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FLAVONOIDS OF FOUR SPECIES OF *PARTHENIUM* (COMPOSITAE)

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Key Word Index—*Parthenium hysterophorus*, *P. bipinnatifidum*, *P. glomeratum* and *P. rollinsianum*; Compositae; North–South American disjunctions; quercetin and kaempferol 3-*O*-glycosides; quercetin; 6-hydroxykaempferol and quercetagetin methyl ethers.

Abstract—Kaempferol and quercetin 3-*O*-glycosides were found in the closely related species, *Parthenium hysterophorus*, *P. bipinnatifidum* and *P. glomeratum*; the major aglycone flavonols in *P. hypterophorus* are quercetagetin 3,7-dimethyl ether and a new flavonoid, 6-hydroxykaempferol 3,7-dimethyl ether. The North–South American species-pair *P. glomeratum* (Argentina) and *P. bipinnatifidum* (Mexico) yielded quercetagetin 3,7,3′-trimethyl ether as the major aglycone. The desert species *P. rollinsianum* yielded five methylated flavonols: quercetin 3,3′-dimethyl ether, penduletin, quercetagetin 3,6,7-trimethyl ether, polycladin and artemetin.

INTRODUCTION

As part of our investigation of the genus *Parthenium* [1–3] we report here some of the flavonoid chemistry of four species of *Parthenium*. The flavonol glycosides of three species, *P. hysterophorus* L., *P. bipinnatifidum* (Ortega) Rollins and *P. glomeratum* Rollins, were similar. Indeed, the latter two species, *P. glomeratum* from Argentina and *P. bipinnatifidum* from Mexico, had essentially identical flavonoids, in accord with the previous report that their sesquiterpene lactones were identical [4]. All four species investigated here, including *P. rollinsianum* Rzedowski, were characterized by methyl ethers of quercetagetin, quercetin and 6-hydroxykaempferol; the aglycones for *P. rollinsianum* (its glycoside pattern was not determined) were the same as, or similar to those identified in *P. incanum* H.B.K. (sect. *Parthenichaeta*) and species of the section *Bolophytum* [5–6].

RESULTS

Aqueous methanol extraction of air-dried, leaf material of *P. hysterophorous* yielded as the major aglycone quercetagetin 3,7-dimethyl ether (**1**), a compound previously isolated from *P. tomentosum* and incorrectly designated as the 3,3′-dimethyl ether [2]. However, we had concluded later [5] on the basis of considerable data that this substance was in fact the 3,7-dimethyl ether, and this was subsequently confirmed when the UV and MS spectra of **1** were shown to be identical with those obtained for synthetic quercetagetin 3,7-dimethyl ether (provided by H. Wagner). Also present in small quantities in *P. hysterophorus* is 6-hydroxykaempferol 3,7-dimethyl ether (**2**), a new flavonol (this substance was subsequently synthesized by H. Wagner, private communication; the natural and synthetic substances were identical by UV). The MS of the new substance gave a base peak

Table 1. Flavonoids of four species of *Parthenium* (Compositae)

Taxon	Flavonoids 1	2	3	4	5	6	7	8	9	10	11	12
Sect. *Argyrochaeta*												
P. hysterophorus Austin, Texas* (ER-170)	+	+							+	+	+	
P. bipinnatifidum Pablillo, Mexico (ER-139)			+						+	+		+
P. glomeratum Yavi, Argentina (Dillon and Rodríguez-480)			+						+	+		+
Sect. *Parthenichaeta*												
P. rollinsianum Santa Ana de Pozos, Mexico (ER-140)				+	+	+	+	+				

* Collection sites and numbers. Voucher specimens are deposited at the University of Texas at Austin Herbarium (TEX), Austin, Texas.

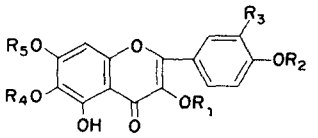
Table 2. UV data of flavonoid methyl ethers* from *Parthenium*

Compound	MeOH	NaOMe	$AlCl_3$	$AlCl_3$–HCl	NaOAc	NaOAc–H_3BO_3	Color Test UV → UV/NH_3
1†	350	392	436	386	368	360	
	276	265	370*sh*	292	260	280*sh*	Purple → Yellow-green
	258		296*sh*	267		264	
			276				
2	339	378	374	363	358	337	
	277	296*sh*	299	294	274	284	Purple → Yellow-green
		270*sh*	238*sh*	237*sh*			
3	351	400	433*sh*	377	395	355	
	280	275	391	294	260	285	Purple → Yellow-brown
	260*sh*		295	265			
7	345	408	404*sh*	402*sh*	415*sh*	350	
	273*sh*	277	385	369	356	275*sh*	
	255		302*sh*	283*sh*	217*sh*	260*sh*	Purple → Yellow-brown
			283*sh*	267	260*sh*		

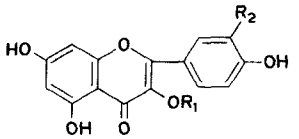
* See refs. [6,8,9] and [10] respectively for published UV, NMR and MS data on compounds **4**, **6** and **8**. A synthetic sample of polycladin, kindly supplied by Prof. H. Wagner, was found to be identical with natural material.

