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COMPARATIVE STUDY OF THE FLAVONOIDS OF SOME LOCAL MEMBERS OF THE UMBELLIFERAE

NABIEL A. M. SALEH, SABRY I. EL-NEGOUMY, MOHAMED N. EL-HADIDI* and HASNAA A. HOSNI*

National Research Centre, El-Dokki, Cairo, Egypt; *Department of Botany, Faculty of Science, Cairo University, Egypt

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Abstract—Thirty-six species belonging to 27 genera of the sub-family Apioideae, family Umbelliferae, were investigated for their leaf and stem flavonoids. Fourteen flavonoid glycosides of the aglycones kaempferol, quercetin, isorhamnetin, apigenin and luteolin were identified. Chemosystematic relationships are discussed.

In the Umbelliferae, flavonoids, phenylpropanoids, acetylenes, terpenoids and coumarins are characteristic chemical constituents [1, 2]. Kaempferol, quercetin, apigenin and luteolin are the most common flavonoid aglycones. Isorhamnetin, chrysoeriol, diosmetin and acacetin occur less frequently and flavanones rarely [3]. Glycosylation is common in position 3 for flavonols and position 7 for flavones [3]. Sulphated flavonoids have also been reported in the family [4].

On the basis of fruit morphology, taxa with spines on both the primary and secondary ridges of the fruits, are grouped in the Caucalideae by Bentham and Hooker [5] and Boissier [6]. But Drude [7] divided these species between two tribes: the Scandiceae (sub-tribe Caucalinae) and the Dauceae. The largest genus in the Caucalinae is *Torilis* and in Dauceae is *Daucus*. At the tribal level, Harborne [3] from the flavonoid evidence, divided the family into two broad groups: the first group of nine tribes in which flavones are rare or absent; and the second group of four tribes in which flavones are common or predominant (Apieae, Dauceae, Laserpitieae and Scandiceae *sensu* Drude). Similar patterns were observed in the present study of 36 species belonging to the sub-family Apioideae (Table 1).

Harborne [3] carried out a detailed study of the flavonoid constituents of the tribe Caucalideae *sensu* Boissier. The study concentrated on the fruit flavonoids and to a lesser extent on those in leaf and flowers. A correlation between flavonoids and evolutionary progression within the Caucalideae was based on the presence or absence of flavones versus flavonols. It has been suggested that flavones represent advancement by loss mutation over the corresponding flavonols [8]. This correlates with advanced and primitive characters in the Umbelliferae [3] and the Oleaceae [9].

The data reported in the present study correlate with the results previously reported in the fruits by Harborne [3] as well as the survey of aglycones by Crowden *et al.* [10]. The most common flavonol glycoside is the 3-glucoside followed by the 3-rutinoside, while the most common flavone glycoside is the 7-glucoside (Table 1).

Although the chromosomal data [11] do not correlate with the tentative grouping of the tribes of the Apioideae based on the presence or absence of flavones and flavonols [10], a close similarity between the distribution of numbers in the Scandiceae and Dauceae support their close relationship based on chemical evidence [3, 10]. Furthermore, serological data confirm that in the Scandiceae and Dauceae greater changes in protein chemistry have occurred [12]. Also, both tribes have evolved stomatal characters [13]. The serological evidence, however, did not support Bentham and Hooker's [5] treatment of placing *Torilis* and *Daucus* in the tribe Caucalideae. Both species contain flavone 5-glycosides, which indicate a rather specialized character (Table 1 and results in ref. [3]) It is interesting to note that all *Torilis* species examined only contained flavone glycosides, while *Daucus* species proved to contain both flavone and flavonol glycosides (see Table 1 and ref. [3]).

Serological data indicated a great protein similarity between tribes Coriandreae and Ammineae, as well as a close correspondence among both tribes and Peucedaneae [12]. All three tribes contain mainly flavonols as their major glycosides, with the exception of *Pimpinella etbacia*, *Cuminum cyminum* and *Ammoides pusilla* which contain flavone glycosides (Table 1). Pollen grain characters indicated that *Bupleurum* species (tribe Ammineae) showed primitive characters [14]. All species investigated in the present study only contained flavonol glycosides, and similar results are also reported in the literature for other *Bupleurum* species [10].

It is interesting to note that in the case of *Bupleurum semicompositum* two chemical races exist, one with the 3-rutinosides of quercetin and isorhamnetin as the major glycosides and the second with the 3-glucosides as well as the 3-rutinosides. Similarly, *Foeniculum vulgare* also proved to have two chemical races [15].

EXPERIMENTAL

Plant material. Fresh material was used whenever possible. Herbarium samples of all investigated taxa are deposited at the Herbarium, Department of Botany, Cairo University.

Isolation and identification of flavonoid constituents. The plant material (leaf and stem) was extracted with 70% EtOH. Flavonoid glycosides were isolated using elution techniques, and identified according to standard methods [16, 17].

