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## Flavonoids as chemosystematic markers in the tribe Cichorieae of the Asteraceae<sup>☆</sup>

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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.

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### 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.

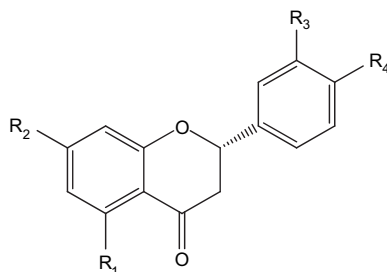
Though flavonoids are poor markers on a higher level, because even rare compounds occur scattered throughout the plant kingdom – e.g. isoetin, which was first described from the pteridophyte genus *Isoetes*, but also occurs *inter alia* in some genera of the Cichorieae – on the generic level and below 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

<sup>☆</sup> 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 <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Name
1	7-hydroxyflavanone	H	OH	H	H	
2	7-methoxyflavanone	H	OCH <sub>3</sub>	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 <sub>3</sub>	H	OH	sakuranetin
7	naringenin 7,4'-dimethyl ether	OH	OCH <sub>3</sub>	H	OCH <sub>3</sub>	
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 <sub>3</sub>	
11	hesperitin 7-O-rutinoside	OH	O-RUT	OH	OCH <sub>3</sub>	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).

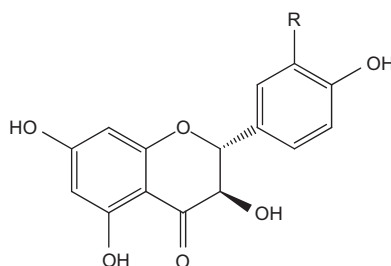
## 2. Summary of literature data

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  $\beta$ -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).



	Semi-systematic name	R
<b>12</b>	aromadendrin	H
<b>13</b>	3'-O-methyltaxifolin	OCH <sub>3</sub>

Fig. 2. Flavanonols (Group II. Flavanonols).

**Andryala** [C5SC1] – *A. ragusina* L. (MeOH/aerial parts/Spain) yielded four flavones apigenin **17**, apigenin 7-*O*-neohesperidoside **29**, luteolin **42**, and luteolin 7-*O*-glucoside **53**. Moreover, a new luteolin 7-*O*-galactoglucuronide **57** was found but the interglycosidic linkage was not established (Recio et al., 1993). Additionally, quercetin 3-*O*-glucoside **107** was reported from this taxon (Mañez et al., 1994).

**Arnoseris** [C5SC3] – *A. minima* (L.) Schweigg. & Korte (MeOH/whole plants/Spain) yielded three flavones luteolin **42**, luteolin 4-*O*-glucoside **45**, and luteolin 7-*O*-glucoside **53** as well as the methoxyflavonol 3-*O*-methylquercetin **102** (Zidorn et al., 2005b).

**Babcockia** – This genus is following Kilian et al. (2009) regarded to be part of the genus *Sonchus* in this review.

**Catananche** [C3] – *C. caerulea* L. (95% EtOH/aerial parts/France) yielded luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-rhamnoside **58**, luteolin 7-*O*-gentiobioside **61**, the C-diglycosylflavones isoschaftoside **39**, schaftoside **40**, 3-hydroxyisoschaftoside **70**, and 3'-hydroxyischaftoside **71** (Proliac, 1972; Proliac et al., 1973, 1974; Proliac and Raynaud, 1977). Flowering heads yielded apigenin 7-*O*-glucuronide **25**, delphinidin **123**, and malvidin **124** (Proliac and Combier, 1974; Proliac et al., 1974).

**Chondrilla** [C4SC4] – *C. juncea* L. (MeOH/aerial parts/Spain) yielded luteolin **42**, luteolin 7-*O*-glucoside **53**, and quercetin 3-*O*-galactoside **104**. Moreover, a luteolin 7-*O*-galactosylglucuronide **57** was reported but the exact linkage of the sugars was not established (Terencio et al., 1993; Mañez et al., 1994).

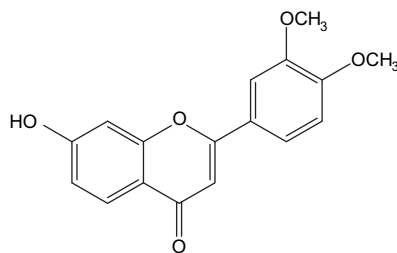
An ethanolic extract of *C. piptocoma* Fisch. Mey. & Avé-Lall. yielded apigenin **17**, 3'-*O*-methyluteolin **47**, and luteolin 7-*O*-glucoside **53** (Zhao et al., 2005).

**Cicerbita** [C4SC1] – *C. plumieri* (L.) Kirsch. yielded kaempferol **86** (Rees and Harborne, 1984).

**Cichorium** [C5SC3] – Rees and Harborne (1984) reported luteolin 7-*O*-glucuronide **54**, kaempferol 3-*O*-glucoside **89**, kaempferol 3-*O*-glucuronide **92**, quercetin 3-*O*-galactoside **104**, quercetin 3-*O*-glucuronide **109**, and isorhamnetin 3-*O*-glucuronide **114** from *C. endivia* L., *C. intybus* L., *C. pumilum* Jacq., and *C. spinosum* L.

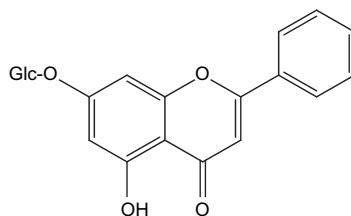
DuPont et al. (2000) analyzed flavonoid composition and content of three varieties of *C. endivia* (MeOH:H<sub>2</sub>O:CH<sub>3</sub>COOH 70:30:5/fresh whole plants/UK): *C. endivia* cvar. coarse frisée, *C. endivia* cvar. fine frisée Glory, and *C. endivia* cvar. escarole. Kaempferol 3-*O*-glucoside **89**, kaempferol 3-*O*-(6-*O*-malonyl)-glucoside **90**, and kaempferol 3-*O*-glucuronide **92** were identified in all cultivars. Kaempferol 3-*O*-rhamnoside **94** was observed only in *C. endivia* cvar. coarse frisée (Woeldecke and Herrmann, 1974; DuPont et al., 2000).

*C. intybus* yielded apigenin **17**, apigenin 7-*O*-arabinoside **23**, luteolin 7-*O*-glucoside **53**, quercetin 3-*O*-galactoside **104**, and quercetin 3-*O*-rhamnoside **111** (Dem'yanenko and Dranik, 1973). Aboul-Ela et al. (2002) reported quercetin **96** from the aerial parts of *C. intybus* (90% EtOH/aerial parts/Egypt). El-Lakany et al. (2004) reported isoscutellarein **84** and kaempferol **86** from the roots of *C. intybus* (90% EtOH/aerial parts/Egypt).



**14** 7-hydroxy-3',4'-dimethoxyflavone

Fig. 3. 7,3',4'-Trihydroxyflavones (Group III. Flavones).



**15** chrysin 7-*O*-glucoside (aequinoctin)

**Fig. 4.** 5,7-Dihydroxyflavones (Group III. Flavones).

Innocenti et al. (2005) studied phenolic compounds from fresh aerial parts of different chicory (*C. intybus*) cultivars: green chicory, cvar. Catalogna; two red chicory cultivars, radicchio rosso di Chioggia and radicchio rosso di Treviso; and white chicory cvar. Witloof (EtOH:H<sub>2</sub>O 7:3/fresh aerial parts/Italy). Cyanidin 3-*O*-glucoside **121**, cyanidin 3-*O*-(6-*O*-malonyl-β-D-glucoside) **122**, and delphinidin 3-*O*-(6-*O*-malonyl-β-D-glucoside) **125** were the major phenolic compounds in the red cultivars (Bridle et al., 1984). Luteolin 7-*O*-glucuronide **54** and quercetin 3-*O*-glucuronide **109** were absent in cultivar Witloof (Innocenti et al., 2005).

Four anthocyanins delphinidin 3,5-di-*O*-β-D-glucoside **126**, delphinidin 3-*O*-β-D-glucoside-5-*O*-(6-*O*-malonyl)-β-D-glucoside **127**, delphinidin 3-*O*-(6-*O*-malonyl)-β-D-glucoside-5-*O*-β-D-glucoside **128**, and delphinidin 3,5-*O*-di-(6-*O*-malonyl)-β-D-glucoside **129** were isolated from the blue perianth of *C. intybus* (50% MeCN + 0.5% trifluoroacetic acid/freeze-dried perianth/Denmark) (Norbaek et al., 2002).

*C. pumilum* (hot EtOH/aerial parts/Egypt) yielded the flavonol quercetin 3-*O*-α-D-glucoside **106** (Saleh et al., 1975).

*Crepis* [C4SC3] – Mañez et al. (1992) reported luteolin **42** and luteolin 7-*O*-glucoside **53** from *C. capillaris* (L.) Wallr. (MeOH/aerial parts/Spain). Flowering heads of the same species (MeOH:(CH<sub>3</sub>)<sub>2</sub>CO:H<sub>2</sub>O, 3:1:1, v:v:v/New Zealand) yielded luteolin **42**, luteolin 7-*O*-glucoside **53**, and luteolin 7-*O*-glucuronide **54** (Zidorn et al., 2005a).

Mañez et al. (1994) studied the chemotaxonomic significance of flavonoids, phenolic acids, and coumarins in the subtribe Crepidinae (Cichorieae, Asteraceae) investigating a total of 20 species. *C. capillaris* and *C. versicaria* L. contained luteolin **42** and luteolin 7-*O*-glucoside **53**. Moreover, luteolin 4'-*O*-glucoside **45** was detected in *C. capillaris*.

*C. divaricata* Boss. & Heldr. and *C. pygmaea* L. yielded luteolin **42** and quercetin **96** (Rees and Harborne, 1984).

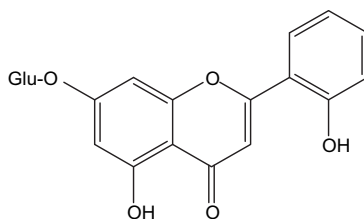
*C. micrantha* Czerep. (90% EtOH/fresh aerial parts/Egypt) yielded apigenin **17** and luteolin **42** (Kassem, 2007).

Isoetin **73** and scutellarein **85** were reported from leaves of *C. senecioides* Delile and *C. tectorum* L. (Harborne, 1978).

Mañez et al. (1992) reported luteolin **42**, luteolin 4'-*O*-glucoside **45**, and luteolin 7-*O*-glucoside **53** from *C. versicaria* L. (MeOH/aerial parts/Spain).

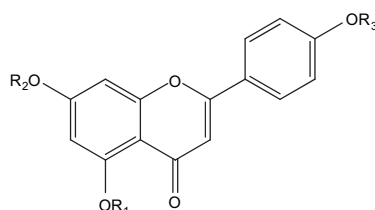
Recently, Zidorn et al. (2008) published a comparative phytochemical HPLC study on phenolics from MeOH/(CH<sub>3</sub>)<sub>2</sub>CO/H<sub>2</sub>O (3/1/1, v/v/v) extracts of flowering heads of various *Crepis* taxa. Luteolin **42**, its 4'-*O*-glucoside **45**, its 7-*O*-glucoside **53**, its 7-*O*-glucuronide **54**, and its 7-*O*-gentiobioside **61** were identified and quantified by HPLC/MS and HPLC/DAD, respectively. The occurrence of these compounds was reported as follows: *C. alpestris* (Jacq.) Tausch (Austria) **42**, **45**, **53**, **54**, and **61**; *C. aurea* (L.) Cass. (Austria) **42**, **53**, and **54**; *C. biennis* L. (Austria) **42**, **53**, **54**, and **61**; *C. capillaris* (Austria) **42** and **53**; *C. conyzifolia* (Gouan) Kern. (Austria) **42**, **45**, **53**, and **54**; *C. foetida* L. (Italy) **42**, **53**, and **61**; *C. froelichiana* DC. (Italy) **42**, **45**, **53**, and **54**; *C. jacquinii* Tausch subsp. *kernerii* (Rech.f.) Merxm. (Italy) **42** and **53**; *C. mollis* (Jacq.) Asch. (Austria) **42**, **53**, **54**, and **61**; *C. nemausensis* Gouan (Italy) **42**, **45**, **53**, and **54**; *C. paludosa* (L.) Moench (Germany) **42**, **45**, **53**, and **54**; *C. pygmaea* L. (Italy) **42**, **53**, **54**, and **61**; *C. rhaetica* Hegetschw. (Austria) **42**, **53**, and **54**; *C. terglouensis* (Hacq.) A.Kern. (Switzerland) **42**, **53**, **54**, and **61**; and *C. tingitana* Ball (Spain) **42**, **45**, **53**, and **54**.

*Dendroseris* [C4SC2] – This genus was regarded by Kilian et al. (2009) to be part of the genus *Sonchus* s.l. However, recently the genus has “for the time being” been accepted by the same group (Hand et al., 2009) as one of the examples for a paraphyletic genus which is needed to establish a taxonomy reflecting evolution (Brummitt, 2002, 2008; Hörandl, 2007).



**16** 5,7,2'-trihydroxyflavone 7-*O*-glucoside

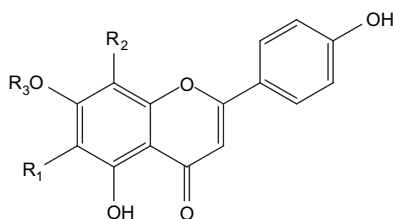
**Fig. 5.** 5,7,2'-Trihydroxyflavones (Group III. Flavones).



	Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Trivial Name
17	apigenin	H	H	H	apigenin
18	apigenin 4'-methyl ether	H	H	CH <sub>3</sub>	acacetin
19	apigenin 4'- <i>O</i> -glucoside	H	H	GLC	
20	apigenin 4'- <i>O</i> -glucuronide	H	H	GLU	
21	apigenin 7-methyl ether	H	CH <sub>3</sub>	H	genkwain
22	apigenin 7,4'-dimethyl ether	H	CH <sub>3</sub>	CH <sub>3</sub>	
23	apigenin 7- <i>O</i> -arabioside	H	ARA	H	
24	apigenin 7- <i>O</i> -glucoside	H	GLC	H	cosmetin
25	apigenin 7- <i>O</i> -glucuronide	H	GLU	H	scutellarin A
26	apigenin 7- <i>O</i> -glucuronide methylester <sup>a</sup>	H	GLU-CH <sub>3</sub>	H	
27	apigenin 7- <i>O</i> -galacturonide	H	GAU	H	
28	apigenin 7- <i>O</i> -gentiobioside	H	GEN	H	
29	apigenin 7- <i>O</i> -neohesperidoside	H	NHP	H	rhoifolin
30	apigenin 7- <i>O</i> -rutinoside	H	RUT	H	isorhoifolin
31	genkwain 4'- <i>O</i> -rutinoside	H	CH <sub>3</sub>	RUT	
32	acacetin 7- <i>O</i> -rutinoside	H	RUT	CH <sub>3</sub>	linarin
33	apigenin 5- <i>O</i> -diglucoside	GLC-GLC <sup>b</sup>	H	H	

<sup>a</sup> Probably an artifact resulting from extraction of the glucuronide with methanol. <sup>b</sup> Interglycosidic linkage not established.

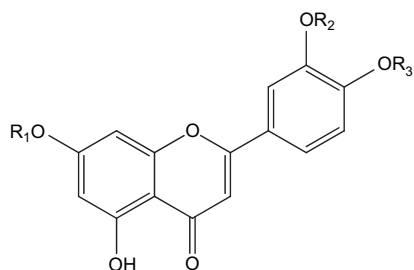
Fig. 6. Apigenin, methoxy derivatives, and *O*-glycosides (Group III. Flavones).



	Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Trivial Name
34	apigenin 8- <i>C</i> -glucoside	H	GLC	H	vitexin
35	apigenin 6- <i>C</i> -glucoside	GLC	H	H	isovitexin
36	apigenin 6- <i>C</i> -( <i>O</i> -xylosyl)-glucoside	GLC- <i>O</i> -XYL*	H	H	
37	apigenin 6- <i>C</i> -glucoside 7-methyl ether	GLC	H	CH <sub>3</sub>	swertisin
38	apigenin 6- <i>C</i> -xyloside-8- <i>C</i> -glucoside	XYL	GLC	H	vicenin-1
39	apigenin 6- <i>C</i> -arabioside-8- <i>C</i> -glucoside	ARA	GLC	H	isoschaftoside
40	apigenin 6- <i>C</i> -glucoside-8- <i>C</i> -arabioside	GLC	ARA	H	schaftoside
41	apigenin 6,8- <i>C</i> -diglucoside	GLC	GLC	H	vicenin-2

\* Interglycosidic linkage not established.

Fig. 7. Apigenin *C*-glycosides and methoxyapigenin *C*-glycosides (Group III. Flavones).



Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Name
<b>42</b> luteolin	H	H	H	
<b>43</b> luteolin 4'-methyl ether	H	H	CH <sub>3</sub>	diosmetin
<b>44</b> luteolin 4'-O-arabinoside	H	H	ARA	
<b>45</b> luteolin 4'-O-glucoside	H	H	GLC	juncein
<b>46</b> luteolin 4'-O-glucuronide	H	H	GLU	
<b>47</b> luteolin 3'-methyl ether	H	CH <sub>3</sub>	H	chrysoeriol
<b>48</b> luteolin 3'-O-(6-O-coumaryl)-glucoside	H	COU-6-GLC		
<b>49</b> luteolin 7-methyl ether	CH <sub>3</sub>	H	H	
<b>50</b> luteolin 7-O-arabinoside	ARA	H	H	
<b>51</b> luteolin 7-O-galactoside	GAL	H	H	
<b>52</b> luteolin 7-O-galacturonide	GAU	H	H	
<b>53</b> luteolin 7-O-glucoside	GLC	H	H	cynaroside
<b>54</b> luteolin 7-O-glucuronide	GLU	H	H	
<b>55</b> luteolin 7-O-glucuronide methyl ester <sup>a</sup>	GLU-CH <sub>3</sub>	H	H	
<b>56</b> luteolin 7-O-glucuronide ethylester <sup>b</sup>	GLU-CH <sub>2</sub> CH <sub>3</sub>	H	H	
<b>57</b> luteolin 7-O-galactosylglucuronide	GAL-GLU <sup>c</sup>	H	H	
<b>58</b> luteolin 7-O-rhamnoside	RHA	H	H	
<b>59</b> luteolin 7-O-(6-O-xylosyl)-glucoside	XYL-6-GLC	H	H	
<b>60</b> luteolin 7-O-sophoroside	SOP	H	H	
<b>61</b> luteolin 7-O-gentiobioside	GEN	H	H	
<b>62</b> luteolin 7-O-rutinoside	RUT	H	H	scolymoside
<b>63</b> luteolin 7,4'-O-diglucoside	GLC	H	GLC	
<b>64</b> luteolin 7-O-gentiobioside-4'-O-glucoside	GEN	H	GLC	
<b>65</b> luteolin 7,3'-O-diglucoside	GLC	GLC	H	

<sup>a</sup> Probably an artifact resulting from extraction of the glucuronide with methanol. <sup>b</sup> Probably an artifact resulting from extraction of the glucuronide with ethanol. <sup>c</sup> Interglycosidic linkage not established.

Fig. 8. Luteolin, methoxy derivatives, and O-glycosides (Group III. Flavones).

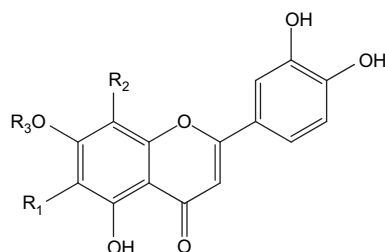
Eleven *Dendroseris* species, *D. berteriana* Hook. & Arn., *D. gigantea* Johow, *D. litoralis* Skottsbo., *D. macrantha* Skottsbo., *D. macrophylla* D. Don, *D. marginata* Hook. & Arn., *D. micrantha* Hook. & Arn., *D. nerifolia* Hook. & Arn., *D. pinnata* Hook. & Arn., *D. pruinata* Skottsbo., and *D. regia* Skottsbo. from the Chilean Juan Fernandez Islands were investigated employing TLC (Pacheco et al., 1991). Flavonoids detected in these taxa were mono- and diglucosides of apigenin **17**, luteolin **42**, and quercetin **96**. The flavonoid glycosides showed different  $R_f$  values in various solvent systems suggesting the existence of either isomeric forms of glucose (pyranose or furanose) in the flavonoid glucosides or differing linkage positions of the glucose moiety to the aglyca (Pacheco et al., 1991).

**Embergeria** – This genus is following Kilian et al. (2009) regarded to be part of the genus *Sonchus* in this review.

**Hedypnois** [C4SC5] – The rare flavone isoletin **73** was detected in leaves of *H. arenaria* (Schousboe) DC. and *H. cretica* (L.) Dum.-Courset (Harborne, 1978).

**Helminthotheca** [C4SC5] – *H. echioides* (L.) J. Holub (synonym: *Picris echioides* L.) (MeOH/aerial parts/Spain) yielded luteolin 7-O-glucoside **53** and quercetin 3-O-glucoside **107** (Rios et al., 1992). Plants from Serbia (80% EtOH/aerial parts/Serbia) yielded apigenin **17**, apigenin 7-O-glucoside **24**, 6-hydroxykaempferol **95**, and 4,4,6,7-tetrahydroxyaurone (helmon) **135** (Milovanovic et al., 2002).

**Heywoodiella** – This genus is following Kilian et al. (2009) regarded to be part of the genus *Hypochaeris* in this review.

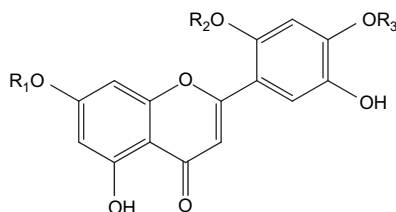


	Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Name
<b>66</b>	luteolin 8-C-glucoside	H	GLC	H	orientin
<b>67</b>	luteolin 6-C-glucoside	GLC	H	H	isoorientin
<b>68</b>	luteolin 6-C-glucoside 7-methyl ether	GLC	H	CH <sub>3</sub>	swertiajaponin
<b>69</b>	luteolin 6-C-xyloside-8-C-glucoside	XYL	GLC	H	lucenin 1
<b>70</b>	luteolin 6-C-arabinoside-8-C-glucoside	ARA	GLC	H	3'-hydroxy-isoschaftoside
<b>71</b>	luteolin 6-C-glucoside-8-C-arabinoside	GLC	ARA	H	3'-hydroxy-schaftoside
<b>72</b>	luteolin 6,8-C-diglucoside	GLC	GLC	H	lucenin 2

Fig. 9. Luteolin C-glycosides and methoxyapigenin C-glycosides (Group III. Flavones).

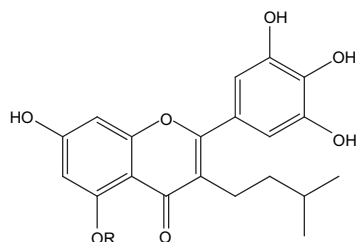
*Hieracium* s.str. (i.e. excluding *Pilosella*) [C55C1] – *H. murorum* L. subsp. *grandidens* (Dahlst.) Zahn var. *minoriceps* Zahn (H<sub>2</sub>O/flowering heads and leaves/France) yielded apigenin **17** and luteolin **42**. In addition, luteolin 7-O-glucoside **53** was reported from the flowering heads and an unspecified luteolin 7-O-diglycoside from the leaves (Haag-Berrurier and Duquenois, 1969).

Leaf excretions of *H. intybaceum* All. [(CH<sub>3</sub>)<sub>2</sub>CO/leaves/Austria] yielded naringenin 7-O-methyl ether **6**, naringenin 7,4'-dimethyl ether **7**, apigenin **17**, apigenin 4'-methyl ether (acacetin) **18**, apigenin 7,4'-dimethyl ether **22** (Wollenweber, 1984).



	Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Name
<b>73</b>	isoetin	H	H	H	
<b>74</b>	isoetin 4'-O-glucuronide	H	H	GLU	
<b>75</b>	isoetin 2'-O-xyloside	H	XYL	H	
<b>76</b>	isoetin 2'-O-(4-O-acetyl)-xyloside	H	4-O-acetyl XYL	H	
<b>77</b>	isoetin 7-O-glucoside	GLC	H	H	sonchoside
<b>78</b>	isoetin 7-O-glucoside-2'-O-arabinoside	GLC	ARA	H	
<b>79</b>	isoetin 7-O-glucoside-2'-O-xyloside	GLC	XYL	H	
<b>80</b>	isoetin 7-O-glucoside-2'-O-(4-O-acetyl)-xyloside	GLC	4-O-acetyl XYL	H	
<b>81</b>	isoetin 7-O-glucoside-2'-O-glucoside	GLC	GLC	H	

Fig. 10. Isoetin and derivatives (Group III. Flavones).



Semi-systematic name		R
<b>82</b>	asplenetin	H
<b>83</b>	asplenetin 5-O-neohesperidoside	NHP

Fig. 11. Asplenetin and derivative (Group III. Flavones).

Leave excretions of *H. amplexicaule* L. [(CH<sub>3</sub>)<sub>2</sub>CO /leaves/Austria] yielded naringenin 7-O-methyl ether **6**, naringenin 7,4'-dimethyl ether **7**, and apigenin 7,4'-dimethyl ether **22** (Wollenweber et al., 1997).

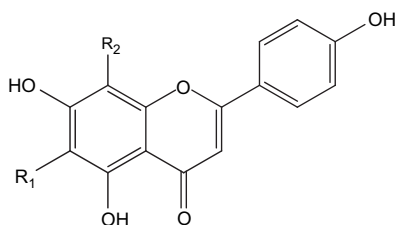
Several papers specifically report on the chemotaxonomic significance of flavonoids from the genus *Hieracium*.

Guppy and Bohm (1976) investigated flavonoids from whole plants of five *Hieracium* species from British Columbia: *H. albertinum* Farr., *H. albiflorum* Hook., *H. cynoglossoides* Arv.-Touv., *H. gracile* Hook., and *H. umbellatum* L. All species contained apigenin **17**, apigenin 4'-O-glucoside **19**, apigenin 7-O-glucoside **24**, luteolin **42**, luteolin 4'-O-glucoside **45**, and luteolin 7-O-glucoside **53**. Additionally, chrysoeriol **47** was detected in *H. albertinum*, *H. cynoglossoides*, *H. gracile*, and *H. umbellatum*. Apigenin 7-O-glucuronide **25** and luteolin 7-O-glucuronide **54** were found in *H. albiflorum*, *H. gracile*, and *H. umbellatum*. Apigenin 7-O-arabinoside **23**, luteolin 4'-O-arabinoside **44**, luteolin 7-O-arabinoside **50**, and quercetin 3-O-glucoside **107** were detected only in *H. umbellatum*. Apigenin 4'-O-glucuronide **20** and luteolin 4'-O-glucuronide **46** were only detected in *H. cynoglossoides*. In addition, the authors observed several flavonoid di- and triglycosides using two-dimensional TLC. However, the positions of the sugar linkages were not established for these compounds (Guppy and Bohm, 1976).

Christy (1985) studied artificial hybrids of *H. gronovii* L., *H. paniculatum* L., *H. scabrum* Michx., and *H. venosum* L. from eastern North America including their chemistry. Apart from the fact flavones were found in all species and hybrids no details were reported in the published abstract (Christy, 1985).

