CHAPTER - I

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The Euphorbiaceae are a large family comprising about 220 genera and 4000 species (Willis 1973). But the exact number of genera and species varies according to different authors. Lawrence (1951) recognised 283 genera and 7300 species. Good (1953) gives the number of genera as 300 genera incorporating 5750 species, and ranks it as the sixth largest family of Angiosperms.

The family is of cosmopolitan distribution but concentrated mainly in the tropics and extending into the temperate regions of Northern and Southern hemispheres. The most familiar members of this large, widely distributed, family are the herbaceous and cactus like Euphorbias. Fifteen genera have more than 100 species each and the larger ones include Euphorbia (1600 sp.), Croton (700), Phyllanthus (480), Acalypha (430), Glochidion (280), Macaranga (240), Manihot (160), Jatropha (150) and Tragia (140).

Many members are broad leaved shrubs and trees whilst a few other genera are ericoid in habit. Tragia and related genera are stem climbers. Members forming the section xylophylla have their ultimate branches leaf like (Phylloclades), the leaves being reduced to scales.

The only character which binds all the members of the family, is the superior, tricarpellary, syncarpus pistil with three separate styles. The inflorescence varies from large terminal dichasial panicles (Jatropha) to solitory axillary flowers (Phyllanthus) and 'Super evolved' flower like cyathium. The flowers range from elaborate, pentamerous pentacyclic, harmaphrodite ones to monochlamydous or achlymedous, unisexual, few or one membered structures with or without vestigeal organs of the other sex. Due to this diversity in floral and morphological structure, the taxonomic positions assigned to the family in different systems of classification show much variation.

I.1 Placement of the Euphorbiaceae

Bentham and Hooker (1862-83) placed the Euphorbiaceae in the series unisexuales of the group monochlamydeae alongwith the urticaceae, casuarinaceae and some amentiferous families. Wettestein (1931) included them in the order Tricocceae and considered them as a primitive family allied to centrospermales. Baillon (1874) placed the Euphorbiaceae next to the Geraniaceae. Engler and Prantl (1897) as well as Bessey (1951) and Lawrence (1951) considered Euphorbiaceae as closely related to Geraniaceae group of families and treated their tricocceae as a suborder of Gerniales; while Rendle (1959) kept the Tricocceae an independent order. Pulle (1937) put Tricocceae between Geraniales and Malvales. Hutchinson (1969) placed the family singly in the order Euphorbiales while Hallier (1912) placed the

Euphorbiaceae along with the passifloraceae, Turnaraceae and salicaceae in the passionales of polypetalae (Table - 1).

Table - 1. Placement of the Euphorbiaceae by a few taxonomists

	ORDER	Sub-order	Families
1. Bentham & Hooker (1862-83)	Unisexuales	-	Euphorbiaceae Platanaceae Urticaceae, Casuarinaceae.
2. Engler & Prantl(1897)	Geraniales	Tricoccea	Euphorbiaceae
3. Hallier(1912)	Passionales	-	Passifloraceae Euphorbiaceae Turneraceae Salicaceae
4. Bessey(1915)	Gerniales	-	Euphorbiaceae Callitrichaceae
5. Cronquist (1968)	Euphorbiales	-	Buxaceae Euphorbiaceae Daphniphyllaceae Aextoxicaceae Pandaceae
6. Hutchinson (1969)	Euphorbiales	-	Euphorbiaceae
7. Takhtajan (1980)	Euphorbiales	-	Euphorbiaceae Pandaceae Dichapetalaceae Aextoxicaceae.

I.2. Intrafamilial classification

Muell-Arg(1865) established two groups, stenolobeae and platylobeae within this family, the former characterised by the cotyledons narrower than the radicle and the latter by cotyledons broader than the radicle. The stenolobeae were divided further into 3 tribes caletieae, Ricinocarpeae and Amphereae, the first with two ovules in each loculus of the ovary, the second and third with one ovule. The platylobeae were divided into tribes the phyllantheae, Bridelieae, Crotoneae, Acalypheae, Hippomaneae, Dalechampieae and Euphorbieae. The first two tribes had two ovules per loculus and the rest had only one in each loculus.

Pax (1897) maintained stenolobeae and platylobeae but reversed the sequence by placing the stenolobeae at the end. He has also divided platylobeae into two subfamilies, phyllanthoideae and Corotonoideae. He further divided phyllanthoideae into 3 tribes; phyllantheae, Bridelieae and Daphiphylleae and Crotonoideae into 8 tribes viz. Crotoneae, Acalypheae, Jatropheae, Maniho teae, cluytieae, Gelonieae, Hippomaneae and Euphorbieae.

