

## RESULTS AND DISCUSSION

## CHAPTER IV

RESULTS AND DISCUSSIONRESULTS

Of the 102 plants screened, 82 plants showed various types of flavonoids in the leaves. The various flavonoids met with were, flavonols, flavones, glycoflavones and proanthocyanidins.

Flavones

Flavones formed the predominant flavonoid pigment having been located in 64 plants. Flavones, as O-glycosides, were present in 63 plants and as C-glycosides in 11 plants. Of the 19 flavone aglycones obtained, seven were 6-oxygenated. 6-Deoxygenated flavones were seen in 56 plants. In nine plants they co-occurred with 6-oxygenated flavones and in nine plants with glycoflavones. They were found together with proanthocyanidins in two plants and in three plants 6-deoxygenated, 6-oxygenated flavones and glycoflavones co-occurred. In only one plant both the C-glycosidic flavone and 6-oxygenated flavone were seen together. 6-Oxygenated flavones were seen in 17 plants of which in one plant it occurred together with proanthocyanidins and a flavonol quercetin and in another with proanthocyanidins.

Flavones formed the predominant flavonoid pigment in the families Scrophulariaceae and Pedaliaceae. 6-Oxyflavones

were noticed only within the Scrophulariaceae. The various 6-deoxyflavones located were apigenin, acacetin, 7'-OMe apigenin, 7,4'-diOMe apigenin, luteolin, 3'-OMe luteolin, 4'-OMe luteolin, 7-OMe luteolin, 3',4'-diOMe luteolin, 7,4'-diOMe luteolin, 7,3',4' triOMe luteolin and tricetin. Scutellarein, 6-OMe scutellarein, 4'-OMe scutellarein, 6,4'-diOMe scutellarein, 6-OH luteolin, 6-OMe luteolin and 6,7'-diOMe luteolin were the 6-oxygenated flavones identified. The glycoflavones located include vitexin, 4-OMe vitexin, 6,4-diOMe vitexin and 7,4'-diOMe vitexin.

#### Flavonols

Flavonols were seen in 18 plants. Apart from a single occurrence in the family Scrophulariaceae, the flavonols were confined to the family Solanaceae. The flavonols identified were quercetin, kaempferol, and their methoxylated derivatives like 3'-OMe quercetin, 4'-OMe quercetin, 3',4'-diOMe quercetin, 4'-OMe kaempferol, 7'-OMe kaempferol and 7,4'-diOMe kaempferol.

#### Proanthocyanidins

These compounds had a limited distribution within the families analysed and were located only in six plants. Of the six plants, five were from the Scrophulariaceae and one from the Orobanchaceae. Proanthocyanidins were not detected from the Solanaceae, Pedaliaceae, Gesneriaceae and Lentibulariaceae.

### Phenolic acids

In all, eight benzoic acids viz. p-OH benzoic, protocatechuic, vanillic, syringic, gentisic, melilotic,  $\beta$ -resorcylic and 2-OH, 6-OMe benzoic acids as well as five cinnamic acids viz. caffeic, p-coumaric, o-coumaric, ferulic and sinapic acids were observed in the families studied. In most of the families, the benzoic acids occurred in large amounts.

### Quinones

Quinones had only a limited occurrence in the families being present in 14 plants of which 12 were from the Scrophulariaceae. In 10 plants they co-occurred with flavonoids while in four plants they replaced the flavonoids.

### Iridoids

Iridoids were observed in 27 species wherein 25 were from the Scrophulariaceae. Iridoids were not located in the members of the Solanaceae, Orobanchaceae and Pedaliaceae.

### Alkaloids

In all, 26 plants were observed to have alkaloids in them. They were widely distributed in the family Solanaceae and were observed in 15 plants. Alkaloids were not spotted in the families Pedaliaceae, Orobanchaceae and Gesneriaceae.

### Saponins

Nearly 50% of the plants showed the occurrence of saponins.

In the family Scrophulariaceae saponin distribution was at random in 27 plants. They were observed throughout the Solanaceae. Within Pedaliaceae only Martynia annua showed the presence of saponins. In the members of the Orobanchaceae, they were scarce, and remained absent from the families Gesneriaceae and Lentibulariaceae.

### Tannins

Besides the Orobanchaceous members viz. Orobanch<sup>o</sup> alba and O. cernua, tannins were not located in any other plants investigated.

The distribution of flavonoids and other chemical markers in the various families screened is shown in Tables VI-XI.

### SCROPHULARIACEAE

The major phenolic pigments of the family were flavones. These compounds were located in 59 out of the 72 plants screened. Among the various aglycones obtained, 6-oxygenated flavones were rare in occurrence. These compounds were located in 17 plants, of which nine contained 6-deoxy flavones (simple flavones) also. 6-Deoxy flavones were more frequent in the sub family Rhinanthoideae. Glycoflavones (obtained from nine plants) were common in the subfamily Scrophularioideae (7/9). Here they were often accompanied by simple flavones. Only in three plants i.e. Scoparia dulcis (Rhinanthoideae), Limnophila indica and Lindenbergia muraria (Scrophularioideae) all the three groups of flavones (6-oxy, 6-deoxy and glycoflavones) occurred together.

TABLE VI

DISTRIBUTION OF FLAVONOIDS AND QUINONES IN THE FAMILY SCROPHULARIACEAE (PLANTS ARRANGED AFTER BENTHAM AND HOOKER, 1876)

Sr. No.	Plant Name	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
	Series A. Pseudosolanaceae (Verbascoideae)																										
	Tribe II Aptosimeae																										
1.	<u>Anticharis senegalensis</u> (Walp.) Bhandari																										
	Tribe III Verbasceae																										
2.	<u>Verbasum chinensis</u> (L.) Santapau																										
3.	<u>V. thapsus</u> L.																										
	Series B. Antirrhinoideae (Scrophularioideae)																										
	Tribe V. Hemimerideae																										
4.	<u>Angelonia salicariaefolia</u> Humb. & Bonpl.																										
	Tribe VI Antirrhineae																										
5.	<u>Antirrhinum majus</u> Linn.																										
6.	<u>Kickxia incana</u> (Wall.) Pennell																										

Table VI (Contd.)

Sr. No.	Plant Name	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
7.	<u>Kickxia ramossissima</u> (Wall.) Jauchten				+																						
8.	<u>Linaria dalmatica</u> (L.) Mill.																										
9.	<u>Maurandya erubescens</u> (Don.) Gray																										
10.	<u>Schweinfurthia papilionacea</u> Boiss.																										
	Tribe VII Cheloneae																										
11.	<u>Penstemon gloxinoides</u> Hort																										
12.	<u>Russelia equisetiformis</u> Schlecht. & Cham.																										
13.	<u>R. floribunda</u> H.B. & K.																										
14.	<u>Scrophularia decomposita</u> Royle, ex Bth.																										
15.	<u>S. koetzi</u> Pennell																										
16.	<u>S. lucida</u> Linn.																										
17.	<u>S. polyantha</u> Royle, ex Bth.																										

Table VI (Contd.)

Sr. No.	Plant Name	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
18.	<u>Scrophularia robusta</u> Pennell.																										
	Tribe VIII Manuleae																										
19.	<u>Sutera dissecta</u> (Del.) Walp.											+					+				+						
	Tribe IX Gratiroleae																										
	Subtribe I Mimuleae																										
20.	<u>Mazus delavayii</u> Bonati																										
21.	<u>M. pumilus</u> (Burm.f.) Steenis																										
	Subtribe II Stenodieae																										
22.	<u>Limnophila aromatica</u> (Lam.) Merr.																										
23.	<u>L. heterophylla</u> (Roxb.) Benth.																										+
24.	<u>L. indica</u> (L.) Druce																										+
25.	<u>L. repens</u> Benth.																										+
26.	<u>Lindenbergia indica</u> (Linn.) Vatke																										+



Table VI (contd)

Sr. No.	Plant Name	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
	Subtribe V Limoselleae																										
40.	<u>Glossostigma diandrum</u> (L.) O.Ktze											+															
	Series C. Rhinanthoideae																										
	Tribe X Digitalaeae																										
	Subtribe I Sibthorpieae																										
41.	<u>Hemiphragma heterophyllum</u> Wall.																										
42.	<u>Mecardonia procumbens</u> (Mill.) Sm.																										
43.	<u>Scoparia dulcis</u> L.																										
	Subtribe II Eudigitalaeae																										
44.	<u>Digitalis lanata</u> Ehrh.																										
45.	<u>D. purpurea</u> L.																										
	Subtribe III Veroniceae																										
46.	<u>Picrohiza kurrooa</u> Royle.																										
47.	<u>Veronica agrestis</u> Linn.																										
48.	<u>V. anagallis-aquatica</u> Linn.																										
49.	<u>V. arvensis</u> Linn.																										
50.	<u>V. beccabunga</u> L.																										

Table VI (Contd.)

Sr. No.	Plant Name	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	
51.	<u>Veronica biloba</u> L.	+			+					+																		
52.	<u>V. campylopoda</u> Boiss.																											
53.	<u>V. didyma</u> Tenore										+																	
54.	<u>V. lanosa</u> Royle, ex Bth.																											
55.	<u>V. laxa</u> Benth.																											
56.	<u>V. melissaefolia</u> Poir.																											
57.	<u>V. oxycarpa</u> Boiss.																											
58.	<u>V. persica</u> Hort, ex Poir.																											
59.	<u>V. salina</u> Schur.																											
60.	<u>V. serpyllifolia</u> Linn.																											
61.	<u>V. spicata</u> L.																											
62.	<u>V. stewartii</u> Pennell																											
	Tribe IX Geradieae																											
	Subtribe III Buchnereae																											
63.	<u>Buchnera hispida</u> Buch-Ham.																											
64.	<u>Striga angustifolia</u> (D. Don.) Sald.																											

Table VI (Contd.)

Sr. No.	Plant Name	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
65.	<u>Striga asiatica</u> (Linn.) O.Kutze.									+																	
66.	<u>S. densiflora</u> (Bth.)Bth. Subtribe IV Eugerardieae		+	+						+																	
67.	<u>Sopubia delphinifolia</u> (L.) G.Don. Tribe XIII Euphrasieae									+																	
68.	<u>Euphrasia laxa</u> L.																										
69.	<u>Pedicularis bicornata</u> Klotzsch																										
70.	<u>P.oederi</u> Vahl.																										
71.	<u>P.pectinata</u> Wall.ex.Bth.										+	+															
72.	<u>P.punctata</u> Decne.																										

1. Apigenin, 2. Acacetin, 3. 7'-OMe Apigenin, 4. Scutellarein, 5. 6'-OMe Scutellarein, 6. 4'-OMe Scutellarein 7. 6,4'-diOMe Scutellarein, 8. 7,4'-diOMe Apigenin, 9. Luteolin, 10. 3'-OMe Luteolin, 11. 4'-OMe Luteolin, 12. 7'-OMe Luteolin, 13. 6-OH Luteolin, 14. 6'-OMe Luteolin 15. 6'-OMe Luteolin, 16. 3',4'-diOMe Luteolin, 17. 7,4'-diOMe Luteolin, 18. 6,3',4'-triOMe Luteolin, 19. Tricin, 20. Vitexin, 21. 4-OMe vitexin, 22. 6,4-diOMe Vitexin, 23. 7,4'-diOMe vitexin, 24. Quercetin, 25. Proanthocyanidins, 26. Quinones.