Giner et al. (1992c) investigated phenolic compounds from *H. amplexicaule* and *H. compositum* Lapeyr. (MeOH/aerial parts/Spain). Both species yielded apigenin **17**, apigenin 7-O-glucoside **24**, luteolin **42**, diosmetin **43**, luteolin 7-O-glucoside **53**, and luteolin 7-O-rhamnoside **58**.

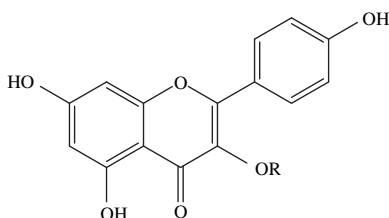
Petrović et al. (1999b) investigated flavonoids from *H. gymnocephalum* Griseb. ex Pant., *H. suborieni* (Zahn) P.D. Sell & C. West, *H. bleicii* Niketic, *H. coloriscapum* Rohlena and Zahn, *H. guentheri-beckii* Zahn, *H. naegelianum* Pancic, and *H. rotundatum* Kit. ex Schultes (MeOH/aerial parts/ Montenegro) by using HPLC/DAD. Apigenin 7-O-glucoside **24**, luteolin **42**, luteolin 7-O-glucoside **53**, luteolin 7-O-β-D-xylosyl-(1 → 6)-β-D-glucoside **59**, and luteolin 7-O-rutinoside **62** were reported from all species, except diglycosides **59** and **62** which were missing in *H. rotundatum*. Apigenin **17** was only detected in *H. suborieni* Petrović et al., 1999b. The flavone diglycosides luteolin 7-O-β-D-xylosyl-(1 → 6)-β-D-glucoside **59** and luteolin 7-O-α-L-rhamnosyl-(1 → 6)-β-D-glucoside **62** were reported from *H. gymnocephalum* (Petrović et al., 1999a).



Semi-systematic name		R <sub>1</sub>	R <sub>2</sub>
<b>84</b>	isoscutellarein	H	OH
<b>85</b>	scutellarein	OH	H

Fig. 12. Isoscutellarein and scutellarein (Group III. Flavones).





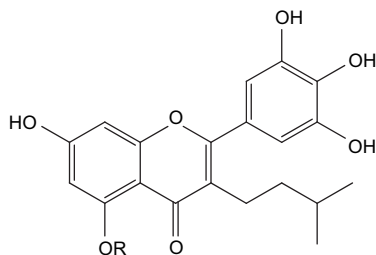
	Semi-systematic name	R	Name
<b>86</b>	kaempferol	H	
<b>87</b>	kaempferol 3- <i>O</i> -galactoside	GAL	trifolin
<b>88</b>	kaempferol 3- <i>O</i> -(6- <i>O</i> -rhamnosyl)-galactoside	RHA-6-GAL	biorobin
<b>89</b>	kaempferol 3- <i>O</i> -glucoside	GLC	astragaln
<b>90</b>	kaempferol 3- <i>O</i> -(6- <i>O</i> -malonyl)-glucoside	MAL-6-GLC	
<b>91</b>	kaempferol 3- <i>O</i> -rutinoside	RUT	nicotiflorin
<b>92</b>	kaempferol 3- <i>O</i> -glucuronide	GLU	
<b>93</b>	kaempferol 3- <i>O</i> -glucuronide methyl ester	GLU-CH <sub>3</sub>	
<b>94</b>	kaempferol 3- <i>O</i> -rhamnoside	RHA	afzelin

Fig. 13. Kaempferol and kaempferol *O*-glycosides (Group IV. Flavonols).

Švehlíková et al. (2002) studied phenolic constituent composition in leaves of *H. rohacsense* Kit., *H. borsanum* Mráz, *H. ratezaticum* (Nyáz. & Zahn) Mráz, and *H. pseudocaesium* Degen & Zahn (MeOH/leaves/Slovakia). Apigenin 4'-*O*-glucuronide **20**, luteolin 4'-*O*-glucuronide **46**, and luteolin 7-*O*-glucoside **53** were detected in all species (Švehlíková et al., 2002).

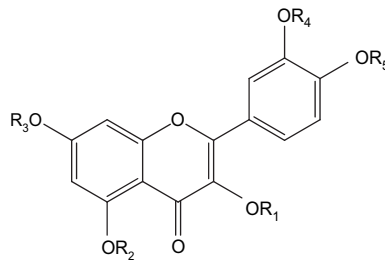
Zidorn et al. (2002) analyzed phenolic acids and flavonoids in flowering heads of 76 taxa belonging to 66 species of *Hieracium* subgenera *Hieracium* and *Pilosella* using HPLC/DAD and HPLC/MS. The following flavonoids were detected: apigenin 4'-*O*-glucuronide **20**, luteolin **42**, luteolin 4'-*O*-glucoside **45**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-glucuronide **54**, and isoetin 4'-*O*-glucuronide **74**. HPLC results revealed only a limited degree of qualitative variation between the different taxa. The peak corresponding to apigenin 4'-*O*-glucuronide **20** was not separated from the peak of a minor compound. Therefore the quantification results of apigenin 4'-*O*-glucuronide **20** were not reported. The following chemosystematic data were reported:

*H. alpinum* L. **42, 45, 53, 54**, and **74**; *H. amplexicaule* **42, 45, 53, 54**, and **74**; *H. atratum* Fr. **42, 45**, and **53**; *H. bifidum* Kit. ex Hornem. subsp. *caesiiflorum* (Almq. ex Norrl.) Zahn **42, 45, 53**, and **74**; *H. bocconeii* Griseb. subsp. *bocconeii* **42, 45**, and **53**; *H. brevifolium* Tausch **42, 45**, and **53**; *H. glaucinum* Jord. **42, 45, 53**, and **54**; *H. glaucinum* Jord. subsp. *basalticum* (Sch.Bip.) J.Duvign. **42, 45, 53**, and **54**; *H. glaucinum* Jord. subsp. *heteroschistum* (Zahn) Soó **42, 45**, and **53**; *H. gorfenianum* Bornm. & Zahn **42, 45, 53**, and **54**; *H. intybaceum* **42, 45, 53, 54**, and **74**.; *H. inuloides* Tausch subsp. *tridentatifolium* (Zahn) Zahn **42, 45, 53**, and **54**; *H. jurassicum* Griseb. **42, 45**, and **53**; *H. kofelicum* Gottschl. **42, 45**, and **53**; *H. kuekenthalianum* (Zahn) Zahn **42, 45**, and **53**; *H. laevigatum* Willd. subsp. *laevigatum* **42, 45**, and **53**; *H. lycopifolium* Froel. subsp. *lycopifolium* **42, 45, 53**, and **54**; *H. macilentum* Fr. **42, 45, 53**, and **54**; *H. maculatum* Schrank subsp. *commixtum* (Jord.) Zahn **42, 45, 53**, and **54**; *H. maculatum* Schrank



	Semi-systematic name	R
<b>82</b>	asplenetin	H
<b>83</b>	asplenetin 5- <i>O</i> -neohesperidoside	NHP

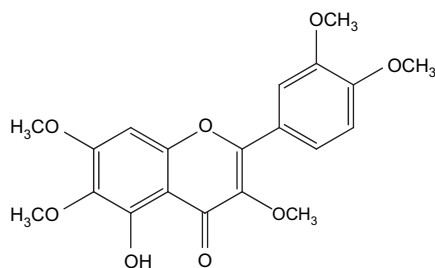
Fig. 14. 6-Hydroxykaempferol (Group IV. Flavonols).



	Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Name
96	quercetin	H	H	H	H	H	
97	isorhamnetin	H	H	H	CH <sub>3</sub>	H	
98	quercetin 7,3',4'-trimethyl ether	H	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	
99	quercetin 7-O-glucoside	H	H	GLC	H	H	quercimeritrin
100	quercetin 7-O-gentiobioside	H	H	GEN	H	H	
101	quercetin 5-O-glucoside	H	GLC	H	H	H	saxifragin
102	quercetin 3-methyl ether	CH <sub>3</sub>	H	H	H	H	
103	quercetin 3-O-arabinoside	ARA	H	H	H	H	guaijaverin
104	quercetin 3-O-galactoside	GAL	H	H	H	H	hyperin
105	quercetin 3-O-(6-O-caffeoyl)-galactoside	CAF-6-GAL	H	H	H	H	
106	quercetin 3-O-α-D-glucoside	αGLC	H	H	H	H	
107	quercetin 3-O-β-D-glucoside	GLC	H	H	H	H	isoquercitrin
108	quercetin 3-O-(6-O-malonyl)-glucoside	MAL-6-GLC	H	H	H	H	
109	quercetin 3-O-glucuronide	GLU	H	H	H	H	miquelianin
110	quercetin 3-O-(2-O-caffeoyl)-glucuronide	CAF-2-GLU	H	H	H	H	
111	quercetin 3-O-rhamnoside	RHA	H	H	H	H	quercitrin
112	quercetin 3-O-rutinoside	RUT	H	H	H	H	rutin
113	isorhamnetin 3-O-glucoside	GLC	H	H	CH <sub>3</sub>	H	
114	isorhamnetin 3-O-glucuronide	GLU	H	H	CH <sub>3</sub>	H	
115	isorhamnetin 3-O-rutinoside	RUT	H	H	CH <sub>3</sub>	H	narcissin
116	rhamnocitrin 3-O-rutinoside	RUT	H	CH <sub>3</sub>	H	H	
117	rhamnazin 3-O-rutinoside	RUT	H	CH <sub>3</sub>	CH <sub>3</sub>	H	
118	quercetin 3,7-O-diglucoside	GLC	H	GLC	H	H	
119	quercetin 3-O-(6-O-malonyl)-glucoside-7-O-glucoside	MAL-6-GLC	H	GLC	H	H	

Fig. 15. Quercetin, methoxy derivatives, and O-glycosides (Group IV. Flavonols).

subsp. *maculatum* **42**, **45**, **53**, and **54**; *H. onosmoides* Fr. subsp. *crinigerum* (Fr.) Zahn **42**, **45**, and **53**; *H. oxyodon* Fr. subsp. *muretii* (Gremli) Zahn **42**, **45**, and **53**; *H. pallidiflorum* Jord. ex Hausm. subsp. *huteri* (Hausm. ex Bamb.) Zahn **42**, **45**, **53**, and **54**; *H. picroides* Vill. **42**, **45**, and **53**; *H. piliferum* Hoppe subsp. *piliferum* **42**, **45**, **53**, and **54**; *H. pilosum* Schleich. ex Froel. **42**, **45**, **53**, **54** and **74**; *H. porrifolium* L. subsp. *porrifolium* **42**, **45**, **53**, and **74**; *H. pospichalii* Zahn subsp. *pospichalii* **42**, **45**, **53**, and **54**; *H. prenanthoides* Vill. subsp. *bupleurifolioides* Zahn **42**, **45**, and **53**; *H. racemosum* Waldst. & Kit. ex Willd. **42**, **45**, and **53**; *H. sabaudum* L. **42**, **45**, **53**, and **54**; *H. saxifragum* Fr. subsp. *vulpii* Zahn **42**, **45**, and **53**; *H. schmidtii* Tausch. subsp. *graniticum* (Sch.Bip.) Gottschl. **42** and **53**; *H. sommerfeltii* Lindab. **42** and **53**; *H. sparsum* Friv. subsp. *vierhapperi* Zahn **42**, **45**, **53**, and **54**;



120 Artemitin

Fig. 16. Artemitin (Group IV. Flavonols).

*H. umbellatum* L. subsp. *umbellatum* **42**, **45**, **53**, and **54**; *H. venostorum* (Zahn) Gottschl. **42**, **45**, and **53**; *H. vetteri* (Zahn) Ronniger **42**, **45**, and **53**; *H. villosum* Jacq. subsp. *villosum*. **42**, **45**, **53**, **54**, and **74**; and *H. wiesbaurianum* Uechtr. subsp. *semicinerascens* Bornm. & Zahn **42**, **45**, **53**, and **54** (Zidorn et al., 2002).

**Hispidella** [C5SC1] – Isoetin **73** was detected in flowering heads and leaves of *H. hispanica* Bernad. ex Lam. (Harborne, 1978).

**Hyoseris** [C4SC2] – *H. lucida* L. (95% EtOH/roots/Egypt) yielded apigenin **17**, apigenin 7-*O*-glucoside **24**, luteolin **42**, and luteolin 7-*O*-glucuronide **53** (Ghazy and Mahmoud, 1987).

Rees and Harborne (1984) reported luteolin **42** and quercetin **96** from *H. radiata* L. (Rees and Harborne, 1984).

**Hypochaeris** [C4SC5] – Eight European species of the genus *Hypochaeris*, *H. achyrophorus* L., *H. cretensis* (L.) Bory & Chaub., *H. glabra* L., *H. illyrica* K.Maly, *H. laevigata* (L.) Cesati, Passer. & Gibelli, *H. maculata* L., *H. radicata* L. subsp. *neapolitana* (DC.) Guadagno, and *H. robertia* (Sch.Bip.) Fiori were analyzed for their array of leaf flavonoids using HPLC and 2D TLC. Luteolin 7-*O*-glucoside **53**, isoetin 7-*O*-glucoside-2'-*O*-xyloside **79**, and isoetin 7-*O*-glucoside-2'-*O*-(4-*O*-acetyl)-xyloside **80** were identified in all species. Luteolin 7-*O*-rutinoside **62** was detected only in *H. cretensis*, *H. illyrica*, *H. laevigata*, *H. maculata*, and *H. radicata* subsp. *neapolitana* (Fiasson et al., 1991).

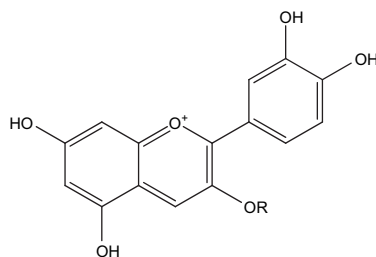
In flowering heads of *H. radicata* collected in New Zealand luteolin **42**, luteolin 4'-*O*-glucoside **45**, luteolin 7-*O*-glucoside **53**, and luteolin 7-*O*-glucuronide **54** were detected by HPLC/DAD and HPLC/MS (Zidorn et al., 2005a).

