CHEMOSYSTEMATICS OF THE CARYOPHYLLACEAE

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INTRODUCTION

The family Caryophyllaceae (the pink family) has a widespread distribution, but is more common in temperate regions of the Northern hemisphere. The Caryophyllaceae consist of about 75 genera and 2000 species (Cronquist,1981).

The economically important members of this family include Stellaria, Saponaria and Silene, which contain saponins and which are used as cardiac stimulants and fish-poisons. This family contains a number of ornamentals such as Dianthus, Gypsophila etc.

The members of the Caryophyllaceae are predominantly herbs with swollen nodes. The leaves are simple, entire, narrow and often connected by tranverse lines at the base. Phyllotaxy is generally opposite except in Corrigiola, where it is alternate. The inflorescence is generally a dichasial cyme, though solitary flowers are not rare (Dianthus). Flowers are regular, perfect and hypogynous, but in Scleranthus, it is perigynous. Sepals are distinct or connate into an evident tube (Silene). Petals are of various types or sometimes absent. Stamens, 5 to 10 (sometimes 1-4) arranged in one or two cycles. Filaments are variously hypogynous, free and distinct or basally adnate to the petals to form a more or less elongate tube often

adnate to the gynophore. Anthers are Tetrasporangiate and dithecal opening by longitudinal slits. Gynoecium is of 2-5 carpels united to form a compound ovary with distinct or, more or less united styles. Ovary is superior (often on a gynophore) and unilocular, but more or less distinctly partitioned towards the base at least when young. Ovules are numerous (sometimes fewer or even solitary) bitegmic, crassinucellar, hemitropous to more commonly campylotropous. Fruit is a capsule or an achene.

TAXONOMY

The Caryophyllaceae have been divided by Bentham and Hooker (1865) in to 3 tribes viz. the Sileneae, Alsineae and Polycarpeae. The distinguishing morphological features of each tribe are :-

Tribe Sileneae

A gynophone, 4-5 lobed calyx, clawed petals, stamens inserted on an elongated gynophore, free styles and the absence of stipules. Based on the nature of capsules, seeds and embryo the tribe sileneae is further classified into three subtribes, the Dianthene, Drypideae and Lychnideae. An indehiscent capsule, 2-styles, peltate seeds, a fascial hilum and a straight embryo demarcate the subtribe Dianthene. Drypideae are distinguished by an indehiscent capsule, lateral

hilum and curved embryo, whereas the Lychnideae possess a capsule which bursts by short or long valves, a lateral hilum and an annular embryo.

Tribe Alsineae

Sepals free or connate at the base, petals subsessile, stamens inserted on an annular disk and free styles.

Tribe Polycarpeae

Free sepals, petals subsessile, stamens 5 inserted on an annular disk, 2-3 combined styles and scarious (rarely absolute) stipules.

In addition to these tribes, Bentham and Hooker placed a number of genera (16) at the end of the Caryophyllaceae, which are sometimes included in the caryophyllaceae (Cronquist,1981) or excluded from it (Hutchison,1959). Some of the genera included in this section are Heriniaria, Illecebrum,Paronychia, and Scleranthus.

Pax (1927) classified the family into two subfamilies viz. the Alsinoideae and Caryophylloideae (Silenoideae). The former possesses polysepalous flowers and perigynous stamens whereas the latter has gamosepalouscaby in hypogynous flowers. The Alsinoideae are further divided into 6 tribes viz. the Alsineae, Sperguleae, Polycarpeae, Paronychieae, Scleranthеae

and Pterantheae. Caryophylloideae contains two tribes viz. the Lychnideae and Caryophyllineae (Dianthcae).

Thorne (1968) recognized three subfamilies, the Paronchyioideae (Illecebraceae), Alsinoideae and Caryophylloideae (Silenoideae). This classification is accepted by many later workers including Cronquist (1981).

