulata show presence of both flavone and flavonol. 6-hydroxy, 3'-4'-di methoxy kaempferol is identified only from Tecomella undulata. Quercetin has also been found in Tabebuia argentea.

Quercetin and kaempferol as reported earlier by Harborne (1967) in Tecoma stans are found to be absent from the same plant material.

From the distribution pattern of flavonoids (flavones and flavonols) within the tribe Tecomeae, 4 sub-groups can be formed on the basis of present chemical work.

1. Those containing only flavonols -
Spathodea campanulata, Tabebuia pentaphylla.
2. Those with only flavones -
Dolichandrone falcata, Haplophragma, Heterophragma,
Paulownia and Radermachera.
3. Those with both flavones and flavonols -
Tabebuia argentea and Tecomella undulata.
4. Those without flavone/flavonols -
Dolichandrone atrovirens, Stereospermum personatum,
Stereospermum suaveolens, Tecoma stans, Tecoma alata,

Tecomaria capensis, Tabebuia rosea and Tabebuia spectabilis.

The members which do not have flavone/flavonol, show presence of quinones.

The two representatives from tribe Jacarandae also show presence of both flavones/flavonols. The percentage incidence of occurrence of flavones is higher than that of flavonols within the tribe. Apigenin, Acacetin and Luteolin along with the flavonol Quercetin have been identified from Jacaranda. Presence of Scutellarein reported by Subramanian et al. (1972) could not be confirmed. The other taxa screened viz., Parmentiera shows presence of 4'-methoxy kaempferol, a flavonol.

The three members of the tribe Crescentieae appear significantly different from those of the other three tribes of the family on chemical grounds. Crescentia cujete and Kigelia pinnata are totally devoid of flavonoids. The third member, Phyllarthron comorense however, shows presence of 4'-methoxy kaempferol, a flavonol, although in traces.

Glycoflavones :

Out of the 31 plants screened, only 8 members contain glycoflavones. 4 members of tribe Bignonieae, 2 of Tecomeae

and 2 of Jacarandaeae show glycoflavones. The tribe Crescentieae is found to be devoid of glycoflavones.

The various glycoflavones identified are vitexin and glycoflavone based on 7-Ome apigenin in Millingtonia hortensis, 8-glucosyl acacetin from Adenocalymma aliaceum and Oroxylum indicum, and 3'-Ome Orientin from Bignonia magnifica. Although glycoflavones have been recorded in the Bignonieae, it is only Millingtonia hortensis which shows their ample presence, a fact hitherto not reported (Subramanian et al., 1971).

Haplophragma adenophyllum and Heterophragma roxburghii of tribe Tecomeae show vitexin and glycoflavone based on 7-Ome luteolin respectively.

Jacaranda mimosifolia and Parmentiera cereifera of Jacarandaeae possess glycoflavones based on 7-Ome Orientin and 7-Ome apigenin.

The leucoanthocyanin test was negative in all the plants screened except Stereospermum suaveolens and Spathodea campanulata of Tecomeae which show only weak positive reaction.

Phenolic Acids :

In all fifteen phenolic acids have been detected in the

present work (Tables 6 a, 6 b, 6 c, 7). Vanillic acid has 100% occurrence, while p-hydroxy benzoic acid has 93.5% occurrence. The p-Coumaric, Ferulic, Gentisic and Melilotic acids have percentage distribution of 83.87%, 67.74%, 67.41%, and 61.29% respectively.

All other phenolic acids are randomly distributed among the five tribes. Syringic acid is found in all the five tribes having percentage distribution next to Melilotic acid (51.61%). The chlorogenic acid also shows fair distribution (48.38%) in 3 tribes of the Bignoniaceae.

O-Coumaric acid is totally absent from the tribe Tecomeae. It is present in 2 members of tribe Oroxyleae, one member each of tribe Jacarandaeae and Crescentieae. The Protocatechuic acid, is more or less confined to 3 members of tribe Tecomeae, however, detected from only one member of tribe Crescentieae, Phyllarthron comorense. Similarly 2-hydroxy, 6-methoxy benzoic acid is identified only from Parmentiera cereifera, 2-hydroxy 5-methoxy benzoic acid from Jacaranda and caffeic acid from Heterophragma roxburghii.

Thus the phenolic acid distribution reveals that p-hydroxy benzoic, vanillic syringic, p-coumaric and ferulic acids are common to all the five tribes, while some of the phenolic acids are confined to one or more tribes. Tribe

Table : 6 a. The Distribution of Phenolic acids in the Bignoniaceae

Sr. No.	NAME OF THE PLANT	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
TRIBE I. BIGNONIEAE																
1.	<u>Adenocalymma aliaceum</u> Miers.	+			+				+	+			+	+	+	+
2.	<u>Amphilophium paniculatum</u> (L.) H.B.K.	+	+		+	+			+	+						+
3.	<u>Bignonia magnifica</u> Bull.	+			+	+	+			+						
4.	<u>B. capreolata</u> L.	+	+		+	+	+		+				+			
5.	<u>Macfadyena unguis-cati</u> (L.) Gentry	+			+	+										+
6.	<u>Pyrostegia venusta</u> (Ker.) Miers.	+	+		+	+	+		+	+	+		+			+
TRIBE II. OROXYLEAE																
7.	<u>Millingtonia hortensis</u> Linn. f.	+	+		+	+			+		+			+		+
8.	<u>Oroxylum indicum</u> (L.) Vent.	+	+		+	+	+		+	+	+					

Key : 1. = p-OH Benzoic Acid; 2. = Gentisic; 5. = Vanillic; 6. = Syringic;
8. = O-Coumaric; 9. = Melilotic; 10. = p-Coumaric; 13. = Ferulic;
14. = Sinapic; 15. = Chlorogenic.

