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The flavonoids of the *Fagonia bruguieri* complex (*Zygophyllaceae*)*

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Abstract: Seven flavonol glycosides were identified from the main taxa of the *F. bruguieri* complex. Of these, kaempferol 3-rhamno-galactoside, Quercetin 3-rhamnogalactoside and Quercetin 3-galactoside are new records for the genus *Fagonia* L. and the *Zygophyllaceae* s. str. The distribution of these flavonoid glycosides is discussed with respect to the morphology, chemosystematics, and possible phylogeny of the complex and the genus.

According to EL-HADIDI (1973), the *Fagonia bruguieri* complex comprises four closely allied species with 4 sulcate-angular internodes. All taxa have petiolate and essentially 3-foliolate leaves on their lower nodes. Within this complex *F. kassasii* HADIDI is rather primitive by its trifoliolate leaves and petioles 3–5 cm long. Advanced taxa such as *F. bruguieri* DC. var. *bruguieri* and *F. schimperi* PRESL are characterized by lower tri- and upper unifoliolate leaves with petioles not exceeding 1 cm. *F. bruguieri* var. *bruguieri* is glandular while *F. schimperi* is almost glabrous. In the most advanced taxa, viz. *F. bruguieri* var. *rechingeri* EL-HADIDI and *F. olivieri* var. *olivieri*, the plants are strictly unifoliolate and the latter is almost glabrous.

SALEH & EL-HADIDI (1977) studied the flavonoids in representatives of three of the seven subfamilies of the *Zygophyllaceae* s. lat. The aglycones identified were kaempferol, quercetin, isorhamnetin, herbacetin and herbacetin-8-O-methyl ether while glycosidic patterns elucidated range from mono- to tri-glycosides. The distribution of these flavonoid glycosides was discussed with respect to their chemosystematic significance.

Chemosystematic investigations of several species of the genus *Fagonia* L. is in progress. These include the species of the *Fagonia arabica* complex (EL NEGOUMY & al. 1986) and *F. mollis* complex (AL WAKEEL & al.1986). In this account the chemosystematics of the main taxa of the *F. bruguieri* complex will be surveyed and discussed in relation to both of the earlier investigated complexes.

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Table 1. Chromatographic, hydrolytic, and oxidation data

	R_f (× 100)				
	BAW	TBA	HOAC	H_2O	PhOH
Kaempferol (K)					
3-glucoside	55	67	34	31	65
3-rutinoside	48	53	66	45	57
3-rhamnogalactoside	52	54	68	58	43
Quercetin (Q)					
3-galactoside	43	56	51	28	46
3-rhamnogalactoside	44	45	69	45	40
3-rutinoside	41	44	56	39	42
Isorhamnetin (I)					
3-rutinoside	46	48	65	34	70

Table 2. UV data (λ max, nm) for flavonoids

Compound	MeOH	NaOMe	$AlCl_3$
Kaempferol			
3-glucoside	352, 295 sh, 265	403, 326, 274	397, 350, 304, 274
3-rutinoside	350, 300 sh, 265	400, 325, 272	395, 302 sh, 272
3-rhamnogalactoside	345, 300 sh, 265	390, 320, 272	397, 350, 300 sh, 272
Quercetin			
3-galactoside	355, 259	407, 320, 277	415, 345 sh, 299 sh, 268
3-rhamnogalactoside	351, 332 sh, 262 sh, 257	400, 325, 272	395, 302 sh, 272
3-rutinoside	345, 300 sh, 265	390, 320, 272	397, 350, 300 sh, 272
Isorhamnetin			
3-rutinoside	355, 266, 255	420, 335, 284	406, 366, 300, 276 sh, 268

Materials and methods

Fresh plant material was collected, chopped, extracted with 70% EtOH. Investigated specimens are: *Fagonia bruguieri* DC. var. *bruguieri* (Galala desert, Cairo Suez Road, March 1985, EL-HADIDI & al.); *F. schimperi* PRESL (Sinai, St Catherine area, Gabel el Dier, April 1985, El Garf); *F. kassasii* HADIDI (Gabel Elba, NW & W, slopes of Gabel Asotriba, January 1962, V. TÄCKHOLM & al.): *F. olivieri* DC. var. *olivieri* (Kuwait Ras el Guleia, November 1966, El Halwagy). Vouchers are deposited at the Herbarium, Faculty of Science, Cairo University (CAI).

