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A CHEMOSYSTEMATIC STUDY OF SOME GERANIACEAE

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Key Word Index—*Geranium*; *Erodium*; *Monsonia*; Geraniaceae; flavonoid glycosides; chemosystematics.

Abstract—The flavonoids of five *Geranium*, fourteen *Erodium* and four *Monsonia* species were studied. Quercetin was the most common aglycone with lesser amounts of kaempferol, myricetin and luteolin. Glycosylation was found mainly in the 3- and/or 4′-positions and to a lesser extent in the 7-position. Chemosystematic relationships are discussed.

INTRODUCTION

The Geraniaceae is represented in Egypt by three native genera (*Geranium* L., *Erodium* L'Hérit. and *Monsonia* L.) comprising about 23 species mainly restricted to the Mediterranean coastal region and the Eastern Desert. In addition, several species of *Pelargonium* L'Hérit. are cultivated as ornamentals.

Forsskäl [1] reported four "Geraniums" now treated as *Erodium* species, of which *E.crassifolium* L'Hérit. (= *Geranium hirtum* Forssk.) was described from Egypt. Later Boissier [2] reported eight *Erodium* and two *Monsonia* species from this region, among which *E. arborescens* (Desf.) Willd. (= *E. hussonii* Boiss.), *E. neuradifolium* Del. ex. Godr. (= *E. aegyptiacum* Boiss.) and *E. oxyrrhynchum* M. Bieb. subsp. *bryoniifolium* Schönbeck-Temesy (= *E. bryoniaefolium* Boiss.) were described from Egypt. Täckholm and Chrtek [3] added four *Geranium* species new to the flora of Egypt: *G. yemense* Defl., *G. trilophum* Boiss., *G. mascatense* Boiss. and *G. rotundiflium L. Monsonia senegalensis* Guill. and Perr. was reported by Täckholm [4], while *M. densiflora* Täck & Boulos was first described from the South Eastern Desert of Egypt [5].

There are very few reports of flavonoid glycosides from members of the Geraniaceae. However, the anthocyanins of some *Geranium* and *Pelargonium* species [6, 7] have been identified and the flavonoid aglycones of 60 *Geranium* species have been reported. Quercetin and kaempferol were found as the most common constituents and myricetin was found in only a few species. The presence of flavonols and proanthocyanidins have been correlated with the geographic distribution of some *Geranium* species [8].

In the present study, five *Geranium*, fourteen *Erodium* and four *Monsonia* species were studied. Their flavonoid glycosides were identified and the results discussed in correlation with their systematics.

RESULTS AND DISCUSSION

Systematic background

According to Täckholm and Chrtek [3] the genus *Geranium* is represented in Egypt by six species, which are closely related morphologically. The three closely related species *G. yemense* Defl., *G. trilophum* Boiss. and *G. mascatense* Boiss. which are confined to the Gebel Elba region, are only differentiated on the basis of mericarp and seed characters [3]. The dissected leaves of *G. dissectum* L. clearly distinguishes this taxon from the other species growing in Egypt.

In a revision of the genus *Erodium* in Egypt [9] 14 species are recognized which are divided into two sections: *Plumosa* Boiss. and *Erodium* (= section *Barbata* Boiss.). Section *Plumosa* is characterized by a decideous mericarp beak (soft plumose on inner side) and a mericarp with two pits, one on either side, beneath the beak. Within section *Plumosa*, the position of *Erodium oxyrrhynchum* M. Bieb subspecies *oxyrrhynchum* Schönbeck-Temesy and *bryoniifolium* Schönbeck-Temesy is of interest. Both were mentioned as two distinct species [10]. Later, Zohary [11] doubted this separation and combined both in *E. bryoniifolium*. *E. oxyrrhynchum* has a very characteristic long beak, as well as a distinctive habit and mericarp. This taxon is restricted to Sinai. *E. bryoniifolium* was previously treated in the Egyptian flora as a distinct species, however the present evidence [9] is in favour of placing it as a subspecies of *E. oxyrrhynchum*.

On the other hand, section *Erodium* is divided into four subspecies: *Gruina* Lange, *Absinthioidea* Brumh., *Malacoidea* Lange and *Cicutaria* Lange. The first two monospecific subsections, *Gruina* and *Absinthioidea*, have very distinct fruit characters if compared with the remaining local members of the *Geraniaceae*.