Table 1. Distribution of flavonols and flavones in the sub-family Apioideae

Sub-family Apioideae (*sensu* Drude)	No. of samples	Flavonols*									Flavones†					
		Kaempferol		Quercetin					Isorhamnetin		Apigenin		Luteolin			
		3Glc	3Glur	3Glc	3Gal	3Glur	3Rut	3Poly	3Glc	3Rut	7Glc	7Glur	7Glc	7Glur	5Glc	5Glur
Tribe I : Echinophoreae																
Pyconcycla tomentosa Decne	1	+++	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tribe II : Scandiceae																
Subtribe 1: Scandicinae																
Scandix pecten-veneris L.	1	–	–	–	–	–	–	–	–	–	+	–	+++	–	–	–
Scandicium stellatum (Sol.) Thell. var. *hirsutum* (C. Koch.) Thell.	1	–	–	–	–	–	–	–	–	–	+	–	+++	–	–	–
Subtribe 2: Caucalinae																
Torilis nodosa (L.) Gaertner	1	–	–	–	–	–	–	–	–	–	+	+	+++	+	–	–
Torilis radiata Moench	2	–	–	–	–	–	–	–	–	–	+	–	+++	+	–	–
Torilis bracteosa Bianca ex Nym.	2	–	–	–	–	–	–	–	–	–	+	+	+++	+	–	–
Torilis arvensis (Hudson) Link	1	–	–	–	–	–	–	–	–	–	+	–	+	?	+++	+
Caucalis tenella Del.	1	–	–	–	–	–	–	–	–	–	+	–	++	+	+++	–
Pseudorlaya pumila (L.) Grande	1	–	–	–	–	–	–	–	–	–	+	–	+++	–	–	–
Tribe III: Coriandreae																
Coriandrum sativum L.	1	–	+	+	–	++	+++	++	–	–	–	–	–	–	–	–
Tribe IV: Ammineae																
Subtribe 1: Carinae																
Bupleurum lancifolium Hornem.	1	–	–	–	–	–	+++	–	–	+++	–	–	–	–	–	–
Bupleurum falcatum L. var. *linearifolium* (Boiss.) Tackh.	1	–	–	+	–	–	++	–	+	++	–	–	–	–	–	–
Bupleurum nanum Poir.	1	–	–	+	–	–	+++	–	+	+++	–	–	–	–	–	–
Bupleurum semicompositum L.	4	–	–	+	–	–	+++	–	–	+++	–	–	–	–	–	–
	4	–	–	+++	–	–	+++	–	+++	+++	–	–	–	–	–	–
Pituranthos tortuosus (Desf.) Benth. & Hook. f.	1	–	–	–	–	–	?	–	–	+++	–	–	–	–	–	–
Ammi majus L.	3	–	–	–	–	–	–	–	+++	+	–	–	–	–	–	–
Ammi visnaga (L.) Lam.	1	–	–	–	–	–	–	–	+++	++	–	–	–	–	–	–
Berula erecta (Hudson) Coville	1	–	–	+++	–	–	–	+	–	–	–	–	–	–	–	–
Pimpinella etbacia Schweinf.	1	–	–	–	–	–	–	–	–	–	–	+++	–	+++	–	–
Ridolfia segetum (L.) Moris	1	–	–	–	–	+++	–	–	–	–	–	–	–	–	–	–
Apium leptophyllum (Pers.) F. Muell. ex Benth.	5	++	+++	++	–	+++	–	+	–	–	–	–	–	–	–	–
Apium graveolens L.	2	–	–	++	+++	–	–	+	–	–	–	–	+	–	–	–
Helosciadium nodiflorum (L.) Koch	1	–	–	+++	–	–	–	+	–	–	–	–	–	–	–	–
Carum carvi L.	1	–	–	+++	–	–	–	–	–	–	–	–	–	–	–	–

Cuminum cyminum L.	1	–	–	–	–	–	–	–	–	–	+‡	–	+++‡	–	–	–
Ammoides pusilla (Brot.) Breistr.	1	–	–	–	–	+	–	–	–	–	–	–	+++	–	–	–
Subtribe 2: Seselinae																
Foeniculum vulgare (L.) Mill. sub. *piperitum* (Ucria) Coutinho	2	–	++	+	–	+++	–	–	–	–	–	–	–	–	–	–
Foeniculum vulgare (L.) Mill. sub. *vulgare*	1	–	++	+	–	+++	–	–	–	–	–	–	–	–	–	–
Crithmum maritimum. L.	1	–	–	+	–	–	–	+	–	–	–	–	+++	–	–	–
Anethum graveolens L.	1	–	–	–	–	+++	–	–	–	–	–	–	–	–	–	–
Tribe V : Peucedaneae																
Subtribe 1: Ferulinae																
Ferula marmarica Asch. & Taub.	1	–	–	+++	–	–	–	++	–	–	–	–	–	–	–	–
Ducrosia ismaelis Asch.	1	–	–	+++	–	–	–	++	–	–	–	–	–	–	–	–
Subtribe 2: Tordylinae																
Malabaila suaveolens Coss.	1	–	–	–	–	–	–	–	§	–	–	–	–	–	–	–
Zosima orientalis Hoffm.	1	–	–	+‖	–	–	–	+¶	–	–	–	–	–	–	–	–
Tribe VI: Dauceae																
Daucus littoralis Sibth. & Sm.	1	–	–	+++	–	–	–	–	–	–	–	–	+**	–	–	–
Tribe VII: Smyrnieae																
Astoma seselifolium DC.	1	–	–	–	–	–	–	–	–	–	–	–	+++	–	–	–

*3 Glc, 3-glucoside; 3 Gal, 3-galactoside; 3 Glur, 3-glucuronide; 3 Rut, 3-rutinoside; 3 Poly, 3-polyglycoside.
†7 Glc, 7-glucoside; 7 Glur, 7-glucuronide; 5 Glc, 5-glucoside; 5 Glur, 5-glucuronide.
‡7-Polyglycosides also present.
§Isorhamnetin is the major aglycone.
‖Quercetin 7-glucoside.
¶Quercetin 3,7-diglucoside.
**Traces of a *C*-glycoside were detected.

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