Similarly pax and Hoffmann (1931) divided the family Euphorbiaceae into two main taxa on the basis of embryo characters viz. platylobeae (cotyledons much broader than the radicle) and stenolobeae (cotyledons as broad as radicle). The platylobeae were divided into two subfamilies the phyllanthoideae (3 tribes) and crotonoideae (8 tribes), while stenolobeae are divided into two subfamilies, the Proanthero-ideae and Ricinocarpoideae.

Recently Webster (1975), using palynological characters classified the family into 5 subfamilies; the phyllanthoideae, Oldfieldoideae, Acalyphoideae, Crotonoideae and Euphorbioideae.

The phyllanthoideae was further subdivided into 13 tribes the Acalyphoideae into 18, the Crotonoideae into 11 and the Euphorbioideae into 5 tribes.

Baillon (1858) in his "Etude generalae due groupe des Euphorbiaces" recognised 12 series for the family Euphorbiaceae. There were no well defined tribes or divisions. Later Baillon Himself gave a more detailed account of the family in the 5th volume of his "Historie des Plantes (1874), wherein he recognised 150 genera including Daphniphyllum (Daphniphyllaceae), Callitriche (callitrichaceae) and Dichapetalaceae. Boissier (1879) divided the sub order Euphorbiaceae into two tribes viz. Euphorbieae, the male flowers without a calyx (calyculus) and Anthostemeae, the male flowers with a distinct calyx.

Bentham (1862-83) also grouped the plants belonging to the family into six tribes the Euphorbieae, Stenolobeae, Buxeae, Phyllantheae, Galiarieae and Crotoneae. The Crotoneae was further divided into 8 subtribes; Jatropheae, Eucrotoneae, Chrozophoreae, Adrianeae, Acalypheae, Gelonieae, Plukenetieae and Hippomaneae. The tribe Buxeae, since Bentham (l.c.) had mostly been treated as a separate family, although it was included within Euphorbiaceae in Engler and Prantl's "Pflanzenfamilien". The tribe Crotoneae is distinct from most of the remainder of the family by the presence of single ovule in each loculus of the ovary in contrast to the two ovules.

Hutchinson (1969) recognised 40 tribes which are

Table - 2. A few taxonomic treatments of the family Euphorbiaceae

1.	Bentham & Hooker (1862-83)	Family	:	Euphorbiaceae
		Tribe	:	(a) Euphorbieae
				(b) Stenolobeae
				(c) Buxeae
				(d) Phyllantheae
				(e) Galiarieae
				(f) Crotoneae.
		Tribe	:	Crotoneae
		Subtribes	:	(1) Jatropheae
				(2) Eucrotoneae
				(3) Chrozophoreae
				(4) Plukenetieae
				(5) Adrianeae
				(6) Acalypheae.
2.	Muell-Arg(1865)	Family	:	Euphorbiaceae
		Group	:	(i) Stenolobeae
				(a) Caletieae
				(b) Ricinocarpeae
				(c) Amphereae
		Group	:	(ii) Platylobeae
				(a) Phyllantheae
				(b) Bridelieae
				(c) Crotoneae
				(d) Acalypheae

Table - 2 (Contd.)

		(e) Hippomaneae
		(f) Dalechampieae
		(g) Euphorbieae
3. Boissier (1879)	Suborder :	Euphorbieae
	Tribes :	Euphorbieae
		Anthostemeae
4. Pax & Hoffman (1931)	:	Euphorbiaceae
	Taxa (i)	Platylobeae
	Subfamily :	(1) Phyllanthoideae (3 tribes)
		(2) Crotonoideae (8 tribes)
	Taxa (ii)	Stenolobeae
	Subfamily	(1) Porantheroideae
		(2) Ricinocarpoideae
5. Hutchinson (1969)	Family :	Euphorbiaceae (40 tribes)
		Glochideae → Euphorbieae
6. Webster (1975)	Family :	Euphorbiaceae
	Subfamily :	(1) Phyllanthoideae (13 tribes)
		Oldfieldoideae
		Acalyphoideae (18 tribes)
		Crotonoideae (" ")
		Euphorbioideae (5 tribes)

arranged in a probable polyphyletic sequence by placing tribe Glochideae in the beginning and Euphorbieae at the end (Table - 2).

