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BENZOFURANS AND METHYLATED FLAVONOIDS OF *GERAEA* (ASTERACEAE)

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Key Word Index—*Geraea*; Asteraceae; benzofurans; flavonoids; chemosystematics.

Abstract—Phytochemical analysis revealed the presence of several rare benzofurans and C-8 oxygenated flavonoids in *Geraea canescens*. *Geraea viscida*, the only other species in the genus, lacked benzofurans and yielded simple flavonols without extra oxygenation. The flavonoids of both species were found to be deposited on the leaf surface. The chemical data suggest a close affinity between *Geraea canescens* and the genus *Enceliopsis* and less closely with the genus *Encelia*. The systematic affinity of *Geraea canescens* to *Geraea viscida*, however, seems unclear judged from the divergent chemical data obtained.

INTRODUCTION

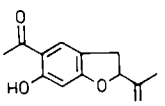
Geraea Torr. and Gray is a small genus comprising two annual or biennial species that are found in the southwestern U.S.A. and adjacent Mexico [1]. *Geraea canescens* Torr. and Gray is restricted to arid environments whereas *Geraea viscida* (Gray) Blake is confined to semiarid chaparral. *Geraea* is a member of the tribe Heliantheae and has been assigned either to the subtribe Helianthinae [2] or Ecliptinae [3]. Robinson considers *Geraea* to belong to a group of related genera including *Enceliopsis*, *Encelia*, *Flourensia* and *Phoebanthus*; they share morphological features such as pale anther thecae and sterile rays [3]. Historically, this group of genera has been a difficult subject for systematic study. The generic boundaries have been repeatedly redefined and several species have been transferred between genera of this group. Reproductive barriers are lacking within the genera, since intergeneric hybrids have been obtained [4].

As part of a larger investigation on the phytochemistry of this group of genera we previously studied *Enceliopsis* and *Encelia* and have been focussing on chromene (benzopyran) and benzofuran derivatives which are among the dominant natural products accumulated in these genera [5–15] as well as in *Flourensia* [16]. We have now extended our study to *Geraea* and wish to report on the benzofurans and flavonoids isolated from this genus.

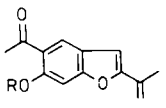
RESULTS AND DISCUSSION

Several collections of flowering *Geraea canescens* representing different populations were available for this study. The individual plants were separated into flowering heads, stems and leaves and exhaustively extracted. TLC revealed the presence of numerous benzofuran derivatives exhibiting bright orange or bluish fluorescence under long wave UV light. Co-chromatography with authentic standards isolated previously from *Encelia* and *Enceliopsis* led to the unequivocal identification of all major compounds, including 6-hydroxytremetone (**1**), euparin (**2**), 6-methyleuparin (**3**), 2,5-diacetyl-6-hydroxybenzofuran (**4**), 2-acetyl-5-(1ξ-hydroxyethyl)-6-methoxybenzofuran (**5**) and 2-isopropylidene-5-(1ξ-hydroxyethyl)-6-methoxybenzofuran (**6**). While compounds **1–3** are known from many genera of the Asteraceae [7], benzofurans **4–6** represent rare structural types in this family, isolated so far only from *Encelia* [11] and *Enceliopsis* [14, 15]. This set of major benzofurans was found to be identical in flowering heads, stems and leaves of all different collections analysed and thus they reflect conservative chemical characters of this species. Previous populational analysis of various *Encelia* and *Enceliopsis* taxa had likewise shown the chromene and benzofuran patterns to be stable chemical markers in these related genera [12, 14]. *Geraea viscida* in comparison was found to lack any chromene or benzofuran derivatives.

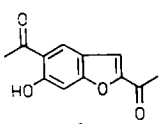
Leaves and stems of *Geraea canescens* and *G. viscida* were further analysed for methylated flavonoids found as



1



2 R = H
3 R = Me



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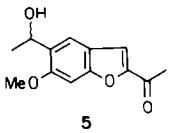

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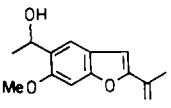


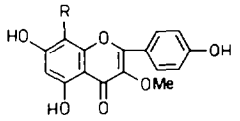
6

constituents of the epicuticular resins of both species. The major flavonoids present were subsequently isolated and identified by their UV and mass spectra as well as by co-chromatography with authentic standards. Flavonol and flavone derivatives, all with extra oxygenation at C-8 of the molecule, were found to be characteristic for *Geraea canescens*. The compounds identified included methylated derivatives of the flavonols herbacetin and gossypetin (**8**, **11**, **12**) as well as of the flavone isoscutellarein (**13**). Additional minor flavonoids present were characterized as flavanone or dihydroflavonol derivatives due to their characteristic UV spectra. The mass spectra again indicated extra oxygenation of the A-ring, possibly also located at C-8 of the respective molecules. Complete structural identification of these dihydro compounds, however, failed due to their low concentrations in the resin.