Table VII

DISTRIBUTION OF FLAVONOIDS AND QUINONES IN PEDALIACEAE, OROBANCHACEAE, GESNERIACEAE AND

LENTIBULARIACEAE

Sr. No.	Plant Name	*	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		
	<u>PEDALIACEAE</u>																													
1.	<u>Martynia annua</u> L.	+	+																											
2.	<u>Pedaliium murex</u> L.	+	+																											
	<u>OROBANCHACEAE</u>																													
1.	<u>Orobancha alba</u> Steph. ex Willd.	+																												
2.	<u>O.cernua</u> Loefl.																													
	<u>GESNERIACEAE</u>																													
1.	<u>Didymocarpus pygmaea</u> Cl.																													
	<u>LENTIBULARIACEAE</u>																													
1.	<u>Utricularia aurea</u> Lour																													
2.	<u>U.inflexa</u> Forsk var. <u>stellaris</u> (Lin.f.) Taylor																													
3.	<u>U. sp.</u>																													

\* See Table VI.

Table VIII

DISTRIBUTION OF FLAVONOIDS AND QUINONES IN SOLANACEAE (PLANTS  
ARRANGED AFTER BENTHAM AND HOOKER, 1876)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11
Sub Family Solanoideae												
Tribe Solaneae												
1.	<u>Capsicum annuum</u> L.	+										
2.	<u>Lycopersicon lycopersicum</u> (L.) Karst.											
3.	<u>Physalis minima</u> L.								+	+		
4.	<u>Solanum sisymbriifolium</u> Lamk.			+			+					
5.	<u>S. melongena</u> L.			+					+			
6.	<u>S. nigrum</u> L.											
7.	<u>S. torvum</u> Swartz.								+			
8.	<u>S. seaforthianum</u> Andr.										+	
9.	<u>S. surattense</u> Burm.f.								+			
10.	<u>S. roxburghi</u> Dun.		+				+					
11.	<u>Withania coagulans</u> Dun.			+								
12.	<u>W. somnifera</u> (L.) Dun.			+							+	
Tribe II Atropeae												
13.	<u>Lycium barbarum</u> L.											
Tribe III Hyoscyameae												
14.	<u>Datura innoxia</u> Mill		+									
15.	<u>D. metel</u> L.			+					+			
16.	<u>Hyoscyamus niger</u> L.								+			
Subfamily Cestroideae												
17.	<u>Cestrum diurnum</u> L.					+						

Table VIII (Contd.)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11
18.	<u>Cestrum nocturnum</u> L.			+								
19.	<u>Nicotiana tabacum</u> L. Tribe V Salpiglossideae							+				
20.	<u>Brunfelsia americana</u> L.				+	+						
21.	<u>B. bicolor</u> L.											
22.	<u>Petunia hybrida</u> Vilm.											+

1. Apigenin,            2. Kaempferol,            3. 4'-OMe kaempferol,  
4. 7'-OMe Kaempferol    5. 7,4'-diOMe Kaempferol,  
6. Quercetin,            7. 3'-OMe quercetin    8. 4'-OMe Quercetin,  
9. 3',4'-diOMe Quercetin,    10. Proanthocyanidins,  
11. Quinones.

Table IX

THE DISTRIBUTION OF PHENOLIC ACIDS, TANNINS, SAPONINS, IRIDIDS, AND ALKALOIDS WITHIN  
SCROPHULARIACEAE (PLANTS ARRANGED AFTER BENTHAM AND HOOKER, 1876)

Sr.No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
Series A. <i>Pseudopslameae</i>																			
Tribe II Aptosimeae																			
1.	<u>Anticharis senegalensis</u> (Walp.) Bhandari	+	+																
Tribe III Verbasceae																			
2.	<u>Verbascum chinensis</u> (L.) Santapau																		++
3.	<u>V. thapsus</u> L.																		++
Series B. Antirrhinoideae (Scrophularioideae)																			
Tribe V Hemimerideae																			
4.	<u>Angelonia salicariaefolia</u> Humb. & Bonpl.																		+++
Tribe VI Antirrhineae																			
5.	<u>Antirrhinum majus</u> Linn.																		+++
6.	<u>Kickxia incana</u> (Wall.) Pennell																		+
7.	<u>K. ramossissima</u> (Wall.) Jaunchen																		++

Table IX (Contd.)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
8.	<u>Linaria dalmatica</u> (L.) Mill.	+	+	+	+	+	+	+							+		++		
9.	<u>Maurandya erubescens</u> (Don.) Gray	#	+	+	+	+						+					++		++
10.	<u>Schweinfurthia papilionacea</u> Boiss.																++	+++	++
11.	Tribe VII Cheloneae																		
11.	<u>Penstemon gloxinoides</u> Hort																		
12.	<u>Russelia equisetiformis</u> Schlecht. & Cham.	+	+	+	+	+						+					?		++
13.	<u>R. floribunda</u> H.B. & K.	+	+	+	+	+						+					++		++
14.	<u>Scrophularia decomposita</u> Royle, ex Bth.																		++
15.	<u>S. koetzi</u> Pennell	+	+	+	+	+													++
16.	<u>S. lucida</u> Linn.	+	+	+	+	+						+					?		?
17.	<u>S. polyantha</u> Royle, ex Bth.											+							
18.	<u>S. robusta</u> Pennell	+	+	+	+	+													
	Tribe VIII Manuleae																		
19.	<u>Sutera dissecta</u> (Del.) Walp.	+	+	+	+	+						+							
	Tribe IX Gratiroleae																		
	Subtribe I Mimuleae																		

Table IX (Contd)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
20.	<u>Mazus delavayii</u> Bonati	+	+	+	+	+	+	+				+							
21.	<u>M. pumilus</u> (Burm.f.) Steenis	+	+	+	+	+	+					+					?	++	++
	Subtribe II Stemodieae																		
22.	<u>Limnophila aromatica</u> (Lam.) Merr.	+	+	+	+	+	+					+							
23.	<u>L. heterophylla</u> (Roxb.) Benth.	+	+	+	+	+	+					+						+	
24.	<u>L. indica</u> (L.) Druce	+	+	+	+	+	+					+						++	++
25.	<u>L. repens</u> Benth.	+	+	+	+	+	+											++	
26.	<u>Lindenbergia indica</u> (Linn.) Vatke	+																	
27.	<u>L. muraria</u> (Roxb.) P. Bruehl	+	+	+	+	+	+											+	+++
28.	<u>Stemodia serrata</u> Bth.	+	+	+	+	+	+					+							+++
29.	<u>S. viscosa</u> Roxb.	+	+	+	+	+	+					+						+	++
	Subtribe III Herpestideae																		
30.	<u>Bacopa monnieri</u> (Linn.) Pennell	+	+	+	+	+	+											+++	
31.	<u>Dopatrium junceum</u> (Roxb.) Buch-Ham. ex Bth	+	+	+	+	+	+					+						+++	+++
32.	<u>D. lobelioides</u> (Retz.) Benth.	+	+	+	+	+	+											++	
	Subtribe IV Vandelleae																		
33.	<u>Lindernia anagallis</u> (Burm.f.) Pennell	+	+	+	+	+	+												
34.	<u>L. ciliata</u> (Colsm.) Pennell	+	+	+	+	+	+												+

Table IX (contd)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
35.	<u>L. crustaceae</u> (L.) F. Muell.	+	+	+	+	+	+	+				+						?	?
36.	<u>L. pusilla</u> (Willd.) Boldingh	+	+														+++		
37.	<u>L. pyxidaria</u> Pursh		+	+	+	+	+												
38.	<u>Torenia bicolor</u> Dalz.	+	+	+	+	+	+				+	+					+++		
39.	<u>T. travencorica</u> Gamble		+	+	+	+	+												
	Subtribe V Limoselleae																		
40.	<u>Glossostigma diandrum</u> (L) O.Ktze			+			+	+											
	Series C Rhinanthoideae																		
	Tribe X Digitalaeae																		
	Subtribe I Sibthorpieae																		
41.	<u>Hemiphragma heterophyllum</u> Wall.			+			+								+				
42.	<u>Mecardonia procumbens</u> (Mill.) Sm.	+	+				+												
43.	<u>Scoparia dulcis</u> L.	+	+	+	+	+	+				+						+++		++
	Subtribe II Eudigitaleae																		
44.	<u>Digitalis lanata</u> Ehrh.	+	+				+				+	+			+				
45.	<u>D. purpurea</u> L.	+	+	+	+	+	+				+	+							++
	Subtribe III Veroniceae																		

Table IX (Contd)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
46.	<u>Picrorhiza kurrooa</u> Royle	+	+	+	+	+	+												
47.	<u>Veronica agrestis</u> Linn.	+	+	+	+						+						++	+++	
48.	<u>V. anagallis-aquatica</u> Linn.	+	+	+					+									?	
49.	<u>V. arvensis</u> Linn.	+	+	+					+								+		++
50.	<u>V. beccabunga</u> L.	+	+	+					+								?		
51	<u>V. biloba</u> Linn.	+	+	+															++
52	<u>V. campylopoda</u> Boiss.	+																	
53.	<u>V. didyma</u> Tenore		+	+															
54.	<u>V. Lanosa</u> Royle, ex Bth.	+		+											+				
55.	<u>V. laxa</u> Benth	+	+	+								+					++	++	++
56.	<u>V. melissaefolia</u> Poir.	+		+										+			+		++
57.	<u>V. oxycarpa</u> Boiss	+	+	+								+							
58.	<u>V. persica</u> Hort. ex Poir.	+	+	+													++	++	
59.	<u>V. salina</u> Schur	+	+	+															
60.	<u>V. serpyllifolia</u> Linn.	+		+													+		
61.	<u>V. spicata</u> L.	+		+													++	++	++
62.	<u>V. stewarti</u> Pennell	+	+	+															+

Table IX (contd)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
	Tribe XI Gerardieae																		
	Subtribe III Buchnereae																		
63.	<u>Buchnera hispida</u> Buch-Ham.	+	+	+	+	+	+	+	+	+	+	+	+	+	+		++	+++	
64.	<u>Striga angustifolia</u> (Don.) Sald.	+	+	+	+	+	+	+	+	+	+	+	+	+	+		++	+++	
65.	<u>S. asiatica</u> (Linn.) Kuntze.	+	+	+	+	+	+	+	+	+	+	+	+	+	+		++	+++	
66.	<u>S. densiflora</u> (Bth.) Bth.	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+++	+++	+++
	Subtribe IV Eugerardieae																		
67.	<u>Sopubia delphinifolia</u> (L.) G. Don.	+	+	+	+	+	+	+	+	+	+	+	+	+	+			+++	
	Tribe XII Euphrasieae																		
68.	<u>Euphrasia laxa</u> L.	+	+	+	+	+	+	+	+	+	+	+	+	+	+		++	+++	+
69.	<u>Pedicularis bicornata</u> Klotzsch.	+	+	+	+	+	+	+	+	+	+	+	+	+	+				
70.	<u>P. oederi</u> Vahl	+	+	+	+	+	+	+	+	+	+	+	+	+	+				
71.	<u>P. pectinata</u> Wall. ex. Bth.	+	+	+	+	+	+	+	+	+	+	+	+	+	+				
72.	<u>P. punctata</u> Decne.	+	+	+	+	+	+	+	+	+	+	+	+	+	+				
	1. p-OH Benzoic acid																		
	2. Protocatechic acid																		
	3. Vanillic acid																		
	4. Syringic acid																		
	5. Gentisic acid																		
	6. Melilotic acid																		
	7. $\beta$ . resorcylic acid																		
	8. Phloretic acid																		
	9. 2-OH 6-O-Me Benzoic acid																		
	10. Caffeic acid																		
	11. p-Coumaric acid																		
	12. O-Coumaric acid																		
	13. Ferulic acid																		
	14. Sinapic acid																		
	I. Tannins																		
	II. Saponins																		
	III. Iridoids																		
	IV. Alkaloids																		