Table : 6 b.

TRIBE III. TECOMEAE.

Sr. NAME OF THE PLANT No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
9. <u>Campsis grandiflora</u> Loisel.		+	+		+				+	+		+		+	
10. <u>Dolichandrone atrovirens</u> (Heyne ex Roth.) Sprague+						+				+		+		+	
11. <u>D. falcata</u> Seem.		+	+		+					+		+			
12. <u>Haplophragma adenophyllum</u> (Wall ex G. Don) Dop.	+	+			+	+			+	+		+		+	
13. <u>Heterophragma quadriloculare</u> (Roxb.) Schum.	+		+		+	+			+	+		+	+	+	
14. <u>Paulownia tomentosa</u> (Thunb.) Steudel.	+	+			+	+			+	+		+			
15. <u>Radermachera xylocarpa</u> (Roxb.) Schum.	+	+			+	+			+	+					
16. <u>Stereospermum personatum</u> (Hassk.) Chatt.	+				+	+			+	+		+	+	+	
17. <u>S. suaveolens</u> (Roxb.) DC.	+	+	+		+					+		+	+		
18. <u>Spathodea campanulata</u> Beauv.	+	+			+						?			+	
19. <u>Tabebuia argentea</u> Britt.	+	+			+	+			+	+		+		+	
20. <u>T. pentaphylla</u> (L.) Hemsl.	+	+			+				+	+		+			
21. <u>T. rosea</u> (Bertol.) DC.	+				+				+			+			
22. <u>T. Spectabilis</u> L.	+				+	+			+					+	
23. <u>Tecoma Stans</u> (L.) Juss ex H.B.K.	+				+				+						
24. <u>T. aiata</u> DC.	+	+			+	+			+					+	
25. <u>Tecomella undulata</u> (Sm.) Seem.	+	+			+				+	+		+			
26. <u>Tecomaria capensis</u> (Thunb.) Spach.	+	+			+				+	+				+	

Key : 1. = p-OH Benzoic acid, 2. = Gentisic acid, 3. = Protocatechuic acid, 5. = Vanillic acid,
 6. = Syringic acid, 9. = Isellitic acid, 10. = p-Coumaric acid, 11. = Phloretic acid.
 13. = Ferulic acid, 14. = Sinapic acid, 15. = Chlorogenic acid, 12. = Caffeic acid.

table : 6 c.

Sr. No.	NAME OF THE PLANT	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
TRIBE IV. JACARANDEAE																
27.	<u>Jacaranda mimosifolia</u> D. Don	+				+		+	+	+	+					
28.	<u>Parmentiera cereifera</u> Seem.	+			+	+	+				+		+			+
TRIBE V. CRESCENTEAE																
29.	<u>Crescentia cujete</u> L.	+	+			+		+		+						
30.	<u>Kigelia pinnata</u> (Jacq.) DC.		+			+		+		+					+	
31.	<u>Phyllarthron comorensis</u> DC.	+	+	+		+		+		+	+				+	

Key : 1. = p-Hydroxy benzoic acid, 2. = Gentisic acid, 3. = Protocatechuic acid,
 4. = 2-Hydroxy 6-methoxy benzoic acid, 5. = Vanillic acid, 6. = Syringic acid,
 7. = 2-Hydroxy, 5-methoxy benzoic acid, 8. = O-coumaric acid, 9. = Melilotic acid,
 10. = p-Coumaric acid, 13. = Ferulic acid, 15. = Chlorogenic acid.

Table : 8. The distribution of leucoanthocyanins, Alkaloids, Iridoids, Saponin, Tannin and various Quinones in members of the Signoniaceae.

Sl. No. OF THE PLANT	Leuco- antho- cyanin	Alkaloids	Iri- doids	Saponin	Tannin	Antara- quinone	Benzo- quinone	Naphtha- quinone
TRIBE I. SIGNONIACEAE								
1. <u>Adenocalymna alacum</u> Miers.		+		+++				+
2. <u>Amphilobium paniculatum</u> (L.) H.B.K.				++				+
3. <u>Signonia magnifica</u> Will.		+		+				+
4. <u>S. capreolata</u> L.		+	+ Pl. Gr.					+
5. <u>Macfadyena unguis-cati</u> (L.) (Gentry)				++				+
6. <u>Durostea venusta</u> (Vahl) Wight.		+		+				+
TRIBE II. OROXYLACEAE								
7. <u>Mallincktonia hortensis</u> L. f.		+		+				+
8. <u>Oroxylum indicum</u> (L.) Vent.		+		++				
TRIBE III. TROCHELACEAE								
9. <u>Campsis grandiflora</u> Loisel.		+	+ Gr. Br.					+
10. <u>Dolichandrone atrovirens</u> (Heyne ex Roth.) Sprengue		+						+
11. <u>D. falcata</u> Seem.		+		+				
12. <u>Haplophragma adenophyllum</u> (Vahl, ex G. Don) Dop.		+		+			+	+
13. <u>Heterophragma quadriloculare</u> (Roxb.) Schum.		+		+				+
14. <u>Paulownia tomentosa</u> (Thunb.) Steud. l.		+						+
15. <u>Radermachera xylocarpa</u> (Roxb.) Schum.				+			+	+
16. <u>Stereospermum personatum</u> (Hassk.) Chatter.	+	+		+				+
17. <u>S. suaveolens</u> (Roxb.) DC.				+				+

Contd..