Standard procedures for the separation and identification of flavonoids were applied (HARBORNE 1967 and MABRY & al. 1970). The extract was subjected to column chromatography on polyamide (MN polyamide SC, 6 Macherey Nagel). Acid hydrolysis was carried out with 2 N HCl, mild acid hydrolysis with 0.1 N HCl. Enzymatic hydrolysis was carried out at pH 5 (acetate buffer) at 37 °C (HARBORNE 1965). For H_2O_2 oxidation the method described

of flavonoid glycosides from *Fagonia bruguieri* var. *bruguieri*

Acid hydrolysis		H_2O_2 oxidation
Strong (2 N HCl)	Mild (0.1 N HCl)	
K, glucose	–	glucose
K, glucose, rhamnose	K, K-3-glucoside	rutinose
K, galactose, rhamnose	K, K-3-galactoside	rhamnogalactose
Q, galactose	–	galactose
Q, galactose, rhamnose	Q, Q-3-galactoside	rhamnogalactose
Q, glucose, rhamnose	Q, Q-3-glucoside	rutinose
I, glucose, rhamnose	I-3-glucoside	rutinose

from *Fagonia bruguieri* var. *bruguieri*

$AlCl_3$-HCl	NaOAc	NaOAc/HB_3O_3
395, 346, 303, 274	372, 302, 274	352, 295, 265
395, 307, 300 sh, 272	385, 305, 272	355, 295 sh, 315 sh, 265
395, 345, 300 sh, 272	362, 300 sh, 270	350, 300 sh, 265
403, 360, 300 sh, 271	392, 325 sh, 260	371, 263
395, 307, 300 sh, 272	385, 305, 272	355, 295 sh, 315 sh, 265
395, 345, 300, 272	362, 300 sh, 270	350, 300 sh, 265
400, 360, 300, 274 sh, 268	410, 322, 273	260, 300 sh, 270 sh, 255

by CHANDLER & HARPER (1961) was applied. For chromatography Whatman No. 1 paper was used for the following solvent systems BAW (n BuOH – HOAc – H_2O, 4 : 1 : 5), upper phase, H_2O, 15% HOAc, 80% PhOH, TBA (t BuOH-HOAc-H_2O 3 : 1 : 1). Sugars were identified by cellulose TLC against standard marker in pyridine EtOAc : HOAc : H_2O, 36 : 36 : 7 : 21) and detected by spraying with aniline phthalate. All fractions were purified by standard procedures (MABRY & al. 1970 and MABRY & MARKHAM 1975) over sephadex LH-20 (Pharmacia) using MeOH prior to spectral analysis. Chemical structures of compounds were elucidated using UV, ^1H NMR and chromatographic techniques in conjunction with comparison of appropriate reference compound (when available), using the standard procedure described by MABRY & al. (1970), MABRY & MARKHAM (1975). UV spectra were recorded in a Beckman 34 ultraviolet spectrophotometer ^1H NMR, spectra of trimethylsilyl ether were recorded on a Varian EM 390, 90 MHz spectrometer in CCl_4 with TMS as internal standard.

Table 3. ^{1}H NMR data of *Fagonia bruguieri* var. *bruguieri* flavonoids. Isorhamnetin was (δ-scale) relative to TMS

Flavonoids as	H-2′	H-6′	H-5′	H-3′	H-8	H-6
Kaempferol						
3-glucoside	7.9	7.85	6.92	6.85	6.45	6.2
3-rutinoside	7.85	7.75	6.9	6.8	6.45	6.2
3-rhamnogalactoside	7.92	7.85	6.92	6.85	6.45	6.2
Quercetin						
3-galactoside	7.5	7.4	6.9	–	6.5	6.18
3-rhamnogalactoside	7.5	7.4	6.9	–	6.45	6.2
3-rutinoside	7.55	7.4	6.85	–	6.45	6.2
Isorhamnetin						
3-rutinoside	7.8	7.55	6.85	–	6.45	6.15

Table 4. Distribution of flavonoid glycosides in the *Fagonia bruguieri* complex. + + + major; + + strong, + weak, t trace, * new record for the *Zygophyllaceae*

	Kaempferol			Quercetin			Isorhamnetin
	3-glucoside	3-rutinoside	3-rhamnogalactoside	3-rutinoside	3-rhamnogalactoside*	3-galactoside*	3-rutinoside
F. kassasii	+	+	+ + +	+ +	+ +	+	+
F. bruguieri	+	+	+ + +	+ +	+ +	+	t
F. olivieri	t	+ +	+ + +	+ +	+	t	+
F. schimperi	t	+ +	+ + +	+ +	+	t	+