The features such as a sessile unilocular ovary, single style, one or rarely 2 ovules, which are erect or pendulous from a funicle and an achene like fruit in the subfamily Illecebraceae prompted Hutchison (1959) to raise this taxon as a separate family. Due to the absence of petals, presence of stipule, straight or curved embryo and copious endosperm the features which are seen in the Polygonaceae - he included the Illecebraceae in Polygonales. The main genera included in this family Illecebraceae are Illecebrum, Paronychia, Hernaria, Scleranthus, Corrigiola and Pteranthus.

PREVIOUS CHEMICAL WORK

The known chemical data of various Caryophyllaceae members include flavonoids, steroids, saponins and related compounds.

Flavonoids reported from this family include flavones like apigenin, variously glycosylated isomollupentin, luteolin, and a flavone derivative Wogonin. Kaemperfol is the

TABLE - 13 . SOME OF THE BIOLOGICAL WORKS IN THE CARYOPHYLLACEAE

Sr.No.	Name of the Plant	Organs	Name of the compound	Reference
			FLAVONOIDS	
1.	Cerastium arvense ssp. arvense	Whole plant	C-glactosyl-6-C-arabinosyl-8-apigenin and iso carymboside, C-xylosyl-6-C-arabinoxyl-8-apigenin	Dubois et al.(1982)
2.	Cerastium arvense	Lvs and flowers	8-C-glycosyl flavone-O-glyeside isomollupentin-7-O-glucoside isomollupentin-4'-O-glucoside and iso mollupentin 2"-O-glucoside	Dubois et al.(1985)
3.	Dianthus barbatus	Arieal part	Kaempferol 3-O-β-D-Sophoroside	Corduil et al.(1977)
4.	Gypsophylla sp.	Lvs	Apigenin, Saponaetrin 4-β -D-glucopyranoside and vitexin	Kryvenchuk et al. (1968)
5.	Melandrium album	-	Apigenin, Lutcolin(Aglycone) homo orientin and iso saponarin (C-glycoside)	Zykovan. (1976)
6.	Silene pratensis	Lvs	Isovitexin	Niemann et al.(1983)

(Contd....)

TABLE - 15 (Contd.)

Sr.No.	Name of the Plant	Organs	Name of the compound	Reference
7.	Stellaria dichotama var. lanceolata	root	Flavone derivative sapogenin	Yasuhawa et al. (1981)
8.	STEROIDS AND RELATED COMPOUNDS			
8.	Acanthophyllum peniculata	-	Gypsogenin(triterpenoid saponin)	Putieva, et al. (1972)
9.	Drymaria drummondii	Whole plant	Oleanolic acid acetate β-amyrin acetate iso/ursenol acetate	Dominquez et al. (1975)
10.	Dianthus barbatas	Areal part	Barbatoside A and B(Saponin)	Cordell et al. (1977)
11.	Dianthus saperbus var. longicalycimon		Dianoside C,D,E and F	Oshima et al. (1984)
12.	Heriniaria glabra		Saponin	Karting et al. (1972)
13.	Herba heriniaria		Saponin	Karting et al. (1972)
14.	Hereniaria glabra		Galotroside B and C β-D-glucopyronoside(1-6)- β-D-glucopyranoside (B) β-D-glycopyranoside(1-4) β-C-Rhamnopyrenoside β-D-fucopyranoside(1-2)	Lukhariv et al. (1970)

(Contd....)

TABLE - 13 . (Contd.)

Sr.No.	Name of the plant	Organ	Name of the compound	Reference
15.	Stellaria Cerastium		Triterpenoid saponin	Yukhanaev, et al. (1972)
16.	Saponaria officinalis		23-oxo 3 -16∝ -olеandiol 17,13 olide	Henry et al.(1982)
17.	Silene praemixta	leaves and inflorescence	2-Deoxy β -ecdysterone 2-deoxy ecdysterone 5-β -Cholest 7-ene-14- -22R, 25. trihydroxy-3-6 dione (Silenosterone)	Saatov et al.(1979)
18.	Silene braechica	root	22-6- β -D galactoside (Ecdysterone)	Saatov et al.(1981)
19.	Silene braechica	root	Sileneoide D-ecdysterone-3-O β-D galactopyranoside (Phytoecdysteroids)	Saatov et al.(1985)

only flavonol reported. Vitexin, isovitexin and orientin are the glycoflavones located so far.