† For published NMR and MS data for compound **1** see ref. [2]

at *m/e* 330 in accord with a flavone containing three hydroxyl and two methoxyl groups. The UV spectral data (see Table 2) established the presence of a 4′-hydroxyl group (NaOMe data: 39 nm bathochromic shift of band I with an increase in intensity) and a 3-*O*-substituent ($AlCl_3$–HCl data). That the new compound was oxygenated at C_6 and contained a C_5 hydroxyl group was evident from the $AlCl_3$–HCl spectrum which gave a band I bathochromic shift of 24 nm relative to the methanol spectrum. The NaOAc spectrum did not exhibit a band I bathochromic shift suggesting that the C_7 hydroxyl group was substituted. A strong MS fragment ion for [M-H]+ at *m/e* 329 (83%) supported the presence of a free C_6 hydroxyl group [8]. Thus, since the MS data established the presence of three hydroxyl and two methoxyl groups in the new flavonol, and the UV data established the presence of 5,6 and 4′-hydroxyl groups, the new substance must be 6-hydroxykaempferol 3,7-dimethyl ether.



(**1**) R_1 = Me, R_2 = H, R_3 = OH, R_4 = H, R_5 = Me
(**2**) R_1 = Me, R_2 = H, R_3 = H, R_4 = H, R_5 = Me
(**3**) R_1 = Me, R_2 = H, R_3 = OMe, R_4 = H, R_5 = Me
(**5**) R_1 = Me, R_2 = H, R_3 = H, R_4 = Me, R_5 = Me
(**6**) R_1 = Me, R_2 = H, R_3 = OH, R_4 = Me, R_5 = Me
(**7**) R_1 = Me, R_2 = H, R_3 = OMe, R_4 = Me, R_5 = Me
(**8**) R_1 = Me, R_2 = Me, R_3 = OMe, R_4 = Me, R_5 = Me



(**4**) R_1 = Me, R_2 = OMe
(**9**) R_1 = Glc, R_2 = OH
(**10**) R_1 = Glc, R_2 = OH
(**11**) R_1 = Glc-O-Ara, R_2 = H
(**12**) R_1 = Gal, R_2 = H

The major aglycone in the species-pair *P. bipinnatifidum* and *P. glomeratum* was identified as quercetagetin 3,7,3′-trimethyl ether (**3**). The MS of **3** gave a parent peak at *m/e* 360 for a flavone containing three hydroxyl and three methoxyl groups. A relative strong peak at *m/e* 359 (50%) was indicative of a C_6 hydroxyl group. The NaOMe spectrum established the presence of a C_4-hydroxyl group (a band I bathochromic shift of 39 nm with an increase in intensity relative to the MeOH spectrum). The NaOAc–H_3BO_3 and NaOAc spectra exhibited no significant shifts in bands I and II, respectively, indicative of methoxyl groups at the C_3 and C_7 positions.

Quercetin 3-*O*-glucoside and kaempferol 3-*O*-glucoside were present in all three species with kaempferol 3-*O*-arabinoglucoside being detected in *P. hysterophorus*, while kaempferol 3-*O*-galactoside was found in both *P. bipinnatifidum* and *P. glomeratum*.

Extractions of *P. rollinsianum* (whole plant) yielded the known compounds quercetin 3,3′-dimethyl ether (**4**), 6-hydroxykaempferol 3,6,7-trimethyl ether (penduletin) (**5**), quercetagetin 3,6,7-trimethyl ether (**6**), quercetagetin 3,6,7,3′-tetramethyl ether (polycladin) (**7**) and quercetagetin 3,6,7,3′,4′-pentamethyl ether (artemetin) (**8**) (see Table 2 and the Experimental).

DISCUSSION

On the basis of the similar flavonoid and sesquiterpene lactone chemistry detected for the disjunct species *P. glomeratum* and *P. bipinnatifidum*, we suggest that the South American species is derived from an extant population(s) of *P. bipinnatifidum*. The occurrence of highly methylated flavonols in *P. rollinsianum* supports the taxonomic placement of this species in the sect. *Parthenichaeta* with close ties to species of the section *Bolophytum*.

EXPERIMENTAL

Air-dried and ground plant material of *Parthenium hysterophorus*, *P. bipinnatifidum*, *P. glomeratum* and *P. rollinsianum* was extracted first with $CHCl_3$ and then with aqueous MeOH (85%). The MeOH extract was concentrated *in vacuo* and subsequently examined by 2-D PC. The chromatograms were de-

veloped first in TBA (*t*-BuOH–HOAc–H_2O, 3:1:1) and then in 15% HOAc. All UV spectra were obtained using standard procedures [7]. The methoxylated flavonols and glycosides from the $CHCl_3$ and methanol extractions were separated in large quantities by polyamide and Sephadex chromatography, respectively. The known compounds were identified by standard procedures including UV (for all), NMR (for **1**, **6** and **8**), MS (for **1**–**6**) and co-chromatography (for **4**–**8**) and GC analysis of the trimethylsilyl ethers of the sugars obtained upon hydrolysis of **9**–**12**.

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