Flowering heads of *Hypochaeris oligocephala* (Svent. & Bramwell) Lack (formerly also known as *Heywoodiella oligocephala* Svent. & Bramwell) yielded isoetin **73** and isoetin 7-*O*-glucoside **77** (Harborne, 1978, 1991). Isoetin **73** was also reported from leaves of *H. achyrophorus*, *H. oligocephala*, *H. radicata*, and *H. uniflora* Vill. (Harborne, 1978).

*H. radicata* (MeOH/aerial parts/Spain) yielded luteolin 4'-*O*-glucoside **45**, luteolin 7-*O*-glucoside **53**, and quercetin 3-*O*-glucoside **107** (Rios et al., 1992; Giner et al., 1993).

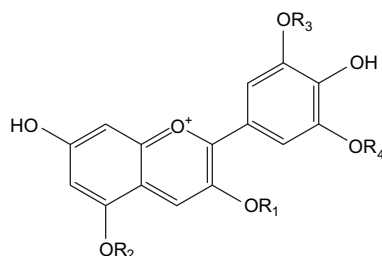
2D TLC investigations of *H. laevigata* and of diploid and tetraploid samples of *H. maculata* proved the occurrence of luteolin 7-*O*-glucoside **53**, a luteolin 7-*O*-diglycoside, luteolin 7-*O*-rutinoside **62**, isoetin 2'-*O*-xyloside **75**, isoetin 2'-*O*-(4-*O*-acetyl)-xyloside **76**, isoetin 7-*O*-glucoside-2'-*O*-xyloside **79**, and isoetin 7-*O*-glucoside-2'-*O*-(4-*O*-acetyl)-xyloside **80** in all taxa investigated (Gluchoff-Fiasson et al., 1991).

**Ixeridium** [C4SC3] – The Tibetan medicinal plant *I. gracile* (DC.) Shih (85% EtOH/whole plants/China) yielded the flavanones **1**, **2**, **3**, and **4**, luteolin 7-*O*-glucoside **53**, kaempferol **86**, quercetin **96**, quercetin 3-*O*-galactoside **104**, the isoflavone isomucronulatol **130**, and the chalcones **132** and **133** (Ma et al., 2007; Zhang et al., 2007).



Semi-systematic name	R
<b>121</b> cyanidin 3- <i>O</i> -glucoside	GLC
<b>122</b> cyanidin 3- <i>O</i> -(6- <i>O</i> -malonyl)-glucoside	MAL-6-GLC

Fig. 17. Cyanidin and derivatives (Group V. Anthocyanidins).



	Semi-systematic name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
123	delphinidin	H	H	H	H
124	malvidin	H	H	CH <sub>3</sub>	CH <sub>3</sub>
125	delphinidin 3- <i>O</i> -(6- <i>O</i> -malonyl)-glucoside	MAL-6-GLC	H	H	H
126	delphinidin 3,5-di- <i>O</i> -glucoside	GLC	GLC	H	H
127	delphinidin 3- <i>O</i> -glucoside -5- <i>O</i> -(6- <i>O</i> -malonyl)-glucoside	GLC	MAL-6-GLC	H	H
128	dephinidin 3- <i>O</i> -(6- <i>O</i> -malonyl)-glucoside-5- <i>O</i> -glucoside	MAL-6-GLC	GLC	H	H
129	delphinidin 3,5-di- <i>O</i> -(6- <i>O</i> -malonyl)-glucoside	MAL-6-GLC	MAL-6-GLC	H	H

Fig. 18. Delphinidin, methoxy derivatives, and *O*-glycosides (Group V. Anthocyanidins).

*I. gramineum* (Fisch.) Tzvelev yielded luteolin **42** and luteolin 7-*O*-glucoside **53** (Liu et al., 2006).

**Ixeris** [C4SC3] – *I. denticulata* (Houtt.) Nakai ex Stebbins f. *pinnatipartita* (Makin) Stebbins (hot water/whole plants/China) yielded luteolin 7-*O*-glucoside **53** and luteolin 7-*O*-glucuronide methyl ester **55** (Ma et al., 1999).

*I. laevigata* (Blume) Yaman yielded apigenin **17**, apigenin 7-*O*-glucoside **24**, and luteolin 7-*O*-glucoside **53** (Ho et al., 1989). The latter was also detected in *I. sonchifolia* Hance (Feng et al., 2000a; Han et al., 2005). Feng et al. (2000a,b) reported apigenin 7-*O*-glucuronide methyl ester **26**, luteolin 7-*O*-glucuronide methyl ester **55**, and luteolin 7-*O*-glucuronide ethyl ester **56** from *I. sonchifolia* Hance (70% EtOH/whole plants/China). In addition, luteolin **42**, luteolin 7-*O*-sophoroside **60**, and luteolin 7-*O*-gentiobioside **61** were isolated from *I. sonchifolia* (Lu et al., 2002). *I. laevigata* Sch.Bip. var. *oldhami* Kitam. yielded apigenin **17**, apigenin 7-*O*-glucoside **24**, luteolin **42**, and luteolin 7-*O*-glucoside **53** (Lu et al., 2000).

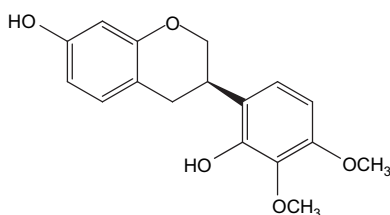
*I. repens* A.Gray. [synonym: *Lactuca repens* Benth. & Hook.f.] yielded luteolin 7-*O*-glucoside **53** (Nakaoki and Morita, 1960).

**Koelpinia** [C2]: *K. linearis* Pall. yielded quercetin **96** (Rees and Harborne, 1984).

**Krigia** [C5SC2] – Leaves of *K. virginica* (L.) Willd. yielded quercetin 3-*O*-glucoside **107** (Harborne, 1977).

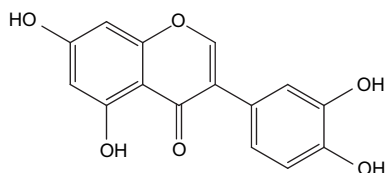
**Lactuca** [C4SC1] – Rees and Harborne (1984) analyzed flavonoid spectra from leaves of 13 *Lactuca* species using 2D paper chromatography. Apigenin **17**, luteolin **42**, and quercetin **96** were detected. Luteolin **42** was the major compound in all species investigated. Moreover, the authors reported unspecified flavone 7-*O*-glycosides and flavonol 3-*O*-glycosides. In detail, *L. acanthifolia* (Willd.) Boiss. yielded **42** and **96**; *L. aculeata* Boiss. **17** and **42**; *L. altaica* Fischer & C.A. Mey. **42** and **96**; *L. graeca* Boiss. **42** and **96**; *L. perennis* L. **17** and **42**; *L. saligna* L. **42** and **96**; *L. sativa* L. **42** and **96**; *L. serriola* L. **17**, **42** and **96**; *L. tatarica* C.A. Mey. **17**, **42** and **96**; *L. tenerrima* Pourr. **17** and **42**; *L. triquetra* Benth. & Hook.f. **17** and **42**; and *L. virosa* L. **17**, **42** and **96**. *L. tetrantha* B.L. Burt & P.H. Davis [synonym: *Scariola tetrantha* (B.L. Burt & P.H. Davis) Soják] yielded luteolin **42** and quercetin **96** (Rees and Harborne, 1984).

Mañez et al. (1994) performed a chemotaxonomic survey of flavonoids in the genus *Lactuca* yielding the following records: *L. muralis* (L.) Gaertn. (synonym: *Mycelis muralis* Dumort.) **24**, **42**, **53**, **107**; *L. tenerrima* Pourr. **24**, **42**, **53**, **55**, **107**; *L. viminea* J.Presl. & C.Presl. **17**, **42**, **53**, **96**, **107**; and *L. virosa* L. **17**, **42**, **53**, **55**, **96**, and **107**.



**130** isomucronulatol

Fig. 19. Isoflavans (Group VI. Isoflavonoids).



131 isoluteolin (orobol)

Fig. 20. Isoflavones (Group VI. Isoflavonoids).

*Lactuca formosana* Maxim. [synonym: *P. formosana* (Maxim.) C. Shih] (90% EtOH/aerial parts/Taiwan) yielded apigenin **17**, apigenin 7-*O*- $\beta$ -D-glucuronide **25**, apigenin 7-*O*- $\beta$ -D-galacturonide **27**, luteolin **42**, luteolin 7-*O*- $\beta$ -D-galacturonide **52**, luteolin 7-*O*- $\beta$ -D-glucoside **53**, luteolin 7-*O*- $\beta$ -D-glucuronide **54**, and quercetin 3-*O*- $\beta$ -D-glucoside **107**; in this report, sugar stereochemistry was established by NMR and optical methods (Lin and Chou, 2002).

*L. indica* L. yielded apigenin 7-*O*-glucoside **24**, luteolin 7-*O*-glucoside **53**, and quercetin 3-*O*-galactoside **104** (Kaneta et al., 1978). Moreover, *L. indica* (hot water/whole plants/Taiwan) yielded luteolin 7-*O*-glucoside **53** and quercetin 3-*O*-glucoside **107** (Wang, et al., 2003). Korean plants (80% MeOH/aerial parts/Korea) from the same species yielded 5,7,2'-trihydroxyflavone 7-*O*-glucoside **16**, luteolin 7-*O*-glucuronide **54**, quercetin 5-*O*-glucoside **101**, quercetin 3-*O*-glucoside **107**, and quercetin 3-*O*-rutinoside **112** (Kim, et al., 2007).

*L. perennis* L. (EtOH/aerial parts/Poland) yielded apigenin **17**, apigenin 7-*O*-glucoside **24**, and luteolin **42** (Kisiel and Ziełńska, 2000).

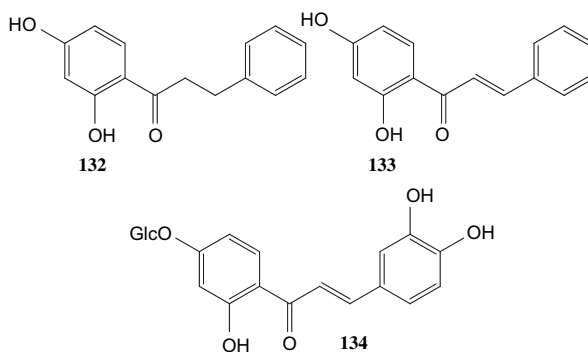
Apigenin **17**, luteolin **42**, and quercetin 3-*O*-glucoside **107** were isolated from aerial parts of *L. quercina* L. and *L. tatarica* (EtOH/fresh aerial parts/Poland). In addition, apigenin 7-*O*-glucoside **24** and kaempferol 3-*O*-glucoside **89** were isolated from *L. tatarica* and luteolin 7-*O*-glucoside **53** was isolated from *L. quercina* (Kisiel, 1998).

*L. saligna* L. (aerial parts/Egypt) yielded apigenin **17**, luteolin **42**, and 7-*O*-methylluteolin **49** (El-Din et al., 1987).

Bilyk and Sapers (1985) reported the occurrence of kaempferol **86** and quercetin **96** from leaves of the following thirteen cultivars of lettuce (*L. sativa* L.). Leaf salads: cvar. *crispy sweet*, cvar. *green ice*, cvar. *ruby*, and cvar. *salad bowl*; head salads: cvar. *augusta*, cvar. *buttercrunch*, cvar. *minneto*, cvar. *summer bibb*, and cvar. *tom thumb*; white head lettuces: cvar. *barcarolle*, cvar. *burpee bipp*, cvar. *fordhook*, and cvar. *paris* (Bilyk and Sapers, 1985).

Eight cultivars of lettuce (*L. sativa*), cvar. *iceberg Salad*, cvar. *green batavia Vanity*, cvar. *cos Remus*, cvar. *green salad bowl Hrizet*, cvar. *green oak leaf*, cvar. *red oak leaf*, cvar. *lollo biondo Ciereo*, and cvar. *lollo rosso Malibu* were analyzed for their flavonoid composition and content (DuPont et al., 2000). Luteolin 7-*O*-glucuronide **54**, quercetin 3-*O*-glucoside **107**, quercetin 3-*O*-(6-*O*-malonyl)-glucoside **108**, and quercetin 3-*O*-glucuronide **109** were identified in all cultivars. Quercetin 3-*O*-galactoside **104** was found in the *cos*, *green salad bowl*, *green oak leaf*, *lollo biondo*, and *lollo rosso* cultivars. Quercetin 3-*O*-rhamnoside **111** was found in the *green salad bowl*, *green oak leaf*, *red oak leaf*, *lollo biondo*, and *lollo rosso* cultivars. Rutin **112** was found only in the *cos* cultivar, and quercetin 3-*O*-(6-*O*-malonyl)-glucoside-7-*O*-glucoside **119** was detected only in the two *lollo* cultivars. Two cyanidins, cyanidin 3-*O*-glucoside **121** and cyanidin 3-*O*-(6-*O*-malonyl)-glucoside **122** were identified in the red-leafed cultivars *lollo rosso* and *red oak leaf* (DuPont et al., 2000).

*L. viminea* (MeOH/aerial parts/Spain) yielded apigenin **17**, luteolin **42**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-glucuronide methyl ester **55**, quercetin **96**, and quercetin 3-*O*-glucoside **107** (Woeldecke and Herrmann, 1974; Terencio et al., 1992).

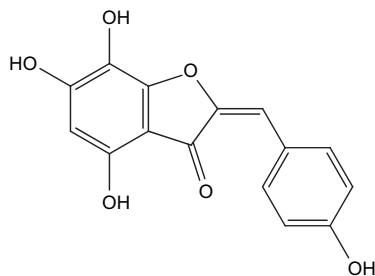


132 2',4'-dihydroxydihydrochalcone

133 2',4'-dihydroxychalcone

134 butein 4'-*O*-glucoside (coreopsin)

Fig. 21. Chalcones (Group VII. Chalcones).