It is clear from the above account that the status and delimitation of subfamilies and the tribe within this large family remained always controversal. No two classification are similar even in the treatment of the major taxa. The conflicting views aired by the taxonomists came in way of understanding the true evolutionary trends and interrelationships operating within the family. In the present work chemical characters have been resorted to examine the existing classificatory schemes and to assess the relationships existing between the taxa. All the available Euphorbiaceae members have been screened for various chemical markers like flavonoids, Phenolic acids, Proanthocyanidins, Iridoids, Saponins and Alkaloids. The chemical data thus obtained have been considered along with data from other disciplines. A cladistic analysis of the various genera has been attempted in this dissertation to chart out the probable course of evolution within the family.

The present dissertation merely represents a beginning in that direction. In this time bound Ph.D. programme of two years 67 members belonging to 29 representative genera of the Euphorbiaceae have been screened. Initially the only consideration has been to set the ball rolling by screening all the plants, which could be relatively easily collected from diverse geographical areas of India. The work is to be continued to include as many taxa as possible with the help of various governmental and private agencies. Conclusions tentatively drawn on the basis of a small sample will have to be tested and confirmed or rejected in the light of further work.

I.3 The Chemical characters used in the present study:

The extensive use of chemical data in systematics led to the recognition of Chemosystematics or Chemotaxonomy as one of the disciplines of Taxonomy. During the past 25 years comparative Phytochemistry has been accepted by many plant taxonomists as a auxiliary tool valuable to plant classification. During this period there was a progress in the chemistry of natural products which was overwhelming and the data on the distribution of chemical compounds found a place in the taxonomic deliberations. This is well exemplified by papers of Heywood (1973), Turner (1963), Kubitzki (1969), Meeuse(1970) and Cronquist (1968). A large part of the recent chemotaxonomic literature has been produced by organic chemists, Biochemists and plant physiologists who became interested in the natural classification of plants.

The two classes of compounds which are being used for taxonomic and evolutionary purposes are (1) the high molecular weight and essentially polymeric molecules such as nucleic acids and proteins and (2) relatively low molecular weight non-polymeric metabolic and products such as non-protein amino acids, alkaloids, flavonoids, betalains, glycosides, terpenoids etc. commonly referred to as secondary constituents.

I.3.1 Flavonoids

Among the various secondary constituents, flavonoids are recognised as being the most valuable systematic marker in plants (Gardner, 1977, Cronquist, 1977). They have the advantage of Universal distribution and great ease of detection and the data on their distribution can be interpreted in terms of phylogeny. Harborne (1967) and Swain (1975) have studied these aspects in detail and proposed evolutionary schemes for flavonoids. Swain (1975) presents a tree showing the evolution of the flavonoid molecule in terms of modification to the aglycone and glycosylation patterns. The criteria for assigning advanced vs primitive status in flavonoids is based on (1) the presece of these compounds in primitive vs advanced plants (2) relative position of the flavonoid in the biosynthetic pathway (3) correlations between flavonoid distribution and evolutionary trends in morphological and/or other mechanical characters. Harborne (1967) provided an evolutionary sequence for flavonoid characters (Table 3 & 4) based on the biosynthesis as well as correlation studies.

The term flavonoids in a wider sense includes not only

Table - 3. Evolution of some flavonoid characters in angiosperms according to Harborne(1967,1972)

Character	Primitive state	Advanced state
Anthocyanin in petal	Cyanidin	Delphinidin or Pelargonidin
	3-deoxygenation (1967)	3-oxygenation
	3-oxygenation	3-deoxygenation
	O-acylation absent	O-acylation present
	Simple glycosylation	Complex glycosylation absent
Proanthocyanin in leaf	Present	Absent
Flavonols/Flavones in leaf	Flavonols incl. myricitin	Quercetin & Kaempferol only
	Flavones absent	Flavones present
	O-methylation absent	O-methylation present
	Simple glycosylation	Complex glycosylation
Extra A-ring hydroxylation	Absent	Present
.............if present	At 8-position	At 6-position
2-oxygenation	Absent	Present
c-glycosylation in leaf	Present	Absent
Biflavonyls in leaf	Present	Absent
Flavonones	Present	Absent
Yellow anthochlors in flowers	Chalcones	Chalcones & aurones
C-acylation	Present	Absent

In addition, three "isolated (advanced) characters were recognized: 1. replacement of anthocyanins by betalains 2. presence of isoflavones 3. presence of 5-deoxygenation.