Analysis of the resin flavonoids of *Geraea viscida* revealed only common and ubiquitous derivatives of kaempferol and quercetin (**7**, **9**, **10**). No dihydro compounds and no C-8 substituted flavonoids were observed.

The benzofurans isolated from *Geraea canescens* are virtually identical to those found in *Enceliopsis* and *Encelia* [12, 14, 15]. Especially the cooccurrence of the biogenetically unusual and rare derivatives of 2,5-diacetylbenzofuran supports an alignment of *Geraea canescens* with the other two genera as suggested by morphological characters [3]. According to our phytochemical results, however, *Geraea canescens* shows a closer affinity to *Enceliopsis* than to *Encelia*. *Geraea canescens* as well as all taxa of *Enceliopsis* lack benzopyran derivatives, which are found in addition to benzofurans in all *Encelia* taxa [12]. The flavonoids of *Geraea canescens* with characteristic oxygenation at C-8 have furthermore recently been found in *Enceliopsis nudicaulis*, *E. nudicaulis* var. *corrugata* and *E. covillei* (Proksch, P. unpublished results).

Striking differences in regard to the natural products analysed in this study were observed between *Geraea canescens* and *G. viscida*. The latter species does not accumulate any benzofurans and the flavonoids found are of a simple type lacking any extra oxygenation of the molecule. It should be pointed out that the diversity in leaf flavonoid data is not reflected in the floral constituents, since both *Geraea* species contain an 8-oxygenated flavonol glycoside, 8-methyl gossypetin 3-glucoside, in the petals [17]. This pronounced chemical diversity in leaf constituents of the two species of *Geraea* can perhaps partly be explained by their different ecological habitats with *Geraea viscida* being a member of the semi-arid chaparral community and *G. canescens* being a desert plant. Considering that the generic boundaries of *Geraea* and related genera are still in a state of flux, a re-evaluation of the generic status of *Geraea canescens* and *G. viscida* in view of these new chemical data seems desirable.



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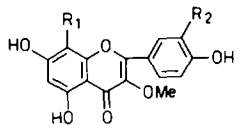
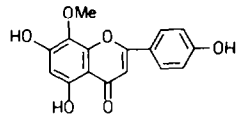
8 R = OMe



9 R_1 = H, R_2 = OH
10 R_1 = H, R_2 = OMe
11 R_1 = OMe, R_2 = OH
12 R_1 = OMe, R_2 = OMe



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EXPERIMENTAL

All plant collections except *G. viscida* collection numbers 1 and 2 were provided and identified by Professor C. Clark, California State, Pomona. Voucher specimens are deposited there. Collection numbers of *G. canescens* were 245, 246 and 286, collection numbers of *G. viscida* were 1, 2 and 170. Dates and localities of collection can be obtained from the authors.

For the analysis of benzofurans the plants were separated into leaves, stems and, when available, flowering heads. The plant material was ground and exhaustively extracted with acetone. Aliquots of the concentrated extracts were chromatographed on silica gel TLC plates with CH_2Cl_2–MeOH (99:1) as eluent. The benzofurans were detected on the plates by their bright fluorescence under $UV_{366\,nm}$. For preparative isolation bulk samples were extracted and separated by CC on silica gel with mixtures of CH_2Cl_2 and MeOH as eluent followed by CC on Sephadex LH-20 with MeOH as eluent. Compounds were identified by co-chromatography with authentic standards.

For the analysis of methylated flavonoids intact leaves and stems were briefly rinsed with MeOH. The concentrated extracts were chromatographed on Sephadex LH-20 with MeOH as eluent, followed by prep TLC on polyamide DC-6 with various mixtures of C_6H_6, MeCOEt and MeOH as eluent. Detection was achieved by viewing the plates under $UV_{366\,nm}$. Compounds were identified by their UV spectra, mass spectra (EI, 70 eV) and by co-chromatography with authentic standards on polyamide DC-6 and DC-11 [18].

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