The third subsection, *Malacoidea*, is characterized by its cordate–ovate leaves which are lobate to pinnatisect, beak 2–6 (9) cm long. Within this subsection, three species are difficult to distinguish, having similar flowers and fruit characters: *E. laciniatum* (Cav.) Willd., *E. pulverulentum* (Cav.) Willd. and *E. chium*. (L.) Willd.

The last subsection, *Cicutaria*, is different from the other Egyptian *Erodium* species in having compound leaves with distinct leaflets. All species are closely related and are only distinguished by sepal venation, the form of stamen filaments, staminode apex and mericarp characters [9].

The genus *Monsonia* is represented in Egypt by four species: *M. senegalensis* Guill. et Perr., *M. densiflora* Täck. & Boulos, *M. nivea* Decne ex Webb and *M. heliotropoides* (Cav.) Boiss. Characters which proved to be helpful in

Table 1. Flavonoid glycosides of some species of the Geraniaceae

Genus Section Subsection Species	Kaempferol	Quercetin							Myricetin		Luteolin
	3Rut4′G	3G	3Gl	3Rut	7G	4′G	3,7G	3Rut4′G	3G	3Rut	7G
Geranium											
G. yemens Defl.	+*	–	–	–	–	–	–	–	–	–	–
G. trilophum Boiss.	–	+†	–	–	–	–	–	–	–	–	–
G. mascatense Boiss.	–	–	–	–	–	–	–	–	–	+++	–
G. dissectum L.	–	+	+++	–	–	–	+	–	–	–	–
G. rotundifolium L.	+‡	–	–	–	–	–	–	–	–	–	–
Erodium											
Plumosa											
E. crassifolium L'Hérit	–	+++	–	+++	–	t	–	–	t	–	–
E. oxyrrhynchum											
subsp. *oxyrrhynchum* M. Bieb.	–	+++	–	+++	–	+++	–	–	t	–	–
subsp. *bryoniifolium* (Boiss.) Schönbeck-Temesy	–	+++	–	+++	–	+++	–	–	t	–	–
E. arborescens (Desf.) Willd.	–	+++	–	+++	–	t	–	–	t	–	–
E. glaucophyllum (L.) L'Hérit	–	+++	–	+++	–	t	–	–	t	–	–
Erodium											
Gruina											
E. gruinum (L.) L'Hérit	–	+	–	–	–	–	–	–	–	–	+++
Absinthioidea											
E. ciconium (L.) L'Hérit	–	+	–	–	–	–	–	–	–	–	+++

Malacoidea											
E. malacoides (L.) Willd.	++	t		++	+	+		+++			
E. neuradifolium Del. ex Godr.	++	t	–	++	+	t	–	+++	–	–	–
E. pulverulentum											
subsp. *pulverulentum* (Cav.) Willd.	++	+	–	++	+	t	–	+++	–	–	–
subsp. *bovei* (Del.) Schönbeck-Temesy	++	+	–	++	+	t	–	+++	–	–	–
E. laciniatum (Cav.) Willd.	++	+	–	++	+	+	–	+++	–	–	–
E. chium (L.) L'Hérit	++	+		++	+	+	–	+++	–	–	–
Cicutaria											
E. moschatum (L.) L'Hérit	–	+	–	+++	–	–	–	–	–	–	–
E. touchyanum Del. ex Godr.	–	+	–	+++	–	–	–	–	–	–	–
E. cicutarium (L.) L'Hérit	–	+		+++	–	–	–	–	–	–	–
Monsonia											
M. senegalensis Guill. and Perr.	–	+++	+	+	–	+	–	–	–	–	–
M. densiflora Täck. and Boulos	–	+++	+	++	–	+	–	–	–	–	–
M. nivea (Decne.) Decne ex Webb	–	+++	+	++	–	+	–	–	–	–	
M. heliotropoides (Cav.) Boiss.	–	+++	+	++		+	–	–	–	–	–

Key: +++ = Major, ++ = strong, + = weak, t = trace, 3G = 3-glucoside, 3Gl. = 3-glucuronide, 3Rut = 3-rutinoside, 7G = 7-glucoside, 4'G = 4'-glucoside, 3,7G = 3,7G-diglucoside and 3Rut4'G = 3-rutinoside-4'-glucoside.

* Major aglycone = kaempferol and traces of myricetin.

† Major aglycone = quercetin and traces of myricetin.