135 4,6,7,4'-tetrahydroxyaurone (helmon)

Fig. 22. Aurones (Group VIII. Aurones).

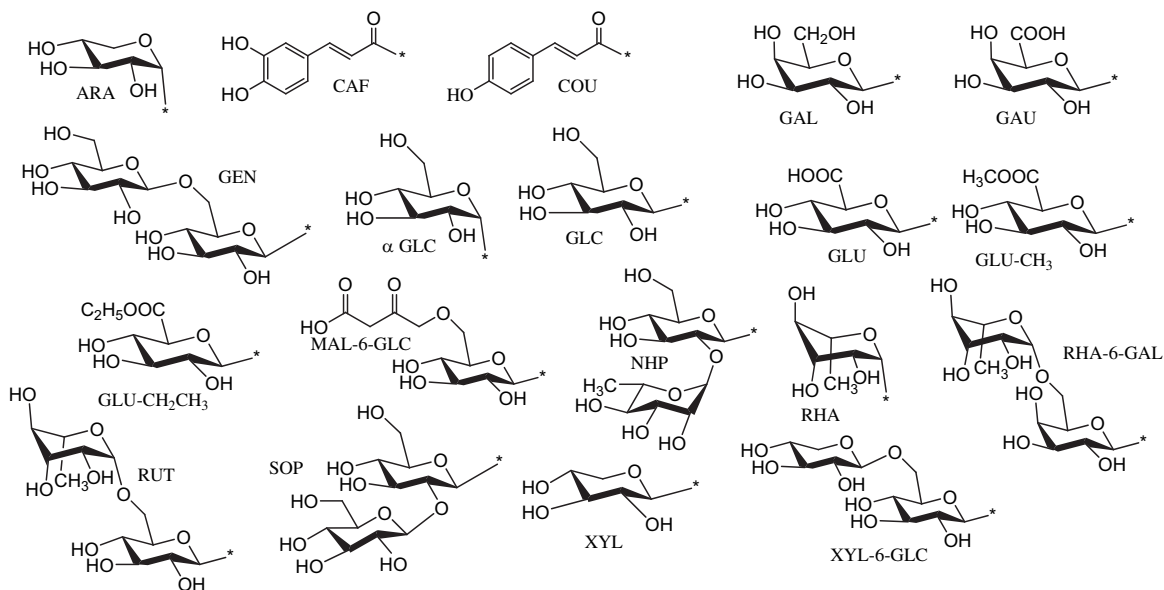
**Lapsana** [C4SC3] – *L. communis* L. subsp. *communis* (EtOH:H<sub>2</sub>O, 1:3/aerial parts/France) yielded luteolin **42**, luteolin 7-*O*-glucuronide **54**, and isoquercetin **107** (Fontanel et al., 1998).

**Launaea** [C4SC2] – *L. arborescens* Murb. (MeOH/aerial parts/Spain) yielded the flavones apigenin 7-*O*-glucoside **24**, luteolin **42**, luteolin 7-*O*-glucoside **53**, and luteolin 7-*O*-rhamnoside **58**. HPLC/DAD analyses revealed that methanolic extracts of *L. acanthoclada* Maire and *L. resedifolia* Druce contained the same set of compounds identified in *L. arborescens* Murb. (Giner et al., 1992b; Mañez et al., 1994).

*L. aspleniifolia* Hook.f. (EtOH/whole plants/India) yielded 7-hydroxy-3',4'-dimethoxyflavone **14**, apigenin **17**, apigenin 7-*O*-glucoside **24**, vitexin **34**, luteolin **42**, luteolin 7-*O*-glucoside **53**, and delphinidin **123** (Gupta et al., 1985). Moreover, the flavones asplenitin **82** and asplenitin 5-*O*-neohesperidoside **83** were found (Gupta and Ahmed, 1985).

*L. mucronata* (Forsk.) Muschl. (95% EtOH/whole plants/Egypt) yielded apigenin 7-*O*-glucoside **24**, luteolin **42**, and luteolin 7-*O*-glucoside **53** (Abdel-Salam et al., 1982).

*L. nudicaulis* Hook.f. (70% EtOH/whole plants/Egypt) yielded apigenin 7-*O*-glucoside **24**, apigenin 7-*O*-gentiobioside **28**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-gentiobioside **61**, luteolin 7-*O*-rutinoside **62**, luteolin 7,4'-*O*-diglucoside **63**, luteolin 7-*O*-gentiobioside-4'-*O*-glucoside **64**, and luteolin 7,3'-*O*-diglucoside **65**. These eight glycosides were also detected in five other *Launaea* species: *L. capitata* (Spreng.) Dandy, *L. cassiniana* Muschl., *L. resedifolia* Druce, *L. spinosa* Sch.Bip., and *L. tenuiloba* Muschl. Apigenin 7-*O*-glucoside **24** and luteolin 7-*O*-glucoside **53** were the major compounds in all six species investigated (Mansour et al., 1983a; Sarg et al., 1984; Sarg et al., 1987). Additionally, an apigenin 5-*O*-diglucoside **33** was reported from *L. resedifolia*; however, the position of the interglycosidic linkage was not established (Saleh et al., 1988).



**Fig. 23.** Structures of sugar and acyl moieties. Abbreviations: ARA  $\alpha$ -L-arabinosyl; CAF caffeoyl; COU coumaroyl; GAL  $\beta$ -D-galactosyl; GAU  $\beta$ -D-galacturonyl; GEN  $\beta$ -D-gentiobiosyl;  $\alpha$ GLC  $\alpha$ -D-glucosyl; GLC  $\beta$ -D-glucosyl; GLU  $\beta$ -D-glucuronyl; GLU-CH<sub>3</sub>  $\beta$ -D-glucuronyl methyl ester; GLU-CH<sub>2</sub>CH<sub>3</sub>  $\beta$ -D-glucuronyl ethylester, MAL-6-GLC 6-*O*-malonyl- $\beta$ -D-glucosyl; NHP  $\beta$ -D-neohesperidosyl; RHA  $\alpha$ -L-rhamnosyl; RHA-6-GAL 6-*O*- $\alpha$ -L-rhamnosyl- $\beta$ -D-galactosyl; RUT  $\beta$ -D-rutinosyl; SOP  $\beta$ -D-sophoroside; XYL  $\beta$ -D-xylosyl; XYL-6-GLC 6-*O*- $\beta$ -D-xylosyl- $\beta$ -D-glucosyl.

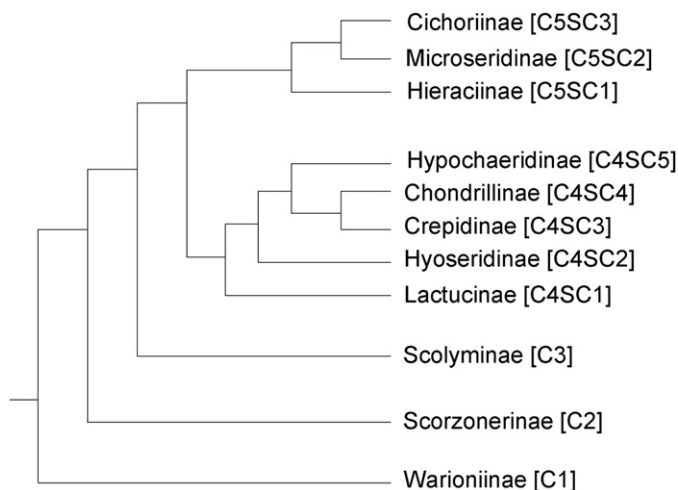


Fig. 24. Current system of the Cichorieae based on (macro-)molecular data (Kilian et al., 2009).

*L. tenuiloba* (EtOAc/aerial parts/Egypt) yielded apigenin **17**, apigenin 7-*O*-glucoside **24**, and luteolin 7-*O*-glucoside **53**; additionally, an apigenin 7-*O*-diglucoside (probably identical to compound **28** found in some other *Launaea* species) was isolated but the glycosidic linkage was not established (Abdel Salam et al., 1986).

**Leontodon** [C4SC5] – Recent molecular investigations resulted in a split of the genus *Leontodon* s.l. into *Leontodon* s.str. and *Scorzoneroides*. The latter is identical in its delimitation to the former *Leontodon* subgenus *Oporinia* (Greuter et al., 2006; Samuel et al., 2006). For members of this taxon please refer to the *Scorzoneroides* section.

Leaves of *L. crispus* Vill., *L. hispidus* L., *L. maroccanus* (Pers.) Ball, and *L. saxatilis* Lam. s.str. [synonym: *L. taraxacoides* (Vill.) Merat subsp. *taraxacoides*] yielded isoetin **73** (Harborne, 1978). In flowering heads of *L. hispidus* and *L. incanus* (L.) Schrank luteolin **42**, luteolin 4'-*O*-glucoside **45**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-glucuronide **54**, and luteolin 7-*O*-gentiobioside **61** were detected by HPLC/DAD and HPLC/MS (Zidorn, 1998, 2008a). Moreover, Zidorn (1998) investigated phenolics including flavonoids in MeOH/(CH<sub>3</sub>)<sub>2</sub>CO/H<sub>2</sub>O (3:1:1, v:v:v) extracts of flowering heads of various *Leontodon* taxa. Luteolin **42**, its 4'-*O*-glucoside **45**, its 7-*O*-glucoside **53**, its 7-*O*-glucuronide **54**, and its 7-*O*-gentiobioside **61** were reported from the following taxa: *Leontodon anomalus* Ball (Italy) **42**, **45**, **53**, **54**, and **61**; *L. berinii* (Bartl.) Roth (Italy) **42**, **45**, **53**, **54**, and **61**; *L. crispus* Vill. (Italy) **42**, **45**, **53**, **54**, and **61**; *L. hispidus* subsp. *dubius* (Hoppe) Pawlowska (synonym: *L. scaber* Miel.) (Austria, Italy, Slovenia) **42**, **45**, **53**, **54**, and **61**; *L. hispidus* subsp. *hispidus* (Austria, Belgium, Germany, Italy, Netherlands, Switzerland) **42**, **45**, **53**, **54**, and **61**; *L. hispidus* subsp. *hyoseroides* (Welw. ex Rchb.) Murr (Austria, Switzerland) **42**, **45**, **53**, **54**, and **61**; *L. incanus* (Austria, Germany, Italy, Slovenia) **42**, **45**, **53**, **54**, and **61**; *L. longirostris* (Finch et P.D. Sell) Talavera (Spain) **42**, **45**, **53**, **54**, and **61**; *L. maroccanus* (Pers.) Ball (Spain) **42**, **45**, **53**, and **54**; *L. saxatilis* (Germany) **42**, **45**, **53**, and **54**; *L. tenuiflorus* (Gaudin) Rchb. (Italy) **42**, **45**, **53**, **54**, and **61**; and *L. tuberosus* L. (Israel) **42**, **45**, **53**, and **54**.

*L. saxatilis* [synonym: *L. taraxacoides* (Vill.) Merat] (MeOH/aerial parts/Spain) yielded apigenin **17**, apigenin 7-*O*-glucoside **24**, luteolin **42**, luteolin 4'-*O*-glucoside **45**, luteolin 7-*O*-glucoside **53**, and quercetin 3-*O*-glucoside **107** (Rios et al., 1992; Giner et al. 1993).

**Microseris** [C5SC2] – Leaves of *M. heterocarpa* (Nutt.) Chamb. and *M. linearifolia* (DC.) Sch.Bip. yielded quercetin 3-*O*-glucoside **107** (Harborne, 1977).

**Mycelis** – This genus is following Kilian et al. (2009) regarded to be part of the genus *Lactuca* in this review.

**Nabalus** [C4SC3] – Fusiak and Schilling (1984) reported apigenin 7-*O*-glucoside **24**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-glucuronide **54**, luteolin 7-*O*-(6-*O*-xylosyl)-glucoside **59**, luteolin 7,4'-diglucoside **63**, and luteolin 7,3'-diglucoside **65** from *N. altissimus* Hook. [synonym: *Prenanthes altissima* L.], *N. roanensis* Chick. (synonym: *Prenanthes roanensis* (Chick.) Chick.), and *N. serpentarius* Hook. (synonym: *Prenanthes serpentaria* Pursh) (Fusiak and Schilling, 1984).

**Notoseris** [C4SC1] – Whole plants of *N. gracilipes* C.Shih yielded luteolin 7-*O*-glucoside **53** (Ye et al., 2001).

Whole plants of the Chinese endemic *N. rhombiformis* C.Shih yielded luteolin 7-*O*-glucoside **53** (Liao et al., 2002).

**Picris** [C4SC5] – Harborne (1978) reported isoetin **73** from the leaves of *P. hieracioides* L. and *P. hispanica* (Willd.) P.D.Sell. Four flavonoids chrysin 7-*O*-glucoside **15**, apigenin **17**, luteolin **42**, and luteolin 7-*O*-glucoside **53** were isolated from *P. radicata* (Forssk.) Less. (Al-Easa et al., 1994).

**Pilosella** [C5SC1] – Apigenin **17**, luteolin **42**, luteolin 7-*O*-glucoside **53**, and isorhamnetin **97** were reported from *P. officinarum* F.W. Schultz & Sch.Bip. (synonym: *Hieracium pilosella* L.) in a number of early papers (Haag-Berrurier and Duquenois, 1962, 1963; Shelyuto et al., 1977). Additionally, Harborne (1978) reported isoetin **73** from flowering heads and leaves of this taxon.

