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FLAVONOIDS OF THREE LOCAL *SENECIO* SPECIES

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Key Word Index—*Senecio gallicus*; *S. hoggariensis*; *S. vulgaris*; Compositae; chemosystematics; flavonol glycosides; sulphated flavonols.

Abstract—Two isorhamnetin glycosides and two sulphated derivatives are reported for the first time in the genus *Senecio*.

The flavonoids of *Senecio* L. species were first studied when rutin (quercetin 3-rutinoside) was reported in *S. erraticus* Benth. subsp. *barbareifolius* Koch. [1], as well as the flowers of *S. jacobaea* L. [2]. The 3-glucosides and 3-rutinosides of both kaempferol and quercetin, and apigenin 7-glucoside as well as the rare 3-methylquercetin were later identified in 25 *Senecio* species [3]. Also present was the rare 6,8-di-*C*-rhamnosylapigenin and, in one species only (*S. tamoides*), the xanthone *C*-glucosides, mangiferin and isomangiferin [3].

In the present study, three local species were studied. The flavonoids present were identified as the 3-glucosides of quercetin and isorhamnetin and isorhamnetin 3-rutinoside. Also present were the 3-monosulphate and 3,7(?)-disulphate of isorhamnetin (see Table 1). No *C*-glycosides of flavones or xanthones were detected.

The presence of quercetin 3-glucoside is common in the Compositae [4, 5]. On the other hand, the variation in the flavonoid chemistry within the *Senecio* species is not unexpected. *Senecio* is a cosmopolitan genus with about 1500 species, and chromosome numbers ranging from $x = 5$ to 90 [6]. This represents the largest variation within the tribe Senecioneae.

EXPERIMENTAL

Plant material. A sample of *S. gallicus* Chaix (= *S. desfontainei* Druce = *S. coronopifolius Desf.*) was collected 1 km W. of Koum Ushim, El-Fayoum. The two other samples (*S. hoggariensis* Battand. and Trab. and *S. vulgaris* L.) were herbarium samples collected from the NW slopes of Gebel Elba and from Sidi Gaber, Alexandria respectively.

Flavonoid identification. The plant material was extracted with 70% EtOH. The flavonoids were isolated, purified and identified by standard procedures [7, 8]. Co-chromatography was carried out with authentic samples of isorhamnetin glycosides [9]. The sulphates were identified by electrophoresis in HOAc buffer (pH 2) for 2 hr [10]. The monosulphate travelled 2 cm, the disulphate 5.5 cm and isorhamnetin 3-glucoside 0 cm. Both sulphated derivatives gave isorhamnetin on treatment with 0.5 N HCl in the cold. The UV data indicated that the monosulphate was sulphated in position 3, while the disulphate was sulphated in positions 3 and 7 (not clear).

Table 1. Distribution of flavonoid glycosides in local *Senecio* species

	Flavonoids identified†				
	Q 3-glucoside	I 3-glucoside	I 3-rutinoside	I 3-monosulphate†	I disulphate‡
Senecio gallicus Chaix	−	++	++	+	+
S. hoggariensis Battand and Trab.	+	−	t	t	−
S. vulgaris L.	++	++	++	+	+

†Q = quercetin, I = isorhamnetin, t = trace.
‡See Experimental for details.

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TWO FLAVONOIDS FROM THE FROND EXUDATE OF *PITYROGRAMMA TRIANGULARIS* VAR. *TRIANGULARIS*

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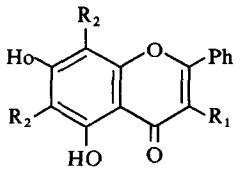
Key Word Index—*Pityrogramma triangularis* var. *triangularis*; Gymnogrammoideae; Pteridophyta; frond exudate; trace constituents; novel flavonoids; 5,7-dihydroxy-3-methoxy-6,8-dimethylflavone; 5,7-dihydroxy-6,8-dimethoxyflavone.

From a recently published review on flavonoid patterns in the farinose exudate of *Pityrogramma* species [1], it is apparent that *P. triangularis* (Kaulf.) Maxon is outstanding in its farina chemistry. Only in the members of this species-complex are *C*-methylated flavonoids found. The following representatives have been reported so far: ceroptin, pityogrammin [2] and triangularin [3] from var. *triangularis*; a *C*-methylated dihydrochalcone from var. *viscosa* D. C. Eaton [4] and three *C*-methylated flavanones from var. *pallida* Weath. [5]. The farinose frond exudate of the 'ceroptin-type' of var. *triangularis* [6] contains a series of trace constituents, as yet unidentified. Two of these have now been isolated in small amounts [7]. One of them is a novel *C*-methylated flavonol, the other a novel flavone.

Compound **1** appears as a dark spot on polyamide (UV 366), which turns reddish-brown after spraying with 'Naturstoffreagenz A' (β-aminodiethyl ether of diphenyl boric acid). It therefore appears to be a flavonol methylated at C-3. According to its molecular peak at *m/z* 312, it could be either a flavone or a 3-methylflavonol [8],



1 R_1 = OMe, R_2 = Me
2 R_1 = H, R_2 = OMe

but this assumption does not agree with its polarity (R_f 0.56 in solvent A). However, the ^{1}H NMR data reveal the existence of one OMe group (δ 3.87 ppm) and two Me groups (δ 2.11, *s*; 2.29, *s*). Thus, in addition, there are two OH groups, one of which can be readily placed at C-5 (δ 12.80, broad signal). Since the ^{1}H NMR signals, as well as characteristic MS-fragments at *m/z* 235 (M − 77) and 105 ('Pic C' accord. to ref. [9]), prove the presence of an unsubstituted B-ring, the second OH group must also be located on the A-ring and at C-7, although in the UV spectrum no shift is observed on addition of NaOAc. The