THE OCCURRENCE OF IRIDOID GLYCOSIDES IN THE SCROPHULARIACEAE

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SUMMARY

A study was made of the occurrence of iridoid glycosides (giving a colour reaction with anisidine) in the *Scrophulariaceae*. Aucuboside, catalpol and antirrhinoside were found in many species: in addition some hitherto unknown, presumably iridoid glycosides were found. Most tribes were homogeneous as to the types of glycosides present, while the subfamilies were not.

On the basis of the prevailing glycosides the family can be segregated into the following groups:

1. taxa devoid of glycosides (most *Gratioleae*, the *Calceolarieae*, most *Digitaleae*, *Sphenandra*, *Sutera* p.p., and *Nemesia*).
2. taxa containing aucuboside and (or) catalpol (*Verbasceae*, *Scrophularieae*, *Collinsieae* *Hemiphragmeae*, *Buchnereae*, *Veroniceae*, *Rhinantheae*, *Sutera* p.p., *Limosella*, *Mazus*, *Zaluzianskya*, *Angelonia*, *Diascia*, *Erinus*, and *Rehmannia*).
3. taxa containing antirrhinoside (*Antirrhineae*).
4. the *Selaginoideae* with unidentified glysosides.

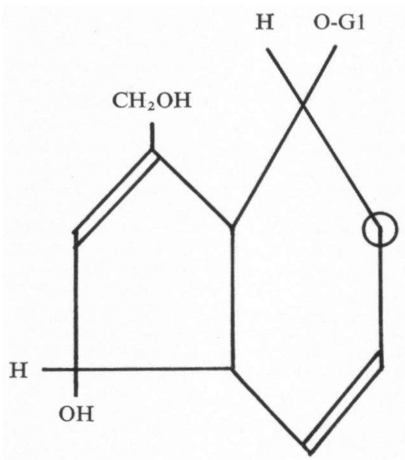
The genera *Leucocarpus*, *Halleria*, and *Alonsoa* have aberrant, but presumably iridoid glycosides, and therefore do not fit in any of the groups mentioned.

1. INTRODUCTION

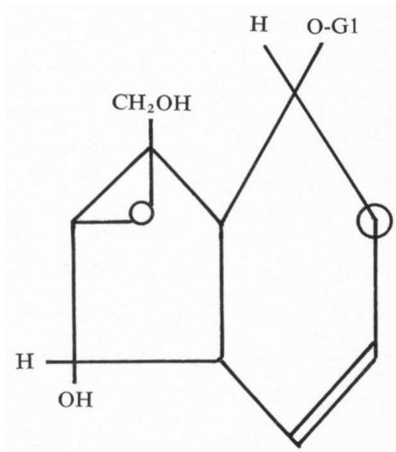
Aucuboside (I) has been recognized as a constituent of a fair number of *Scrophulariaceae* (see *e.g.* BRAECKE 1923; PARIS & CHASLOT 1955). Other iridoid glycosides known to occur in this family are catalpol (II) (WIEFFERING 1966), antirrhinoside (III) (SCARPATI *et al.* 1968) and derivatives of harpagide (IV) (KITAGAWA *et al.* 1967). Catalpol has been found in a *Verbascum* and in three *Veronica* species, antirrhinoside in two *Antirrhinum*, and harpagide derivatives in a *Scrophularia* species; a cinnamoyl ester of catalpol occurs in a *Picrorhiza* species (KITAGAWA *et al.* 1969).

JIRAWONGSE (1964) studied the occurrence of aucuboside in a fairly large number of *Scrophulariaceae* and found that the presence or absence of aucuboside is rather strongly correlated with Pennell's classification of this plant family as outlined in ENGLER's Syllabus (1964). It should be noted, however, that Jirawongse's method of identification did not lend itself to differentiating aucuboside from some other iridoid glycosides; antirrhinoside as well as catalpol, harpagide and some as yet unidentified glycosides were probably recorded as aucuboside.