Various type of steroids found to occur in this family include gypsogenin (Triterpenoid sapogenin), arinariose A and B, barbatoside A and B, and dianoside, C, D, E and F. (TABLE-13)

In the present work, 24 members of Caryophyllaceae have been screened for leaf phenolics and for other chemical markers such as tannins, saponins, iridoids, proanthocyanidins and quinones. These plants belong to all the three subfamilies of Thorne.

MATERIALS AND METHODS

Most of the plants were collected from Kashmir. Plants were also procured from Kerala, Tamilnadu and Gujarat. All the voucher specimens have been deposited in the Herbarium of the M.S.University of Baroda, Baroda, India (Appendix 2)

Standard procedures were followed for the extraction, isolation and identification of various chemical markers (ref. Chapter 2).

RESULTS

The distribution of flavonoids, phenolic acids, alkaloids, saponins, and steroids in the leaves of various Caryophyllaceae members screened is presented in Table-14 and 15.

TABLE - 14. DISTRIBUTION OF FLAVONOIDS IN THE FAMILY ~~THE~~ CARYOPHYLLACEAE*

Sl.No.	Name of the Plants	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	TRIBE - SILENEAE																	
1.	Cucubalus baccifer Linn.												+					
2.	Dianthus barbatus Linn.													+				
3.	D.jacquemontii Edgew.																	+
4.	Lychnis himalayensis Edgew.																	
5.	L.apetala Linn.													+				
6.	L.coronoria Lamk.										+			+	+			
7.	Saponaria vaccaria Linn.													+				
8.	Silene tenuis Wild.													+				
9.	S.vulgaris (Moench) Garcke												+					
10.	S.conoideae Linn.																	+
11.	TRIBE - ALSINEAE																	
11.	Arenaria foliosa Royl emss				+								+					
12.	A.festucoides Benth.			+				+						+				
13.	A.neelgerrensis Wight													+				
14.	A.kashmirica Edgew.					+							+			+		
15.	Cerastium monosperma Linn.		+										+					
16.	Cerastium tomentosum Linn.																	

(Contd...)

TABLE - 14 (Contd.)

Sl.No.	Name of the Plants	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
17.	Holosteum umbellatum Linn.																	
18.	Sagina procumbens Linn.	+	+			+								+	*			
19.	Spergula arvensis Linn.													+	*			
20.	Stellaria media Linn.												+					
21.	Stellaria alsine Grimm.														+			
	TRIBE-POLYCARPEA																	
22.	Polycarpea corymbosa Lamk.		+	+								+						+
23.	Vaccaria pyramidata Medic												+					
24.	Herniaria hirsuta Linn.							+	+		+							

1. Apigenin, 2. Acacetin, 3. 3'-OMe Luteolin, 4. 3',4'-diOMe Luteolin, 5. 7-OMe Luteolin, 6. 7-OMe Luteolin, 7. Kaempferol, 8. 4'-OMe Kaempferol, 9. 7,4'-diOMe Kaempferol, 10. Quercetin, 11. 7,3 diOMe-Quercetin, 12. Vitexin, 13. 4'-OMe Vitexin, 14. 7,4'-diOMe Vitexin 15. Isovitexin, 16. 7'-4'-Isovitexin 17. Orientin.

* After Bentham and Hooker (1865).