Results and discussion

Aqueous ethanolic extracts of *Fagonia bruguieri* var. *bruguieri* yielded after chromatographic separation seven flavonol glycosides (Table 1). Subsequent, analysis of the glycosides was carried out by chemical (Table 1) and conventional UV and ^{1}H NMR spectroscopy (Tables 2 & 3). The flavonoids of *F. bruguieri* var. *bruguieri* are based upon kaempferol, quercetin and isorhamnetin. All glycosides are linked at position three. The main flavonoid glycoside is kaempferol 3-rham-

separated from *F. schimperi.* Spectra were recorded in CCL_4; values are given in PPM as an internal standard

Glycosyl				O-methyl
"H 1	"H 1 (C-1 rhamnosyl)	Non-aromatic	CH_3 (rhamnosyl)	
5.9	–	3.5–3.85	–	–
5.85	4.25	3.5–3.9	1.25	–
5.65	4.2	2.25–3.9	1.25	–
5.7	–	3.45	–	–
5.6	4.2	3.35–3.9	1.25	–
5.9	4.2	3.3–3.6	1.2	–
5.9	4.25	3.3–3.6	1.15	3.85

Table 5. Distribution of flavonoids in three *Fagonia* complexes. ± *major* compound

	Kaempferol			Quercetin			Isorhamnetin		Herbacetin	Herbacetin-8-methylether			
	3-glucoside	3-rhamnogalactoside	3-rutinoside	3-galactoside	3-rhamnogalactoside	3-rutinoside	3-glucoside	3-rutinoside	8-rutinoside	aglycone	3-rutinoside	3,7-diglucoside	3-rutinoside-7-glucoside
F. arabica complex							+	+	+		±	+	+
F. mollis complex			±					±		+			
F. bruguieri complex	+	±	+	+	+	+		+					

nogalactoside which is a new record to the genus *Fagonia* as well as the other genera of *Zygophyllaceae* s. str. (SALEH & EL-HADIDI 1977).

It may be noticed that the species of *F. bruguieri* complex (Table 4) are characterized by the presence of quercetin (3-galactoside, 3-rhamnogalactoside and 3-rutinoside). Of these, quercetin 3-galactoside and 3-rhamnogalactoside are new records for the *Zygophyllaceae* s. str. The three flavonoid glycosides (kaempferol 3-rhamnogalactoside, quercetin 3-rutinoside and isorhamnetin 3-rutinoside) are