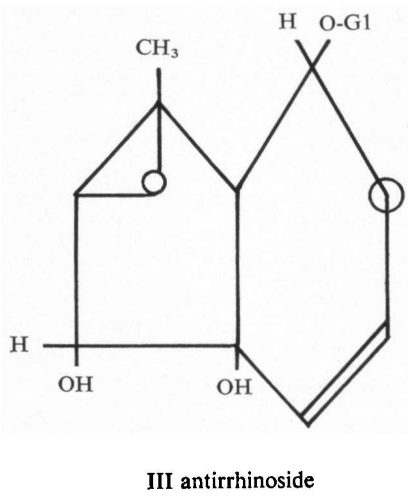
In order to compare the distribution pattern of iridoid glycosides in the *Scrophulariaceae* with infrafamilial classifications a number of species of the family were investigated during the present study. Since a concensus on a natural system of the *Scrophulariaceae* is lacking (see THIERET 1967) the phytochemical data in this study may be useful for future attempts at reclassification.



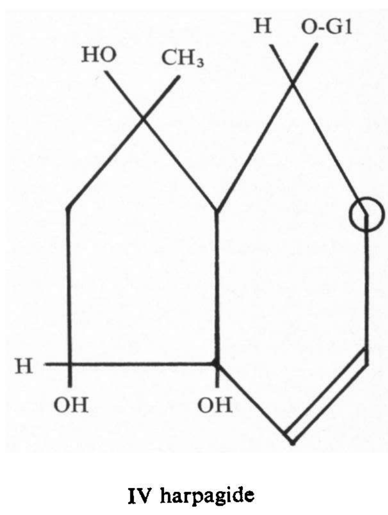
I aucuboside



II catalpol



III antirrhinoside



IV harpagide

2. MATERIALS AND METHODS

Part of the investigated seeds were present in the Seed Collection of the Laboratory of General and Technical Biology. Most of the seed samples tested were obtained *via* the seed-lists of horti. To avoid erroneous results caused by misnamed samples either extracts were prepared in duplicate or triplicate from samples of two or three horti; or from the samples used for extraction part was sown and the resulting plants were identified. Most samples of vegetative parts were from specimens cultivated in the Botanical Garden of this Laboratory, the other samples were collected from plants growing in their natural habitats.

Extracts were prepared by heating seeds or vegetative parts in 50% ethanol and concentrating the extracts to thin syrups. The latter were examined by paper chromatography in n-butanol-ethanol-water (40:11:19 v/v) and spraying the dried chromatograms with p-anisidine phosphate reagent, consisting of p-anisidine (0.5 g), concentrated phosphoric acid (3 ml), and 70% ethanol (100 ml). After heating the chromatograms at 105° for 1 minute the spots of the following iridoid glycosides are visible: aucuboside (R_F 0.41, dark brownish grey), catalpol (R_F 0.32, orange), and Asarina glycoside (R_F 0.13, pink-orange). Then the chromatograms were sprayed again, with the acidic p-anisidine reagent which in addition to the reagent mentioned contained concentrated hydrochloric acid (1 ml per 100 ml of reagent). After heating the chromatogram (1 minute at 105°) the spots of aucuboside and catalpol are somewhat more intensive while harpagide, antirrhinoside, Antirrhinum glycoside B, and Alonsoa glycoside (which react weakly with the first reagent) show up fully (harpagide R_F 0.36, violet-brown; antirrhinoside R_F 0.24, brown; Antirrhinum glycoside B R_F 0.11, brown-yellow; Alonsoa glycoside R_F 0.64, brownish red). In ultraviolet light the spots are more intensive than in daylight, while the colours are more or less different; the antirrhinoside and Antirrhinum glycoside B spots fluoresce blue.

When aucuboside and (or) catalpol are present there are sometimes one or two fast spots present in addition. They have either the colour of the aucuboside or of the catalpol spot and have R_F values of 0.7–0.8; probably they are esters of these glycosides. In one case, *Penstemon barbatus* hybr., a glycoside with R_F 0.68 was shown to be an ester of catalpol while on treatment with alkali the compound was converted into catalpol. This substance was not identical with catalposide. The occurrence of an aucuboside ester in extracts of *Rhinanthus glaber* was demonstrated by FIKENSCHER *et al.* (1969).

Several species yielded unknown spots (*e.g. Alonsoa, Hebenstreitia*); their colours, and also a positive copper reaction (TRIM & HILL 1951) strongly suggest that these compounds have iridoid characters. Some of the as yet unknown glycosides were isolated by application of the carbon adsorption and elution method (HILL & VAN HEYNINGEN 1951) followed by preparative paper chromatography using the same solvent as for qualitative paper chromatography. One of the isolated glycosides (Hebenstreitia glycoside B) could be obtained in a crystalline form; it is identical with the glycoside occurring in *Stachytarpheta*

Table 1. Characteristics of some unidentified iridoid glycosides.