TABLE - 15 . SHOWING DISTRIBUTION OF PHENOLIC ACIDS, SAPONINS, STEROIDS, AND ALKALOIDS IN THE FAMILY CARYOPHYLLACEAE*

Sl.No.	Name of the Plants	1	2	3	4	5	6	7	8	9	10	11	12
	TRIBE-SILENEAE												
1.	Cucubalus baccifer Linn.	+		+							+	+	
2.	Dianthus barbatus Linn.	+	+		+						+	+	
3.	D.jacquemontii Edgew.	+	+	+			+				+	+	
4.	Lychnis himalayensis, Edgew.	+		+							+	+	
5.	L.apetala Linn.	+	+	+							+	+	
6.	L.coronaria Lamk.	+	+	+							+	+	
7.	Saponaria vaccaria Linn.	+		+							+	+	
8.	Silene tenuis Wild.	+		+			+				+	+	
9.	S.vulgaris (Moench) Garcke	+		+							+	+	
10.	S.conoidea Linn.	+	+	+							+	+	
	TRIBE-ALSINEAE												
11.	Arenaria foliosa Roylemss	+					+		+		+	+	
12.	A.festucoides Benth.	+		+				+			+	+	
13.	A.neelgerrensis Wight	+	+	+				+			+	+	

(Contd....)

TABLE - 5 (Contd.)

Sl.No.	Name of the Plants	1	2	3	4	5	6	7	8	9	10	11
14.	Arenaria keshmirica Edgew.	+	+	+							+	+
15.	Cerastium monospermum Linn.	+		+			+	+			*	+
16.	Cerastium tomentosum Linn.	+		+		+		+			+	+
17.	Holosteum umbellatum Linn.	+		+			+				+	+
18.	Sagina procumbens Linn.	+		+			+				+	+
19.	Spergula arvensis Linn.	+		+			+	+			+	+
20.	Stellaria media Linn.	+	+	+							+	+
21.	Stellaria alsine Grimm.	+		+		+		+			+	+
	TRIBE - POLYCARPEA											
22.	Polycarpea corymbosa Lamk.	+	+		+						+	+
23.	Vaccaria pyramidata Medic	+	+	+							+	+
24.	Herniaria hirsuta Linn.	+	+	+			+			+	+	+

1. Vanillic, 2. Syringic, 3. p-OH Benzoic, 4. Gentisic, 5. p-Coumaric
6. Cis and Trans Ferulic, 7. Cis and trans Synapic, 8. O-Coumaric,
9. Phloritic, 10. Saponins 11. Steroids.

* After Bentham and Hooker (1865).

Glycoflavones were found to be the major phenolic leaf pigments of this family. Nineteen out of twentythree plants contained one or the other type of glycoflavones. The various glycoflavones detected in this family were vitexin, 4'-OMe-vitexin, 7,4'-diOMe vitexin, isovitexin, and orientin. Glycoflavones were the only flavnoids of the subfamily Silenoideae.

Flavones were present in 6 species. The different flavones encountered were apgienin, acacetin, 3'-OMe luteolin, 7-OMe luteolin and 3',4'-diOMe luteolin. All these compounds except 3'-OMe luteolin were confined to the subfamily Alsinodeae.

4'-OMe kaempferol (Herniaria hirsuta, Arenaria festucoides), kaempferol, quercetin (Herniaria hirsuta) and 7,4'-di OMe quercetin (Polycarpea corymbosa) were the flavonols detected in this family.

Glycoflavones located singly in 9 members. Flavones co-occurred with glycoflavones in 6 species, whereas flavones, together with flavonols and glycoflavones ~~in 6 species, wheres~~ were present in Arenaria festucoides and Polycarpea corymbosa. Herniaria hirsuta was the only member with flavonol alone. Lychnis himalayensis, Cerastium tomentosum and Holosteum umbellatum were the three species without flavonoids.