Table X

THE DISTRIBUTION OF PHENOLIC ACIDS, TANNINS, SAPONINS, IRIDIDS AND ALKALOIDS IN THE FAMILIES  
 PEDALIACEAE, OROBANCHACEAE, GESNERIACEAE AND LENTIBULARIACEAE

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
<u>PEDALIACEAE</u>																			
1.	<u>Martynia annua</u> L.	+	+	+	+	+	+	+	+	+	+	+	+	+	+		++		
2.	<u>Pedaliium murex</u> L.	+	+	+	+	+	+	+	+	+	+	+	+	+	+				
<u>OROBANCHACEAE</u>																			
1.	<u>Orobancha alba</u> Steph.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
2.	<u>O. cernua</u> Loefl.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
<u>GESNERIACEAE</u>																			
1.	<u>Didymocarpus pygmaea</u> Cl.	+	+	+															+
<u>LENTIBULARIACEAE</u>																			
1.	<u>Utricularia aurea</u> Lour																		
2.	<u>U. inflexa</u> Forsk var. <u>stellaris</u> (Linn.f.) Taylor																		+
3.	<u>U. Sp</u>	+	+	+															+
1.	p-OH Benzoic acid																		
2.	Protocatechuic acid																		
3.	Vanillic acid																		
4.	Syringic acid																		
5.	Gentisic acid																		
6.	Melilotic acid																		
7.	resorcylic acid																		
8.	Phloretic acid																		
9.	2-OH-6-OMe Benzoic acid																		
10.	Caffeic acid																		
11.	p-Coumaric acid																		
12.	O-Coumaric acid																		
13.	Ferulic acid																		
14.	Sinapic acid																		
I.	Tannins																		
II.	Saponins																		
III.	Iridoids																		
IV.	Alkaloids																		

Table XI

DISTRIBUTION OF PHENOLIC ACIDS, TANNINS, SAPONINS, IRIDOIDS AND ALKALOIDS IN SOLANACEAE  
(PLANTS ARRANGED AFTER BENTHAM AND HOOKER, 1876)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV	
	Subfamily Solanoideae																			
	Tribe Solaneae																			
1.	<u>Capsicum annuum</u> L.	+	+	+													+++		+++	
2.	<u>Lycopersicon lycopersicum</u> (L.) Karst.			+	+												+		+	
3.	<u>Physalis minima</u> L.	+	+	+													++		++	
4.	<u>Solanum sisymbriifolium</u> Lamk.	+	+	+	+														+	
5.	<u>S. melongena</u> L.	+	+	+	+					+							?		+	
6.	<u>S. nigrum</u> L.				+	+				+	+						++			
7.	<u>S. torvum</u> Swartz.	+	+	+													++		+	
8.	<u>S. seaforthianum</u> Andr.	+	+	+													+++		+++	
9.	<u>S. surattense</u> Burm.f.				+												+++		+++	
10.	<u>S. roxburghii</u> Dun.				+					+	+						++		++	
11.	<u>Withania coagulans</u> Dun.				+	+											++		++	
12.	<u>W. somnifera</u> (L.) Dun.	+	+	+													+		++	

Table XI (Contd.)

Sr. No.	Plant Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	I	II	III	IV
	Tribe II Atropeae																		
13.	<u>Lycium barbarum</u> L.	+		+													++		?
	Tribe III Hyoscyameae																		
14.	<u>Datura innoxia</u> Mill.			+		+											++		+++
15.	<u>D. metel</u> L.	+		+		+											+++		+++
16.	<u>Hyoscyamus niger</u> L.	+		+		+		+									++		+++
	Subfamily Cestroidae																		
	Tribe IV Cestrineae																		
17.	<u>Cestrum diurnum</u> L.	+		+		+											+++		+++
18.	<u>C. nocturnum</u> L.			+		+											+++		+++
19.	<u>Nicotiana tabacum</u> L.	+		+				+									++		+++
	Tribe V Salpiglossideae																		
20.	<u>Brunfelsia americana</u> L.			+		+						+	+	+			+++		+++
21.	<u>B. bicolor</u> L.			+		+		+				+	+				+++		+++
22.	<u>Petunia hybrida</u> Wilm.			+		+		+				+	+				++		++

1. p-OH Benzoic acid, 2. Protocatechuic acid, 3. Vanillic acid, 4. Syringic acid,  
5. Gentisic acid, 6. Melilotic acid, 7.  $\beta$ -resorcylic acid, 8. Phloretic acid,  
9. 2-OH 6-OMe Benzoic acid, 10. Caffeic acid, 11. p-Coumaric acid, 12. o-Coumaric acid,  
13. Ferulic acid, 14. Sinapic acid, I. Tannins, II. Saponins, III. Iridoids, IV. Alkaloids.

The single occurrence of flavonol in the family was noticed in Dopatrium junceum (Scrophularioideae). Here quercetin was located along with 6-OH luteolin and proanthocyanidins.

Proanthocyanidins were observed in five plants and quinones in nine. Twenty five plants gave a positive test for iridoids. These plants were almost equally distributed in the various sub-families of the family. An equal number of plants contained saponins. Alkaloids were rare (9/72) and tannins absent.

Benzoic acids were widely distributed than cinnamic acids. Vanillic acid was ubiquitous. p-OH Benzoic and melilotic acids had more than 60% frequency of distribution. Syringic acid was located in less than 25% of the plants screened. The three cinnamic acids, p-coumaric, o-coumaric and ferulic acids, occurred in 20-40% of plants. The rare phenolic acids of the family were gentisic, protocatechuic, 2-OH-6-OMe benzoic  $\beta$ -resorcylic, sinapic and caffeic acids.

#### Subfamily - Pseudosolaneae (Verbascoideae)

This subfamily was represented by only three plants viz. Anticharis senegalensis (tribe Aptosimeae), Verbascum chinensis and V. thapsus (tribe Verbasceae). All the three plants contained 6-deoxygenated flavones. A glycoflavone, 4-OMe vitexin, was observed in Verbascum chinensis. Both the species of Verbascum contained saponins, whereas iridoids were noticed only in V. thapsus. None of the plants contained proanthocyanidins

quinones or alkaloids. Cinnamic acids were not observed in Anticharis whereas in Verbascum, they were represented by ferulic acid. The lesser number of plants screened does not permit drawing taxonomic conclusions on the various taxa of this subfamily.

Subfamily - Antirrhinoideae (Scrophularioideae)

Most of the tribes of the subfamily Scrophularioideae viz. the Hemimerideae, Antirrhineae, Cheloneae, Manuleae and Gratioleae were represented in the present study. Among the 37 plants studied in this subfamily, 22 plants contained 6-deoxygenated flavones and seven plants contained glycoflavones. Most of the plants with 6-deoxyflavones and glycoflavones, belonged to the tribe Gratioleae. 6-Oxygenated flavones were noticed in 13 plants. Though these plants were distributed within the tribes Antirrhineae, Cheloneae and Gratioleae, their relative incidence was more in the tribe Antirrhineae. In five plants 6-deoxyflavones occurred together with 6-oxyflavones and in another six plants with glycoflavones. 6-Oxyflavones and glycoflavones co-occurred in only three plants of which two are from the tribe Gratioleae. In Limnophila indica and Lindenbergia muraria (tribe Gratioleae), all the three groups of flavones viz. 6-deoxy, 6-oxy and glycoflavones occurred together. Flavonols, which were otherwise absent in the family Scrophulariaceae, were located in Dopatrium junceum (tribe Gratioleae). Proanthocyanidins were seen in four plants and quinones in nine. Iridoids were seen in 12 plants and were

concentrated more in the tribe Antirrhineae. The tribe Gratioleae had a very poor representation of iridoids. However, the tribe Gratioleae showed a frequent presence of saponins, which was noticed in nine plants of the tribe. Saponins were seen in 14 plants. Of the six plants with alkaloids, three were from the tribe Antirrhineae. Among the cinnamic acids, ferulic acid was frequent throughout the subfamily. Ortho and paracoumaric acids were seen rarely. Sinapic acid, observed in Kickia ramossissima and caffeic acid in Russelia equisetiformis, were not seen anywhere else in the subfamily. Both the tribe Antirrhineae and Cheloneae had larger number of benzoic acids in them.

On the whole, the incidence of 6-oxygenated flavones, glycoflavones, proanthocyanidins, alkaloids and cinnamic acids was more in this subfamily when related with the other two subfamilies the Verbascoideae and Rhinanthoideae.

The tribe Gratioleae is noteworthy because of the higher incidence of 6-deoxygenated flavones, glycoflavones, saponins and quinones as well as by the poor representation of iridoids, proanthocyanidins and alkaloids. Moreover, flavonols were detected only from this tribe. The tribe Manuleae, represented here by Sutera dissecta, is similar to the tribe Gratioleae in having 6-deoxyflavones and glycoflavones. The tribes Antirrhineae and Hemimerideae, the latter tribe represented by a single plant Angelonia salicariaefolia were distinguished by

the higher incidence of 6-oxygenated flavones, iridoids and alkaloids. Glycoflavones, quinones, saponins and proanthocyanidins were scarce in the tribe Antirrhineae. Angebonia salicariaefolia was devoid of glycoflavones but found to contain proanthocyanidins, quinones and saponins. Tribe Cheloneae could be chemically demarcated by the absence of glycoflavones, proanthocyanidins and alkaloids. Saponins, iridoids and quinones were rare in this tribe.

#### Tribe Gratiolleae

Twentyone plants belonging to nine genera were studied within this tribe. These plants were distributed within five subtribes viz. Mimuleae (Mazus-2), Stemodieae (Limnophila-4, Lindenbergia-2 and Stemodia-2), Herpestideae (Bacopa-1 and Dopatrium-2), Vandelleae (Lindernia-5 and Torenia-2) and Limoselleae (Glossostigma-1).

6-Deoxygenated flavones were widespread in the tribe having been observed in 13 plants. Four plants contained glycoflavones and six, 6-oxygenated flavones. All these three groups of flavones (i.e. 6-deoxygenated, 6-substituted and C-glycosides) were seen together in Limnophila indica and Lindenbergia muraria. 6-Deoxy flavones co-occurred with glycoflavone in four plants and with 6-oxygenated flavones in three plants. A flavonol quercetin was identified along with 6-OH luteolin and proanthocyanidins in Dopatrium junceum. Apart from this, flavonols were not located in the family. The incidence of quinones was

relatively high and these compounds were spotted in 6-plants. Proanthocyanidins were noticed in two plants and an equal number contained alkaloids. Six plants were observed to have iridoids in them. Saponins were noticed in almost 50% of the plants. The tribe showed poor distribution of cinnamic acids. Except for the subtribe Vandelleae where Lindernia and Torenia were found to be chemically similar in containing both 6-deoxyflavones and C-glycosides, other subtribes do not possess any distinct chemical identity.

On the basis of the presence of iridoids the nine genera studied in this tribe can be grouped into two. The first group possessing iridoids include Mazus, Limnophila, Lindenbergia, Stemodia and Dopatrium. The second group with Bacopa, Lindernia, Torenia and Glossostigma was devoid of these compounds. In the first group, except for Mazus, which possessed 6-deoxyflavones, all the other plants contained 6-oxygenated flavones. Nevertheless Dopatrium proved an exception in having flavonols. In Stemodia only 6-substituted flavones were noticed. But both Limnophila and Lindenbergia possessed the three groups viz. 6-deoxyflavones, 6-oxygenated flavones and glycoflavones. However, quinones and cinnamic acids were seen only in Limnophila spp.