Glycoside	R_F in solvent[a]				Reaction with silver reagent[b]	$[\alpha]_D$ in water	Reaction with Trim and Hill reagent[c]	Remarks
	A	B	C	D				
Alonsoa	0.64	0.64	0.68	0.53		- 62°	purple	
Antirrhinum B	0.11	0.09	0.24	0.02	w	- 21°	purple	
Asarina	0.13	0.14	0.31	0.04	+	- 55°	brown	
Hebenstreitia A	0.73	0.74	0.78	0.66	—	- 54°	blue	
„ B	0.47	0.49	0.60	0.30	—	-133°	bluish green	m.p. 138–140°
„ C	0.29	0.30	0.46	0.13	—		blue	
Penstemon A	0.68	0.73	0.76	0.58	—	- 52°	brown	ester of catalpol

[a] solvents: A: n.butanol-ethanol-water (40:11:19 v/v); B: n-butanol-acetic acid-water (5:1:4 v/v); C: n-butanol-pyridine-water (6:4:3 v/v); D: n.butanol saturated with water.
[b] TREVELYAN *et al.* (1950)
[c] TRIM & HILL (1952)

species (*Verbenaceae*). The Hebenstreitia glycoside C is chromatographically identical with a glycoside occurring in both *Duranta plumieri* Jacq. (*Verbenaceae*) and *Phlomis russeliana* Benth. (*Labiatae*) while Hebenstreitia glycoside A is an ester of glycoside C. The preparations were characterized by the data in *table 1*.

3. RESULTS AND DISCUSSION

In *table 2* the investigated species of the *Scrophulariaceae* are recorded. They are arranged according to the system in ENGLER's Syllabus (1964) with the following exceptions: *Lindenbergia* is transferred from the *Gratioleae* to the *Rhinantheae*, *Nemesia* from the *Antirrhineae* to the *Hemimerideae*, *Synthyris* from the *Digitaleae* to the *Veroniceae*, and *Leucocarpus* from the *Scrophularieae* to the *Gratioleae*. Reference to the literature pertinent to these transfers is given by THIERET (1967).

Tables 2 and *3* show that within the tribes the occurrence or absence of iridoid glycosides is fairly consistent.

The *Gratioleae* are devoid of iridoid glycosides giving coloured products with the anisidine reagents. Exceptions are *Limosella* and *Mazus* which contain aucuboside and catalpol, and *Leucocarpus* which contains an unknown, presumably glycosidic compound reacting with the reagents.

In the *Verbasceae* aucuboside and catalpol occur generally together with one or two other glycosides which are probably esters of aucuboside and catalpol.

The *Scrophularieae* also generally contain both aucuboside and catalpol. In many *Penstemon* species catalpol is the main component, aucuboside being present in traces or lacking, while in *Scrophularia* the presence of catalpol is often dubious; in the latter genus one or more other glycosides occur, one of them being an ester of harpagide (KITAGAWA *et al.* 1967; this observation on *Scr. buergeriana* Miq. could be confirmed with *Scr. nodosa* by the present author). *Halleria* contains an unknown glycoside and is therefore exceptional in this tribe. The transfer of *Leucocarpus* to the *Gratioleae* makes the *Scrophularieae* more coherent, without, however, contributing to the homogeneity of the *Gratioleae*.

The *Manuleae* are heterogeneous in respect of the presence of iridoid glycosides; even the genus *Sutera* is heterogeneous.

In *Collinsia* (tribe *Collinsieae*) all species tested contain catalpol accompanied by traces of aucuboside; in some species probably esters of catalpol are present.

The *Calceolarieae* are devoid of iridoid glycosides, while the *Hemimerideae* are heterogeneous: *Alonsoa* contains a glycoside which has very probably an iridoid structure; in *Angelonia* and *Diascia* aucuboside occurs; and from *Nemesia* iridoid glycosides are absent. The transfer of the latter genus to the *Hemimerideae* therefore increases the inhomogeneity of the tribe in respect of the presence of iridoid glycosides.

