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Some observations on the chemistry and taxonomy of the tribe Bignonieae

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Abstract. Chemotaxonomy of 12 taxa of the tribe Bignonieae investigated resemble one another in the presence of syringly radicals, caffeic acid, gentisic acid, vanillic acid unknown phenolic compound L(68/89) uniformly positive activity of polyphenolase and overlapping incidence of several classes of secondary chemical constituents, phenolic compounds and unusual (non-protein) amino acids. The quantified chemical data indicate that Bignonieae are homogenous taxon and the taxa are closely related. The present study does not support the creation of Pyrostegineae and Oroxyleae.

Keywords. Chemotaxonomy; chemical constituents; Bignoniaceae.

1. Introduction

The Bignoniaceae comprise of 120 genera and 650 species (Willis 1973) which are mainly tropical in distribution and few are temperate. Bentham and Hooker (1862–1893) recognized 4 tribes viz. Bignonieae, Crescentieae, Jacarandeae and Tecomeae. The present study deals with the chemotaxonomy of 12 species distributed in 10 genera belonging to the tribe Bignonieae.

2. Materials and methods

The materials have been collected from various places in India as shown in table 1 and the voucher specimens are deposited in the Department of Botany, Nizam College (Osmania University), Hyderabad. The leaves and stem material were screened for different classes of secondary chemical constituents, phenolic compounds and free amino acids following standard phytochemical methods (Gibbs 1974; Harborne 1973). The unidentified similar chromatographic spots were designated by certain code letters. The chemical data were analysed according to Ellison *et al* (1962).

3. Results

The data on the distribution pattern of different classes of secondary metabolites are presented in table 2, from which it is evident that the members of the tribe share certain chemical characters. The taxa included in the present study are characterized by the presence of syringyl radicals and are uniformly positive to the activity of polyphenolase as evidenced by the Maule test and cigarette and hot water tests respectively. There is uniform absence of anthraquinones, aurones, cyanogenic glycosides, juglone and saponins. Besides the above similarities the taxa however,

Table 1. List of taxa investigated.

S. No.	Name of the taxa	Place of collection	Voucher specimen number
1.	*Adenocalymma alliaceum* Miers.	Nizam College, Hyderabad	MS 11
2.	*Amphilophium mutisii* H B and K	Indian Botanic Garden, Howrah	MS 20
3.	*Anemopaegma scandens* Mello and Schum	Public garden, Hyderabad	MS 35
4.	*Bignonia chamberlaynii* Sims	Indian Botanic Garden, Howrah	MS 21
5.	*B. diversifolia* H B and K	Lalbagh garden, Bangalore	MS 39
6.	*B. magnifica* Bull	Public garden, Hyderabad	MS 34
7.	*Clytostoma callistegoides* Bur	Kakatiya University, Warangal	MS 31
8.	*Doxantha unguis-cati* Rehd	Nizam College, Hyderabad	MS 10
9.	*Millingtonia hortensis* L. f	Begumpet, Hyderabad	MS 6
10.	*Oroxylum indicum* (Vent) L	Indian Botanic Garden, Howrah	MS 22
11.	*Pyrostegia ignea* Presl	Nizam College, Hyderabad	MS 8
12.	*Radermachera xylocarpa* (Roxb) K Schum	Lalbagh garden, Bangalore	MS 42

Table 2. Distribution pattern of the different classes of secondary metabolites.

Chemical constituents	Name of the taxon*											
	1	2	3	4	5	6	7	8	9	10	11	12
Alkaloids												
Alkaloids										+		
Indoles		+										
Flavonoids												
Aurones												
Dihydrochalcones	+		+							+	+	+
Flavones		+										
Flavonols					+	+	+					
Flavanones				+				+	+			
Proanthocyanidins						+		+				
Quinones												
Anthraquinones												
Juglones												
Tannins												
Catechol tannins								+				
Ellagic acid	+				+	+	+		+	+	+	+
Tannins										+		
Terpenoids												
Aucubin compounds			+			+		+			+	
Iridoids	+	+	+	+	+	+		+	+	+	+	+
Saponins												
Triterpenoids/steroids	+		+	+		+	+		+		+	
Others												
Cyanogenic glycosides												
Polyphenolase activity	+	+	+	+	+	+	+	+	+	+	+	+
Syringin								+				
Syringyl radicals	+	+	+	+	+	+	+	+	+	+	+	+