The genus Mazus contained only 6-deoxyflavones and was devoid of glycoflavones, proanthocyanidins, quinones, saponins and alkaloids. Iridoids also were present. Ferulic acid was the only cinnamic acid observed. Between the two species of

Mazus i.e. M.delavayii and M.pumilus, luteolin derivatives, protocatechuic and syringic acids were observed only in the former, and gentisic acid was noticed only in the latter. The various species of Limnophila were also chemically distinguishable. Thus, L.heterophylla was devoid of flavonoid pigments, instead they possessed quinones. Though quinones were present in L.indica they contained flavones (both 6-deoxy and 6-oxygenated) and C-glycosides. Glycoflavones were absent in L.aromatica. This plant had 6-OMe apigenin and 7',4'-diOMe apigenin. Flavonoids within L.repens could not be identified due to their trace amounts. Apart from 6-deoxyflavones which were present in Lindenbergia indica, the presence of 6-OH luteolin and 6,4-diOMe vitexin in L.muraria characterize the latter plant from the former. Though both Stemodia serrata and S.viscosa were characterized by 6-oxygenated flavones the presence of quinones in the latter distinguished it from the former. Furthermore, 2-OH-6-OMe benzoic acid which was otherwise absent in the subfamily Scrophularioideae was observed in S.serrata.

In the second group, invariably all the plants contained 6-deoxygenated flavones. Lindernia and Torenia distinguish themselves in producing glycoflavones. Between these two genera proanthocyanidins in Torenia provide enough evidence for the separate identity of this genus. Cinnamic acids were absent in Glossostigma. Bacopa contained only 3',4'-diOMe luteolin. Among the species of Lindernia, flavonoids could not be identified in L.ciliata and L.pusilla, due to the trace amount

of these compounds. The presence of glycoflavones in L. anagallis demarcated it from L. crustacea and L. pyxidaria. Lindernia crustacea was further characterized by quinones. The two species of Torenia also showed chemical dissimilarities. T. bicolor could be distinguished from T. travencorica by the presence of glycoflavones, proanthocyanidins, quinones and cinnamic acids in the former and by their absence in the latter.

#### Tribe Antirrhineae

This tribe is represented by six plants belonging to 5 genera i.e. Antirrhinum (1), Kickxia (2), Linaria (1), Maurandya (1) and Schweinfurthia (1). Of these, three contained 6-oxygenated flavones. In Schweinfurthia they co-occurred with 6-deoxyflavones. Apart from this plant, 6-deoxyflavones were present in three more plants. Glycoflavones were noticed in two plants, where they co-occurred with 6-deoxyflavones in one plant and with 6-oxygenated flavone in the other. Proanthocyanidins were observed in Linaria and quinones in Antirrhinum. Except for Maurandya, all other plants contained iridoids. Alkaloids were noticed in three plants and saponins in two. Sinapic acid which was otherwise absent in the subfamily was noticed in Kickxia ramossissima. The plants were either devoid of cinnamic acids or when present, were represented by lesser number. Benzoic acids were more common in the tribe.

In having 6-deoxyflavones Antirrhinum, Linaria and Maurandya are alike in nature. Glycoflavones and quinones isolate Antirrhinum (A. majus) from the other two genera. Though

both Linaria (L.dalmatica) and Maurandya (M.erubescens) contained only 6-deoxyflavones, the former contained proanthocyanidins also. Except Linaria, all other plants in this group contained alkaloids. The absence of iridoids demarcated Maurandya.

The species of Kickxia and Schweinfurthia were distinct from the former group in possessing 6-substituted flavones. Nevertheless, 6-deoxyflavones accompanying 6-substituted flavones and the presence of alkaloids as well as saponins provide Schweinfurthia (S.papilionacea) its identity. Moreover, this plant distinctly possessed vanillic acid in very large quantities. The species of Kickxia contained 6-oxyflavones and were devoid of saponins and alkaloids. However, the presence of glycoflavone in K.ramosissima gave it a separate identity from K.incana.

#### Tribe Cheloneae

Penstemon (1), Russelia (2) and Scrophularia (5) were the three genera analysed from this tribe. Of the 8 plants studied three contained 6-deoxyflavones and three, 6-oxygenated flavones. None of the plants contained glycoflavones, proanthocyanidins or alkaloids. Quinones, iridoids and caffeic acid were noticed only in Russelia equisetiformis. Two plants possessed saponins in them. In its phenolic acid distribution the tribe was similar to the tribe Antirrhineae. Flavonoids could not be identified in Russelia floribunda, Scrophularia lucida and S.robusta due to their trace amounts.

Russelia showed more affinity with Scrophularia in possessing 6-oxygenated flavones. Nevertheless Scrophularia, decomposita contained only 6-deoxyflavones; thereby is chemically similar to Penstemon. (P. gloxinoides). Scrophularia polyantha was characterized by the presence of both 6-deoxy and 6-oxygenated flavones. Though both Russelia equisetiformis and S. koetzi were similar in having 6-substituted flavones, the presence of quinones and iridoids in the former demarcated this plant from the latter.

#### Subfamily Rhinanthoideae

In subfamily Rhinanthoideae, 6-deoxyflavones, saponins, iridoids and benzoic acids were predominant. 6-oxyflavones, cinnamic acids, alkaloids, glycoflavones, proanthocyanidins and quinones were rare. Thirtytwo plants distributed within the tribes Digitaleae (22), Gerardieae (5) and Euphrasiaeae (5) were studied in this subfamily. Flavonoids were identified in 29 plants of which 27 plants contained 6-deoxyflavones. In three plants of the tribe Digitaleae viz. Digitalis lanata, Veronica serpyllifolia and V. spicata, flavonoids were replaced by quinones. In V. campylopoda and Euphrasia laxa flavonoids were not identified due to their trace amounts. Only four plants possessed 6-substituted flavones and a single plant Scoparia dulcis contained glycoflavone. The plants with 6-substituted flavones and glycoflavones were confined to the tribe Digitaleae. Apart from Veronica spicata (tribe Digitaleae) all the plants of this subfamily were devoid of proanthocyanidins. Tests for tannins,

saponins and alkaloids could be conducted in only 16 plants (due to the non-availability of plant materials) of which 11 plants showed saponins, four had alkaloids and none had tannins. Iridoids were tested in 17 plants among which 11 plants were observed to have these compounds. The subfamily was rich in benzoic acids but was poor in cinnamic acids.

The presence of 6-substituted flavones, glycoflavones, quinones and proanthocyanidins keep the tribe Digitaleae distinct from the Gerardieae and Euphrasieae. Convincing characters were not observed to demarcate the tribes Gerardieae and Euphrasieae.

#### Tribe Digitaleae

Hemiphragma (1), Mecardonia (1), Scoparia(1), Digitalis(2), Picrorhiza(1), and Veronica (16) were the genera studied in this tribe. The first three genera belong to the subtribe Sibthorpieae, Digitalis in Eudigitaleae and the remaining two in Veroniceae. Of the 22 plants studied, 18 plants contained 6-deoxyflavones and in four plants, they were accompanied by 6-oxygenated flavones. 14 plants were screened for tannins, saponins, iridoids and alkaloids of which saponins were spotted in 10 plants, iridoids in seven and alkaloids in two.

The presence of iridoids demarcate the subtribe Veroniceae. Both subtribe Veroniceae and Sibthorpieae contain 6-substituted flavones. The absence of iridoids, 6-oxygenation in flavones, glycoflavones and abundance of saponins distinguished subtribe Eudigitaleae.

Subtribe Sibthorpieae

Of the three genera analysed, Mecardonia (M.procumbens) possessed only 6-deoxy flavones. Both Hemiphragma (H.heterophyllum) and Scoparia (S.dulcis) contained 6-oxyflavones alongwith 6-deoxy flavones. Glycoflavones and alkaloids were seen in Scoparia belonging to this subtribe.

Subtribe Eudigitaleae

This subtribe was represented by two species of Digitalis (D.lanata and D.purpurea) only. Both the plants were rich in saponins as well as cinnamic acids and were devoid of iridoids and alkaloids. These two species were distinct in flavonoid chemistry. Apigenin, 7'-OMe apigenin, 7,4'-diOMe apigenin were noticed in D.purpurea whereas flavonoids were replaced by quinones in D.lanata.

Subtribe Veroniceae

Picrorhiza (1) and Veronica (16) were the genera studied in this subtribe. Both these genera resembled in their flavonoids and phenolic acids. Picrorhiza (P.kurrooa) contained acacetin and 3'-OMe luteolin, the flavones which were common in the species of Veronica. Of the 16 spp. of Veronica screened, 13 contained 6-deoxy flavones and in two plants (V.biloba and V.persica) they were accompanied by 6-substituted flavones. Proanthocyanidins were seen only in V.spicata. In V.serpyllifolia and V.spicata the flavonoids were replaced by quinones. Of the 11 plants

analysed for tannins, saponins, iridoids and alkaloids none contained tannins. Saponins were observed in seven plants and an equal number showed iridoids. Only in V.laxa alkaloids were observed. Picrorhiza was not tested for tannins, saponins, iridoids and alkaloids. Cinnamic acids were poorly represented within the subtribe.

On the basis of the iridoid content the species of Veronica can be grouped into two. The first group consisting of V.agrestis, V.arvensis, V.biloba, V.laxa, V.melissaefolia, V.persica and V.spicata possessed iridoids and the second group which is devoid of iridoids include V.anagallis-aquatica, V.beccabunga, V.oxycarpa and V.salina. Iridoids were not tested in other plants. In the former group V.biloba and V.persica were distinct for having 6-substituted flavones in them. Flavonoids couldn't be identified in V.campylopoda due to their trace amounts.

#### Tribes Gerardieae and Euphrasiaeae

The members belonging to these tribes were very similar in their chemical constitution and therefore a line of demarcation could not be drawn. These two tribes were rich in 6-deoxyflavones and iridoids. Of the ten plants belonging to Buchnera (1), Striga (3), (Tribe Gerardieae, subtribe-Buchneraeae), Sopubia (Tribe-Gerardieae, subtribe-Eugerardieae), Euphrasia(1) and Pedicularis (4) (Tribe-Euphrasiaeae) analysed, all the plants except Euphrasia laxa contained 6-deoxyflavones. 6-Substituted

flavones, glycoflavones, proanthocyanidins and quinones were not located in any of these plants. Species of Buchnera, Striga, Sopubia and Euphrasia were tested for iridoids and all gave a positive result. Alkaloids were spotted in Striga densiflora and Euphrasia laxa. The various species analysed possessed different assortment of chemical characters useful for their identification.

#### PEDALIACEAE

Martynia annua and Pedaliium murex were the plants studied in this family. Both the plants contained only flavones and were devoid of proanthocyanidins, quinones, iridoids and alkaloids. A glycoflavone vitexin was seen alongwith apigenin and acacetin in Martynia annua, whereas in Pedaliium murex only apigenin, acacetin and luteolin were observed. Saponins were noticed in Martynia annua. p-OH Benzoic, vanillic, gentisic, melilotic and ferulic acids were the phenolic acids, seen in Martynia annua. p-OH Benzoic and ferulic acid were lacking in Pedaliium murex which contained protocatechuic, p-coumaric and o-coumaric acid additionally.

