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FLAVONOID PATTERN AND SYSTEMATICS OF THE GENUS *LEUCOCYCLUS*

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Key Word Index—*Leucocyclus*; Anthemideae; Compositae; flavonoid profile; *C*-glycosylflavones; flavonol 3-*O*-glycosides; flavone 7-*O*-glycosides; infra-generic distribution patterns; infra-generic systematics; generic relationships.

Abstract—The flavonoid pattern of the monotypic Turkish genus *Leucocyclus* consists of *C*-glycosylflavones (isovitexin; isoorientin and derivatives; several di-*C*-glycosylapigenins; schaftoside, isoschaftoside and vicenin-3; lucenin-2), of flavonol 3-*O*-glycosides (quercetin and kaempferol 3-*O*-rhamnoglucoside) and trace amounts of luteolin 7-*O*-rhamnoglucoside. The systematic significance of the flavonoid diversification within *Leucocyclus* as well as possible relationships to other genera of the Anthemideae are discussed.

INTRODUCTION

The monotypic Turkish genus *Leucocyclus* Boiss. (Anthemideae–Compositae) can be characterized best by its vermiform leaves with reduced primary leaflets standing transverse and imbricate and by the large, solitary capitules with white ligules. *Leucocyclus formosus* Boiss. comprises only two subspecies, namely ssp. *formosus* distributed in the Taurus region, and ssp. *amanicus* (Rech. fil.) Hub.-Mor. and Grierson, which is endemic in the Amanus region [1]. Several morphological features suggest relationships to other Anthemidean genera: fruit morphological characters especially point to a close affinity with *Anacyclus* [2], whereas leaf structures resemble those of *Achillea* sect. *Santolinoidea* and sect. *Arthrolepis* [3]. The first surveys on polyacetylenes and other root constituents [9] as well as flavonoids [3] indicate that *Achillea* and *Leucocyclus* are closely related within the *Anacyclus–Anthemis–Achillea* assemblage (cf. ref. [4]). Apart from this, the flavonoid diversification within the genus *Leucocyclus* appears to be of systematic interest.

RESULTS

Leucocyclus formosus is characterized by the predominance of *C*-glycosylflavones and flavonol 3-*O*-glycosides. Flavone 7-*O*-glycosides occur only in small amounts. Different accumulation trends, however, can be noticed at the subspecies level. Thus in ssp. *formosus* *C*-glycosylflavones predominate, whereas ssp. *amanicus* mainly accumulates flavonol 3-*O*-glycosides (Table 1).

L. formosus ssp. *formosus* contains a range of glycoflavones. The mono-*C*-glycosylflavones are mainly based on luteolin, i.e. isoorientin, but the di-*C*-glycosylated types, however, are mostly apigenin derived. The rather widespread isoorientin is accompanied in *Leucocyclus* by its 2″-arabinoside and an isoorientin caffeoyl ester. The di-*C*-glycosylapigenins are represented by isoschaftoside and a mixture of schaftoside and vicenin-3. Of the corresponding di-*C*-glycosylluteolins only lucenin-2 is accumulated. A similar pattern of several *C*-glycosylflavones has also been observed in *Achillea* [3].

Beside the *C*-glycosylflavones, quercetin 3-*O*-rhamnoglucoside and trace amounts of luteolin 7-*O*-rhamnoglucoside were found in ssp. *formosus*. *L. formosus* ssp. *amanicus*, on the other hand, seems to lack most of the *C*-glycosylflavones which are typical of ssp. *formosus*, containing mainly quercetin and kaempferol 3-*O*-rhamnoglucoside together with isoschaftoside. Thus the accumulation of isoschaftoside and of the nearly ubiquitous quercetin 3-*O*-rhamnoglucoside appear to be the only common flavonoid characters of the two subspecies.

DISCUSSION

In comparison with the related genus *Achillea* [3], flavonoid diversification in *Leucocyclus* seems to be most significant at the subspecies level. Together with morphological differences the flavonoid data suggest that these subspecies should be given species status. This is mainly underlined by different achene structures (concerning the size of the marginal wings [1]) and by the difference in the colour of the disc florets (yellow for ssp. *formosus*, white for ssp. *amanicus*) (Sorger, F., personal communication).

In addition to this the flavonoid data clearly indicate a very close relationship to *Achillea*. In particular ssp. *amanicus* appears to be very near to *Achillea* sect. *Arthrolepis*. Such a relationship is also indicated by common morphological characters: this subspecies was originally described as *Achillea amanica* Rech. fil. belonging to sect. *Arthrolepis* [5]. On the other hand, the flavonoid pattern of ssp.