*As in table 1.

differ in the restricted distribution of other classes of chemical constituents. Alkaloids and ellagitannins (hydrolysable tannins) are detected in *Oroxylum indicum* and are absent in the rest. There is an isolated instance of indoles in *Amphilophium mutisii*. While the iridoids (monoterpenoid cyclopentanoid lactones) are present in all the taxa except *Cyclostoma callistegoides*, the specific type of iridoid, namely aucubin, is found in *Anemopaegma scandens*, *Bignonia magnifica*, *Doxantha ungus-cati* and *Pyrostegia ignea*. The aucubin compounds are absent in the remaining 8 taxa. The presence of catechol-tannins (condensed tannins) and syringin is noticed only in *D. ungus-cati*, as shown by the positive results of Isenberg Buchnann's and Syringin tests respectively. The occurrence of ellagic acid in the independent state is recorded in *Adenocalymma alliaceum*, *Bignonia diversifolia*, *B. magnifica*. *C. callistegoids*, *Millingtonia hortensis*, *O. indicum*, *P. ignea* and *Radermachera xylocarpa* and its absence is recorded from *Amphilophium mutissii*, *A. scandens*, *Bignonia chamberlaynii* and *D. unguis-cati*. Judging from the colour reactions carried out, 5 major types of flavonoids are recorded in different taxa of the tribe. Proanthocyanidins are present in *B. magnifica* and *D. unguis-cati* and absent in the remaining 10 species. Triterpenoids/steroids are found in all the members excepting *A. mutisii*. *B. diversifolia*, *D. unguis-cati*, *O. indicum* and *R. xylocarpa*.

The distribution pattern of phenolic constituents is presented in table 3. The caffeic acid, gentisic acid, vanillic acid and the unidentified phenolic compound L (hR_f 68/89) are shared by all the taxa included in the present study. From among the identified phenolic acids, *p*-OH benzoic acid and *p*-coumaric acid are present in all the taxa of the tribe excepting *A. mutisii* and *O. indicum*. Gallic and salicylic acids seem to be of restricted distribution. The former is found in *B. diversifolia*, *C. callistegoides* and *D. unguis-cati* and the latter in *A. mutisii* and *A. scandens*.

Table 3. Distribution pattern of different phenolic constituents.

Phenolic constituents	Name of the taxon*											
	1	2	3	4	5	6	7	8	9	10	11	12
p-OH Benzoic acid	+		+	+		+	+	+	+		+	+
Caffeic acid	+	+	+	+	+	+	+	+	+	+	+	+
p-Coumaric acid	+		+	+	+	+	+	+	+		+	+
Gallic acid					+		+	+				
Gentisic acid	+	+	+	+	+	+	+	+	+	+	+	+
Salicylic acid		+	+									
Vanillic acid	+	+	+	+	+	+	+	+	+	+	+	+
A (13/24)	+								+			
B (27/26)	+	+	+	+		+	+	+	+		+	+
C (36/5)								+		+		
D (36/75)											+	
E (40/30)	+	+		+	+	+	+	+	+	+		+
F (52/12)									+		+	
G (52/84)					+					+		
H (59/93)								+		+		
I (62/50)												+
J (66/82)									+			+
K (68/36)					+							
L (68/89)	+	+	+	+	+	+	+	+	+	+	+	+

*As in table 1.

Numbers in parentheses indicate the hR_f ($100 \times R_f$) values in I and II directions.

From among the unidentified phenolic constituents, B (hR_f 27/26) and E (hR_f 40/30) are wide spread in distribution. The distribution of the rest of the phenolic constituents is sparse.

The data on the distribution pattern of free amino acids in the tribe are presented in table 4. From the table it is evident that there is apparent absence of certain protein amino acid, which are otherwise ubiquitous and there is discontinuous distribution of unusual amino acids.

