Flavonoids of *Ericameria laricifolia* (Asteraceae)

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Z. Naturforsch. **39 c**, 1184–1185 (1984);
received July 25, 1984

Ericameria laricifolia, Asteraceae, Leaf Resin, 19 Flavonoid Aglycones

Nineteen flavonoid aglycones have been identified from the external stem and leaf resin of *Ericameria laricifolia* by thin layer co-chromatography with authentic samples. Kaempferol, quercetin, apigenin, and their methyl ethers have been found, along with luteolin and 6-methoxy luteolin. It is suggested that future flavonoid chemosystematic studied of resin-exuding species would best focus on aglycones as opposed to glycosides.

Ericameria is a genus of about 20 shrubby, resinous species found in the southwestern US and adjacent Mexico. It had been submerged into the large genus, *Haplopappus* [1], but has been more recently treated at the genus rank once again [2]. Previous chemo-systematic studied have addressed the relationship between *Ericameria* and other *Haplopappus* segregates [3], but to a limited extent. In our ongoing effort to survey these groups of taxa in the tribe Asterae, subtribe Solidaginae, for systematically useful flavonoid patterns, we have now examined *E. laricifolia.*

Experimental

Leaves and stems of *Ericameria laricifolia* were collected along Four Peaks Rd., Maricopa Co., Arizona, 7.7 miles east of Beeline Hwy., in April, 1984. A voucher specimen (Clark 84-1) is deposited in the herbarium at ASU. Leaves and green stems (2.08 kg) were immersed for ca. 2 min in acetone, which was quickly filtered and evaporated to a thick syrup (258 g). 17 g of this syrup were dissolved in methanol and chromatographed by CC over Sephadex LH-20 in methanol. 25 fractions (100 ml) were collected, with fractions 7–24 being flavonoid-rich. The identities of all compounds were determined according to ref. [4] using comparative TLC with authentic samples on polyamide (polyamide DC-11, Macherey-Nagel), visualized under UV light (366 nm) both before and after spraying with Naturstoffreagenz A (*β*-amino-ethylester of diphenyl boric acid; C. Roth, Karlsruhe). The reference compounds were isolated from various sources, as referred to in [5].

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0341-0382/84/1100-1184 $ 01.30/0

Results and Discussion

The following 19 known compounds were identified from the leaf and stem resin of the sample plant material: the flavones apigenin (**1**), ap-7-methyl ether (**2**), ap-4′-Me (**3**), ap-7,4′-diMe (**4**), luteolin (**5**), and 6-methoxyluteolin (**6**); the flavonols kaempferol (**7**), kae-7-Me (**8**), kae-4′-Me (**9**), kae-3-Me (**10**), kae-3,4′-diMe (**11**), kae-3,7-diMe (**12**), kae-3,7,4′-triMe (**13**), quercetin (**14**), qu-3-Me (**15**), qu-3′-Me (**16**), qu-3,7-diMe (**17**), qu-3,3′-diMe (**18**), and qu-3,7,4′-triMe (**19**).

Eight of these compounds (**4, 6, 8–12, 13**) were also found in one population of *E. diffusa* [6], an overlap which would seem to indicate a significant relationship between these two species. However, two populations of *E. diffusa* shared only three compounds [6], which were also found in *E. laricifolia* (**4–6**). The data available at this time indicate a critical need both for further species surveys and, in particular, for studies on the variability of these compounds within species and populations.

Nevertheless, two trends can be observed based on the current study and that by Urbatsch *et al.* [6]. The first is that simple methyl esters of kaempferol and quercetin typify the species examined so far, with additional divergence into the formation of several flavones in *E. laricifolia* and of galangin-3-Me and kae-3,5,7-triMe in one population of *E. diffusa.* The second is that the diversity of aglycones exceeds that of glycosides in this species [3]. We have also found this trend in the related genera *Hazardia* [7, 8] and *Haplopappus* [9–11]. In addition, all of the glycosides in *Ericameria, Hazardia,* and *Haplopappus* are based on aglycones also found in the leaf exudates. We suggest, therefore, that future studies on these resinous genera should focuse on the flavonoid aglycone patterns found in the exudates as opposed to the internal glycoside derivatives.

Acknowledgement

We thank the Alexander von Humboldt Foundation for a fellowship to W. D. C. during the period this work was completed. Financial support from the Deutsche Forschungsgemeinschaft (E. W.) is also acknowledged.

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