Flavonoid Aglycones in the Leaf Exudate of the Genus *Leucocyclus* (Compositae)

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The monotypic genus *Leucocyclus*, consisting of only two subspecies, was investigated for its exudate flavonoids. Major flavonoid aglycones were polymethoxyderivatives of 6-hydroxyflavones and, to a lesser extent, of 6-hydroxyflavonols. The two subspecies differed in their accumulation trends, but populational variation reduced the significance of taxonomic implications. Cultivated material corresponded largely to the original material collected from nature. The accumulation trends of *Leucocyclus* coincide with those of the closely related genus *Achillea*.

Introduction

The monotypic genus *Leucocyclus* Boiss. (Compositae-Anthemideae), occurring in Turkey, is closely associated with the genus *Achillea* [1, 2]. Major distinctive features are the anatomy and morphology of the cypselas [1], whereas the vermiform leaves correspond to those of sections *Achillea* and *Arthrolepsis* of the genus *Achillea* [2]. The species of both sections are distributed in Turkey and adjacent regions [2].

The close relationship between *Leucocyclus* and *Achillea* is also reflected in the accumulation tendencies of root acetylenes and amides [3] as well as of leaf flavonoid glycosides [2, 4]. A preliminary survey indicated that *Leucocyclus* accumulates free flavonoid aglycones in the leaf exudates, as do many species of *Achillea* [5–7]. We now wish to report on the distribution of these aglycones in the two recognized subspecies, *i.e. L. formosus* Boiss. subsp. *formosus* and subsp. *amanicus* (Rech. fil.) Hub. Mor. & Grierson, which are distinguished mainly by floral characters [8].

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Materials and Methods

Dried material from wild populations, cultivated plants and herbarium specimens were used for analysis. Voucher specimens are deposited either at the Herbarium of the Institute of Botany, University of Vienna (WU) or at the Museum of Natural History, Vienna (W.).

L. formosus subsp. *formosus:* 1) Turkey, C 3 Isparta, Beysehir Lake (Hübl, Meusel & Valant 1978/7-14-3, WU); 2) Turkey, C 3 Isparta, Cicek Dagi (Sorger 67-5-33, W); 3) Turkey, C 2 Antalya, Irmasan (Hübl, Meusel & Valant 1978/7-27-12, WU);

L. formosus subsp. *amanicus:* 4) Turkey, C 6 Adana, Amanus region (Hübl, Meusel & Valant 1978/7-21-1, WU); 5) cultivated from cypselas of 4 (A-1539, WU).

Leaves were shortly rinsed with acetone to dissolve the epicuticular material. Bulk material was column chromatographed on Sephadex LH-20 to separate the flavonoids from the dominating terpenoid constituents. Comparative TLC was carried out on silica and on polyamide in several solvent systems [9]. Individual compounds were identified on the basis of co-chromatography with authentic standards, both directly from the exudate solution and after isolation by prep. CC and/or TLC, as well as by UV-spectroscopy. In critical cases, the proposed structures were confirmed by MS-data.

Results and Discussion

Major flavonoid compounds in the leaf exudates of *Leucocyclus* were the 6-hydroxyflavones scutellarein 6,7-dimethylether (cirsimaritin), the -6,7,4′-trimethyl ether (salvigenin) as well as 6-hydroxyluteolin 6-methylether (nepetin), the -6,7-dimethyl ether (cirsiliol), the -6,7,4′-trimethyl ether (eupatorin) and the -6,7,3′,4′-tetramethyl ether. Thus, both the apigenin and the luteolin derivatives exhibited similar substitution patterns. Of the corresponding flavonols, only 6-hydroxykaempferol 3,6,7,4′-tetramethyl ether and quercetagetin 3,6,7-trimethyl ether (chrysosplenol-D) and the -3,6,7,3′,4′-pentamethyl ether (artemetin) were accumulated. The distribution patterns observed within the two subspecies of *Leucocyclus* are given in Table I.

The variation encountered in subsp. *formosus* is notable. The populations 1 and 2 accumulated both the 6-hydroxyluteolin derivatives and quercetagetin 3,6,7-trimethyl ether, but they differed in the ac-

Table I. Flavonoid aglycones of *Leucocyclus*.

Compounds	*Leucocyclus formosus* subsp. *formosus* population: 1	2	3	subsp. *amanicus* 4	5
scu 6,7-diMe	●	0	0	●	0
scu 6,7,4′-triMe			●	●	0
6OHlu 6-Me	+	+	+	+	
6OHlu 6,7-diMe	0	●		+	
6OHlu 6,7,4′-triMe			0	●	0
6OHlu 6,7,3′,4′-tetraMe			●	●	0
6OHkae 3,6,7,4′-tetraMe				+	+
queg 3,6,7-triMe	+	0			
queg 3,6,7,3′,4′-pentaMe			+	●	0

scu = scutellarein; 6OHlu = 6-hydroxyluteolin; 6OHkae = 6-hydroxykaempferol; queg = quercetagetin.
● = large amounts; 0 = small amounts; + = traces.

cumulation of scutellarein 6,7,4′-trimethyl ether (Table 1). Another population (No. 3) correlated even to the population of subsp. *amanicus*, thus contrasting markedly to Nos. 1 and 2. Cultivated plants of subsp. *amanicus* and their parent plants collected in Turkey exhibited similar profiles being more diversified than that of subsp. *formosus*. However, there were no data obtained on the infraspecific variability of subsp. *amanicus* aglycones. The flavonoid composition of No. 3, although corresponding to subsp. *amanicus*, does not indicate a taxonomic misplacement, particularly as the morphological features are well in accordance with subsp. *formosus*. Possible explanations like hybridisation or introgression should be ruled out due to geographical isolation of the two subspecies [8].

The exudate flavonoids of the genus *Leucocyclus* are similar to those of *Achillea* species [5–7]. Thus, aglycone profiles serve as additional indicator for the close relationship between the two genera as already proposed on the basis of common morphological features [1] and glycoside chemistry [2, 4]. However, the aglycones do not as strongly suggest to assign species status to the subspecies, as did the diversification trends of glycosides [4]. With respect to the ecology of *Leucocyclus*, this genus affords a further example of Compositae plants from arid regions to accumulate flavonoid aglycones in its exudate [10].

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