Zidorn et al. (2002) investigated phenolic acids and flavonoids in MeOH/(CH<sub>3</sub>)<sub>2</sub>CO/H<sub>2</sub>O (3:1:1, v:v:v) extracts of flowering heads of 76 taxa belonging to 66 species of *Hieracium* subgenera *Hieracium* and *Pilosella* by using HPLC/DAD and HPLC/MS. *Pilosella* was traditionally part of the genus *Hieracium*. Many authors in Central and Southern Europe, which are centers of

biodiversity in the group, still regard *Pilosella* as a subgenus of *Hieracium* (Gottschlich, 2009). Therefore, not all taxa of *Hieracium* subgenus *Pilosella* have a valid name in the genus *Pilosella*, yet. One new combination needed for this review is provided here:

*Pilosella rubriflora* (Zahn) Zidorn comb. nov.; basionym: *Hieracium rubriflorum* Zahn in Schinz & Keller, Fl. Schweiz, ed. 2, 2: 253 (1905).

The occurrence of luteolin **42**, luteolin 4'-O-glucoside **45**, luteolin 7-O-glucoside **53**, luteolin 7-O-glucuronide **54**, and isoetin 4'-O-glucuronide **74** was reported as follows (Zidorn et al., 2002): *P. arvicola* (Nägeli & Peter) Soják **42**, **45**, **53**, **54**, and **74**; *P. aurantiaca* (L.) F.W. Schultz & Sch.Bip. **42**, **45**, **53**, **54**, and **74**; *P. auriculoides* (Láng) Arv.-Touv. subsp. *trichocymum* Touton & Zahn **42**, **45**, and **53**; *P. bauhinii* (Schult.) Arv.-Touv. **42**, **45**, and **53**; *P. brachiata* (Bert. ex DC.) F.W. Schultz & Sch.Bip. **42**, **45**, **53**, **54**, and **74**; *P. caespitosa* (Dumort.) P.D. Sell & C. West subsp. *caespitosum* **42**, **45**, **53**, **54**, and **74**; *P. caespitosa* (Dumort.) P.D. Sell & C. West subsp. *colliniforme* (Peter) P.D. Sell & C. West **42**, **45**, **53**, **54**, and **74**; *P. calodon* (Tausch ex Peter) Soják subsp. *pseudofallax* Touton **42**, **45**, and **53**; *P. cymosa* (L.) F.W. Schultz & Sch.Bip. subsp. *cymosum* **42**, **45**, **53**, and **74**; *P. derubella* (Gottschl. & Schuhw.) S.Brüt. & Greuter **42**, **45**, **53**, and **74**; *P. fallacina* (F.W. Schultz) F.W. Schultz subsp. *fallacinum* **42**, **45**, **53**, **54**, and **74**; *P. fallax* (Willd.) Arv.-Touv. subsp. *durisetum* Nägeli & Peter **42**, **45**, **53**, **54**, and **74**; *P. fusca* (Vill.) Arv.-Touv. subsp. *chrysanthes* Nägeli & Peter **42**, **45**, **53**, **54**, and **74**; *P. glomerata* (Froel.) Arv.-Touv. **42**, **45**, **53**, **54**, and **74**; *P. guthnickiana* (Hegetschw.) Soják subsp. *rubricymigerum* (Nägeli & Peter) Zahn **42**, **45**, **53**, **54**, and **74**; *P. hoppeana* (Schult.) F.W. Schultz & Sch.Bip. subsp. *hoppeana* **42**, **45**, **53**, and **74**; *Pilosella hoppeana* (Schult.) F.W. Schultz & Sch.Bip. subsp. *testimonialis* (Nägeli ex Peter) Soják [synonym: *H. macranthum* Ten. subsp. *testimoniale* (Peter) Gottschl.; not *H. macranthelium* subsp. *testimoniale* as erroneously stated in the original publication; for the intricate synonymy of this taxon refer to Gottschlich (2009)] **42**, **45**, **53**, and **74**; *P. hypeuryum* (Peter) Soják **42**, **45**, **53**, **54**, and **74**; *P. kalksburgense* (Wiesb.) Soják **42**, **45**, **53**, and **74**; *P. lactucella* (Wallr.) P.D. Sell & C. West subsp. *lactucella* **42**, **45**, **53**, **54**, and **74**; *P. leptophyton* (Nägeli & Peter) S.Brüt. & Greuter **42**, **45**, **53**, and **74**; *P. leptophyton* (Nägeli & Peter) S.Brüt. & Greuter subsp. *leptophyton* **42**, **45**, **53**, **54**, and **74**; *P. leptophyton* (Nägeli & Peter) S.Brüt. & Greuter subsp. *polyanthemoides* Zahn **42**, **45**, **53**, **54**, and **74**; *P. macranthelium* (Nägeli & Peter) Soják **42**, **45**, **53**, **54**, and **74**; *P. macrostolona* (G.Schneider) Soják **42**, **45**, **53**, **54**, and **74**; *P. officinarum* F.W. Schultz & Sch.Bip. subsp. *peleteriana* (Mérat) T.Tyler **42**, **45**, **53**, and **74**; *P. piloselloides* (Vill.) Soják **42**, **45**, **53**, **54**, and **74**; *P. piloselloides* (Vill.) Soják subsp. *obscurum* (Rchb.) Zahn **42**, **45**, **53**, **54**, and **74**; *P. piloselloides* (Vill.) Soják subsp. *subcymigerum* (Nägeli & Peter) Zahn **42**, **45**, **53**, **54**, and **74**; *P. piloselloides* (Vill.) Soják subsp. *themariense* Bornm. & Zahn **42**, **45**, **53**, **54**, and **74**; *P. rothiana* (Wallr.) F.W. Schultz & Sch.Bip. subsp. *rothianum* **42**, **45**, **53**, and **74**; *P. rubriflora* (Zahn) Zidorn **42**, **45**, **53**, **54**, and **74**; *P. sciadophora* (Nägeli & Peter) Soják subsp. *tridentinum* Nägeli & Peter **42**, **45**, **53**, **54**, and **74**; and *P. sphaerocephalum* (Froel.) P.D. Sell & C. West **42**, **45**, **53**, **54**, and **74**.

Isoetin 4'-O-glucuronide **74** was identified as a useful chemosystematic marker for the characterization of (sub-) genus *Pilosella* and its delimitation from *Hieracium* s.str. (Zidorn et al., 2002).

**Pinaropappus** [C5SC2] – A methanolic extract of *P. roseus* Less. (MeOH/aerial parts/Mexico) yielded kaempferol 3-O-rutinoside **91**, rutin **112**, isorhamnetin 3-O-rutinoside **115**, rhamnocitrin 3-O-rutinoside **116**, and rhamnazin 3-O-rutinoside **117** (Harput et al., 2004).

**Prenanthes** – *P. altissima* L., *P. roanensis* (Chick.) Chick., and *P. serpentaria* Pursh, members of the former genus *Prenanthes* s.l., are now considered to be members of the genus *Nabalus* (Kilian et al., 2009).

**Pterocypsela** [C4SC1] – This genus is following Kilian et al. (2009) regarded to be part of the genus *Lactuca* in this review.

**Pyrrhopappus** [C5SC2] – Five *Pyrrhopappus* species were investigated palynologically, cytogenetically, and chemosystematically (Northington, 1974). Apigenin 7-O-glucoside **24**, luteolin **42**, and luteolin 7-O-glucoside **53** were found in leaves of all investigated taxa: *P. carolinianus* (Walt.) DC., *P. georgianus* Shinners, *P. grandiflorus* (Nutt.) Nutt., *P. multicaulis* DC. var. *geiseri* (Shinners) North., *P. multicaulis* DC. var. *multicaulis* DC., and *P. rothrockii* A.Gray; apigenin **17** was only detected in *P. carolinianus* (Walt.) DC. (Northington, 1974). Northington (1974) found also several minor flavonoid glycosides but did not establish their structure. Moreover, unidentified anthochlor pigments, chalcones and aurones were detected in ligules of the *Pyrrhopappus* species (Northington, 1974). These findings were confirmed by Harborne (1977).

Harborne (1977) investigated anthochlors from fresh flowering heads of *P. carolinianus*, *P. grandiflorus*, *P. multicaulis* var. *geiseri*, *P. multicaulis* var. *multicaulis*, and *P. rothrockii*; in all taxa coreopsin (butein 4'-glucoside) **134** was identified as the main anthochlor in the yellow *Pyrrhopappus* ligules.

**Reichardia** [C4SC2] – Leaves of *R. picroides* (L.) Roth yielded isoetin **73** (Harborne, 1978).

Recio et al. (1992) investigated phenolic compounds from *R. tingitana* (L.) Roth and *R. picroides* (MeOH/aerial parts/Spain). In both species the following seven flavonoid glycosides were detected: apigenin 7-O-glucoside **24**, apigenin 7-O-neohesperidoside **29**, apigenin 7-O-rutinoside **30**, luteolin 7-O-glucoside **53**, luteolin 7-O-rhamnoside **58**, and luteolin 7-O-rutinoside **62**. *R. picroides* additionally contained luteolin 4'-O-glucoside **45** and luteolin 7,3'-O-diglucoside **65** (Recio et al., 1992; Mañez et al., 1994).

**Rhagadiolus** [C4SC3] – *R. stellatus* (L.) Gaertn. yielded quercetin **96** (Rees and Harborne, 1984).

**Rothmaleria** [C5SC3] – *R. granatensis* (Boiss. ex DC.) Font Quer yielded quercetin **96** (Rees and Harborne, 1984).

**Scariola** – This genus is following Kilian et al. (2009) regarded to be part of the genus *Lactuca* in this review.

**Scolymus** [C3] – Aerial parts and flowering heads of *S. hispanicus* L. were investigated for the presence of phenolic compounds. A new flavonoid, quercetin 3-O-(2-O-caffeoyl)-glucuronide **110**, was isolated (Sanz et al., 1993). In addition, kaempferol **86**, kaempferol 3-O-rutinoside **91**, kaempferol 3-O-glucuronide **92**, kaempferol 3-O-glucuronide methyl ester **93**, quercetin **96**, quercetin 5-O-glucoside **101**, quercetin 3-O-galactoside **104**, quercetin 3-O-glucoside **107**, quercetin 3-O-



glucuronide **109**, quercetin 3-O-rutinoside **112**, isorhamnetin 3-O-glucoside **113**, and isorhamnetin 3-O-rutinoside **115** were reported (Rees and Harborne, 1984; Sanz et al., 1993; Rubio-García et al., 1994, 1995; Rubio-García and Diaz, 1995). The fresh aerial parts of *S. hispanicus* yielded apigenin 6,8-di-C-glucoside **41**, kaempferol 3-O-galactoside **87**, biorobin **88**, and quercetin 5-O-glucoside **101** (Romussi and Ciarallo, 1978).

*S. maculata* L. yielded kaempferol **86** (Rees and Harborne, 1984).

**Scorzonera** [C2] – Rees and Harborne (1984) investigated flavonoids from nine taxa of the genus *Scorzonera*, apigenin **17**, luteolin **42**, kaempferol **86**, and quercetin **96** were found. Quercetin **96** was the major compound in all taxa investigated. In detail, the following chemosystematic data were reported: *S. austriaca* Willd. var. *angustifolia* DC. **86** and **96**; *S. crispatula* (Boiss.) Boiss. **42** and **96**; *S. graminifolia* L. **42** and **96**; *S. hirsuta* L. **42**, **86**, and **96**; *S. hispanica* L. **96**; *S. laciniata* L. **17**, **42** and **96**; *S. mollis* M.Bieb. **42** and **96**; *S. pseudolanata* Grossb. **96**; *S. pusilla* Pall. **42** and **96** (Rees and Harborne, 1984).

*S. austriaca* Willd. (95% EtOH/whole plants/Qinghai, China) yielded luteolin 3'-O-(6-O-coumaroyl)-glucopyranoside **48** (Jiang et al., 2007).

*S. columnae* Guss. yielded apigenin **17**, luteolin **42**, quercetin **96**, and quercetin 3-O-(6-O-caffeoyl)-galactoside **105** (Menichini et al., 1994).

**Scorzoneroideis** [C4SC5] – Recent molecular investigations resulted in a split of the genus *Leontodon* s.l. into *Leontodon* s.str. and *Scorzoneroideis*. The latter is identical in its delimitation to the former *Leontodon* subgenus *Oporinia* (Greuter et al., 2006; Samuel et al., 2006). A chemosystematic study of *Scorzoneroideis* (*Leontodon* subgenus *Oporinia*) encompassed *S. autumnalis* (L.) Moench, *S. crocea* (Haenke) J.Holub, *S. duboisii* (Sennen) Greuter, *S. helvetica* (Mérat) J.Holub, *S. montaniformis* (Widder) Gutermann, *S. montana* (Lam.) J.Holub subsp. *melanotricha* (Vierh.) Gutermann, *S. montana* (Lam.) J.Holub subsp. *montana*, *S. pyrenaica* (Gouan) J.Holub, and *S. rilaensis* (Hayek) J.Holub. Flowering heads of all taxa were analyzed by HPLC/DAD and HPLC/MS (Zidorn and Stuppner, 2001). Luteolin **42**, luteolin 4'-O-glucoside **45**, luteolin 7-O-glucoside **53**, luteolin 7-O-glucuronide **54**, and luteolin 7-O-gentiobioside **61** were present in all investigated taxa. Luteolin 4'-O-glucoside **45** was detected in all taxa except in the two investigated subspecies of *S. montana* and in *S. montaniformis* (Zidorn and Stuppner, 2001; Zidorn, 2008a).

Moreover, Zidorn (1998) investigated phenolics including flavonoids in MeOH/(CH<sub>3</sub>)<sub>2</sub>CO/H<sub>2</sub>O (3/1/1, v/v/v) extracts of flowering heads of *Scorzoneroideis palisae* Izuzquiza (Spain) and detected **42**, **45**, **53**, **54**, and **61**. Whole plants (MeOH, Spain) of *S. muelleri* (Sch.Bip.) Greuter & Talavera yielded apigenin **17** and luteolin **42** (Zidorn et al., 2004 and erratum 2007).