Some unidentifiable compounds were also detected in this family. They were brown in UV and gave a light yellow colour with Na_2CO_3. Their absorption maxima (λ max) in MeOH were in the range of 350-363 nm (Band I) and 235-240 nm (Band II). The species in which these compounds were located are Dianthus barbatus (λ_{MeOH}^{max} 350, 240) Lychnis apetala (λ_{MeOH}^{max} 360, 240), Silene tenuis (λ_{MeOH}^{max} 360, 235), Silene vulgaris (λ_{MeOH}^{max} 360, 240), Silene conoidea (λ_{MeOH}^{max} 363,240) Arenaria neelgerrensis (λ_{MeOH}^{max} 360, 240), Cerastium monosperma (λ_{MeOH}^{Max} 355, 240; 345, 240) and Stellaria alsiene (λ_{MeOH}^{Max} 360, 240; 350, 240).

Nine phenolic acids have been identified in the Caryophyllaceae, of which vanillic, syringic, and p-OH benzoic acids were present in all subfamilies. Gentisic and Synapic acids were confined to the subfamily Alsinoideae. p-Coumaric acid was present in all the subfamilies but Alsinoideae, whereas o-coumaric acid was present only in the subfamily Alsinoideae. Phloretic acid was located only in the Paranchyioideae.

Saponins and steroids were widrespread in the family. Tannins, iridoids, quinones and proanthocyanidins were absent in all the members screened.

DISCUSSION

The Paronchyioideae (Illecebraceae) with flavonols as the only flavonoids are unique among the caryophyllaceae members,

which predominantly contain flavones and or glycoflavones. This separate identity of the Illecebraceae is also evident from the palynological studies. The unusual pollen grains of Illecebrum verticillatum and Herniaria glabra with distinct tetrahedral shape and large aperture on each of the three facees have not been found in any other taxa of Caryophyllales However Herniaria hirsuta have the common pantoporate type of pollen (Nowicke and Skvarla, 1977).

The unique flavonoid pattern, and the peculiarities of pollen grains and morphological features justify the creation of a separate family Illecebraceae as was done by Hutchinson (1959). This family is closely allied to the Caryophyllaceae.

The inclusion of Illecebraceae in Polygonales (Hutchinson 1959) does not find any support from the data gathered from chemistry and sieve element plastids. Chemically the Polygonaceae members are with tannins, proanthocyanidins and quinones, but all these compounds were lacking in Herniaria hirsuta. All the investigated members of the caryophyllaceae as well as Herniaria, Illecebrum, Stegnosperma and Limeum showed the presence of P-III subtype plastids with polygonal protein crystalloids (Behnke, 1975,1976). This type of sieve element plastids are not reported outside Caryophyllales and also from the Polygonaceae.

Widespread distribution of glycoflavones and flavones, universal occurrence of saponins and steroids as well as the absence of tannins, iridoids and proanthocynanidins seem to be the common features of the Caryophyllaceae (excluding Illecebraceae).

Within the Caryophyllaceae, the chemical data bring forth the existence of two distinct groups. They are (1) Caryophylloideae (Silenoideae) with glycoflavones and (2) Alsinoideae with glycoflavones in combination with flavone and flavonol. These two distinct groups are in accordance with the subfamilies proposed by Thorne (1968) and therefore the tribal classification proposed by Bentham and Hooker (1865) and subfamilial and tribal classification proposed by Pax (1927) do not get much support from the chemical study. The tribe Sileneae (B and H) is chemically distinct by the presence of glycoflavones alone, but other two tribes Alsineae and Polycarpeae do not show clear demarcation between them, with both the tribes possessing flavonols, flavones and glycoflavones. However the percentage of incidence of flavone, flavonol and glycoflavone combination in the tribe Alsineae is very low (9.09%) when compared to tribe Polycarpeae (100%). The subfamilies and tribes proposed by Pax (1927) were not distinct chemically, nor were the subtribes of Bentham and Hooker (1865).

Both the subfamilies, in the Caryophyllaceae show different rates of advancement. Presence of glycoflavones

a relatively advanced chemical character in the subfamily Silenoideae and the presence of advanced flavones, moderately advanced glycoflavones and primitive flavonols in the Alsinoideae indicate that both of these subfamilies attained the same level of advancement in the evolutionary scale.