Table : 8. Contd.

Sr. No.	NAME OF THE PLANT	Leuco-anthocyanin	Alkaloids Iridoids	Saponin	Tannin	Antiraphan-quinone	Benzoquinone	Naphtha-
18.	<u>Spathodea campanulata</u> Beauv.	+	+					+
19.	<u>Tabebuia argentea</u> Britt.			+				+
20.	<u>T. pentaphylla</u> (L.) Hensl.		+	+				+
21.	<u>T. rosea</u> (Bertol.) DC.		+					+
22.	<u>T. spectabilis</u> L.			+				+
23.	<u>Tecoma stans</u> (L.) Juss. ex H.B.K.		+	+		+		+
24.	<u>T. alata</u> DC.			+		+		+
25.	<u>Tecomella undulata</u> (Sm.) Seem.					+		+
26.	<u>Tecomaria capensis</u> (Thunb.) Spach.		+	Sl.Gr.	+	+		+
TRIBE IV. JACARANDEAE								
27.	<u>Jacaranda rimosifolia</u> D. Don		+	+				+
28.	<u>Parmentiera cereifera</u> Seem.		+	Sl.		+		
TRIBE V. CRESCENTIAE								
29.	<u>Crescentia cujete</u> L.		+					+
30.	<u>Kirelia pinnata</u> (Jacq.) DC.							+
31.	<u>Phyllanthon comorensis</u> DC.		+	Sl.	+			+

Table : 7. Percentage of incidence of phenolic acids in the tribes Bignoniaceae, Oxoxyleace, Tecomeace, Jacarandaceae and Crescentiaceae.

Phenolic Acid	1	2	3	4	5
p-Hydroxy benzoic	100	100	94	100	66
Gentisic	50	100	66	-	100
Protocatechuic	-	-	16	-	33
2-Hydroxy, 6-methoxy benzoic	-	-	-	50	-
Vanillic	100	100	100	100	100
Syringic	82.5	100	44	50	100
2-Hydroxy-5-methoxy benzoic	-	-	-	50	-
O-Coumaric	-	100	-	50	33
Melilotic	66	50	55	50	100
p-Coumaric	66	100	94	100	33
Phloretic	-	-	5.5	-	-
Caffeic	-	-	5.5	-	-
Ferulic	50	-	66	50	66
Sinapic	16	50	16	-	-
Chlorogenic	66	50	50	50	-

1. Bignoniaceae, 2. Oxoxyleace, 3. Tecomeace,
4. Jacarandaceae, 5. Crescentiaceae.

Bignoniaceae, Oxycnemeae and Tecomeae show Gentisic, Melilotic, Sinapic and Chlorogenic acid common to these 3 tribes. However, o-Coumaric acid is restricted to 2 members of the tribe Oxycnemeae. In the same way, Protocatechuic acid is confined to 3 Tecomeae members. Whereas Sinapic acid to Bignoniaceae. This suggests that these three tribes though they share a number of phenolic acids, are distinct from each other.

The presence of phloretic acid is not certain in the case of Spathodea campanulata. The sinapic acid is totally absent in tribes Jacarandaceae and Crescentiaceae. Its presence is noticed in 3 Tecomeae members like Stereospermum personatum, Stereospermum suaveolens and Tecomaria capensis and two members of Bignoniaceae, Adenocalymma aliaceum and Millingtonia hortensis.

Chlorogenic acid is found in 66% of the members of Bignoniaceae, 50% of Tecomeae as well as Jacarandaceae and none in Crescentiaceae. Tribe Jacarandaceae and Crescentiaceae are also distinct from each other in having characteristic phenolic acid distribution. Tribe Jacarandaceae shows presence of 2-hydroxy-6 methoxy benzoic acid, 2-hydroxy,5-methoxy benzoic acid and chlorogenic acid whereas Crescentiaceae members show only Protocatechuic acid.

Iridoids :

The various members belonging to 5 tribes of the Bignoniaceae show scanty distribution of iridoids. Only 5, (2 of Tecomeae and one each of Bignonieae, Jacarandaeae and Crescentieae) gave positive blue colour reaction.

Saponins :

These are present in all the 5 tribes. Totally 21 members gave positive indication for saponins. In all 7 out of 8 Bignonieae members show presence of saponin. Adenocalymma aliaceum shows considerable quantity of saponin (3+). The other genera like Amphilophium, Macfadyena and Oroxylum show lesser quantity of saponin (2+), whereas the remaining members like Bignonia magnifica, Millingtonia hortensis and Pyrostegia venusta show moderate amount of saponin (+).

The 12 Tecomeae members and one each from Jacarandaeae and Crescentieae show presence of saponin in detectable amounts.

Tannins are completely absent in the leaves of members of the family Bignoniaceae.

Quinones :

In all 27 members of the family show quinones. They are

broadly grouped into 3 types, 1. Anthraquinones, 2. Benzoquinone and 3. Naphthaquinone. Each tribe has distinct pattern of quinone distribution. Tribe Bignoniaceae is characterised by naphthaquinone (87%).

An anthraquinone is detected from Pyrostegia venusta, the only member with anthraquinone in tribe Bignoniaceae. The Benzoquinones are completely absent in this tribe.

Tribe Tecomaceae also shows presence of naphthaquinone with a slightly less (83.3%) percentage distribution. They are present in all the Tecomaceae members except Dolichandrone falcata, Spathodea campanulata and Tabebuia rosea. Benzoquinone has been found in 6 members of this tribe. This type of quinones has not been located either in tribe Bignoniaceae or any member of the Crescentiaceae. Members of tribe Jacarandaceae share presence of both benzo- as well as naphthaquinone. In the tribe Jacarandaceae, the Jacaranda mimosifolia contain naphthaquinone whereas benzoquinone is located in Parmentiera cereifera.