In an earlier study Harborne (1978) reported isoetin **73** from leaves of *S. pyrenaica* (synonym: *Leontodon pyrenaicus* Gouan).

**Sonchus** [C4SC2] – Recent molecular investigations revealed that various genera of the *Sonchus* alliance established for species from the Canary Islands (*Chrysoprenanthes*, *Babcockia*, *Lactucosonchus*, *Sventenia*, *Taeckholmia*, *Wildpretia*) and for species from Australia/New Zealand (*Actites*, *Embergia*, *Kirkianella*), respectively, were nested within *Sonchus* (Hand et al., 2009; Kilian et al., 2009). The same was confirmed for the monospecific Mediterranean genus *Aetheorhiza* as well as for the genera *Dendroseris* and *Thamnoseris*, endemic to the Pacific Juan Fernandez and Desventuradas Islands, respectively (Hand et al., 2009). The Canarian, Mediterranean and Australian/New Zealand genera are morphologically only questionably distinct from *Sonchus* and their inclusion in *Sonchus* seems therefore justified (Hand et al., 2009; Kilian et al., 2009). However, *Dendroseris* and *Thamnoseris* are because of their distinct morphology currently accepted as separate genera by Hand et al. (2009) and this assessment is followed here.

Bramwell and Dakshini (1971) investigated phenolics of 20 species of *Sonchus* s.l. from the Canary Islands. *S. abbreviatus* Link, *S. acaulis* Dum.-Cours., *S. brachylobus* Webb & Berthel., *S. capillaris* Svent., *S. fauces-orci* Knoche, *S. filifolius* Svent., *S. gonzalezpadroni* Svent., *S. gummifer* Link, *S. hierrensis* (Pitard) Boulos, *S. jacquinocephalus* Svent., *S. jacquinii* DC., *S. leptocephalus* Cass., *S. microcarpus* (Boulos) U.Reifenb. & A.Reifenb., *S. ortunoii* Svent., *S. oleraceus* L., *S. pinnatus* Aiton, *S. platylepis* Webb & Berthel., *S. radicans* Aiton, *S. tectifolius* Svent., and *S. tuberifer* Svent. (all 90% EtOH/leaves/Canary Islands) were investigated. Luteolin **42** and its 7-O-glucoside **53** occurred in all species except *S. gonzalezpadroni* (Bramwell and Dakshini, 1971).

Bondarenko et al. (1973, 1975, 1976, 1978) investigated phenolic compounds from the whole plants and the flowering heads of *S. arvensis* L. Acacetin 7-O-rutinoside **32**, chrysoeriol **47**, luteolin 7-O-glucoside **53**, quercetin **96**, isorhamnetin **97**, quercetin 7-O-glucoside **99**, and isorhamnetin 3-O-glucoside **113** were isolated from the whole plants (Bondarenko et al., 1975; Bondarenko et al., 1976). Luteolin **42** and its 7-O-glucoside **53** were isolated from flowering heads. Moreover, sonchoside **77** was reported for the first time from this species (Bondarenko et al., 1973; Bondarenko et al., 1978).

*S. asper* (L.) Hill yielded apigenin 7-O-rutinoside **30**, luteolin 7-O-glucoside **53**, and luteolin 7-O-rutinoside **62** (Kaneta et al., 1978). *S. oleraceus* yielded apigenin 7-O-glucuronide **25**, luteolin **42**, and luteolin 7-O-glucoside **53** (Kaneta et al., 1978; Bondarenko et al., 1983).

Mansour et al. (1983b) studied the chemosystematic the phenolics from the whole plants of 32 species of *Sonchus* from the subgenera *Sonchus*, *Dendrosonchus*, and *Oligosonchus*. Moreover, members of the former genera *Embergia* and *Taeckholmia* were investigated.

The following chemosystematic data were reported:

Former genus *Babcockia*: *S. platylepis* yielded apigenin 7-O-glucoside **24**, luteolin 7-O-glucoside **53**, luteolin 7-O-glucuronide **54**, and luteolin 7-O-rutinoside **62** (Mansour et al., 1983b).

Former genus *Embergia*: *S. grandifolius* Kirk yielded luteolin 7-O-glucoside **53** and luteolin 7-O-glucuronide **54** (Mansour et al., 1983b).

Former genus *Taeckholmia*: *S. capillaris*, *S. canariensis* Boulos, *S. heterophylla* Boulos, *S. microcarpa*, and *S. regis-jubae* Pit. yielded apigenin **17** and luteolin 7-*O*-glucoside **53** (Mansour et al., 1983b).

Former genus *Sonchus* s.str., subgenus *Sonchus*: *S. arvensis* L. subsp. *uliginosus* (M.Bieb.) Béguinot **24**, **53**, **54**, and **62**; *S. asper* (L.) Hill subsp. *glaucescens* (Jordan) Ball **24**, **53**, and **54**; *S. bourgeauii* Sch.Bip. var. *imbricatus* (Svent.) Boulos **24**, **53**, and **54**; *S. brachyotus* DC. **24**, **53**, **54**, and **62**; *S. crassifolius* Pourr. ex Willd. **24**, **53**, and **54**; *S. hydrophilus* Boulos **24**, **53**, and **54**; *S. macrocarpus* Boulos & C.Jeffrey **24**, **53**, and **54**; *S. maritimus* L. **24**, **53**, and **54**; *S. oleraceus* L. **24**, **53**, and **54**; and *S. tenerrimus* L. **24**, **53**, and **54** (Mansour et al., 1983b).

Subgenus *Dendrosonchus*: *S. acaulis* **24**, **53**, **54**, and **62**; *S. brachylobus* var. *canariae* (Pitard) Boulos **24**, **53**, **54**, and **62**; *S. canariensis* (Sch.Bip.) Boulos subsp. *orotavensis* Boulos **53**, **54**, and **62**; *S. congestus* Willd. **24**, **53**, **54**, and **62**; *S. fauces-orci* Knoche **24**, **53**, **54**, and **62**; *S. fruticosus* L.f. **24**, **53**, **54**, and **62**; *S. gandogeri* Pitard **24**, **53**, **54**, and **62**; *S. gomeraensis* Boulos **24**, **53**, **54**, and **62**; *S. gummifer* Link **53** and **62**; *S. hierrensis* (Pitard) Boulos **24**, **53**, **54**, and **62**; *S. lidii* Boulos **24**, **53**, **54**, and **62**; *S. palmensis* (Sch.Bip.) Boulos **24**, **53**, **54**, and **62**; *S. pinnatifidus* Cav. **24**, **53**, **54**, and **62**; *S. pinnatus* Aiton **24**, **53**, **54**, and **62**; *S. pitardii* Boulos **24**, **53**, **54**, and **62**; *S. radicans* Aiton **24**, **53**, **54**, and **62**; and *S. ustulatus* Lowe **24**, **53**, **54**, and **62** (Mansour et al., 1983b).

Subgenus *Oligosonchus*: *S. bipontini* Asch. var. *glanduliferus* (R.E. Fries) Robyns **24**, **53**, **54**, and **62**; *S. luxurians* (R.E. Fries) C.Jeffrey **24**, **53**, **54**, and **62**; *S. melanolepis* Fresen **24**, **53**, **54**, and **62**; *S. nanus* Sond. ex Harv. **24**, **53**, **54**, and **62**; and *S. schweinfurthii* Oliv. & Hiern **24**, **53**, **54**, and **62** (Mansour et al., 1983b).

Luteolin 7-*O*-glucuronide **54** was identified as the major glycoside in all subgenera. Luteolin 7-*O*-rutinoside **62** was absent from members of subgenus *Sonchus* but found in subgenera *Dendrosonchus* and *Oligosonchus*. Luteolin 7-*O*-rutinoside **62** was the major constituent in members of subgenus *Dendrosonchus* (Mansour et al., 1983b).

Mañez et al. (1994) studied the chemotaxonomic significance of flavonoids, phenolic acids and coumarins from 20 species of the subtribe Crepidinae (MeOH/aerial parts/Spain) using TLC and HPLC/DAD. The investigated species encompassed five taxa of *Sonchus* and these yielded the following flavonoids: *S. asper* subsp. *asper* **17**, **24**, **42**, and **53**; *S. asper* subsp. *glaucescens* **17**, **24**, **42**, and **53**; *S. maritimus* L. subsp. *aquatilis* (Pourret) Nyman **17**, **24**, and **53**; *S. oleraceus* **42** and **53**; and *S. tenerrimus* **17**, **24**, **42**, and **53** (Mañez et al., 1994).

*S. pustulatus* Willk. yielded apigenin **17**, luteolin **42**, and quercetin **96** (Rees and Harborne, 1984).

**Sorozeris** [C4SC3] – *S. hookeriana* Stebb. subsp. *erysimoides* (Hand.-Mazz) Stebb. (petrol ether:Et<sub>2</sub>O:MeOH 1:1:1/aerial parts/China) yielded diosmetin **43** and isoluteolin **131** (Meng et al., 2000).

**Stephanomeria** [C5SC2]– Five species of annual *Stephanomeria*, *S. diegensis* Gottlieb, *S. exigua* Nutt. subsp. *coronaria* (Greene) Gottlieb, *S. exigua* Nutt. subsp. *exigua*, *S. exigua* Nutt. subsp. *deanei* (J.F. Macbr.) Gottlieb, *S. exigua* Nutt. subsp. *macrocarpa* Gottlieb, *S. paniculata* Nutt., *S. malheurensis* Gottlieb, and *S. virgata* Benth. were investigated for flavonoids using TLC. Eriodicytol 7-*O*-glucoside **8**, eriodicytol 7-*O*-glucuronide **9**, apigenin **17**, apigenin 7-*O*-glucoside **24**, apigenin 7-*O*-glucuronide **25**, luteolin **42**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-glucuronide **54**, kaempferol 7-*O*-glucoside **89**, and quercetin 3-*O*-glucoside **107** were found in all taxa. There was some variation in the occurrence of quercetin 3-*O*-rutinoside **112** which was detected only in *S. diegensis*, *S. exigua* subsp. *macrocarpa*, *S. paniculata*, and *S. virgata* (Bohm and Gottlieb, 1989).

**Taeckholmia** – This genus is following Kilian et al. (2009) regarded to be part of the genus *Sonchus* in this review.

**Taraxacum** [C4SC3] – *T. formosanum* Kitam. (hot MeOH/fresh aerial parts/Taiwan) yielded 4'-*O*-methyluteolin **43** and luteolin 7-*O*-glucoside **53** (Leu et al., 2003).

*T. hallaisanense* Nakai yielded luteolin 7-*O*-glucoside **53** and luteolin 7-*O*-rutinoside **62** (Whang et al., 1994).

*T. mongolicum* Hand.-Mazz. & Dahlst. yielded the flavonols hyperin **104** and isoquercitrin **107** (Ling et al., 1999). Recently, Shi et al. (2008) reported hesperitin **10**, hesperidin **11**, genkwanin **21**, genkwanin 4'-*O*-rutinoside **31**, luteolin **42**, luteolin 7-*O*-galactoside **51**, luteolin 7-*O*-glucoside **53**, isoetin **73**, isoetin derivatives **78**, **79**, and **81**, quercetin **96**, quercetin 7,3',4'-trimethyl ether **98**, quercetin 7-*O*-gentiobioside **100**, quercetin 3,7-*O*-diglucoside **118**, and artemitin **120** from *T. mongolicum* (EtOH/whole plants/China).

*T. officinale* F.H. Wigg. yielded apigenin **17**, luteolin 7-*O*-glucoside **53** (Hörhammer and Wagner, 1962), luteolin 4'-*O*-glucoside **45**, luteolin 7-*O*-glucoside **53**, luteolin 7-*O*-rutinoside **62**, quercetin **96**, quercetin 7-*O*-glucoside **107**, isorhamnetin 3-*O*-glucoside **113**, and quercetin 3,7-*O*-diglucoside **118** (Wolbis et al., 1993). Flavonoid glycosides, luteolin 7-*O*-glucoside **53** and two different luteolin 7-*O*-diglucosides (the authors did not establish the glycosidic linkages), were isolated from flowering heads and leaves of *T. officinale*; flowering heads additionally yielded luteolin **42** and chrysoeriol **47** (Williams et al., 1996).

*T. platycarpum* Dahlst. yielded apigenin **17** and luteolin 7-*O*-glucoside **53** (Kaneta et al., 1978).

The ethanolic extract of whole plants of *T. sinicum* Kitag. yielded apigenin **17**, apigenin 7-*O*-glucuronide **25**, luteolin **42**, diosmetin **43**, and luteolin 7-*O*-glucoside **53** (Ling et al., 1998a, b).

**Tragopogon** [C2] – Whole plants of various *Tragopogon* species, which occur as introduced species in the US, and from two amphidiploid *Tragopogon* species, which spontaneously originated in the US from European ancestors, were studied using paper chromatography. Luteolin and quercetin glycosides, and their C-glycosylflavones were detected. *T. porrifolius* L. yielded apigenin C-glycosides **34**, **35**, **38**, and **41**, luteolin **42** and its C-glycosides **66**, **67**, and **69** as well as quercetin 3-*O*-glucoside **107**. *T. pratensis* L. yielded apigenin **17**, its C-glycosides **35**, **37**, and **41**, luteolin **42**, luteolin 7-*O*-glucoside **53**, luteolin C-glycosides **66**, **67**, **68**, and **72**, and quercetin 3-*O*-glucoside **107**. *T. dubius* Scop. yielded apigenin C-glycosides **35**, **36**, **37**, **38**, and **41**, luteolin **42**, luteolin 7-*O*-glucoside **53**, luteolin C-glycosides **66**, **67**, **68**, and **69**, and quercetin 3-*O*-glucoside **107**. A new C-glycosylflavone, *O*-xylosylisovitexin **36**, was only detected in *T. dubius*. The flavonoids present in the amphidiploid species

corresponded to the combined flavonoid constituents of the two respective parent diploids species. *T. mirus* Ownbey, which originated from hybrids between *T. dubius* and *T. porrifolius*, yielded **34, 35, 37, 38, 41, 42, 53, 66, 67, 68, 69**, and **107**.