Characteristic for the *Antirrhineae* is antirrhinoside which is often accompanied by Anthirrhinum glycoside B and Asarina glycoside. *Lindenbergia* appears

Table 2. Iridoid glycosides in Scrophulariaceae

Tribe	Species	Organ[a]	Spots[b]
Scrophularioideae-Gratioleae	*Bacopa monniera* Wettst.	l, n	–
	Gratiola officinalis L.	l, s	–
	Ilysanthes attenuata (Muhl.) Small	s	–
	Leucocarpus perfoliatus (H.B.K.) Benth.	l, s	1 spot
	Limosella aquatica L.	s	auc (+ cat)
	Lindernia crustacea (L.) F.Muell.	s	–
	Mazus rugosus Lour.	l, s	auc (?) + cat + 2 o
	Mimulus cardinalis Dougl. ex Bth.	l, s	–
	M. guttatus DC.	s	–
	M. lewisii Pursh	s	–
	M. luteus L.	s	–
	M. moschatus Dougl.	n	–
	Peplidium muelleri Benth. var. *longipes*	s	–
	Scoparia dulcis L.	n	–
	Torenia asiatica L.	s	–
	T. baillonii Godefroy ex André	s	–
	T. flava Buch.-Ham. ex Wall.	s	–
	T. fournieri Lind. ex Fourn.	l, s	–
	T. peduncularis Benth.	s	–
	T. violacea (Azaola ex Blanco) Pennell	n	–
Scrophularioideae-Verbasceae	*Celsia arcturus* Jacq.	l, n	auc + cat + 2 o
	C. cretica L.f.	s	auc + cat
	C. orientalis L.	s	auc + cat + 2 o
	C. roripifolia Halácsy	s	auc + cat + 3 o
	C. sinuata Colla	s	auc + cat + 1 o
	Verbascum blattaria L.	l	auc + cat + 1 o
	V. nigrum L.	l, s	auc + cat + 1 o
	V. thapsus L.	l	auc + 2 o
Scrophularioideae-Scrophularieae	*Chelone lyonii* Pursh	l, s	auc + cat
	C. obliqua L.	s	auc + cat
	Dermatobotrys saundersii Bolus	l	auc + cat + 1 ester
	Halleria lucida L.	l	1 spot
	Penstemon albertinus Greene	s	cat
	P. arizonicus Hell.	s	auc + cat
	P. barbatus hybr.	l, n, s	auc + cat + cat ester
	P. barrettae A. Gray	s	cat
	P. centranthifolius Benth.	s	cat
	P. comarrhenus A. Gray	s	cat
	P. corymbosus Benth.	s	cat
	P. heterophyllus Lindl.	s	cat
	P. utahensis Eastwood	s	(auc +) cat
	Phygelius capensis E. Mey. ex Benth.	l, s	auc + cat + 2 o
	Russelia juncea Zucc.	p	auc + cat
	Scrophularia balbisii Hornem.	l	auc + cat + 1 o

