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FOLIAR FLAVONOIDS OF *KECKIELLA TERNATA*

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ABSTRACT

The major foliar phenolics of *Keckiella ternata* are quercetin 3-O-glucoside, kaempferol 3-O-glucoside, and acteoside (= orobanchin). The occurrence of flavonols in *K. ternata* is anomalous compared with other species of *Keckiella* and *Penstemon*, in which leaf flavonoids are based on luteolin and 6-hydroxyluteolin. The occurrence of foliar flavonols in *K. ternata* is interpreted as an advanced, derived condition.

Key words: *Keckiella ternata*, Scrophulariaceae, flavonoids, quercetin 3-glucoside, kaempferol 3-glucoside, acteoside, comparative phytochemistry.

INTRODUCTION

The genus *Keckiella* Straw comprises seven species which have long been recognized as a natural, monophyletic assemblage. These taxa have been treated as section *Hesperothamnus* within *Penstemon* (Keck 1936) and as a separate genus, *Keckiella* (Straw 1966, 1967). Various features of *Keckiella* species have been studied, including cytology (Keck 1951), anatomy (Michener 1981), and reproductive biology (Michener 1982). Little is known of the phytochemistry of the genus. Scogin and Freeman (1987) reported that the floral anthocyanins of all six of the pigmented species of *Keckiella* are a mixture of cyanidin 3-glucoside and cyanidin 3,5-diglucoside. The present work is the first report of foliar phenolic constituents for *Keckiella*.

MATERIALS AND METHODS

Fresh leaves of *Keckiella ternata* (Torr.) Straw were collected from plants cultivated at the Rancho Santa Ana Botanic Garden (Acc. No. 14554) and from the wild (Los Angeles Co., San Gabriel Mts., Glendora Ridge Road). Leaf phenolics were extracted into 80% methanol, concentrated under reduced pressure, and separated by one-dimensional paper chromatography (1D-PC) using BAW as the solvent (Harborne 1967). Compounds detected under UV illumination were eluted and purified by 1D-PC using water as the solvent. Chromatographic and spectroscopic properties of phenolic constituents were determined, and acid and enzymatic hydrolyses were performed using standard methods (Mabry, Markham, and Thomas 1970).

RESULTS

Three major phenolic constituents were detected on chromatograms of leaf extracts of *Keckiella ternata*. Two compounds exhibited the color properties under UV illumination appropriate for flavonols substituted at the 3-position (dark changing to yellow in the presence of ammonia fumes). The third compound fluoresced bright blue and changed to yellow-green in the presence of ammonia

Table 1. Chromatographic properties of *Keckiella ternata* phenolics.

	R _f (× 100)				Forestal (hydrolysis product)
	BAW	TBA	15% HOAc	Water	
Compound 1	65	71	47	13	57
Compound 2	49	51	45	9	40
Compound 3	54	62	82	65	79

fumes, which suggested that it was a phenolic acid derivative. The same compounds were present in garden-cultivated and field-collected plant samples. The two flavonoid compounds yielded kaempferol and quercetin, respectively, upon both acid and enzymatic (glucosidase) hydrolysis. Chromatographic and spectroscopic properties of these compounds and their hydrolysis product are presented in Tables 1 and 2. These data are consistent with reported values for kaempferol 3-O-glucoside (cmpd. 1) and quercetin 3-O-glucoside (cmpd. 2) (Harborne 1967; Hösel and Barz 1970).

The third compound yielded caffeic acid upon acid hydrolysis. The chromatographic and spectroscopic properties of this compound are presented in Tables 1 and 2 and agree well with reported values for the phenylpropanoid glycoside, acteoside (Harborne 1973; Kobayashi, Karasawa, Miyase, and Fushima 1985).

DISCUSSION

During an examination of the foliar flavonoid aglycones of *Keckiella*, Mistretta (1988) noted that *K. ternata* was anomalous among *Keckiella* species. *Keckiella ternata* produces leaf flavonoids based on the flavonols kaempferol and quercetin, whereas the leaves of the remainder of the species of *Keckiella* contain flavonoids based upon some combination of the flavones luteolin and 6-hydroxyluteolin. Leaf flavonoids of species of the closely related genus *Penstemon* also are based on the aglycones luteolin and 6-hydroxyluteolin (Scogin unpub. data). The leaf flavonoids of the Scrophulariaceae in general are most commonly based upon the flavones luteolin, apigenin, and chrysoeriol; and flavonol glycosides occur only uncommonly (Tomas-Barberan, Grayer-Barkmeijer, Gil, and Harborne 1988).

The degree of evolutionary advancement of *Keckiella ternata* indicated by the presence of foliar flavonol glycosides is problematic. Harborne (1977) postulated that among angiosperms as a whole, the accumulation of flavonol glycosides rather than flavone glycosides is the more primitive phytochemical state. In contrast, Gornall and Bohm (1978) have suggested that at lower levels in the taxonomic hierarchy (e.g., within genera), it is difficult to discriminate between primitive and highly advanced flavonoid phenotypes, which in many cases may be identical. I would interpret the occurrence of flavonol glucosides in *K. ternata* as a highly advanced flavonoid phenotype. The highly derived nature of *K. ternata* is supported by morphological features, such as the occurrence of a ternate leaf arrangement, and features of reproductive biology, such as hummingbird pollination. An electrophoretic examination of the allozymes of triose phosphate isomerase reveals an additional allele in *K. ternata* which is absent in all other *Keckiella*

Table 2. Spectroscopic properties of *Keckiella ternata* phenolics. Shoulders on spectra are indicated by parentheses.

	Absorption peaks (nm)		
	Compound 1	Compound 2	Compound 3
MeOH	(258), 266, (296), 351	258, (267), 358	(247), 292, 333
+NaOMe	279, 325, 407	275, 328, 411	
+AlCl	(257), 276, 304, 349, 398	272, 301, 411	
+AlCl/HCl	(256), 275, 303, 347, 398	274, 302, (363), 401	
+NaOAc	(260), 274, 304, 377	268, 301, 377	

species examined (Mistretta 1988). These data also support the derived nature of *K. ternata*.

Keck (1936) suggested a "connection" between *K. ternata* and *K. breviflora* (Lindl.) Straw based upon similarities of habit, but noted that these taxa "are probably not in a direct line of descent" (p. 219). The foliar flavonoid composition of these two species does not support a close alliance between them (Mistretta 1988).

The phenylpropanoid glycoside, acteoside, has been reported from *Penstemon roseus* G. Don [reported as *P. rosseus* (Sweet) G. Don by Lira-Rocha, Diaz, and Jimenez (1987)] and *P. hirsutus* (L.) Willd. (Gering and Wichtl 1987) and appears to be a universal constituent among members of both *Keckiella* and *Penstemon* (Scogin, unpub. data), thus reinforcing the strong alliance between these two genera.

In summary, the flavonoid constituents of *Keckiella ternata* are so anomalous compared with other members of both *Keckiella* and *Penstemon* that they do not suggest any particular alliances. In addition, the flavonol constituents are interpreted as being secondarily derived, rather than retained primitive characters, and indicate, along with morphological features, that *K. ternata* is a highly derived taxon within *Keckiella*.

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