All the 3 members of the tribe Crescentiaceae show presence of naphthaquinone only.

Around 70-75% of the plants gave a weak positive test for alkaloids. However, when the extracts of plant materials were tried chromatographically using BAW as solvent system,

they did not show clearcut bands either in UV light or in iodine chamber nor when sprayed with Dragendroff reagent.

2:6 Discussion

The results clearly point to the homogeneity of the family Bignoniaceae. The distribution of various chemical markers clearly delineate the five tribes. Each tribe has its own characteristic compounds.

Tecomeae

The slightly higher incidence of flavonols, and a definite, though not very common occurrence of leucoanthocyanin in the tribe Tecomeae point to its primitiveness as compared to the Bignonieae.

Within the tribe Tecomeae, Haplophragma and Heterophragma possess flavone and glycoflavone type of compounds; yet, both the genera can be chemically differentiated on the basis of distinct type of flavone derivatives. The former shows presence of apigenin derivative, while the latter contains luteolin type of compound and its methylated derivative. The pollen grains of Haplophragma and Heterophragma are quite distinct. Both have prolate-spheroidal shaped pollen grain but Haplophragma has zonocolporoidate type of pollen grains whereas Heterophragma

has 3-zonocolpate type (Mitra, 1968). The above conclusions are also supported by leaf architectural studies (Jain, 1978).

Similarly the two species of Dolichandrone can be separated on flavonoid pattern. D. falcata show presence of apigenin and acacetin. As against this, D. atrovirens is completely devoid of flavonoid type of compounds. This indicates that both the species of Dolichandrone, screened in the present work are not coherent as far as the chemical data is concerned. The occurrence of oblate spheroidal and 4-zonocolpate pollen grains in D. atrovirens and prolate spheroidal and zonocolporoidate type in D. falcata and chemical differences between these are indicative of distinct status of two species. The presence of uniserriate rays in Dolichandrone, however, suggest its distinct feature among other Tecomeae members.

The systematics of the controversial genus Paulownia has already been discussed in detail in Chapter 2, pp. 31-34. Morphologically and cytological evidences are overwhelmingly in support of placement of Paulownia along with Catalpa in the Bignoniaceae.

The chemical analysis has revealed the presence of Acacetin, 3'-methoxy luteolin and 4'-methoxy luteolin. Presence of luteolin and its methyl derivatives, as reported

from Catalpa (Harborne, 1967), suggest a closer relationship between Paulownia on one hand, and the Bignoniaceous genera on the other. Regarding the doubtful alliance of this controversial genus with the Scrophulariaceae the chemical data (Gibbs, 1974) on the predominantly arborescent Veronica are fairly conclusive.

Table 9 summarises the chemical characters of the genus Veronica (Scrophulariaceae), Paulownia (family position uncertain) and Catalpa (Bignoniaceae)

Table : 9. Comparison of chemical characters.

	<u>Veronica</u> (Scrophulariaceae)	<u>Paulownia</u> (Family position uncertain)	<u>Catalpa</u> (Bignoniaceae)
1. Flavonoids	No reports	Acacetin 3'-methoxy luteolin 4'-methoxy luteolin	Luteolin and its methyl derivatives
2. Iridoids	+	-	-
3. Alkaloids	-	+	-
4. Tannins	+	-	-
5. Saponins	-	-	-
6. Leucoanthocyanins	-	-	-

Chemical data thus is not indicative of relationship of the genus Paulownia with the Scrophulariaceae but secure its position in Bignoniaceae and that too within the tribe

Tecomeae on the basis of similar type of flavones.

Spathodea can be treated as the most primitive taxon in the tribe Tecomeae due to the presence of flavonols and leucoanthocyanin. Cytologically Spathodea is a bit confusing genus (Goldblatt and Gentry, 1979). The range of chromosome numbers recorded so far seem to be most improbable ($2n = 26$; Raghavan and Venkatasubban, 1940; Venkatasubban, 1945; Mehra and Bawa, 1969; $2n = 36$; Nanda, 1962 and $2n = 38$; Mangenot and Mangenot, 1962). It appears that $n = 13$ is the correct count and $n = 19$ and $n = 18$ may represent triploidy ($2n = 39$) with some loss of chromosome (Goldblatt and Gentry, 1979). Palynologically, Spathodea agrees with other Tecomeae members in its characteristic zonocolporoidate type of pollen grains. The presence of small, scale like glands in Spathodea, which serve as a hydathode or water excretory organ, is also indicative of its primitive status.

The other genus Tabebuia can also be treated as equally primitive. This is especially true for T. pentaphylla on the basis of flavonol presence. Paulownia can be considered as advanced taxon within the tribe Tecomeae in the light of higher occurrence of flavones, absence of glycoflavones and leucoanthocyanin.