*T. miscellus* Ownbey, which resulted from hybridization between *T. dubius* and *T. pratensis*, yielded apigenin C-glycosides **35, 37, 38**, and **41**, luteolin **42**, luteolin 7-O-glucoside **53**, luteolin C-glycosides **66, 67, 68, 69**, and **72**, and quercetin 3-O-glucoside **107**. Interestingly compound **36**, which was found only in the diploid species *T. dubius*, was not detectable in any of the amphidiploid species (Kroschewsky et al., 1969).

A methanolic extract of *T. orientalis* L. yielded apigenin **17**, vitexin **34**, luteolin **42**, orientin **66**, isoorientin **67**, and quercetin **96** (Smolarz and Krzaczek, 1988).

*Urospermum* [C4SC5] –; *U. dalechampii* (L.) F.W. Schmidt (MeOH/aerial parts/Spain) yielded luteolin 4'-O-glucoside **45**, luteolin 7-O-glucoside **53**, quercetin 3-O-arabinoside **103**, quercetin 3-O-galactoside **104**, and quercetin 3-O-glucoside **107** (Rios et al., 1992; Giner et al., 1993) as well as naringenin **5**, aromadendrin **12**, and 3-O-methyltaxifolin **13** (Marco et al., 1994).

*U. picroides* (L.) Scop. ex F.W. Schmidt (hot EtOH/aerial parts/Egypt) yielded quercetin **96** and quercetin 3-O-galactoside **104** (Metwally et al., 1973). Giner et al. (1992a) reported luteolin **42**, luteolin 4'-O-glucoside **45**, luteolin 7-O-glucoside **53**, kaempferol 3-O-galactoside **87**, quercetin **96**, quercetin 3-O-galactoside **104**, and quercetin 3-O-glucoside **107** from the same species (MeOH/aerial parts/Spain) (Giner et al., 1992a).

*Youngia* [C4SC3] – *Y. denticulata* (Houtt.) DC. yielded luteolin 7-O-glucoside **53** (Kaneta et al., 1978). *Youngia japonica* (L.) DC. (95% EtOH/whole plants/China) yielded apigenin **17** (Xie et al., 2006) and luteolin 7-O-glucoside **53** (Ooi et al., 2006).

### 3. Chemosystematic analysis of the literature data on sesquiterpenoids

As discussed elsewhere (Zidorn, 2006, 2008a, 2008b), one of the main problems in interpreting phytochemical data is that there is a bias towards the publication of new compounds; in contrast, new sources of known compounds are often not reported at all. However, in the case of flavonoids this problem seems to be less pronounced than in other classes of natural products like, e.g. sesquiterpene lactones (Zidorn, 2008b). Currently, there are a total of 1613 chemosystematic reports (compound/taxon) for 135 different compounds found in 354 different source taxa representing 299 species. However, not only most species but also about sixty percent of the genera of the Cichorieae have not been investigated for their flavonoid profile yet. Fig. 24 displays the major clades of the Cichorieae, which have arisen from recent molecular investigations (Kilian et al., 2009). In Table 1 the chemosystematic flavonoid data outlined in detail above are summarized for these clades, which are treated as subtribes by Kilian et al. (2009). Table 2 is based on these data and contains percentages of the respective natural product classes and sub-classes in the various sub-tribes of the Cichorieae.

In addition to the insufficient or lacking coverage for many genera the data have to be interpreted with care because techniques of differing reliability (e.g. TLC versus NMR) were used in compound identification and flavonoids from different organs were investigated (whole plants versus leaves versus flowering heads) in the different compiled publications. All the above factors make systematic data interpretation problematic.

Keeping this in mind the following trends can be described:

**Table 1**

Summary of classes of flavonoids reported for the various clades and subclades of the Cichorieae sensu Kilian et al. (2009). The total number of chemosystematic reports (compound per taxon reports) is 1613. I Flavanones, II flavanonols, III flavones, IV flavonols, V anthocyanidins, VI isoflavonoids, VII chalcones, VIII auronones. Subclasses 1–22 are congruent with structures displayed in Figs. 1–22 and explained in the legend.

Classes	I		II		III								IV				V		VI		VII		VIII		Σ
	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22			
Clades/Subtribes	<i>n</i>	11	2	1	1	1	17	8	24	7	9	2	2	9	1	24	1	2	7	1	1	3	1	135	
Warioniinae	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Scorzonerinae	18	0	0	0	0	0	4	22	18	22	0	0	0	2	0	18	0	0	0	0	0	0	0	86	
Scolyminae	3	0	0	0	0	0	1	3	3	2	0	0	0	7	0	9	0	0	2	0	0	0	0	27	
Lactucinae	42	0	0	0	0	1	18	0	41	0	1	0	0	14	0	71	0	4	0	0	0	0	0	150	
Hyoseriinae	78	0	0	1	0	0	86	1	205	0	2	2	0	0	0	6	0	0	1	0	0	0	0	304	
Crepidinae	41	6	0	0	0	0	15	0	112	0	6	0	2	1	0	16	1	0	0	1	1	2	0	163	
Chondrillinae	2	0	0	0	0	0	1	0	4	0	0	0	0	0	0	1	0	0	0	0	0	0	0	6	
Hypochoeridinae	43	1	2	0	1	0	6	0	132	0	38	0	0	1	1	9	0	0	0	0	0	0	0	192	
Hieraciinae	95	4	0	0	0	0	119	0	337	0	41	0	0	0	0	3	0	0	0	0	0	0	0	504	
Microseridinae	20	16	0	0	0	0	31	0	36	0	0	0	0	9	0	21	0	0	0	0	0	5	0	118	
Cichoriinae	12	0	0	0	0	0	2	0	11	0	0	0	1	19	0	20	0	4	6	0	0	0	0	63	
Σ	354	27	2	1	1	1	283	26	899	24	88	2	3	53	1	174	1	8	9	1	1	7	1	1613	

*n*: Number of taxa investigated for flavonoids/number of flavonoids per flavonoid class reported for the Cichorieae. Σ: Sum of chemosystematic reports (compound per taxon) for this clade/compound class. Flavonoid subclasses (SC): SC1 flavanones, SC2 flavanonols, SC3 7,3',4'-trihydroxyflavones, SC4 5,7-dihydroxyflavones, SC5 5,7,2'-trihydroxyflavones, SC6 apigenin derivatives, SC7 apigenin C-glycosides, SC8 luteolin derivatives, SC9 luteolin C-glycosides, SC10 isoenflavon derivatives, SC11 asplenitin derivatives, SC12 isoscutellarein and scutellarein, SC13 kaempferol derivatives, SC14 6-hydroxykaempferol, SC15 quercetin derivatives, SC16 artemitin, SC17 cyanidin derivatives, SC18 delphinidin derivatives, SC19 isoflavans, SC20 isoflavones, SC21 chalcones, SC22 auronones.

**Table 2**

Summary of relative contributions (in %) of the various classes of flavonoids to the total of chemosystematic reports of each clade and subclade sensu Kilian et al. (2009), respectively. I Flavanones, II flavanonols, III flavones, IV flavonols, V anthocyanidins, VI isoflavonoids, VII chalcones, VIII aurones. Subclasses 1–22 are congruent with structures displayed in Figs. 1–22 and explained in the legend.

Classes	I			II			III						IV				V		VI		VII		VIII	
	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22		
Clades/Subtribes	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–		
Warioniinae	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–		
Scorzonerinae	0.0	0.0	0.0	0.0	0.0	4.7	25.6	20.9	25.6	0.0	0.0	0.0	2.3	0.0	20.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Scolyminae	0.0	0.0	0.0	0.0	0.0	3.7	11.1	11.1	7.4	0.0	0.0	0.0	25.9	0.0	33.3	0.0	0.0	7.4	0.0	0.0	0.0	0.0		
Lactucinae	0.0	0.0	0.0	0.0	0.7	12.0	0.0	27.3	0.0	0.7	0.0	0.0	9.3	0.0	47.3	0.0	2.7	0.0	0.0	0.0	0.0	0.0		
Hyoseriinae	0.0	0.0	0.3	0.0	0.0	28.3	0.3	67.4	0.0	0.7	0.7	0.0	0.0	0.0	2.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0		
Crepidinae	3.7	0.0	0.0	0.0	0.0	9.2	0.0	68.7	0.0	3.7	0.0	1.2	0.6	0.0	9.8	0.6	0.0	0.0	0.6	0.6	1.2	0.0		
Chondrillinae	0.0	0.0	0.0	0.0	0.0	16.7	0.0	66.7	0.0	0.0	0.0	0.0	0.0	0.0	16.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Hypochaeridinae	0.5	1.0	0.0	0.5	0.0	3.1	0.0	68.8	0.0	19.8	0.0	0.0	0.5	0.5	4.7	0.0	0.0	0.0	0.0	0.0	0.0	0.5		
Hieraciinae	0.8	0.0	0.0	0.0	0.0	23.6	0.0	66.9	0.0	8.1	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Microseridinae	13.6	0.0	0.0	0.0	0.0	26.3	0.0	30.5	0.0	0.0	0.0	0.0	7.6	0.0	17.8	0.0	0.0	0.0	0.0	0.0	4.2	0.0		
Cichoriinae	0.0	0.0	0.0	0.0	0.0	3.2	0.0	17.5	0.0	0.0	0.0	1.6	30.2	0.0	31.7	0.0	6.3	9.5	0.0	0.0	0.0	0.0		

Flavonoid subclasses (SC): SC1 flavanones, SC2 flavanonols, SC3 7,3',4'-trihydroxyflavones, SC4 5,7-dihydroxyflavones, SC5 5,7,2'-trihydroxyflavones, SC6 apigenin derivatives, SC7 apigenin C-glycosides, SC8 luteolin derivatives, SC9 luteolin C-glycosides, SC10 isoetin derivatives, SC11 asplenin derivatives, SC12 isoscutellarein and scutellarein, SC13 kaempferol derivatives, SC14 6-hydroxykaempferol, SC15 quercetin derivatives, SC16 artemitin, SC17 cyanidin derivatives, SC18 delphinidin derivatives, SC19 isoflavans, SC20 isoflavones, SC21 chalcones, SC22 aurones.

The most common compounds in the Cichorieae are luteolin 7-O-glucoside **53** (261 taxa), luteolin **42** (229 taxa), luteolin 7-O-glucuronide **54** (146 taxa), luteolin 4'-O-glucoside **45** (111 taxa), apigenin 7-O-glucoside **24** (86 taxa), apigenin 4'-O-glucuronide **20** (80 taxa), and apigenin **17** (74 taxa).

Flavones with 1328 chemosystematic reports (compound/taxon) account for the vast majority of the total of 1613 chemosystematic flavonoid reports in the Cichorieae published so far. Flavonols rank second with 229 chemosystematic reports. The flavone group is dominated by luteolin derivatives (899 compound/taxon reports), apigenin derivatives (283 compound/taxon reports), and isoetin derivatives (88 compound/taxon reports). Flavonol reports are dominated by quercetin (174 compound/taxon reports) and kaempferol (53 compound/taxon reports) derivatives.

When comparing the results obtained for flavonoid data with those of sesquiterpene lactone data published earlier (Zidorn, 2008b) the following points are interesting to note: 1. Compound diversity in sesquiterpene lactones is much higher than in flavonoids (360 versus 135 detected compounds). The total number of investigated taxa is higher for flavonoids (354 taxa) than for sesquiterpene lactones (139 taxa). The average number of compounds reported for each analyzed taxon is slightly higher for sesquiterpene lactones (6.0 compounds pro taxon) than for flavonoids (4.6 compounds pro taxon). Not surprisingly, the average number of source species is much higher for flavonoids (11.9) than for sesquiterpene lactones (2.3). The latter figures are an indication not only of the huge variety of sesquiterpene lactones in the Cichorieae, indeed nearly every thorough investigation results in the description of new sesquiterpene lactones, but also a result of the relative ease with which flavonoids are detectable and identifiable as compared to sesquiterpene lactones.

So far no flavonoids have been reported from the Warioniinae. Based on the sum of chemosystematic reports (compound/taxon) the other subtribes (sensu Kilian et al., 2009) are characterized by the following trends: In the Scorzonerae, C-glycosides of both apigenin and luteolin play a dominant role, whereas luteolin and its O-glycosides are less important than in most other subtribes of the Cichorieae. Quercetin derivatives are the fourth dominant group of flavonoids in this subtribe. The flavonoid profile of the Scolyminae is characterized by the dominance of flavonols and quercetin and kaempferol and their O-glycosides in particular. Lactucinae contain predominantly quercetin O-glycosides but also a significant proportion of luteolin-O-glycosides. Hyoseriinae and Crepidinae are dominated by luteolin O-glycosides but also contain significant shares of apigenin O-glycosides. Crepidinae additionally contain a significant share of quercetin derivatives. Chondrillinae are also dominated by luteolin O-glycosides and contain in addition apigenin O-glycosides and quercetin O-glycosides. Hypochaeridinae are dominated by luteolin O-glycosides but also encompass above average numbers of reports for isoetin derivatives. Hieraciinae are also dominated by luteolin O-glycosides with apigenin O-glycosides and isoetin derivatives being the next most important groups of flavonoids. Microseridinae contain apigenin O-glycosides and luteolin O-glycosides in nearly equal shares and also have a significant percentage of reports for quercetin derivatives and flavanones. Cichoriinae are characterized by quercetin O-glycosides, kaempferol O-glycosides, and luteolin O-glycosides (in decreasing order) as their dominant flavonoid classes.

The authors sincerely hope that the compilation of data provided in the present review will be helpful in the selection of taxa for future investigations. Moreover, the data presented here might provide first indications, which compounds to expect in members of the Cichorieae not investigated, yet.

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