Table 2. Continued

Tribe	Species	Organ[a]	Spots[b]
	S. calliantha Webb et Berth.	l, s	auc (+ cat?) + 2 o
	S. chrysantha Jaub. et Spach	l	auc (+ cat?) + 2 o
	S. glabrata Ait.	l, s	auc (+ cat?) + 2 o
	S. neesii Wirtg.	l	auc (+ cat?) + 2 o
	S. nodosa L.	l, n	auc (+ cat?) + 2 o
	S. nodosa L.	r	auc + cat + CH_3O - cat(?) + harpagide ester
	S. marylandica L.	l	auc (+ cat?)
	S. peregrina L.	l	auc (+ cat?) + 3 o
	Teedia lucida Rudolphi	l, s	auc + cat + 2 o
	Tetranema mexicanum Benth.	l, s	auc + cat + 1 ester
Scrophularioideae-Manuleae	*Sphenandra viscosa* Benth.	n, s	–
	Sutera antirrhinoides Hiern	l	auc (+ cat?) + 4 o
	S. campanulata (Benth.) Kuntze	l	–
	S. foetida Roth	l	–
	Zaluzianskya capensis Walp.	l, s	cat + 3 o
Scrophularioideae-Collinsieae	*Collinsia bicolor* Benth.	l	auc + cat + 2 o
	C. bicolor Benth.	s	(auc +) cat + cat ester?
	C. grandiflora Dougl. ex Lindl.	s	(auc +) cat
	C. parviflora Dougl. ex Lindl.	s	(auc +) cat
	C. tenella (Pursh) Piper	l, s	auc + cat + 1 o
	C. verna Nutt.	s	(auc +) cat
Scrophularioideae-Calceolarieae	*Calceolaria x fruticohybrida* Voss	n	–
	C. gracilis H.B.K.	s	–
	C. scabiosaefolia Sims	l, n, s	–
	Jovellana sinclairii Kränzlin	s	–
Scrophularioideae-Hemimerideae	*Alonsoa meridionalis* (L.f.) O. Kuntze	l, s	alo + 1 o
	A. warszewiczii Regel	l, s	alo + 1 o
	Angelonia grandiflora C. Morr.	l	auc + 2 o
	Diascia barberae Hook. f.	l, s	auc
	Nemesia floribunda Lehm.	s	–
	N. foetens Vent.	s	–
	N. melissaefolia Benth.	s	–
	N. strumosa Benth.	l, s	–
Scrophularioideae-Antirrhineae	*Anarrhinum bellidifolium* Desf.	l	ant B + 2 o
	A. corsicum Jord. et Fourr.	s	ant + 1 o
	Antirrhinum majus L.	l	ant + ant B + some o
	A. maurandioides A. Gray	l	ant + ant B + asa
	A. orontium L.	l, s	ant + ant B
	A. tortuosum Bosc ex Lam.	s	asa + 1 o
	Asarina procumbens Mill.	l, n, s	asa
	A. purpusii (Brandeg.) Pennell	s	ant
	A. scandens (Cav.) Pennell	s	ant + asa
	Chaenorrhinum minus Lange	s	ant (?)
	Ch. origanifolium Fourr.	s	ant B (?) + 2 o
	Galvezia speciosa (Nutt.) A.Gray	s	ant
	Kickxia elatine (L.) Dum.	s	ant + asa + 1 o
	K. spartioides (Brouss. ex Buch) Janchen	s	ant

Table 2. Continued

Tribe	Species	Organ[a]	Spots[b]
	K. spuria Dum.	l, s	ant + some o
	Linaria anticaria Boiss. et Reut.	s	ant + ant B
	L. cymbalaria Mill.	n	ant + 2 o
	L. genistifolia Mill.	s	ant + ant B
	L. purpurea Mill.	s	ant + ant B + 1 o
	Maurandia barclaiana Lindl.	l	ant + ant B (?)
	M. erubescens A.Gray	l, s	ant + ant B + asa
Rhinanthoideae-	*Digitalis ferruginea* L.	s	–
Digitaleae	*D. grandiflora* Mill.	s	–
	D. lanata Ehrh.	s	–
	D. lutea L.	l, s	–
	D. purpurea L.	l, n	–
	Erinus alpinus L.	l	auc + ester + 1 o
	Isoplexis canariensis Steud.	s	–
	Rehmannia angulata Hemsl.	n	(auc +) cat
	Sibthorpia europaea L.	l, s	–
Rhinanthoideae-	*Hemiphragma heterophyllum*		
Hemiphragmeae	Wall.	s	auc + cat
Rhinanthoideae-	*Aureolaria virginica* (L.) Pennell	s	auc
Buchnereae	*A. grandiflora* Pennell		
	var. *pulchra* Pennell	s	auc
	Leptorrhabdos parviflora Benth.	s	auc + cat + 1 o
	Striga lutea Lour.	s	auc
Rhinanthoideae-	*Campylanthus salsoloides* Roth	l	auc + 2 o
Veroniceae	*Hebe andersonii* Cockayne	l	auc + 3 o
	Lagotis minor (Willd.) Standley	s	auc + cat
	Leptandra virginica Nutt.	s	auc + cat + some o
	Ourisia macrophylla Hook.	s	auc + cat
	Parahebe catarractae (Forst. f.)		
	W.R.B.Oliv.	s	auc + cat
	P. lyallii W.R.B.Oliver	s	auc + cat
	Synthyris missurica (Rafin.)		
	Pennell	s	auc + cat
	S. stellata Pennell	s	auc + cat
	Veronica chamaedrys L.	l	auc + cat + 2 o
	V. crassifolia Wierzb. ex Heuff	n	auc + cat + 1 o
	V. derwentiana R.Br.	l, s	auc + cat + 1 ester
	V. gentianoides Vahl	n	cat
	V. virginica L.	s	auc + cat
	Wulfenia carinthiaca Jacq.	l, s	auc + cat + 1 o
Rhinanthoideae-	*Bartsia alpina* L.	s	auc + ester
Rhinantheae	*Bellardia trixago* All.	s	auc
	Bungea trifida (Vahl) C.A.Mey.	s	auc + cat
	Castilleja hyparctica Rebr.	s	auc + cat
	C. raupii Pennell	s	auc + cat
	C. rhexifolia Rydb.	l	cat
	Cordylanthus involutus Wiggins	s	auc
	Euphrasia lutea L.	s	auc + cat + ester + 2 o
	E. minima Jacq.	s	auc