‡ Major glycosides = kaempferol 3-rhamnoside.

distinguishing the different *Monsonia* species are: habit and leaf form, number of flowers per pedicel, size of petals, length of sepals mucro and mericarp characters. *M. senegalensis* differs from the other *Monsonia* species in that the fruit beak is bristly (as opposed to soft plumose hairs), the peduncles are single flowered (as opposed to several flowered) and in being an annual (as opposed to perennial) [12]. The sources of the collected taxa are recorded in the Experimental section.

Chemosystematic relationships

Although the *Geranium* species investigated in the present study only represent a small portion of the genus, they differ from all the *Erodium* and *Monsonia* species in the absence of 4'-glucosides, which are characteristic of the two latter genera. The presence of both quercetin 3-glucoside and quercetin 3-rutinoside in nearly all the *Erodium* and *Monsonia* species examined, further confirms their close relationship. On the other hand, *Monsonia* species are distinguished from the *Erodium* species by the presence of quercetin 3-glucuronide, which was also detected in *Geranium dissectum* (Table 1).

In a study of the proanthocyanidins and flavonol aglycones in the leaves of 60 *Geranium* species Bate-Smith [8] found quercetin and kaempferol in almost every species, but not in the same amounts. Myricetin was only detected in 8 species. Knuth [13] divided 259 *Geranium* species into 30 sections, many with geographical connotation. Yeo [14] suggested a close relationship between sections *Ruberta* (*Robertiana*) and *Anemonifolia*. The results of Bate-Smith [8] indicate that these two sections have identical flavonoid patterns, with both quercetin and kaempferol present. In the present study quercetin 3-glucuronide was the major flavonoid glycoside in *Geranium dissectum* with lesser amounts of quercetin 3-glucoside and 3,7-diglucoside. In *G. rotundifolium* kaempferol 3-rhamnoside is the major flavonoid. As both species belong to section *Columbina* (*sensu* Knuth) these results suggest that flavonoid glycosides may be useful characters in the classification of *Geranium* species.

The four *Monsonia* species studied all have quercetin 3-glucoside as the major flavonoid glycoside with lesser amounts of quercetin 3-rutinoside and traces of quercetin 3-glucuronide and 4'-glucoside. This result is not surprising in view of their similar morphology and further supports the close relationship of these species.

Quercetin 3-glucoside was found throughout both sections of *Erodium*, but section *Plumosa* differs from section *Erodium* in the presence of traces of myricetin 3-glucoside. The only other report of myricetin in the family is in some *Geranium* species [8]. Furthermore, within section *Plumosa*, both subspecies of *E. oxyrrhynchum* produced quercetin 4'-glucoside as their major glucoside. Other species belonging to this section only contained traces of the same glycoside.

Section *Erodium* is divided into four subsections: *Gruina*, *Absinthioidea*, *Malacoidea* and *Cicutaria*. The

Table 2. Details of Geraniaceae specimens examined

Taxon	Collection
Geranium	
G. yemense	Gebel Elba, Khor across Gebel El-Shallal, 1962, Täckholm *et al.* (CAI)
G. trilophum	Gebel Elba, W. Akwamtra, 1967, Osborn and Helmy (CAI)
G. mascatense	Gebel Elba, Bir Shallal, 1962, Täckholm *et al.* (CAI)
G. dissectum	Dakhla Oasis, 1931, Hassib (CAI)
G. rotundifolium	Gebel Catherina, 1940, Hassib (CAI)
Erodium	
E. crassifolium	Sidi Abdel-Rahman, 1978, Merxmüller (CAI)
E. oxyrrhynchum	
subsp. *oxyrrhynchum*	Sinai, El-Raha plain, 1956, Täckholm (CAI)
subsp. *bryoniifolium*	Suez road, 1968, El-Sayed (CAI)
E. arborescens	Wadi Hof, 1950, Ibrahim (CAI)
E. glaucophyllum	Wadi Hof, 1980, Fayed and El-Naggar (CAI)
E. gruinum	Ikingi Mariut, 1908, Maire (CAI)
E. ciconium	Cairo-Alexandria desert road, 1968, Täckholm *et al.* (CAI)
E. malacoides	Dakhla Oasis, Mut, 1952, Täckholm *et al.* (CAI)
E. neuradifolium	Plateau of Sollum, 1975, Amin (CAI)
E. pulverulentum	
subsp. *pulverulentum*	Red Sea Coast, G. Hamata, 1961, Täckholm *et al.* (CAI)
subsp. *bovei*	Sinai, Fairan Oasis, 1961, El-Hadidi (CAI)
E. laciniatum	Ras El-Hekma, 1956, Imam (CAI)
E. chium	Burg El-Arab, 1958, Täckholm *et al.* (CAI)
E. moschatum	Mariut, Amira Satition, 1927, G. Täckholm (CAI)
E. touchyanum	Wadi Liblab, 1952, Kamel, CAI)
E. cicutarium	Dakhla Oasis, El-Hindawi, 1937, Hassib (CAI)
Monsonia	
M. senegalensis	Gebel Elba, 1933, Fahmy and Hassib (CAI)
M. densiflora	W. Sheit, 1961, Täckholm *et al.* (CAI)
M. nivea	Wadi El-Hay, Saff desert, 1960, Täckholm *et al.* (CAI)
M. heliotropoides	Wadi Gernal, Red Sea Coast, 1961, Täckholm *et al.* (CAI)