Thus, based on the chemical data the advanced nature or

primitiveness of the 4 sub-groups within the tribe Tecomeae can be elucidated in the following way :

1. Spathodea campanulata and Tabebuia pentaphylla can be considered as the most primitive sub-group of tribe Tecomeae due to the presence of only flavonols.
2. Taxa like Campsis, Dolichandrone falcata, Haplophragma, Heterophragma, Paulownia, and Radermachera with only the flavones point to the advanced nature of the sub-group. Glycoflavones in traces are present only in Haplophragma and Heterophragma. This indicates a primitive character. However, the higher incidence of flavones, as compared to glycoflavones and absence of leucoanthocyanin point to the advanced nature of this sub-group.
3. This sub-group is represented by Tabebuia argentea and Tecomella undulata. The presence of both flavones and flavonols and the absence of glycoflavone and leucoanthocyanin suggest that this sub-group may be assigned an evolutionary level intermediate between the first and the second sub-groups.
4. It comprises Stereospermum, Dolichandrone atrovirens, Tabebuia rosea, T. spectabilis, Tecoma and Tecomaria. This seems a unique sub-group of tribe Tecomeae. It

shows absence of all flavonoid components (flavone, flavonol, glycoflavone) and thus, chemically appears the most advanced among the four sub-groups. The presence of leucoanthocyanin in Stereospermum as evidenced by weak positive test points to the primitiveness of the taxon.

On cytological grounds, Tecoma and Tecomaria are exceptional members in tribe Tecomeae. They have $n = 18$ (Goldblatt and Gentry, 1979). Venkatasubban (1944) and Sugiura (1931, 1936) have reported $2n = 36$ in Tecoma stans. Thus both chromosome number and unusually small chromosome size in these two genera suggest that they are closely related. Palynologically also they have similar type of pollen grains. They differ only in their pollen shape character.

The two species of Stereospermum are again distinct from each other in respect to palynological characters. Although the overall shape of the pollen grain is spheroidal yet their types are quite different. In Stereospermum personatum pollen are of parasyncolpate type while in S. suaveolens they are of zonocolporoidate type (Mitra, 1968). Anatomically the genus is distinctive, it shows vessels > 200 μ in size as also presence of fibres in wood, a specialised anatomical feature of Stereospermum.

Cytologically the tribe Tecomeae forms the basal group of the family and is heterogenous in nature (Goldblatt and Gentry, 1979). Polynologically however, it shows homogeneity of its various taxa. The basic pollen grain type for this tribe is zonocolporoidate. This clearly separates Tecomeae members from other tribes of the Bignoniaceae. Morphological and anatomical studies of leaves/stem (wood) also reveal some characteristic features of tribe Tecomeae.

Bignonieae and Oroxyleae

The tribe Bignonieae shows dominance of flavones. Of 8 members investigated, 6 show the presence of various flavones in the leaves; only one member - Pyrostegia is found to possess flavonols. All the members except Pyrostegia show one or the other derivative of apigenin, suggesting close chemical affinity. The genus Pyrostegia may be treated chemically as the most primitive taxon in the tribe Bignonieae because of the presence of flavonol type of compounds. At the same time it differs from other members screened, in the pattern of quinone distribution. It is the only member from tribe Bignonieae which show presence of anthraquinone, unlike other members which are characterised by naphthaquinone.

Cytologically also Pyrostegia differs from the rest of

the Bignonieae members in having chromosome count = 60; however it may be a triploid with $3n = 60$ (Joshi and Hardas, 1956). Palynological studies reveal that though Pyrostegia and Bignonia have similar spheroidal pollen grains, the two genera are quite distinct. The former shows spiraperturate type of pollen grain and is the only member in tribe Bignonieae with this type of pollen grain, while the latter has zonocolporate type of pollen grains (Mitra, 1968). Anatomically, Pyrostegia is characterised by presence of calcium oxalate crystals in the leaf (Metcalfe and Chalk, 1950).

Therefore, the creation of sub-tribe Pyrostegineae to accomodate the so different Pyrostegia and Bignonieae to accomodate rest of the genera is being indicated here. However, more work covering the remaining three species of Pyrostegia is necessary before a firm proposal could be made.

The occurrence of flavone and glycoflavone type of compounds in Adenocalymma and Bignonia magnifica forms another group in the ascending evolutionary sequence. The other two taxa namely Amphilophium and Bignonia capreolata can be placed at a still higher level due to presence of flavones only, an advanced chemical feature. The genus Macfadyena can be treated as highly advanced member of the tribe Bignonieae on the basis of complete absence of flavonoid compounds.

Millingtonia and Oroxylum have a number of chemical characters in common such as presence of Scutellarein, glycoflavone and phenolic acids like Gentisic, o-Coumaric and p-Coumaric. Morphologically, on the basis of retention of 5 stamens in the two genera, it is considered that they may be among the most primitive living members of the family. Cytological studies based on chromosome number and chromosome morphology prompted Goldblatt and Gentry (1979) to separate the two genera from tribe Bignoniaceae and elevate them to the tribe Oroxyleae. The present chemical findings also show chemical similarities between these two genera and therefore, support Goldblatt and Gentry (1979) separation of these two genera from tribe Bignoniaceae. Venkatasubban (1945) mentioned $2n = 30$ in case of Oroxylum indicum but did not provide gametic confirmation. Mehra and Bawa (1969) have recorded $n = 15$ in Oroxylum but according to Goldblatt and Gentry (1979) this may be a miscount. They believe that the genera approaching Oroxylum in chromosome number are Spathodea with $2n = 26$ and Millingtonia $2n = 30$. The $n = 14$ in the 5-stamened Oroxylum (Ghatak, 1956; Goldblatt, 1976) along with the high frequency of $x = 20$ in the family as a whole suggest that $x = 7$ as basic number for Bignoniaceae. $n = 20$ is interpreted as hexaploid with the loss of one chromosome. Millingtonia, the other genus of the tribe Oroxyleae known cytologically (Narasimha Rao 1936;

Venkatasubban, 1944; Goldblatt, 1976) has $n = 15$, a number perhaps regarded as tetraploid with the addition of one chromosome.