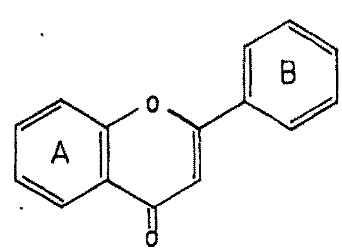
Table-4 **Different character states for angiosperm flavonoids (including anthocyanidins), illustrating possible phylogenetic conditions and the difficulty of distinguishing between primitive and highly advanced types**

Character	Primitive	Advanced	Highly advanced
Deoxygenation	OH	H	-
O-methylation	OH	OMe	OH
Extra A-ring oxygenation	Absent	Present	Absent
...if present	6.H,8-O	6.H,8-H	6-O,8-H
2-oxygenation	Absent	Present	Absent
O-glycosylation	simple (glu & or rham,)	simplex (gluc.gal; arab,xyl & rham)	simple (glu, &/or rhamn.)
Proanthocyanidins	Present	Absent	Absent
O-acylated glycosides	Absent	Present	Absent
C-glycoflavones	Absent	Present	Absent
Biflavones	Absent	Present	Absent
Isoflavones	Absent	Present	Absent

Table-4 (contd)

Character	Primitive	Advanced	Highly advanced
Anthochlors	Absent	Present	Absent
.... if present	Chalcones	Present	Absent
Flavonoid bisulfates	Absent	Present	Absent
C-acylation	Absent	aurones	Chalcones
		present	?
Anthocyanins	Present	Present	Absent
		replaced by	-
		betalains	

the compounds based on flavone (2-phenyl chromone) skeleton, but also a number of related or derived compounds like anthocyanins, isoflavones, neoflavones etc. The flavone skeleton may be considered as containing (i) a C_6-C_3 fragment (Phenyl propane unit) that contains 'B' ring and (ii) a C_6 fragment the 'A' ring. These two are of different biosynthetic origin (Geisman, 1962).

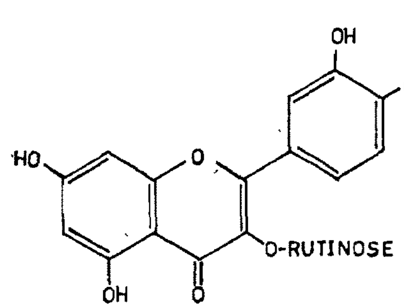


Flavone skeleton

Flavonoids often occur as glycosides in plants, but a number of them are present in the free state too. The sugars involved in glycoside linkages are the usual ones.

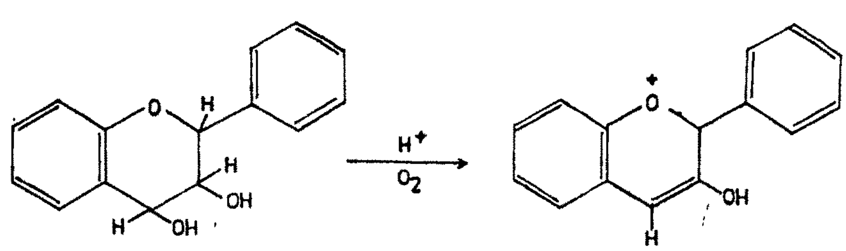
Flavones and flavonols, together known as anthoxantins (yellow flower pigments) are by far the most abundant groups of flavonoids in Angiosperms. Most of them, especially of the latter group, are yellow in color and are responsible for many colors ranging from yellow to white. When they co-occur with anthocyanins they exert a bluing effect in flower color. Flavone itself occurs in primrose flowers and its various hydroxylated and methoxylated derivatives contribute to the light yellow color of many flowers. Apigenin, luteolin are the two hydroxy flavones widespread in plant kingdom. They occur methoxylated and/or glycosylated. The glycosylatin normally occurs at C_7 and the sugar component may be a simple sugar like glucose, galactose or rhamnose or a disaccharide.

Flavonols are 3-OH flavones. They are darker in color and contribute to the deep yellow color of many flowers. The properties of these compounds are very similar to flavones. The three common members of this group are kaempferol, quercetin and myrecetin. Rutin,3-O rutinoside of quercetin,is known as the vitamin P (permeability factor).