#### OROBANCHACEAE

Only two species of Orobanche (O.alba and O.cernua) were studied from this family. Both plants contained tannins and were devoid of saponins, iridoids and alkaloids. O.alba contained a simple flavone, acacetin, while in O.cernua flavonoids were replaced by quinones. Moreover, proanthocyanidins were

seen in the latter plant. Protocatechuic, vanillic, gentisic, melilotic, and ferulic acids were the phenolic acids observed in the family. However, O.cernua was devoid of protocatechuic acid.

#### GESNERIACEAE

Didymocarpus pygmaea was the sole representative studied in this family. This plant possessed a single flavonoid vitexin, a glycoflavone. It also contained iridoids, but was devoid of saponins, tannins and alkaloids. p-OH Benzoic, protocatechuic and vanillic acids were the phenolic acids noticed in the plant.

#### LENTIBULARIACEAE

Three species of Utricularia viz. U.aurea, U.inflexa var stellaris and U.sp. were studied in this family. The plants were devoid of the flavonoid system. In U.inflexa var stellaris quinones were observed. The plants were devoid of proanthocyanidins, tannins and saponins. Iridoids and alkaloids were located in the family, p-OH Benzoic, protocatechuic, vanillic, gentisic, melilotic, ortho coumaric and ferulic acids were the phenolic acids observed in these plants.

#### SOLANACEAE

Twenty two plants distributed within the subfamilies Solanoideae and Cestroideae were studied. Of the various genera, Capsicum (1), Lycopersicon (1), Physalis (1), Solanum (7), Withania (2) (of tribe Solaneae), Lycium (1) (tribe Atropeae),

Datura (2), Hyoscyamus (1) (tribe Hyoscyameae) belonged to the subfamily Solanoideae, and Cestrum (2), Nicotiana (1) (tribe Cestrineae), Brunfelsia (2) and Petunia (1) (tribe Salpiglossideae) belonged to the subfamily Cestroideae. In the family Solanaceae, flavonols formed the major flavonoid pigment, for these compounds were observed in 17 plants. Apart from Capsicum annuum which contained apigenin, the family was also devoid of glycoflavones. The family was also devoid of glycoflavones and proanthocyanidins. Flavonoids were not observed in Lycium barbarum and could not be identified in Lycopersicon lycopersicum, Solanum nigrum and Brunfelsia bicolor.

Kaempferol, 4'-OMe kaempferol, 7-OMe kaempferol, 7,4'-diOMe kaempferol, quercetin, 3'-OMe quercetin, 4'-OMe quercetin and 3',4'-diOMe quercetin were the flavonols identified in these plants. The incidence of quercetin and its derivatives were more in the subfamily Solanoideae than in the subfamily Cestroideae.. Within Cestroideae these compounds were noticed only in Nicotiana tabacum and Petunia hybrida. Apart from this difference, both the subfamilies were similar in their flavonoid chemistry. All the tribes were indistinguishable from each other in their flavonoids.

Invariably, all the plants contained saponins, and alkaloids were noticed in 16 plants. The family was devoid of tannins and iridoids.

p-OH Benzoic, protocatechuic, vanillic, syringic gentisic, melilotic, p-coumaric, o-coumaric and ferulic acids were the phenolic acids observed in the family of which vanillic acid was ubiquitous. Cinnamic acids and protocatechuic acids were seen only in the tribes Solaneae and Salpiglossideae.

#### DISCUSSION

A. Based on a priori weighting of chemical characters in the family Scrophulariaceae

The uniform presence of flavones and the predominance of 6-oxygenated flavones characterize the Scrophulariaceae. The high incidence of saponins and benzoic acids are other features which bind the members of this family together. The rarity of glycoflavones, proanthocyanidins, quinones, alkaloids and tannins are some other common features observed among the various taxa of the Scrophulariaceae.

When the chemical characters have been primarily used to delimit the groups within the Scrophulariaceae, the family tends

to separate into two major groups; one with iridoids and other without them (Table XII). The first group consists of the genera Kickxia, Stemodia, Veronica, Russelia, Angelonia, Dopatrium, Schweinfurthia, Lindenbergia, Limnophila (L.indica), Verbascum, Mazus, Buchnera, Striga, Sopubia, Euphrasia, Pedicularis, Antirrhinum and Linaria. This group comprises almost all the members of the subfamily Rhinanthoideae and a number of plants of Antirrhinoideae. The second group contains the remaining genera i.e. Maurandya, Scrophularia, Lindernia, Bacopa, Glossostigma, Digitalis, Mecardonia, Veronica, Verbascum, Torenia and Limnophila (L.aromatica), mostly from the Antirrhinoideae.

Within the first group further classification is done based on the distribution of 6-oxygenation in flavones. The first sub-group contain predominantly the members of the sub-family Antirrhinoideae while the second group incorporate mostly the members of Rhinanthoideae. In the first subgroup Kickxia, Stemodia, and Veronica (V.biloba and V.persica) form one group (IA ai), Russelia, Stemodia, and Angelonia form the second group (IA aii) and Lindenbergia (L.muraria) and Limnophila (L.indica) form the third group (IA bii). Dopatrium and Schweinfurthia were placed alone in separate groups. Similarly in the second subgroup Verbascum (V.thapsus), Mazus, Veronica, Buchnera, Striga, Sopubia, Euphrasia and Pedicularis are placed

Table XII

CLASSIFICATION OF THE SCROPHULARIACEAE BASED ON A PRIORI WEIGHTING OF CHEMICAL CHARACTERS

The family is characterized by the uniform presence of flavones, predominance of 6-oxygenated flavones, iridoids, saponins and benzoic acids.

CLASSIFICATION BASED ON IRIDOIDS

Total number of plants screened for iridoids - 46

Number of plants with iridoids

Pseudosolaneae - 1

Antirrhinoideae - 12

Rhinanthoideae - 15

I. PRESENCE OF IRIDOIDS

IA. Iridoids with 6-oxygenated compounds

IA(a) Iridoids and 6-oxygenated compounds IA(a)(i) Iridoids and 6-oxygenated compounds with rare occurrence of glycoflavones  
flavonols, quinones and proanthocyanidins.

Kickxia (Antirrhineae)  
Stemodia (Gratiolaeae)  
Veronica biloba &  
V. persica (Digitalaeae)

ii) Iridoids, 6-oxygenated flavones, quinones and proanthocyanidins.

Russelia (Cheloneae)  
Stemodia (Gratiolaeae)  
Anselonia (Hemimerideae)

iii) Iridoids, 6-oxyflavones, flavonols, quinones and proanthocyanidins.

Dopatrium (Gratiolaeae)

Table XII (Contd.)

IA(b)	Iridoids with 6-oxy- and 6-deoxygenated compounds with rare occurrence of glycoflavones, quinones and proanthocyanidins.	IA(b) i)	Iridoids with only 6-oxy and 6-deoxy compounds	<u>Schweinfurthia</u> (Antirrhineae)
		ii)	Iridoids, 6-oxy, 6-deoxy and glycoflavones, rare occurrence of quinones and proanthocyanidins.	<u>Lindenbergia muraria</u> (Gratiolaceae) <u>Limmophila indica</u> (Gratiolaceae)
IB.	<u>Iridoids without 6-oxygenated flavones</u> Rarely with glycoflavones, proanthocyanidins and quinones.	IB(i)	Iridoids with only 6-deoxy flavones	<u>Verbascum thapsus</u> (Verbasceae) <u>Mazus</u> (Gratiolaceae) <u>Veronica</u> (Digitaleae) <u>Buchnera</u> (Gerardiaceae) <u>Striga</u> (Gerardiaceae) <u>Sopubia</u> (Gerardiaceae) <u>Euphrasia</u> (Euphrasieae) <u>Pedicularis</u> (Euphrasieae)
		ii)	Iridoids with 6-deoxyflavones, rarely with glycoflavones, quinones and proanthocyanidins	<u>Antirrhinum</u> (Antirrhineae) <u>Linaria</u> (Antirrhineae) <u>Veronica spicata</u> (Digitaleae)

Except for the 2 species of Veronica the whole group belongs to the subfamily Antirrhinoideae.

Table XII (Contd.)

II.	<u>ABSENCE OF IRIDIODS</u>			
IIA.	With 6-deoxyflavones rarely with glycoflavones, proanthocyanidins and quinones	IIA(i)	6-deoxyflavones with rare occurrence of quinones	<u>Maurandya</u> (Antirrhineae) <u>Scrophularia</u> (Cheloneae) <u>Lindernia</u> (Gratiolaeae) <u>Bacopa</u> (Gratiolaeae) <u>Glossostigma</u> (Gratiolaeae) <u>Digitalis</u> (Digitaleae) <u>Mecardonia</u> (Digitaleae) <u>Veronica</u> (Digitaleae) <u>Verbascum chinensis</u> (Verbasceae) <u>Lindernia</u> (Gratiolaeae) <u>Torenia</u> (Gratiolaeae)
		ii)	6-deoxy and glycoflavones with rare occurrence of quinones and proanthocyanidins	
IIB.	With 6-oxygenated and 6-deoxyflavones			<u>Limnophila aromatica</u> (Gratiolaeae)

in one group (IB i) where as Antirrhinum, Linaria and Veronica (V.spicata) are grouped separately.

The second group contains most of the members of tribe Gratioleae screened and a few members of tribes, Antirrhineae, Cheloneae, Digitaleae and Verbasceae.

These chemical groups are not in total conformity with morphological groups existing. It is significant to note that most of the genera screened here are chemically natural. However, chemical differences do help in their discrimination or identification in the vegetative state, which also is a major contribution.

Though the major chemical trends within the family have been visualized here, an ultimate classificatory system based on chemical characters alone is not advisable any time. Since a very small fraction of the Scrophulariaceae has been screened here, the chemical data procured from the present work in conjunction with data collected from other diverse disciplines are analysed for a proper taxonomic assessment at all levels of hierarchy. During this process all the taxonomic categories within the family have been critically evaluated for their validity, circumscription and subdivisions.

B. Review of the existing classification of the Scrophulariaceae in the light of chemical data

Of the three subfamilies of the Scrophulariaceae viz. the Pseudosolaneae (Verbascoideae), Antirrhinoideae (Scrophularioideae) and Rhinanthoideae (Bentham and Hooker, 1876) only the Rhinanthoideae exhibits their separate chemical identity. Thus the subfamily Rhinanthoideae is distinct by the dominance of 6-deoxyflavones and iridoids. Apart from a single occurrence in Scoparia, the subfamily is free of glycoflavones. Similarly, proanthocyanidins are spotted only in Veronica spicata. Moreover, the Rhinanthoideae are further characterized by the poor incidence of 6-substituted flavones, alkaloids, quinones and cinnamic acids.

The tribe Digitaleae of the subfamily Rhinanthoideae in containing 6-oxygenated flavones, glycoflavones, proanthocyanidins and quinones as well as in the rarity of iridoids is dissimilar to the tribes of the Rhinanthoideae. In containing these chemical features this tribe is very similar to the Antirrhinoideae. Therefore, the removal of Digitaleae from the Rhinanthoideae and inclusion in Antirrhinoideae (Scrophularioideae) as once proposed by Schmid (1906) and Bellini (1907) will result in the formulation of more homogenous Antirrhinoideae and Rhinanthoideae.

The subfamilies Pseudosolaneae and Antirrhinoideae are similar in many respects. Both these subfamilies contain 6-oxygenated flavones, glycoflavones, proanthocyanidins, alkaloids

and cinnamic acids. Iridoids are poorly represented in these taxa. The overwhelming similarities between these subfamilies evidently are in favour of the merger of them as one, the subfamily Antirrhinoideae, as proposed by Pennell (1935). This merger is supported by the similarities in their wood anatomy (Arati and Datta, 1977).