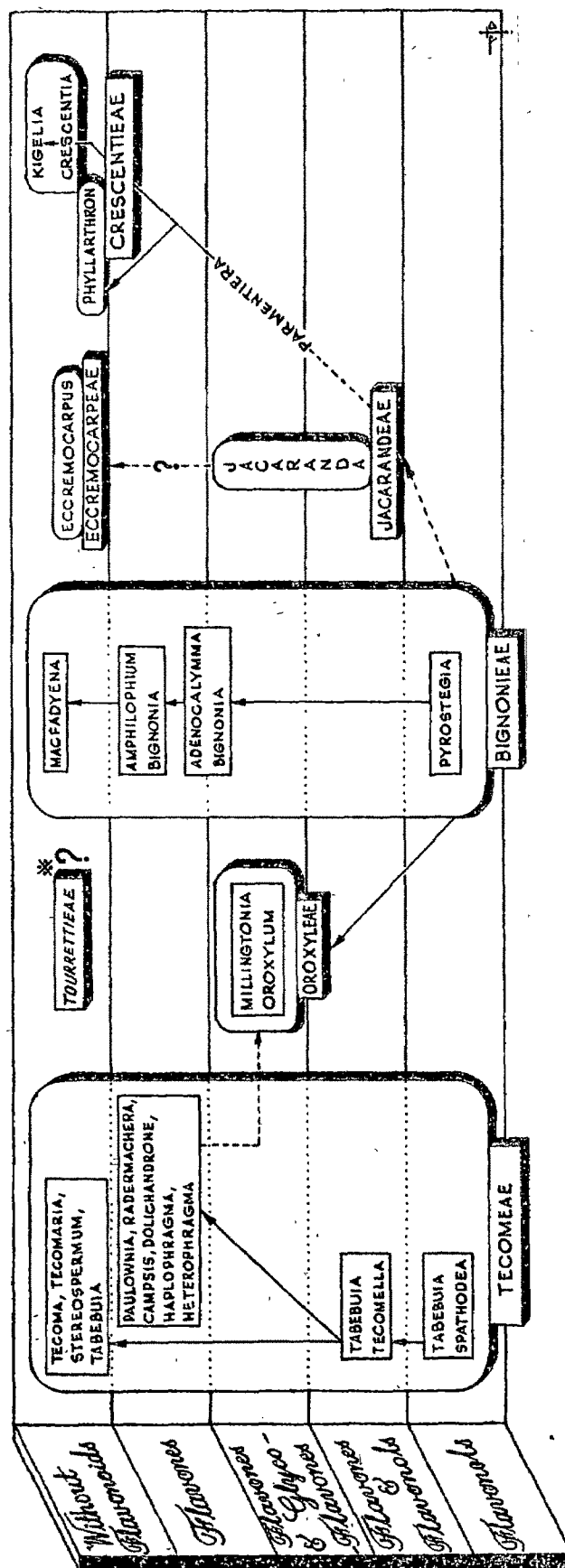
Pollen morphological studies also show common features between these two genera. Both the genera have prolate-spheroidal shaped and 3-zonocolpate type of pollen grains. In addition, leaf architectural studies (Jain, 1978) also reveal marked similarities between them and therefore, support separation of these two genera from tribe Bignonieae, primarily on cytological grounds. Irrespective of the splitting of Bignonieae proposed and supported on various grounds, the dominance of flavones and absence of leucoanthocyanin in all the taxa screened so far suggest an advanced position for the tribe. $X = 20$ as the basic chromosome count in tribe Bignonieae also point to its advanced nature. Palynologically, the tribe is characterised by zonocolpate type of pollen grains. The complete absence of bundle sheath in leaves also provide a distinguishing character for the tribe. Anatomically also the tribe Bignonieae shows a number of characters such as absence of sclerenchyma fibre or spicular cells, presence of simple perforations in vessels of young stem, lignified pith and occurrence of medium-sized vessels in wood etc. which are common to its various members except Adenocalymma and

Crescentieae

Barring Phyllarthron, which shows flavonols in traces, the tribe Crescentieae lacks flavones, flavonols, glycoflavones or leucoanthocyanins. The absence of these compounds may be looked upon as a distinct advancement of the tribe. Chemically, Phyllarthron appears to represent an evolutionary side branch of the basic taxon from which advanced genera like Crescentia and Kigelia have probably evolved.

The characteristic pattern of distribution of the flavonoids delineate all the tribes of the Bignoniaceae. The evolutionary sequence within the family appears to be Tecomeae - Tourrettieae - Oroxyleae - Bignonieae - Crescentieae. The presence of flavone, flavonol and glycoflavone make the Jacarandae an unique and isolated tribe difficult to be assigned a clear evolutionary status. In the rest of the tribes, the flavonol - flavone - noflavonol/flavone - pattern of chemical evolution seems to have been repeated. The higher incidence of flavonols renders the Tecomeae more primitive than either the Oroxyleae or Bignonieae. The dominance of flavones in the Bignonieae, marks the advanced nature of the tribe. Crescentieae represents the peak of evolution due to almost complete absence of the flavonoids (Fig. 2.).