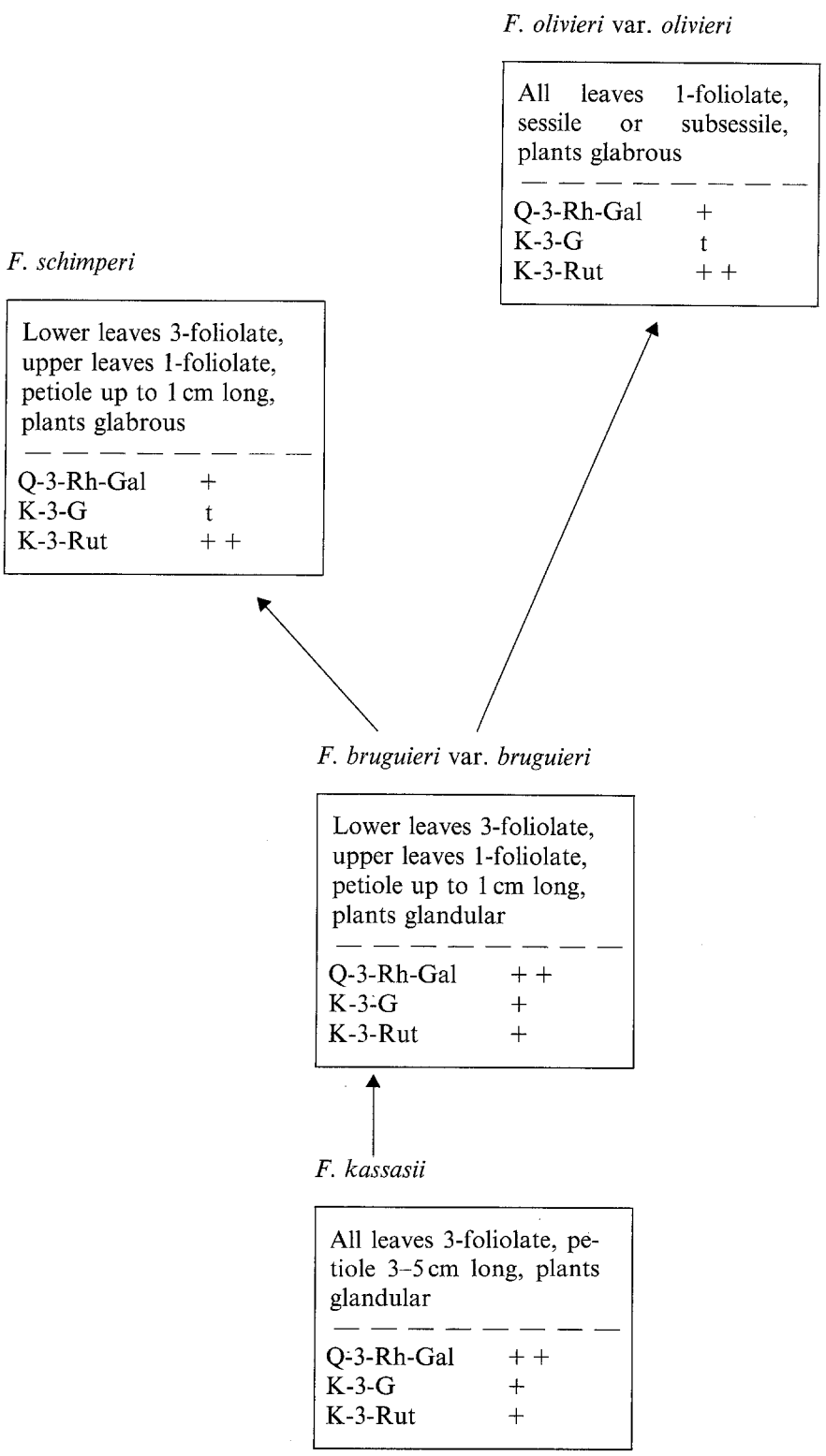

Fig. 1. Diagram of the phylogenetic relationships of the taxa investigated from the *F. bruguieri* complex. Quercetin-3-rhamnogalactoside (Q-3-Rh-Gal), Kaempferol-3-glucoside (K-3-G), Kaempferol-3-rutinoside (K-3-Rut)

occurring quantitatively in similar amounts among the investigated taxa; of these kaempferol 3-rhamnogalactoside is the main glycoside. Quercetin 3-rhamnogalactoside, quercetin 3-galactoside and kaempferol 3-glucoside are quantitatively more common in both, *F. kassasii* and *F. bruguieri* var. *bruguieri*, suggesting a more ancestral position for these taxa, whereas the presence of both flavonoid glycosides in lower amounts or traces in *F. schimperi* and *F. olivieri* var. *olivieri* could be regarded as an advanced feature. Another criterion of apparent advancement is the increase in quantity of kaempferol 3-rutinoside in *F. schimperi* and *F. olivieri* var. *olivieri* as compared with *F. bruguieri* var. *bruguieri* and *F. kassasii*.

Fig. 1 gives a diagram of the relationships between the morphological characters and the recorded flavonoid glycosides among the investigated taxa of the *F. bruguieri* complex. The possibly ancestoral taxa *F. kassasii* and *F. bruguieri* var. *bruguieri*, are glandular shrubs or undershrubs with petiolate and 3-foliolate leaves (at least at the lower nodes). Both have a higher content of quercetin 3-rhamnogalactoside than the more specialized taxa, *F. schimperi* and *F. olivieri* var. *olivieri*. The latter are glabrous, prostrate undershrubs with short petioled or sessile and 3-foliolate leaves on the lower nodes in *F. schimperi* and strictly unifoliolate leaves in *F. olivieri* var. *olivieri*.

Table 5 presents the available information about the distribution of flovonoid glycosides among the investigated *Fagonia* complexes. It may be noticed that isorhamnetin 3-rutinoside is of common occurrence among the taxa of the investigated complexes. Isorhamnetin, herbacetin and herbacetin-8-methyl ether are the aglycones of the *F. arabica* complex. The main flavonoid glycoside is herbacetin-8-methyl ether-3-rutinoside (EL NEGOUMY & al. 1986). Kaempferol, isorhamnetin, and herbacetin-8-methyl ether are the aglycones of the *F. mollis* complex. The main flavonoid glycosides are Kaempferol-3-rutinoside and isorhamnetin-3-rutinoside (AL WAKEEL & al. 1986). Table 5 also shows that three of the flavonoid glycosides known from the *F. bruguieri* complex belong to quercetin which suggests the primitive status and eventual ancestral position of this complex.

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