Though the subfamily Antirrhinoideae contains advanced chemical characters like 6-oxygenation of the flavones, the apparent higher incidence of primitive characters such as glycoflavones, proanthocyanidins, quinones and alkaloids added with infrequent distribution of iridoids and presence of flavonols (in Dopatrium junceum) mark this subfamily as primitive. The absence of most of the above primitive characters, place the Rhinanthoideae as an advanced or 'derived group'. The parasitic mode of habitat and elaborate zygomorphy of the corolla of the two tribes Gerardieae and Euphrasieae corroborate the placement of the subfamily at a higher level in the evolutionary ladder.

Within the subfamilies the different tribes are characterized by the various assortment of chemical characters.

Subfamily Antirrhinoideae (Scrophularioideae)

Within the subfamily Antirrhinoideae (Scrophularioideae), the tribe Gratioleae is distinct from the other tribes in

possessing higher incidence of 6-deoxyflavones, glycoflavones, saponins and quinones as well as in the rarity of iridoids, alkaloids and cinnamic acids. Moreover, the detection of a flavonol, quercetin from Dopatrium, is a character which was not seen anywhere else in the family. In contrast to this, the tribe Antirrhineae shows a predominance of 6-oxygenated flavones, iridoids and alkaloids. This tribe is also characterized by the poor incidence of glycoflavones, quinones, saponins and proanthocyanidins. The tribe cheloneae, though contain 6-oxygenated flavones, is characterized by the absence of glycoflavones, proanthocyanidins and alkaloids. In addition, the rarity of saponins, iridoids and quinones are other distinguishing characters. Since the tribes Hemimerideae and Manuleae are represented by only single plants the chemical identities of these tribes cannot be decisively established at this juncture. However Angelonia salicariaefolia (tribe Hemimerideae) shows chemical similarities with the tribe Antirrhineae and Sutera dissecta (tribe Manuleae) with the Gratiolleae.

#### Tribe Gratiolleae

Apart for the subtribe Vandelleae, wherein the species of Lindernia and Torenia show chemical similarity, the subtribal classification of the tribe does not get any chemical support. But the plants are categorized into two major groups on the basis of their iridoid content. Thus, Mazus, Limnophila,

Lindenbergia, Stemodia and Dopatrium form one group possessing iridoids in them. The genera Bacopa, Lindernia, Torenia and Glossostigma, which are devoid of iridoids, form the second group. The latter group is homogenous, for, all the plants contain 6-deoxyflavones and are devoid of 6-oxygenated flavones. Flavones are 6-oxygenated in most of the plants of the former group, Mazus being the exception (Mazus has only 6-deoxy flavones).

The genus Dopatrium stands out from the rest of the members of the Gratiolaceae (even of the family) in its chemical, morphological and cytological characters. Apart from the presence of the flavone 6-OH luteolin, the plant contains a flavonol quercetin which is very rarely seen in the family (Quercetin is reported from Lindernia section Lindernia, Diaz, 1977). Other compounds present in this plant are quinones and proanthocyanidins. The plant shows advanced floral vasculature and has five sepal traces against the general trend of ten. In contrast to other species of the tribe, the staminodes in Dopatrium are in the position of postero-lateral stamen. The ovary is unilocular with parietal placentation. In situ germination of pollen grains is another distinguishing feature met within Dopatrium (Varghese 1967, 1971). These characters clearly warrant a separate identity to the genus Dopatrium.

The genus Mazus ( of the former group) is distinguished chemically by its 6-deoxyflavones and the absence of 6-oxygenated flavones, glycoflavones, proanthocyanidins, quinones,

saponins and alkaloids. The chemical identity of the two species viz. M. delavayii and M. pumilus is well evident. Limnophila is characterized by the presence of all the three types of flavones (6-deoxy, 6-substituted and C-glycosidic flavones) and quinones. Proanthocyanidins and alkaloids are absent from this genus. The three species of Limnophila (L. heterophylla, L. indica, and L. aromatica) possesses characteristic chemical features to mark their separate identity. Being free of the flavonoid pigment, L. heterophylla stands out as the most advanced species within the tribe. L. indica is the primitive of the three species. Since the flavonoids in L. repens are not identified, its position is not certain in the evolutionary sequence. Lindenbergia is similar to Limnophila in its flavonoid content. However, the absence of quinones and presence of alkaloids in Lindenbergia differentiate this genus from Limnophila. The presence of 6-oxygenated flavone in L. muraria keeps it advanced over L. indica which contain only apigenin. Species of stemodia have uniform presence of 6-oxygenated flavones and alkaloids. S. viscosa is distinct from S. serrata in containing quinones.

The second group of genera in the tribe Gratioleae can be further subdivided into two, on the basis of the presence of absence of glycoflavones. Thus Lindernia and Torenia are grouped together in possessing glycoflavones. Glossostigma and Bacopa are devoid of glycoflavones and

thus form another subgroup.

Though the two genera Lindernia and Torenia are similar in their flavonoid chemistry and in containing quinones, the latter genus is distinguished by their proanthocyanidins and thus the merger of Torenia (in part/ in toto to Lindernia suggested by many authors (Philcox, 1968) does not gain any chemical support. The combination of apigenin and luteolin which cited as characteristic of Torenia (Diaz, 1977) is seen in Lindernia also, and therefore the separation of these two genera on the basis of flavones alone is no longer valid. However, Lindernia crustaceae possesses characters like the presence of proanthocyanidin and ferulic acid which are absent in other species of Lindernia but present in Torenia. This plant is similar to Torenia in its seed characters (Thieret, 1967).

The various species of Lindernia possess characters defending their chemical identities as also the different species of Torenia. Bacopa and Glossostigma are similar in their flavonoid chemistry, but the latter genus is different from the former in not containing cinnamic acids.

The first group of genera mentioned, comprises the plants included in three subtribes viz. Mimuleae, Stemodieae and Herpestideae (in part). Bacopa belonging to the subtribes Herpestideae is included in the second group along with the plants of subtribe Vandelleae and Limoselleae. In their

chemical characters, the former group obviously is advanced over the latter group. Limnophila, in which the flavonoid system is lost, is the termination of the line of evolution in the first group. Dopatrium occupies the basal position with Mazus, Lindenbergia and Stemodia as the intermediate genera. In the second group, Torenia and Lindernia form the basal group from which Bacopa is evolved through Glossostigma.

#### Tribe Antirrhineae

The predominance of 6-oxygenated flavones, iridoids and alkaloids is the characteristic feature of this tribe. Furthermore, the presence of the iridoid antirrhinoside which is often accompanied by antirrhinum glycoside B, asarina glycoside and harpagide (Kooiman, 1970, D'ohot, 1972) help to demarcate this tribe within the subfamily. The low incidence of glycoflavones, quinones, proanthocyanidins and saponins are other characters observed in the tribe Antirrhineae.

Maurandya stands out from the rest of the genera of this tribe in not producing iridoid compounds. But the absence of 6-oxygenated flavones keeps this genus closer to Antirrhinum and Linaria. Antirrhinum is different from both Linaria and Maurandya in possessing C-glycosides and quinones. Linaria possesses proanthocyanidins and thus exhibits its own identity. Though both Antirrhinum and Linaria are kept in the same subtribe Linarineae (Rothmaler, 1954) the two genera are

distinct in their flavonoids, quinones alkaloids (Harkiss, 1972), cytology seed coat character and in pollen morphology (Elisens and Tomb, 1983, Elisens, 1986). The differences existing between these two genera are summarized in table XIII.

Table XIII

COMPARISON OF THE GENERA ANTIRRHINUM AND LINARIA

Sr. No.	Characters	<u>Antirrhinum</u>	<u>Linaria</u>
1.	Flavones	Luteolin, 3', 4'-diOMe luteolin	7, 3', 4'-tri OMe luteolin, eriodictyol glycoside, Scutellarein monomethyl ether Pectolinarin Unranin Linarin
2.	Glycoflavones	Vitexin	absent
3.	Proanthocyanidins	absent	present
4.	Quinones	present	absent
5.	Iridoids	Antirrhinum-glycoside Antirrhinum glycoside B Asarina glycoside	Antirrhinum glycoside Antirrhium glycoside B
6.	Alkaloids	Bases (unidentified)	Peganine
7.	Seed coat	Cristate and medusiform	Tuberculate irregular cristate
8.	Pollen morphology	Fusiform, syncolpate or Apocolpate Microreticulate	Narrowly oblong, Apocolpate Microreticulate
9.	Chromosome Number(n)	8	6

Such magnitude of differences evidently warrant placing these two genera in separate subtribes.

Kickxia and Schweinfurthia are alike in having 6-substituted flavones. Nevertheless Schweinfurthia is distinct in containing 6-deoxyflavones, alkaloids and saponins which are absent in the other genus.

The chemical dissimilarities observed between Kickxia and Linaria are reflected in their cytology also. The former plant possess a basic chromosome number 9 and latter 6 (Vij and Kashyap, 1976; Elisens and Tomb, 1983). In seed morphology though both the genera are categorised under miscellaneous, Kickxia show irregular low cristae as against tuberculate or apiculate tuberculae of Linaria (Elisens and Tomb, 1983). These characters corroborate the distinct identities of these two genera.

Within the tribe Antirrhineae, Maurandya with their simple flavones (6-deoxyflavones) and absence of iridoids is the most primitive taxon. Kickxia occupies the highest position in an evolutionary sequence with Antirrhinum, Linaria and Schweinfurthia positioned in between.

#### Tribe Cheloneae

This tribe is characterized by the poor incidence of 6-oxygenated flavones, variety of iridoids and quinones as well

as by the absence of glycoflavones, proanthocyanidins and alkaloids.

The genus Penstemon is distinct from Russelia and Scrophularia in possessing only 6-deoxyflavones and thereby occupies the lower most level in an evolutionary sequence. Though both Russelia and Scrophularia possess 6-substituted flavones the presence of iridoids differentiates Russelia from Scrophularia which does not contain them. The presence of iridoids keep Russelia as the highly evolved genus. Scrophularia obviously is the intermediate taxon. Each species of Scrophularia are distinguished by its chemical constitution.

Within the Cheloneae, only Russelia showed the presence of quinones, iridoids and caffeic acid. By virtue of these characters and also in containing densely packed long hairs within the loculicidal capsule which occurs nowhere else in the Scrophulariaceae, this taxon warrants a separate tribal status Russelieae as proposed by Thieret (1967).

#### Tribes Aptosimeae and Verbasceae

The tribe Aptosimeae which is represented by Anticharis senegalensis is characterized by the presence of 6-deoxygenated flavones and absence of cinnamic acid, whereas the Verbasceae represented by the species of Verbascum is distinguished by the presence of 6-deoxygenated flavones, glycoflavones and iridoids. Furthermore, the absence of quinones, proanthocyanidins and

alkaloids characterize the latter tribe. This significantly credit the advanced nature of the tribe verbasceae over Aptosimeae.

#### Tribe Digitaleae

Since the shifting of tribe Digitaleae from the subfamily Rhinanthoideae to the subfamily Antirrhinoideae makes the former group more homogenous (as proposed earlier) this tribe is treated here under the subfamily Scrophularioideae.

This tribe exhibits a number of chemical similarities with the tribe Gratioleae such as the higher incidence of 6-deoxyflavones and saponins as well as by the rarity of 6-substituted flavones and iridoids. As observed, the chemical traits clearly delineates the three subtribes analysed viz. the Sibthorpieae, Eudigitaleae and Veroniceae.