Rutin

Proanthocyanidins are 16 dymers of flavones devoid of the Keto group at C_4 and possess a saturated C_3 fragment. They are optically active. The activity is due to the asymetric nature of C_2 and C_3. They are colourless common in woody species. A proanthocyanidin molecule may be a dimer of flavon 3,4-diol or contains a catechin and a flavan 3,4-diol. These compounds as the name suggests yield anthocyanidins on acidic or alkaline hydrolysis along with complex polymeric structures known as phlobaphenes or "tannin reds". The polymeric probaphenes and the proanthocyanidin form the condensed tannins. The production of anthocyanidin from a flavon 3,4-diol is as follows:



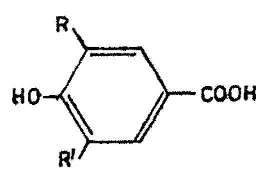
Flavan-3,4-diol

Anthocyanidin

Because of this reaction the proanthocyanidins were known as leucoanthocyanidins. Proanthocyanidins seldom occur as glycosides. The linkages between the two monomer most often is a C-C linkage.

I.3.2 Phenolic acids

This group includes both the benzoic and cinnamic acids (phenyl propanes). p-OH Benzoic acid, vanillic and syringic acid residues are present as components of lignin and so are located in almost all angiosperms.



p-Hydroxybenzoic (R=R'= H)
Protocatechuic (R=OH, R'=H)
Vanillic (R=OMe, R'=H)
Syringic (R=R'=OMe)

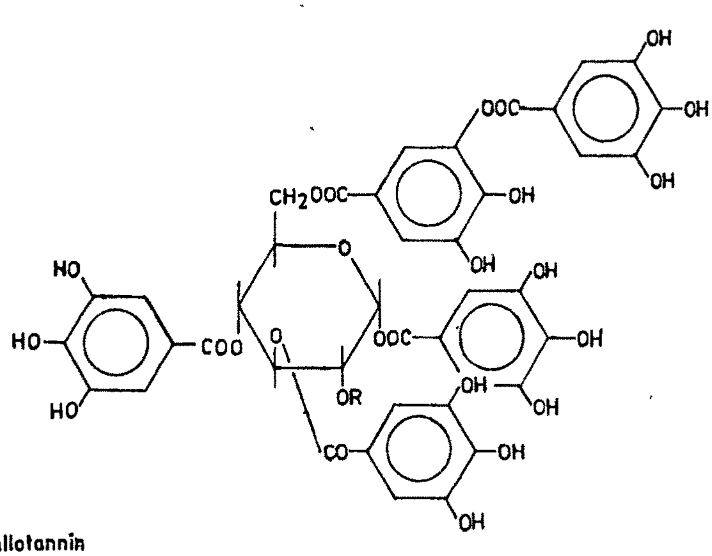
Gentisic and protocatechuic acids are the two other phenolic acids common in higher plants. The gentisic acid has an unusual hydroxylation pattern which is not directly related to either commonly occuring flavonoids nor the lignin (Ibrahim *et al*.1962). Salicylic acid and the related pyrocatechuic acid seem to be characteristic constituents of certain groups like Ericaceae, as also of other genera like *Populus*, *Asclepias*, *Calotropis* and *Vinca*. Gallic acid along with the dimeric ellgic acid form the non-sugar (aglycones) components of gallo-and ellagitannins.

I.3.3 Iridoids

Iridoids are a group of monotropenoid lactones present in many of the advanced orders of dicotyledons. These compounds mostly occur in plants combined with sugar (glycoside). The presence of these compounds in a given group of plants is considered by many (Hegnaur, 1966b, 1969, 1971; Kubitzki, 1969; Meeuse, 1970; Bate-Smith 1972; Swain, 1966; Jensen et al, 1975) to be a valuable chemical character.

I.3.4 Tannins

Tannins are polyphenolic constituents having an astringent taste and ability to convert animal hydes to hard stable leather. Two groups of tannins, hydrolysable and condensed have been located in plants.



Gallotannin

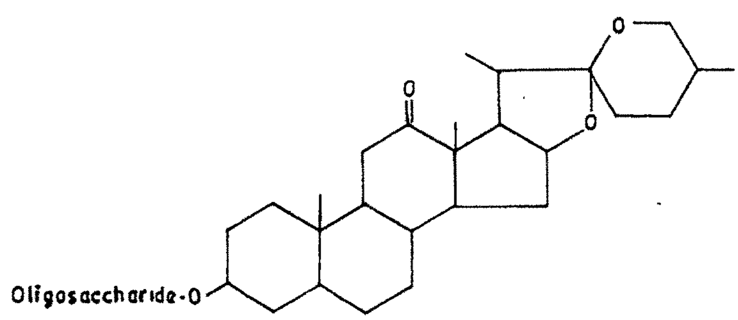
Hydrolysable tannins are complex molecules containing several molecules of a phenolic acid (gallic acid, ellagic acid etc.) esterified to different positions of the sugar molecules and among themselves. Condensed tannins are polyphenols of complex structures which on hydrolysis give polymeric phlobaphenones and/or anthocyanins.

