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Flavonoids as chemosystematic markers in the tribe Cichorieae of the Asteraceae☆

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ABSTRACT

This review summarizes reports on flavonoids from the Cichorieae (Lactuceae) tribe of the Asteraceae family. A total of 135 different compounds have been reported from 354 taxa belonging to 299 species, including many cultivars of common vegetables like chicory and lettuce. The reported compounds encompass flavanones (11 compounds), flavanonols (2 compounds), flavones (72 compounds), flavonols (35 compounds), anthocyanidins (9 compounds), isoflavonoids (2 compounds), chalcones (3 compounds), and an aurone. So far only 43 of the approximately 100 currently recognized genera of the tribe Cichorieae have been investigated for the occurrence of flavonoids. The distribution of the various classes of flavonoids is analyzed with regards to data from the current molecular-based reassessment of the systematics of the tribe.

1. Introduction

Recently, the sesquiterpenoids known from taxa of the Cichorieae (Lactuceae) tribe have been reviewed (Zidorn, 2006, 2008b). The present review is intended as a complementary collection of chemosystematic data for the tribe Cichorieae. Flavonoids of the Cichorieae had been reviewed by Bohm and Stuessy in 2001. Since then a lot of new data both on the molecular phylogeny of the tribe and on the occurrence of flavonoids within the tribe have been published.

Though flavonoids are poor markers on a higher level, because even rare compounds occur scattered throughout the plant kingdom – e.g. isoetin, which was first described from the pteridophyte genus *Isoetes*, but also occurs *inter alia* in some genera of the *Cichorieae* – on the generic level and below the generic level flavonoids represent the class of natural products which is most widely employed for chemosystematic investigations. The frequent use of flavonoids in chemosystematics has mainly practical reasons. Historically flavonoids were among the first natural products comparatively investigated in detail because they are easily detected and separated using simple techniques like paper chromatography and thin layer chromatography combined with UV-shift and/or spraying reagents.

The traditional circumscription of the Cichorieae as a conveniently recognized tribe, diagnosed by the unique combination of homogamous capitula with 5-dentate, ligulate flowers and the presence of milky latex, has been altered recently on the basis of molecular data to include the genera *Gundelia* and *Warionia* (Kilian et al., 2009). Both genera feature milky latex but in contrast to all other Cichorieae they have homogamous capitula with tubular flowers only. Thus, homogamous capitula with 5-dentate, ligulate flowers are not a joint character of all members of the Cichorieae tribe anymore. Conclusively, there is no

☆ Dedicated to Professor Werner Herz (Department of Chemistry/University of Florida, Tallahassee, USA) on the occasion of his 89th birthday.

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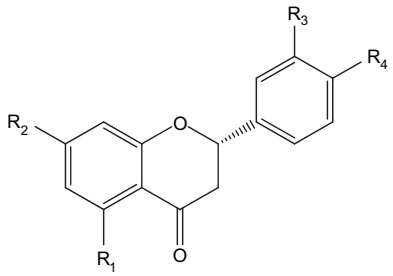

	Semi-systematic name	R_1	R_2	R_3	R_4	Name
1	7-hydroxyflavanone	H	OH	H	H	
2	7-methoxyflavanone	H	OCH_3	H	H	
3	5-hydroxyflavanone	OH	H	H	H	
4	dihydrochrysin	OH	OH	H	H	
5	naringenin	OH	OH	H	OH	
6	naringenin 7-methyl ether	OH	OCH_3	H	OH	sakuranetin
7	naringenin 7,4'-dimethyl ether	OH	OCH_3	H	OCH_3	
8	eriodictyol 7-*O*-glucoside	OH	O-GLC	OH	OH	miscanthoside
9	eriodictyol 7-*O*-glucuronide	OH	O-GLU	OH	OH	
10	hesperitin	OH	OH	OH	OCH_3	
11	hesperitin 7-O-rutinoside	OH	O-RUT	OH	OCH_3	hesperidin

Fig. 1. Flavanones (Group I. Flavanones).

single autapomorphy characterizing the Cichorieae; milky latex, a mutual character of all members of the Cichorioideae also occurs in some genera of the tribes Arctoteae, Cardueae, Liabeae, Mutisieae, and Vernonieae, and even in a few representatives of the Asteroideae (Kilian et al., 2009). The second main phenetic character of the group, homogamous capitula with 5-dentate, ligulate flowers, is not only found in the Cichorieae but also in some genera of Mutisieae (*Catamixis*, *Hyaloseris*, and *Glossarion*) and, by convergent evolution, in the Heliantheae–Coreopsidinae (*Fitchia*) of the subfamily Asteroideae; moreover, 5-dentate, ligulate marginal flowers also occur in the Vernonieae (*Stockesia*) (Kilian et al., 2009). New molecular analyses with a large dataset revealed that *Gundelia* falls within the basal Cichorieae, forming a well supported clade with *Catananche*, *Hymenonema,* and *Scolymus*. The unispecific *Warionia* was found to represent the sister group to all Cichorieae including *Gundelia*. Since a closer relationship of *Warionia* to any other tribe was ruled out, a new subtribe Warioniinae was established, which is at the base of the Cichorieae (Kilian et al., 2009).

2. Summary of literature data

Literature data on flavonoids from the Cichorieae tribe were retrieved based on the earlier review by Bohm and Stuessy (2001) and with the help of the SciFinder database. All entries until the end of 2008 were considered. Both semi-systematic and trivial names are given in the figures for the respective flavonoid subgroups (Figs. 1–22). Sugar moieties and other substituents used in abbreviated form in Figs. 1–22 are shown and explained in Fig. 23. Fig. 24 displays a simplified form of the new molecular system of the Cichorieae provided by Kilian et al. (2009). In the compilation of chemosystematic data below, the assignment of each genus to its corresponding clade (sub-tribe) is indicated in square brackets after the name of the respective genus.

In the following paragraphs, the available information on the distribution of flavonoids in the Cichorieae is compiled. Genera and species within genera are ordered alphabetically. Wherever available, additional information on the investigated plant organ, the solvent used for extraction and the country of origin of the investigated plant material are included. For an overview on the total of the currently recognized genera in the Cichorieae please refer to Bremer (1994), Zidorn (2008b), or Kilian et al. (2009).

Stereochemistry of sugars is often not thoroughly elucidated in the literature. Thus, in the following account, usually only the sugar and the linkage position are indicated, though for example for glucose β-linkage and the D-enantiomer of glucose seem to be the norm and are implied where not elucidated by NMR and optical methods, respectively.

Agoseris [C5SC2] – Leaves of *A grandiflora* (Nutt.) Greene and *A. heterophylla* (Nutt.) Greene yielded quercetin 3-*O*-glucoside **107** and unspecified glycosides of apigenin and luteolin (Harborne, 1977).