DIAGRAMMATIC REPRESENTATION OF THE EVOLUTIONARY TRENDS WITHIN THE TRIBES OF THE 'BIGNONIACEAE'



[* THE LOCATION OF 'TOURRETTIEAE' IN THE DIAGRAM IS TENTATIVE, DUE TO LACK OF RELIABLE CHEMICAL DATA]

FIG. - 2

The distribution of phenolic acids also leads further support to the tribal classification of the Bignoniaceae. Table 7 summarises the chemical findings in respect of phenolic acids and their percentage distribution. In the Bignoniaceae, on the basis of percentage distribution of various phenolic acids, the 5 tribes of the Bignoniaceae stand out. Though a number of phenolic acids are common to all of them, the presence of specific and characteristic phenolic acids delineates the 5 tribes. Tribe Bignonieae, Oroxyleae and Tecomeae show similar pattern for a number of phenolic acids. However, o-Coumaric acid is confined to tribe Oroxyleae, Sinapic acid to Bignonieae and Protocatechuic acid to Tecomeae. Similarly 2-hydroxy, 6-methoxy and 2-hydroxy, 5-methoxy benzoic acids along with chlorogenic acid are restricted to Jacarandaeae and Protocatechuic to Crescentieae.

The chemical data concerning the flavonoids and phenolic acids in the Bignoniaceous taxa studied in the thesis have provided an insight into the classification of the group (Table 10.). There are agreements and disagreements with the established schemes of classification. There are a few classificatory changes which are based on the chemical work presented here.

The limits of Tecomeae of Bentham and Hooker are

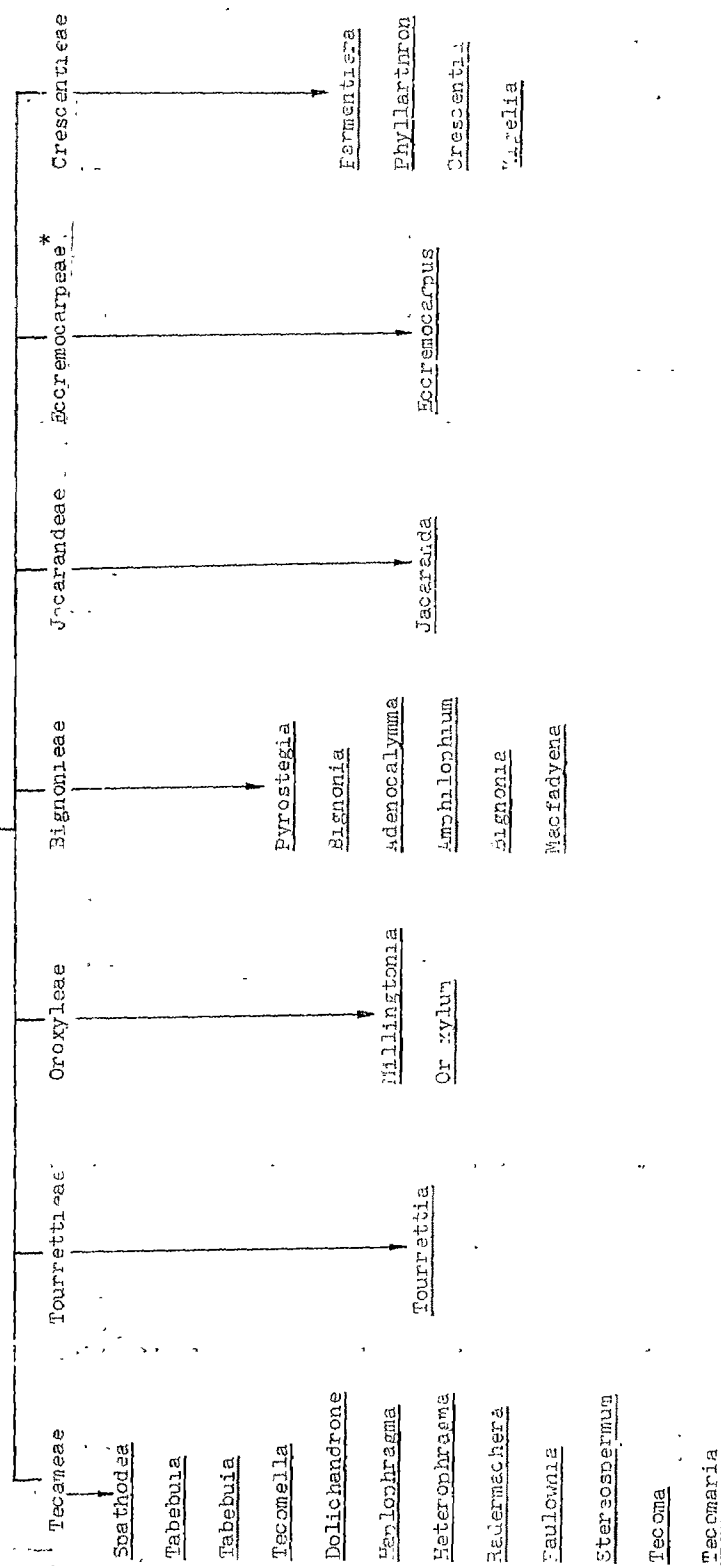
Table : 10.

PROPOSED CLASSIFICATION OF THE TAXA OF THE BIGNONIACEAE

STUDIED IN THE PRESENT WORK

BIGNONIACEAE

(TRIPES)



1. * Have not been studied under the present project.

2. The genera have been arranged according to their evolutionary status.

accepted without reservation. Tourrettieae as visualised by Schumann has been accepted on morphological grounds. No chemical work is available on this monogeneric tribe.

The tribe Bignonieae has been divided into Oroxyleae and Bignonieae following Goldblatt and Gentry (1979). The chemical data is in close agreement with the cytological data presented by them.

A sub-tribe pyrostegineae and Bignonineae have been proposed within the limits of Bignonieae.

The tribe Jacarandae of Benth and Hooker is accepted with considerably changed circumscription. The elevation of Eccremocarpus to tribe Eccremocarpeae (Schumann, 1895) on morphological grounds is supported on chemical grounds.