Table 1. Flavonoid pattern of the genus *Leucocyclus*

Leucocyclus formosus	*C*-Glycosylflavones							Flavonol 3-*O*-glycoside		Flavone 7-*O*-glycoside
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
ssp. *formosus* (1)	*t*	++	++	++	++	+	+	+		*t*
ssp. *formosus* (2)	*t*	++	+	++	++	*t*	+			*t*
ssp. *formosus* (3)	*t*	+	*t*	++	++	+	*t*			*t*
ssp. *formosus* (4)	+	++	++	++	++	*t*				
ssp. *formosus* (5)		++	+	+	++	*t*	*t*			
ssp. *amanicus* (6)		+						+		
ssp. *amanicus* (7)		+						+	++	
ssp. *amanicus* (8)		*t*						*t*	++	
ssp. *amanicus* (9)		*t*						*t*	++	

Key: *A* = isovitexin; *B* = isoschaftoside; *C* = schaftoside + vicenin-3; *D* = isoorientin; *E* = isoorientin-2″-arabinoside; *F* = isoorientin caffeoyl ester; *G* = lucenin-2; *H* = quercetin 3-*O*-rhamnoglucoside; *I* = kaempferol 3-*O*-rhamnoglucoside; *J* = luteolin 7-*O*-rhamnoglucoside. ++ = major component, + = minor component, *t* = trace.

formosus bears great resemblance with that of some species from *Achillea* sect. *Santolinodea* [3]. A close relationship between *Leucocyclus* and *Anacyclus* which is suggested by their achene structures is not fully supported by the flavonoid data. However, certain flavonoid profiles of members from *Achillea* sect. *Arthrolepis* [3] and some species of *Anacyclus* including the closely related genus *Heliocauta* [4], are similar to those of *L. formosus* ssp. *amanicus* (Table 2) and thus once more underline the proposed arrangement of genera within the tribe Anthemideae (cf. refs. [2, 4]).

EXPERIMENTAL

List of plant sources (numbers refer to Table 1): (1) Turkey, C 3 Isparta, Beysehir Lake (Hübl, Meusel & Valant 1978/7-14-3, WU); (2) Turkey, C 3 Isparta, Cicek Dagi near Beysehir Lake (Sorger 67-5-33); (3) Turkey, Bulgar Dag (Kotschy No. 65, WU); (4) Turkey, C 5 Adana, Karaisali, ob Pozanti (Huber-Morath No. 15785, E); (5) Turkey, C 3 Isparta, Dedegöl Dag (Sorger 66-46-5, E); (6) Turkey, C 6 Adana, Amanus region (Hübl, Meusel & Valant 1978/7-21-1, WU); (7) cult. A-1539 (achenes of 1978/7-21-1); (8) Turkey, Mt Amanus (Haradjan No. 789, E); (9) Turkey, C6 Adana, Nur Daglari (Sorger 73-21-23, E). Voucher specimens are

Table 2. Distribution of flavonoid glycosides in some genera of Anthemideae

	CGL	FL3	FL5	FL7	FN7	Ref.
Achillea						
sect. *Santolinoidea*	++	*t*			++	[3]
sect. *Arthrolepis*		++			++	[3]
Leucocyclus formosus						
ssp. *formosus*	++	*t*			*t*	
ssp. *amanicus*	*t*	++				
Heliocauta						
(as *Anacyclus atlanticus*)		++			++	[9]
Anacyclus		++	++	++	++	[9]

Key: CGL = *C*-glycosylflavones; FL3 = flavonol 3-*O*-glycosides; FL5 = flavonol 5-*O*-glycosides; FL7 = flavonol 7-*O*-glycosides; FN7 = flavone 7-*O*-glycosides. Ref. = references. Amounts as in Table 1.

Table 3. hR_f values of *Leucocyclus* compounds on TLC (Cellulose, Merck)

	BAW	CAW (1:1)	15% Acetic acid
Isoorientin	48	39	25
Isoorientin 2″-arabinoside	46	40	67
Isoorientin caffeoyl ester	48	29	37
Lucenin-2	27	27	28
Isoschaftoside	32	39	32
Schaftoside + vicenin-3	37	44	37
Quercetin 3-*O*-rhamnoglucoside	50	40	46
Kaempferol 3-*O*-rhamnoglucoside	62	55	56
Luteolin 7-*O*-rhamnoglucoside	37	38	14

deposited in the Herbarium for the Institute of Botany, University of Vienna (WU), the Herbarium of Edinburgh (E) and in the Herbarium of Dr. F. Sorger.

EtOH leaf extracts were run in 1-D on Whatman No. 3 MM sheets in 15% HOAc, the flavonoid bands eluted and re-chromatographed in BAW (*n*-BuOH–HOAc–H_2O, 4:1:5) and CAW ($CHCl_3$–HOAc, 1:1, 2:1, H_2O saturated) (Table 3). UV analysis was carried out using standard procedures [6] and gave results directly comparable with lit. data. The structures of lucenin-2, isoschaftoside and isoorientin 2″-arabinoside were established by means of MS comparison of permethyl ethers. HPLC of the second vicenin fraction showed a major peak identical with schaftoside and a secondary peak corresponding with vicenin-3 (Chopin, J., personal communication). After acid hydrolysis (1 N HCl, 1 hr, 100°) cinnamic acids were extracted with Et_2O, *C*-glycosylflavones with *n*-BuOH and flavonol and flavone aglycones with EtOAc. Sugar residues were co-chromatographed with authentic samples on TLC (cellulose) in *n*-BuOH–pyridine–H_2O (6:4:3) and sprayed with *p*-anisidine hydrochloride [7]. Cinnamic acids were compared on TLC (cellulose) in 5% HOAc, C_6H_6–HOAc–H_2O (6:7:3) and CAW (2:1). UV and R_f comparison of the hydrolytic products from *F* suggest it is an isoorientin caffeoyl ester. Its UV spectra are in good agreement with data of isoorientin 2″-caffeoyl ester [8], but R_f values are different (Chopin, J., personal communication). Thus the caffeic moiety is probably attached at another position. Amounts available did not allow further identification.

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