Table 2. Continued

Tribe	Species	Organ[a]	Spots[b]
	E. minima subsp. *drosocalyx* (Freyn) Hayek	l	auc (+ cat?) + 1 o
	E. parviflora Fries	l	auc + cat
	E. rostkoviana Hayne	l	auc + cat
	Lathraea clandestina L.	p, n, s	auc + some o
	Lindenbergia philippinensis Benth.	s	auc + cat
	L. ruderalis Voigt	s	cat
	Melampyrum arvense L.	l, s	auc + cat + 1 o
	M. nemorosum L.	s	auc + cat
	Odontites rubra Pers.	s	auc + cat + ester
	O. verna (Bell.) Dum.	s	auc + cat + ester + 1 o
	Orthantha lutea A.Kern. ex Wettst.	l, s	auc + cat + some o
	Orthocarpus luteus Nutt.	s	auc
	Parentucellia latifolia (L.) Car.	s	auc
	P. viscosa (L.) Car.	s	auc + ester
	Pedicularis kerneri D. T.	s	auc + cat + ester
	P. lapponica L.	s	auc + cat
	P. palustris L.	l, s	auc + cat
	P. recutita L.	s	auc
	Rhinanthus buccalis Wallr.	s	auc
	Rh. major Ehrh.	l	auc + cat + 1 o
Selaginoideae-Selagineae	*Dischisma arenarium* E.Mey.	l	4 spots
	D. arenarium E. Mey.	s	2 spots
	Hebenstreitia comosa Hochst.	l	3 spots
	H. dentata L.	l	3 spots
	H. dentata L.	s	1 spot
	H. integrifolia L.	s	1 spot
	Selago alopecuroides Rolfe	s	1 spot
	S. serrata Berg	l	1 spot
	S. thunbergii Choisy	s	2 spots

[a] l = leaves, s = seeds, n = nectar, r = roots, p = vegetative parts (whole plants or stems + leaves)

[b] – = no iridoid glycosides visible on chromatograms; spot = unidentified glycoside present; auc = aucuboside; (auc) = trace of aucuboside; auc? = presumably aucuboside; cat = catalpol; cat ester = ester of catalpol; CH_3O-cat = methoxy-catalpol; ant = antirrhinoside; ant B = Antirrhinum glycoside B; asa = Asarina glycoside; alo = Alonsoa glycoside; 1 o = one other glycoside.

to fit well in this tribe, while the removal of *Nemesia* contributes to its homogeneity.

Apart from *Erinus* and *Rehmannia* which contain aucuboside the *Digitaleae* are devoid of iridoid glycosides. The transfer of *Synthyris* to the *Veroniceae* is justified by the presence of aucuboside and catalpol.

In the *Hemiphragmeae*, *Buchnereae*, *Veroniceae*, and *Rhinantheae* aucuboside and (or) catalpol occur generally. The isolation of a cinnamoyl ester of catalpol from *Picrorhiza kurroa* Royle ex Benth. by KITAGAWA *et al.* (1969) is in harmony with the general occurrence of catalpol and aucuboside in the *Veroniceae*, to which the species belongs.

The *Selagineae* are characterized by the presence of several glycosides of as yet unknown but very probably iridoid structure.

In the present study a limited number of the species (160, 5%) and, to a lesser extent, of the genera (76, 36%) of the *Scrophulariaceae* has been investigated. This restricts the strength of the arguments derived from the results. Still these results may point to a basis for a more natural subfamilial division of the family.

The chemical evidence collected allows the family to be segregated into several groups.