The Jacaranda is the sole genus in Jacarandae. The transfer of Jacaranda to Tecomeae along with Spathodea and Tecoma, though apparently sound on morphological grounds, is not supported on chemical criteria. Spathodea with only flavonols, Tecoma without any flavonoid type of compound and Jacaranda with 3 flavones, 1 flavonol and a glycoflavone are chemically distinct so that their close alliance under a tribe appears illogical.

Cytologically also the genus Jacaranda is unique. Although it shares the same chromosome count $n = 18$ (Simmonds, 1954; Venkatasubban, 1944; Mehra and Bawa, 1969; Kedharnath, 1950 and Nanda, 1962). with Tecoma and Tecomaria, yet it differs from them in the chromosome morphology and size. Both Tecoma and Tecomaria have unusually small chromosomes. Thus, the grouping of Jacaranda with Tecoma and Tecomaria cannot be supported on cytological grounds.

Jacaranda with uniform distribution of ovules on placenta and trigonous seeds with an equitorial fringe forming the membranous wing is quite distinct from Tecoma and Tecomaria where the ovules are arranged in two groups and the winged seeds are ovate-ellipsoidal.

In spite of the overwhelming data against merger of Jacaranda in Tecomeae as proposed by Schumann (1895), the palynological data offers some support. Pollen morphological studies reveal that Spathodea, Tecoma, Tecomaria and Jacaranda have similar type of zonocolporoidate pollen grains (Mitra, 1968).

The realignment of Parmentiera in the Crescentieae on the basis of indehiscent fruit and cauliflory as visualised by Schumann (1895). However, on the basis of available

chemical data Parmentiera appears close to Phyllarthron. Both these genera possess flavonols in traces along with iridoids. Crescentia and Kigelia are marked by total absence of flavonoid type of compounds. All the four genera have $2n = 40$; however, Goldblatt and Gentry (1979) have grouped Parmentiera with Crescentia under Crescentieae as a new world taxon and Kigelia with Phyllarthron under Coleeae as an Afro-madagascarian taxon. Present chemical data do not support such a taxonomic splitting based merely on the geographical distribution.

Therefore, it is clear that Bentham and Hooker's (1865) placement of Jacaranda and Parmentiera under the tribe Jacarandaeae though supported on a few morphological as well as embryological characters (Govindu, 1950), cannot be supported on the basis of chemical (present study), anatomical (Metcalfe and Chalk, 1950) and cytological (Goldblatt and Gentry, 1979) criteria.

Eccremocarpeae and Tourrettieae

The genera Eccremocarpus and Tourrettia assigned to the Jacarandaeae and Tecomeae respectively by Bentham and Hooker (1865) have been separated into tribes Eccremocarpeae and Tourrettieae by Schumann (1895). Eccremocarpeae, a monogeneric tribe is characterised by complete absence of

flavonoid pigments (Harborne, 1967). Such chemical evidence supports separation of Eccremocarpus and raising its level and places it at a higher evolutionary status. Tourrettia belonging to monogeneric Tourrettieae seems to be little worked out chemically. Morphologically, however, the tribe is quite distinct in its quadrilocular ovary and bivalvular capsule filled with barbed bristles. Cytologically, however, the tribe has the same chromosome count $2n = 40$, which characterises the rest of the taxa of Tecomeae.

The 6-hydroxylation pattern, a common structural feature of the Bignoniaceae flavonoids reported here, is of great taxonomic interest. 6-hydroxylated flavones are also reported from members of the Lamiaceae, Scrophulariaceae and Verbenaceae, the taxa with which the Bignoniaceae are traditionally allied. The higher incidence of flavones links the Bignoniaceae to Acanthaceae and Gesneriaceae (Harborne, 1967) which also possess flavones as regular leaf or petal constituents. The chemical data thus delineates and separates the Bignoniaceae from the predominantly actinomorphic Solanaceae and Convolvulaceae.

The embryological literature on the Bignoniaceae is very meagre and relates mainly to megasporogenesis and endosperm development with only scanty references about anther development and embryogeny. The available literature

has been reviewed earlier by Schnarf (1931), Mauritzon (1935) and recently by Davis (1966). The most recent embryological studies in the family are those of Gupta and Nanda (1978) and Nanda and Gupta (1978) who studied development of anther wall in Pyrostegia venusta and Tecoma stans with special reference to tapetal ontogeny and Kate (1978) who studied male and female gametophytes of Tecoma radicans.

The ovules are hemianatropous to anatropous, unitegmic and tenuinucellate and embryo sac development conforms to the polygonum type. Endosperm development is of the cellular type while embryogeny corresponds to the capsella type. The Embryological information is not sufficient and not of much help for taxonomic considerations at infra-familial level. However, morphological and embryological data in general, are in favour of placing the Bignoniaceae in close proximity of the Verbenaceae and Boraginaceae under Engler's Tubiflorae.

Out of a total of 31 plants screened under the present research programme, only 5 showed the presence of iridoids. The presence of these compounds is considered as an advanced chemical character of great systematic significance (Jensen, et al., 1975). The presence of iridoids and that too of aucubin type is a definite pointer to the overall advancement of the family.

All the 31 Bignoniaceae taxa were screened for their leaf alkaloids with the intention of utilising such data for a better appraisal of phylogenetic consideration in the family. Nearly 75% of the samples showed presence of alkaloids though in fairly small quantities. However, the even distribution of this chemical marker in the entire taxon has rendered the character quite unimportant from the point of view of phylogeny.

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