#### Subtribe Sibthorpieae

The presence of 6-oxygenated flavones and the absence of iridoids characterize this subtribe from the other two subtribes. However, within the subtribe, Mecardonia is different from other members due to the lack of 6-oxygenated flavones. The observation of glycoflavones clearly demarcate Scoparia from Hemiphragma. Moreover the genus Scoparia is distinct within this subtribe for having gentisic and 2-OH,6-OMe benzoic acids. Chemically Hemiphragma appears to be the most evolved within

the subtribe with Scoparia as the most primitive.

#### Subtribe Eudigitaleae

Being rich in anthraquinones, saponins and cinnamic acids this subtribe apparently is distinct from other subtribes. The absence of 6-substituted flavones and iridoids are other distinguishing characters. Within the subtribe Eudigitaleae, the two species of Digitalis viz. D. purpurea and D. Lanata exhibit chemical distinctiveness.

#### Subtribe Veroniceae

In addition to their 6-oxygenated flavones, the presence of iridoids separates the subtribe Veroniceae from the subtribe Sibthorpieae and Eudigitaleae. The genera Picrorhiza and Veronica are similar in their flavonoid chemistry. The species of Veronica can be allied into two groups based on the presence of iridoids. Thus V. agrestis, V. arvensis, V. biloba, V. laxa, V. melissaefolia, V. persica and V. spicata form the first group with iridoids and the second group which is devoid of iridoids consists of V. anagallis-aquatica, V. beccabunga, V. oxycarpa and V. salina. In the former group V. biloba and V. persica are highly evolved for the bounty presence of 6-oxygenated flavones. V. spicata is the primitive taxon because of the presence of proanthocyanidins and quinones as well as by the absence of 6-substituted flavones. Furthermore the plant is reported to

6-oxygenated flavones, C-glycosidic flavones, proanthocyanidins and quinones. This is further corroborated by their wood anatomical (Arati and Dutta, 1977) and pollen morphological (Dutta and Chanda, 1979) studies. However Kooiman (1970) treats this subfamily as the most primitive group within the family Scrophulariaceae because of the infrequent presence of iridoids observed within the members of this tribe, a view held by Pennell (1935), Melchior (1964), Thieret (1967) and others, based on the floral and other exomorphological characters. Therefore, the tribe Gratioleae can be placed as the most primitive tribe within the Scrophularioideae. The frequent presence of 6-oxygenated flavones and iridoids in the tribe Antirrhineae warrant this tribe as the climax group within the Antirrhinoideae. This view is further strengthened by the iridoid analysis (Kooiman, 1970), wood anatomy (Arati and Datta, 1977) and the advanced morphological characters such as the varying forms of transverse capsule ruptures, diverse seed shapes and elaborate corolla modifications (Pennell, 1935). The tribes Manuleae, Aptosimeae, Digitaleae; Verbasceae, Cheloneae and Hemimerideae in the sequence presented, can be arranged in an ascending series between the Gratioleae and the Antirrhineae.

#### Comments on the Controversial Genera within the Antirrhinoideae

Lindenbergia, the affinity of which to Rhinanthoideae and Antirrhineae is debated, shows more chemical similarities to the other members of the tribe Gratioleae in having the combination

of 6-deoxy, 6-oxy and C-glycosidic flavones. Thus the plant can be very well reinstated in the tribe Gratioleae itself. This view gains support by the critical study of this genus by Prijante (1969) and the vascular trace studies by Varghese (1971).

The genus Scoparia shows a lucid chemical affinity with the members of gratioleae. The characteristic combination of 6-deoxy, 6-substituted and glycoflavones which is confined to the tribe gratioleae is seen in Scoparia too. Therefore the logical position of Scoparia seems to be in the tribe Gratiolaeae. So the shifting of this genus from the tribe Digitaleae and to the Gratiolaeae as done by Pennell (1935) is supported on chemical evidences.

A similar situation is seen in the case of the genus Sutera of the tribe Manuleae. The chemical affinity the plant exhibited with the members of the tribe Gratiolaeae in having 6-deoxy-flavones and glycoflavones is in favour of its transfer to the latter tribe, as practised by Pennell (1935). Anatomical studies further strengthen this view (Arati and Datta, 1977).

The grouping of Verbascum along with Scrophularia as suggested by Bachmann (1882), Schmid (1906), Hartl (1959) and Thieret (1967) finds no chemical support. Verbascum is devoid of 6-oxygenated flavones, is characterized by the presence of glycoflavones and iridoids. Scrophularia by contrast is

distinguished by the presence of 6-oxygenated flavones as well as by the absence of glycoflavones and iridoids. This obviously justify their placing in the two separate tribes viz. Verbasceae and Cheloneae.

#### Subfamily Rhinanthoideae

With the transfer of the tribe Digitalaeae, the number of tribes screened in this subfamily is reduced to two; tribe Gerardieae and Euphrasieae. These two tribes are almost indistinguishable chemically.

#### Tribes Gerardieae and Euphrasieae

The uniform presence of simple (6-deoxy) flavones, the predominance of iridoids as well as the absence of 6-oxygenated flavones, glycoflavones, proanthocyanidins and quinones characterize the two tribes. The various species and the genera are distinguishable chemically.

Although these plants possess a number of advanced chemical traits (like the predominance of iridoids, absence of glycoflavones, proanthocyanidins and quinones), the absence of 6-oxygenated flavones and presence of alkaloids are some of the primitive features retained by them.

The elevation of the tribe Euphrasieae as the apogee of the family Scrophulariaceae on the basis of its floral anatomy and parasitic mode of habitat (Pennell, 1935) needs a rethinking

in the light of chemical evidences. The reported occurrence of the primitive chemical features like flavonols and tannins from the Spp. of Euphrasia and Pedicularis (Krolikovska, 1967; Karimova, 1974; Potter, 1897; Harkiss and Tammins, 1973) relates this tribe to a primitive position. On the other hand it may be explained that these plants though advanced in floral character and having parasitic mode of habit retained the tannins and flavonols as the defense mechanisms against microbes and insects. The parasitic mode of habit might have necessitated the production of these compounds which function as phytoalexins and antimicrobial agents. If it is accepted that this tribe is evolved from other members of scrophulariaceae containing flavones, the reappearance of these characters may be considered highly advanced. Whatever be the case, the presence of these compounds strongly suggests that the tannin rich Orobanchaceae has evolved from these taxa. The presence of alkaloids in both the Orobanchaceae and Euphrasieae further strengthen this view.

The probable evolutionary trends within the family is shown graphically in figure I.

#### PEDALIACEAE

The prevalence of 6-deoxyflavones and the higher incidence of benzoic acids are the features of this family. In these respects the family Pedaliaceae is similar to the Scrophulariaceae. Furthermore the report of Pedalin (a 6-oxygenated flavone) from Sesamum indicum and iridoids from Harpagophytum procumbens

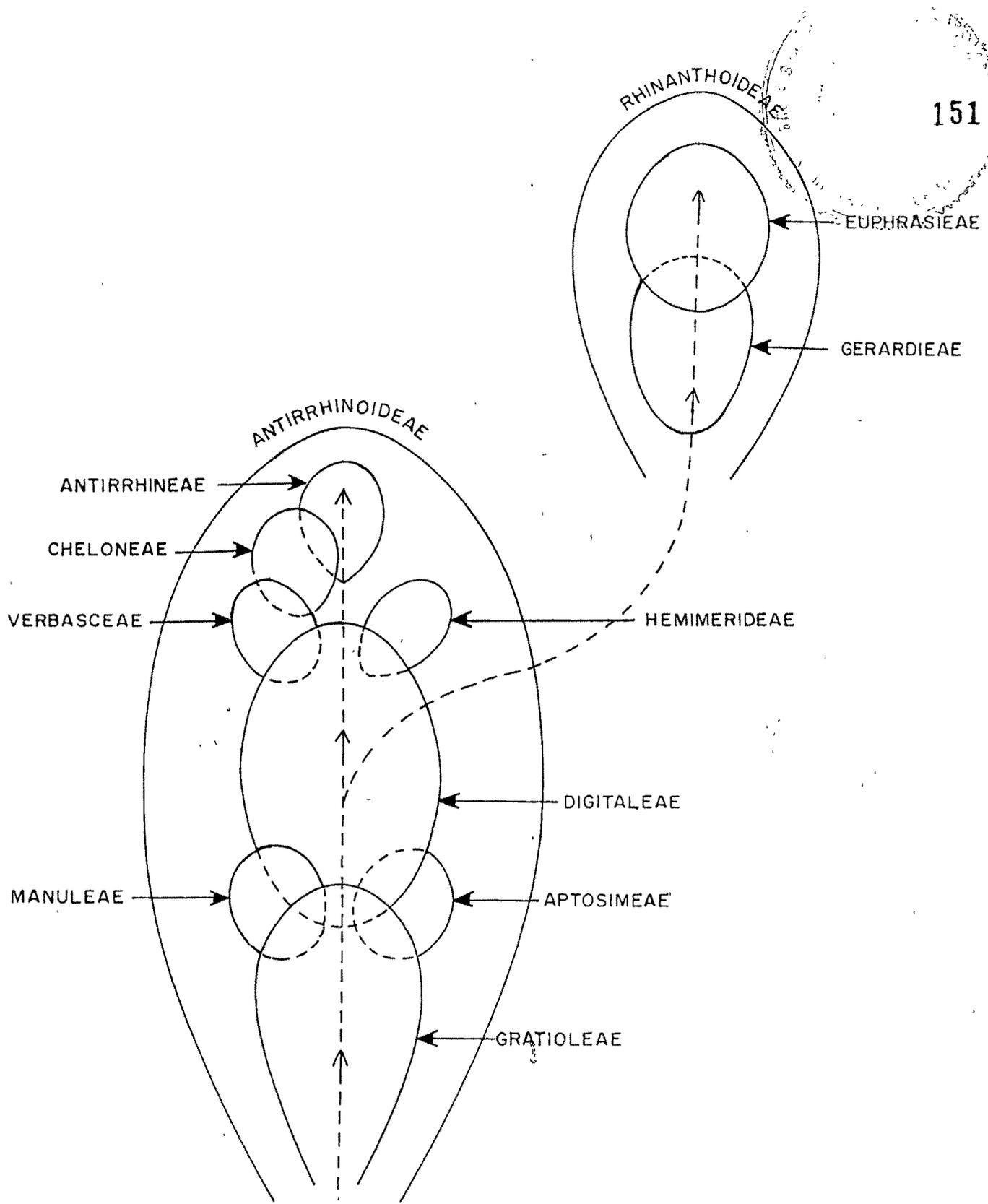


FIG. 1 PROBABLE EVOLUTIONARY TRENDS WITHIN THE SCROPHULARIACEAE

(Krishnaswamy, et al. 1970; Kikuchi, et al. 1983) brings these two families still closer. The Pedaliaceae resemble the Scrophulariaceae in morphological characters too except for the specialized mucilaginous trichomes which make the herbage somewhat slimy. The close relationship between the two families is further strengthened by their embryological similarities (Kulkarni, 1968).

The Martyni<sup>n</sup>aceae which are separated from Pedaliaceae of which a single species Martynia annua is screened in the present study, are distinct from the latter in having glycoflavones, saponins and phenolic acids such as p-OH benzoic acid and ferulic acid. Differences in phenolic acids between these two taxa are observed by Das, et al. (1966). These differences are corroborated by the evidences from epidermal structures and stomatal ontogeny (Inamdar, 1969). The creation of the family Martyniaceae though chemically valid, when the taxa screened are considered, data on the remaining members viz. Cramiolaria and Proboscidea are to be sought to arrive at a final taxonomic judgement.