4. Discussion

From among the different classes of secondary metabolites there is uniform absence of anthraquinones, aurones, cyanogenic glycosides and juglone, in all the taxa studied. However, the presence of all these compounds is reckoned an advanced trait and the absence therefore, indicates the primitiveness. The catechol tannins in *D. unguis-cati* and hydrolysable tannins in *O. indicum* represent relative primitiveness. The presence of alkaloids in *O. indicum*, indoles and flavones in *A. mutisii* and aucubin compounds in 4 of the 12 taxa denote their supremacy over the other taxa.

Table 4. Distribution pattern of different free amino acids.

	Name of the taxon*											
Free amino acid	1	2	3	4	5	6	7	8	9	10	11	12
Alanine								+				
r-Aminobutyric acid	+		+	+		+		+	+	+	+	+
Argenine	+	+				+			+	+		
Aspartic acid			+	+					+			
L-Cysteine HCl					+	+	+					
Glutamic acid				+	+	+					+	+
Glutamine	+		+	+								
Glycine			+				+	+		+		
Histidine					+					+	+	
Hydroxy proline					+				+			
Isoleucine				+		+	+					+
L-Leucine				+		+						+
Methionine		+			+							+
Ornithine		+	+									
Proline	+	+	+	+		+	+	+	+	+	+	+
Serine		+			+	+	+			+	+	+
Threonine	+	+	+				+	+		+		
Tyrosine			+					+				
DL-valine			+	+			+	+	+	+	+	
a (4)		+							+		+	
b (6)	+											
c (8)		+		+								+
d (10)					+				+		+	
e (13)									+			
f (28)			+		+							
g (42)					+	+	+	+			+	
h (55)			+			+						
i (75)							+					

*As in table 1.

Numbers in parentheses indicate the hR_f ($100 \times R_f$) value.

Table 5. Synthetic numerical indices.

Name of the taxon*	Paired affinity: Name of the taxon* 1	2	3	4	5	6	7	8	9	10	11	12	Group affinity	Isolation values
1	100	60	75	80	60	76	75	61	77	64	74	81	883	0·4
2		100	60	71	51	56	53	52	58	55	54	66	736	0·9
3			100	73	54	76	62	61	61	51	74	68	815	0·0
4				100	58	75	73	70	76	55	66	80	877	0·0
5					100	68	72	59	59	62	61	60	764	0·4
6						100	82	73	68	54	75	70	873	0·0
7							100	66	66	51	68	68	836	0·4
8								100	60	57	61	61	781	0·9
9									100	51	76	72	824	0·9
10										100	52	64	664	0·9
11											100	68	761	0·4
12												100	858	0·4

*As in table 1.

There seems to be overlapping incidence of ellagic acid and iridoids in many of the taxa studied. There is complimentarity also between these two classes of compounds, as pointed out by Bate-Smith (1971). Though the syringin is rare there is uniformity in the ratio of syringaldehyde to vanillin. This is indicative of similar cell wall composition in all the taxa studied.

Of the phenolic constituents, it is evident from table 3, that a few of them are uniformly present while many of them are shared by the members.

The common protein amino acids are present in all the taxa, though they appear to be absent in a few. The apparent absence is due to their extreme low concentration in the system. Their incidence has no relevance in taxonomic considerations. On the other hand the occurrence of uncommon (non-protein) amino acids in different taxa, indicate their discontinuous distribution.

The distribution of different classes of secondary constituents, phenolic substances and unusual amino acids is numerically analysed (table 5) to bring about the relationship among them. The pairwise affinity is calculated according to Ellison *et al* (1962). It ranges from 51–82. The affinity of one taxon with all others derived from pairwise affinity is expressed as group affinity (Ellison *et al* 1962) and it ranges from 664–883. The isolation values are negligent. On account of occurrence of alkaloids and ellagic tannins, *Oroxylum* may apparently stand distinct from others but these two constituents however do not warrant its seclusion; as it shares several other features with the rest of the taxa in question. The high paired and group affinity values and low isolation values indicate that Bignonieae are fairly a homogenous taxon and do not support the relegation of *Pyrostegia* into a sub tribe Pyrosteginieae (Padhye and Sabnis 1987) and *Millingtonia* and *Oroxylum* into a separate tribe Oroxyleae (Schumann 1895).

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