flavonoid patterns of subsection *Malacoidea* and *Cicutaria* are distinct. Thus, subsection *Cicutaria* is characterized by quercetin 3-rutinoside as the major component and subsection *Malacoidea* shows a most complex flavonoid pattern, with quercetin 3-rutinoside-4′-glucoside as its major flavonoid and smaller amounts of kaempferol 3-rutinoside-4′-glucoside. Kaempferol is absent from all other *Erodium* species examined. This subsection is also characterized by the presence of traces of quercetin 7-glucoside. The two monospecific subsections *Gruina* and *Absinthioidea* have identical flavonoid profiles and are chemically different from all the other *Erodium*, *Monosonia* and *Geranium* species examined. Although they contain traces of quercetin 3-glucoside (similar to other *Erodium* species), the major flavonoid is luteolin 7-glucoside. It has been suggested that in the dicotyledons flavones represent more advanced characters than flavonols and this was found to correlate with morphological characters in the case of the Umbelliferae [15, 16] and Oleaceae [17]. If this concept is valid then species of the two subsections *Gruina* and *Absinthioidea* may be considered as the most advanced species of the Geraniaceae which have so far been surveyed by us and by Bate-Smith [8].

EXPERIMENTAL

Plant material. Plants were collected as fresh material or herbarium samples, and voucher specimens are deposited in the Herbarium, Cairo University (CAI). Details of collected specimens are given in Table 2.

Identification of flavonoids. Plant material was extracted with 70% EtOH. Flavonoid glycosides were separated and identified according to standard methods [6, 18]. Common flavonoids identified were: quercetin 3-glucoside, 3-glucuronide, 3-rutinoside, 7-glucoside, 3,7-diglucoside, myricetin 3-glucoside, 3-rutinoside and luteolin 7-glucoside. The three uncommon flavonoids were identified as follows:

Kaempferol 3-rutinoside-4′-glucoside. Acid hydrolysis gave kaempferol, glucose and rhamnose. H_2O_2 oxidation gave rutinose, while enzymic hydrolysis (β-glucosidase) gave kaempferol 3-rutinoside. UV in MeOH: 265, 284 sh, 345; NaOMe: 279, 304 sh, 350 sh, 412 (stable); $AlCl_3$: 274, 300 sh, 335 sh, 392; $AlCl_3$–HCl: 274, 300 sh, 335 sh, 391; NaOAc: 266, 280 sh, 354, 400 sh. R_f: BAW 0.11, H_2O 0.51, 15% HOAc 0.58, PhOH 0.52.

Quercetin 4′-glucoside. Acid hydrolysis and enzymic hydrolysis (β-glucosidase) gave quercetin and glucose. UV λ_{max}^{MeOH} nm: 252, 266, 366; NaOMe: 280, 319 sh, 345 sh, 438 (stable); $AlCl_3$: 260, 266, 300 sh, 346 sh, 420; $AlCl_3$–HCl: 260, 268, 300 sh, 346 sh, 420; NaOAc: 273, 320, 384; NaOAc–H_3BO_3: 254, 268, 306 sh, 367. R_f: BAW 0.30, H_2O 0.02, 15% HOAc 0.06, PhOH 0.32.

Quercetin 3-rutinoside-4′-glucoside. Acid hydrolysis gave quercetin, glucose and rhamnose. H_2O_2 oxidation gave rutinose, while enzymic hydrolysis (β-glucosidase) gave rutin. UV λ_{max}^{MeOH} nm: 252, 268, 355; NaOMe: 266, 304 sh, 418 (stable); NaOAc: 256, 268, 360, NaOAc–H_3BO_3: 256, 268, 358. R_f: BAW 0.09, H_2O 0.47, 15% HOAc 0.56, PhOH 0.50.

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