The hydrolysable tannins are abundant in the leaves while condensed tannins are often concentrated in the wood; usually a single species contains only one of these groups but there are instances where both types of tannins co-occur in the same plant.

The association of proanthocyanins and tannins with the woody habit has been established. Highly advanced herbaceous taxa are devoid of tannins or proanthocyanins. Tannins normally correlative well with the more primitive characters in angiosperms.

1.3.5 Saponins

Saponins are the glycosides which show ability to haemolyse blood cells in solution. They possess a steroid or a triterpenoid, aglycone linked to an oligosaccharide. The steroidal saponins are common in monocots while the triterpenoid saponins are found in dicots. Their taxonomic value is less at a higher level of hirarchy although they may be used as useful chemical character at lower levels of classification.



Saponin based on hecogenin

I.3.6 Alkaloids

Alkaloids are secondary plant products which contain a heterocyclic nitrogen. Alkaloids have a limited distribution in the plant Kingdom and their utility as chemical characters are confined to the families which contain them. In families like the Menespermaceae, Solanaceae and Convolvulaceae their presence is a family character. The difficulty in identifying them and their unstability in the laboratory conditions reduce the acceptability of these compounds in chemotaxonomy.

Table - 5. Previous Chemical Work

FLAVONOIDS

No.	Name of the Plant	Organ examined	Chemical Constituents
1.	*Croton oblongifolius*	lvs	Quercetin, isorhamnetin Quercetin 3-galactoside
2.	*C. sparsiflorus*	lvs	Quercetin 3-rhamnosyl glucoside
3.	*Euphorbia dracunculoides*	Whole plant fruit	Derivatives of kaempferol Quercetin, Daphnetin
4.	*E. granculata*	Whole plant	Ellagic acid, rutin Quercetin & Apigenin 7 glucoside
5.	*Euphorbia Hirta*	Dried defatted & powdered	Kaempferol
6.	*E. hypericifolia*	Whole plant	Quercetin-3-α-D galactopyranoside
7.	*Hevea brasiliensis*	lvs	Vitexin, isovitexin
8.	*Jatropha curcas*	lvs	Apigenin, vitexin
9.	*J. gossypifolia*	lvs	Apigenin, vitexin& isovitexin.
10.	*Manihot utilissima*	lvs	Quercetin 3-rhamnosyl glucoside
11.	*Phyllanthys emblica*	lvs	Ellagic acid, kaempferol 3-glucoside
12.	*Phyllanthus niruri*	lvs	Quercetin, isoquercetin Rutin
13.	*Sapium sebiferum*		Quercetin & quercetin 3-glucoside

Table - 5 (Contd.)

STEROLS

Sr.No.	Name of the plant	Organs examined	Chemical constituents
1.	*Croton sparsiflorus*	lvs, stem	β - sitosterol taraxerol
2.	*Euphorbia dracunculoides*	Fruit	Sitosterol, Myricyl alcohol
3.	*Euphorbia pulcherrima*	-	Cholesterol
4.	*E. pulcherrima*	Latex	Setosterol
5.	*Euphorbia tirucalli*	Bark	Cycloarterol, 24-methylene cyclo-artenol-s -sitosterol
6.	*E. tirucalli*	Latex	Tirucallol
7.	*Hevea brasiliensis*	-	Ergosterol
8.	*Hura crepitans*	-	Cycloartenol, 24-methylene cycloartenol
9.	*Jatropha curcas*	Seeds	β-sitosterol, -glucose of β -Sitosterol
10.	*Sapium sebiferum*	lvs, stem	Morentenol, Morentenone
11.	*S. sebiferum*	Bark	Morentenol, Morentenone
12.	*Phyllanthus reticulatus*	lvs	Sitosterol

ALKALOIDS

Sr.No.	Name of the plant	Organs examined	Chemical constituents
1.	*Acalypha indica*	-	Tiracetonamine
2.	*Croton sparsiflorus*	Whole plant	Crotosparine, N-methyl, Crotosparine, Crotosparinine, N-methyl, Crotosparinine, Sparsiflorine

Table - 5 (Contd.)

Sr.No.	Name of the plant	organs examined	Chemical consituents
3.	*Croton tiglium*	-	Crotonosine, Ricinine