Group 1 contains the taxa which are devoid of iridoid glycosides; they comprise the *Gratioleae* (without *Limosella*, *Mazus*, and *Leucocarpus*), the *Calceolarieae*, the *Digitaleae* (without *Erinus* and *Rehmannia*), *Sphenandra* and *Nemesia*.

Group 2 consists of the taxa in which aucuboside and (or) catalpol occur: *Verbasceae*, *Scrophularieae* (*Halleria* is exceptional), *Collinsieae*, *Hemiphragmeae*, *Buchnereae*, *Veroniceae*, *Rhinantheae*, *Sutera* (p.p.?), *Limosella*, *Mazus*, *Zaluzianskya*, *Angelonia*, *Diascia*, *Erinus*, and *Rehmannia*.

Group 3 is formed by the species containing antirrhinoside: the *Antirrhineae*.

Group 4 contains the *Selaginoideae* in which unknown glycosides occur.

Provisionally the remaining taxa with unknown glycosides are put together into group 5, although the chromatographic evidence does not favour combination of these genera into one group: *Leucocarpus*, *Halleria*, and *Alonsoa*.

The division of the *Scrophulariaceae* into five groups of taxa is inconsistent with the subfamilial division as it is presented in Engler's Syllabus. Now the validity of the subfamilies *Scrophularioideae* and *Rhinanthoideae* is not very convincing since the difference between these subfamilies is based on one single character (which is moreover somewhat dubious), *viz.* the aestivation of the corolla lobes. The result of this division is that primitive tribes like the *Gratioleae* are in the same subfamily (*Scrophularioideae*) as the climax group *Antirrhineae* and that such diverse tribes as the *Digitaleae*, *Veroniceae* and the wholly or semi-parasitic taxa making up the remainder of the *Rhinanthoideae* are found together in one subfamily. This situation does not inspire much faith in the naturalness of the present subfamilial division, and has led some botanists to cast doubt on it (SCHMID 1906; BELLINI 1907; HALLIER 1903).

The segregation of the family into the groups mentioned above on the basis of the distribution of iridoid glycosides does not imply that each of these groups should be given subfamilial status; for this groups 1 and 2 are possibly too heterogeneous, while group 3 may have such close links with parts of group 1 or 2 that they outweigh the value of the iridoid character.

It should be noted that one of the tribes lacking iridoid glycosides is the *Gratioleae* which is considered to be the most primitive tribe of the family

Table 3. Distribution of iridoid glycosides in the tribes of the Scrophulariaceae (numbers of species).

	Aucuboside and/or catalpol	Antirrhinoside, antirrhinum glycoside B and/or asarina glycoside	Unknown glycosides	No glycosides
Scrophularioideae				
Gratioleae	2	–	1	17
Verbasceae	8	–	–	–
Scrophularieae	24	–	1	–
Manuleae	2	–	–	3
Collinsieae	5	–	–	–
Calceolarieae	–	–	–	4
Hemimerideae	2	–	2	4
Antirrhineae	–	21	–	–
Rhinanthoideae				
Digitaleae	2	–	–	7
Hemiphragmeae	1	–	–	–
Buchnereae	4	–	–	–
Veroniceae	15	–	–	–
Rhinantheae	29	–	–	–
Selaginoideae				
Selagineae	–	–	7	–

(Pennell 1935; Thieret 1967). Unless among the predecessors of the *Gratioleae* iridoid glycosides once have occurred and the capacity for synthesis of these compounds has been lost in this tribe in the course of evolution, the mechanism for the biosynthesis of these glycosides must have evolved within the other tribes. An alternative and more probable possibility is that a basic mechanism for the biosynthesis of iridoid compounds may be present in the *Gratioleae* and the other tribes of group 1, resulting in iridoid compounds which do not react with the reagent used in the present study. Many such iridoid compounds are known, *e.g.* the monoterpenoid alkaloids occurring in the *Apocynaceae* and *Rubiaceae*, iridoids like the Nepeta-lactones, and alkaloidal actinidine derivatives like indicaine and plantagonine, the latter two occurring in *Pedicularis olgae* Regel and some species outside the *Scrophulariaceae* (Torssell 1968). Thus far iridoid compounds have not been found in the *Gratioleae*, which may, however, be mainly due to the difficulty of demonstrating their presence.

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