#### OROBANCHACEAE

The presence of proanthocyanidins and tannins coupled with the absence of iridoids demarcate the family Orobanchaceae from the rest of the families studied. In containing tannins and 6-deoxy flavones this family shows close similarities with the tribe Euphrasieae, the parasitic tribe of the Scrophulariaceae. This indicate the possible origin of this family

from the parasitic members of the scrophulariaceae. The relation is corroborated by the embryological (Nagendran, et al. 1980) as well as by the morphological and physiological studies. (Heinricher, 1897). The nearly complete continuity of morphological characters from the scrophulariaceae to Orobanchaceae prompted authors like Hallier (1903); Bellini (1907); Beeshore (1920); Glisic (1929) and Tiagi (1956) to unite the two families. But typical members of these families are entirely different from each other in their chemical characters, clearly objecting the merger of these families. Though the family Orobanchaceae is considered evolved from the scrophulariaceae the retention of primitive characters such as proanthocyanidins, alkaloids, tannins and quinones may be viewed as defence mechanism of the plant in accordance with their parasitic habit.

#### GESNERIACEAE

The presence of glycoflavones and iridoids as well as the absence of saponins tannins and alkaloids observed in Didymocarpus pygmaea represent the family characters. The report of iridoid glycosides, chalcones aurones and quinones (Agarwal, et al. 1973; Bhaskar and Seshadri, 1973; Wollenweber, et al. 1981, Harbone, 1967, Inoue, et al. 1983) corroborate the data of the present project and suggest that the family is closely related to the Scrophulariaceae chemically. The similarity between the two families is further supported by pollen characters (Erdtman, 1952). In morphological characters

also the family is very similar to Scrophulariaceae.

#### LENTIBULARIACEAE

The plants screened in this family are characterized by the absence of flavonoid system and their replacement by quinones. In having iridoids the family is related to the Scrophulariaceae. This is supported by the iridoid analysis of Wieffering (1966) in both the families. The elimination of flavonoid system, the characteristic feature of the family is noticed in the aquatic members (tribe Gratiolae) of Scrophulariaceae. Hence, an evolutionary relationship can be drawn from the Scrophulariaceae to the Lentibulariaceae, through the tribe Gratiolae. The relation between the two families is further confirmed by the embryological (Reayat Khan, 1954) and pollen morphological (Erdtman, 1952) studies. Except for the unilocular ovary with free central placentation and insectivorous habit, the two families are similar morphologically. Therefore, there exists no doubt on the placement of Lentibulariaceae alongwith the Scrophulariaceae.

#### SOLANACEAE

The family Solanaceae is characterized by the uniform presence of flavonols and saponins as well as by the absence of flavones (except in Capsicum annuum), glycoflavones, proanthocyanidins, tannins and iridoids. The high incidence of alkaloids is another feature which distinguishes the family from

the other families screened. The two subfamilies within, viz. the Solanoideae and Cestroideae are similar in their flavonoids except for the relative higher frequency of quercetin and its derivatives in the former and kaempferol and its derivatives in the latter.

Morphological variability observed between the two families Solanaceae and Scrophulariaceae are expressed in their chemical traits too. In contrast to the Scrophulariaceae in which flavones and iridoids predominate, the Solanaceae are rich in flavonols as well as alkaloids and are devoid of flavones and iridoids. The tribe Salpiglossideae which is considered as a link between Solanaceae and Scrophulariaceae because of its trend towards zygomorphy, is chemically indistinguishable from the rest of the Solanaceae. It neither possesses flavones nor iridoids which are characteristic to the Scrophulariaceae and thus is very dissimilar to the latter. This is further supported by the impressive array of evidences put forward by Robyns (1931) to prove that Solanaceous zygomorphy is quite different from that of the Scrophulariaceae. Therefore its inclusion in Scrophulariaceae is against all taxonomic judgements. The absence of chemical identity does not warrant a separate family status to this tribe as practised by Hutchinson (1969).

There is no doubt about the placement of the Solanaceae in a related order Solanales. Eventhough on morphological

grounds the Scrophulariaceae is considered derived from the Solanaceae, chemical evidences in favour of this derivation are wanting. The chemical differences between these two taxa are so overwhelming that such a relationship seems to be highly arbitrary.

In addition to the above families a number of other families are placed alongwith the Scrophulariaceae for their similarities in morphology and other characters. Though these families are not taken up in the present study their chemical interrelationships with the Scrophulariaceae are examined in the light of the present investigation and from the data available from literature.

#### BUDDLEJACEAE

This family charactersitically contains aucubins and 6-oxygenated flavones, the typical features of the Scrophulariaceae (Daniel and Sabnis, 1979). In addition to the presence of methylated flavones, the water soluble yellow carotenoid gentiobioside-crocin, which otherwise occurs in Scrophulariaceae, is reported from Buddleja variabilis. Other feature of similarity are the absence of alkaloids, tannins and proanthocyanidins and presence of orobanchin and saponins. The absence of internal phloem, a character cited in favour of removal of Buddlejaceae from the Gentianaceae, is another character bringing these families together. Though the flowers of Buddlejaceae are regular and tetramerous unlike the zygomorphic irregular pentamerous flower of the

Scrophulariaceae, a trend towards zygomorphy is observed in Senango, a genus in Buddlejaceae. Studies on serological (Cronquist, 1981), pollen/morphological and embryological (Difulvia, 1979) characters further strengthen the concept of a close relationship between the Scrophulariaceae and the Buddlejaceae. Thus the inclusion of Buddlejaceae alongwith Scrophulariaceae in the Scrophulariales seems to be in order.

#### OLEACEAE

Daniel and Sabnis (1987) who analysed a number of plants of Oleaceae comments "the Oleaceae with woody habit, high frequency of flavonols in the Jasminoideae and absence of aucubins appear to be the odd man out in the otherwise much advanced Scrophulariales and therefore its retention in the Gentianales is strongly advocated". The presence of 6-substituted flavones such as 6-OH luteolin and 6-OMe apigenin in some of the members of Oleaceae keep the family more evolved than any taxon of the Gentianales. They differ from most of the Gentianales in the absence of alkaloids, internal phloem and in possessing two stamens. For the time being the family Oleaceae may be considered as a link between the two orders Gentianales and Scrophulariales, a view proposed by Piechura (c.f. Cronquist, 1981) based on serological analysis.

#### ACANTHACEAE, THUNBERGIACEAE AND MENDONCIACEAE

Morphological similarity between the Acanthaceae and Scrophulariaceae are so lucid that a line of demarcation becomes

arbitrary. This close affinity is reflected in the chemical characters also in that, both the families are rich in 6-oxygenated flavones and iridoids (Daniel and Sabnis, 1987 a). Moreover, the accumulation of orobanchin is noted in Acanthaceae too. Morphologically the Acanthaceae diverge from the Scrophulariaceae primarily in their explosively dehiscent fruit and specialized funiculus. In addition, the development of cystoliths and reduction of endosperm are the additional features noted in Acanthaceae.

Bremekamp (1953) transferred the subfamily Nelsonioideae of the Acanthaceae to the Scrophulariaceae and placed them near the tribe Rhinanthae based on the presence of well-developed endosperm, the placentation and the dehiscence of the fruit. This view though supported on the basis of palynological evidence (Chaubal, 1966, Raj, 1961) is objected to on the basis of embryological (Mohan Ram and Wadhi, 1965; Johri and Singh, 1959) and morpho-anatomical characters (Ahmed, 1974a). However, a chemical analogy is observed between the tribes Rhinanthae of Scrophulariaceae and Nelsonioideae in the uniform distribution of 6-deoxyflavones and iridoids (Daniel and Sabnis 1987a). Thus the subfamily Nelsonioideae apparently is a connecting link between these two families.

The family Thunbergiaceae which is separated from the Acanthaceae because of its chemical (Daniel and Sabnis, 1987a) morpho-anatomical (Ahmed, 1974b) and embryological (Bremekamp, 1953; Mohan Ram and Wadhi, 1965) characters appears to be

a primitive family within the order Scrophulariales because of the lack of iridoids and the predominance of glycoflavones. The family is also devoid of 6-oxygenated flavones and cinnamic acids.

The Mendonciaceae, often treated as another subfamily of Acanthaceae, is treated as a family by Cronquist (1981) and placed under the order Scrophulariales. He characterized the family from Acanthaceae because of the lack of both cystoliths and the specialized mechanism of seed-dispersal. Except for the presence of tannins and absence of saponins the family is not studied for their chemical traits and hence no taxonomic conclusion are drawn here.

#### BIGNONIACEAE

Though the family Bignoniaceae seems to be advanced over Scrophulariaceae in most of the morphological characters, chemically it is primitive to the latter due to the higher incidence of flavonols and quinones (Padhye, 1982). Furthermore, iridoids are very poorly distributed in this family. The tribe Tecomeae, containing Paulownia which is controversial due to its lack of endosperm (Hence considered as a link between the two families) is closer to the Scrophulariaceae because of the predominance of flavones.

THE ORIGIN OF THE SCROPHULARIALES

The origin of the Scrophulariales is also a debatable question. Though Cronquist (1968) derived this order from the Polemoniales, in a latter treatment (Cronquist, 1981) he relates the order to the primitive Rosales. Hutchinson (1969) is of the opinion that the Personales (containing the herbaceous families of the Scrophulariales) are evolved from his Solanales whereas the Bignoniales containing the woody members ( the families Bignoniaceae, Pedaliaceae and Martyniaceae) are considered evolved from the Loganiales (containing the Buddlejaceae and Oleaceae also). Wettstein (1935) suggested a point of origin for the Tubiflorae (containing Scrophulariales) in Rosales and Rendle (1938) hints at a possible derivation from the Solanaceae and nearby taxa.

Among the related orders of the Scrophulariales, the Solanales are believed to be the closest. Within the order Solanales, the family Solanaceae and the Convolvulaceae are chemically too much specialised (the former in the elaboration of tropane alkaloids and the latter in the production of ergot alkaloids) to be an ancestor to the Scrophulariales. This leaves the families Polemoniaceae and the Menyanthaceae in the field. The families Scrophulariaceae, Myoporaceae, Gesneriaceae and Globulariaceae may find an ancestor in the Polemoniaceae. Menyanthaceae and Lentibulariaceae are similar in their habitat. The woody families such as the Oleaceae, Buddlejaceae and

Bignoniaceae find a closer relation to the Loganiaceae plants than to the Solanales as suggested by Hutchinson. Such a derivation of these families suggests that the order Scrophulariales is not a monophyletic one, a concept which is highly debatable.

The order Rosales combine all the primitive features expected of a probable ancestor of the Scrophulariales. This order contain woody trees as well as succulent herbs. The leaves may be simple or compound. The wood is without internal phloem. Presence of iridoid compounds, sympetalous corolla, stamens isomerous and alternate with the petals, a compound pistil with numerous ovules on axile placenta, unitegmic and tenuinucellar ovules are the other characters of the order which can be cited in favour of deriving the Scrophulariales from the Rosales. The Saxifragaceae with two carpels, swollen placenta bearing several layers of ovules can easily give rise to Scrophulariaceae plants. Similarly the woody members of the Scrophulariales may be derived from the woody members of Cunoniaceae / Encryphiaceae / Connaraceae / Brunelliaceae. The families Acanthaceae and Gesneriaceae may be derived from the family Grossulariaceae which possess unicellular pointed hairs and unilocular more or less intruded parietal placentation.