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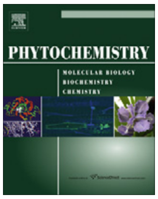

Review

Sesquiterpene lactones and their precursors as chemosystematic markers in the tribe Cichorieae of the Asteraceae

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ABSTRACT

This review summarizes all reports on sesquiterpene lactones and their immediate precursors from the Cichorieae (Lactuceae) tribe of the Asteraceae. A total of 360 compounds have been reported from this tribe. The reported substances belong to three classes of sesquiterpenoids: guaianolides (243 compounds), eudesmanolides (73 compounds), and germacranolides (44 compounds). Sources of these compounds encompass 139 taxa from 31 different genera. The distribution of these lactones within the tribe Cichorieae is discussed in a chemosystematic context. Moreover, some general ideas about the interpretation of chemosystematic data are discussed.

Contents

1. Introduction

The Cichorieae (synonym: Lactuceae) encompass approximately 100 genera and 1500 species (Bremer, 1994). Systematics of the tribe Cichorieae are still in a state of flux (Greuter, 2003; Samuel et al., 2006). Therefore, the system of Bremer, which is currently the most widely accepted, is generally followed here. Deviations from Bremer's monograph are summarized in Table 1 and are additionally mentioned in the accounts of the respective genera. The Cichorieae encompass a number of genera which are used as vegetables or for salads (e.g. *Cicerbita*, *Cichorium*, *Lactuca*, *Scorzonera*, *Taraxacum*, and *Tragopogon*) as well as a number of genera used in folk medicine (e.g. *Crepidiastrum*, *Ixeris*, *Lactuca*, *Pilosella*, *Taraxacum*, and *Youngia*). Knowledge about secondary metabolites from these commercially interesting genera is generally quite good. However, most of the other genera of the Cichorieae have not been studied phytochemically at all.

In contrast to other tribes of the Asteraceae (Zdero and Bohlmann, 1990), which contain numerous different types of basic carbon skeletons, the Cichorieae so far have yielded only eudesmanes, germacranes, and guaianes. A common feature of sesquiterpenoids from the Cichorieae tribe is the presence of sugar or carboxylic acid residues in the molecules.

Many sesquiterpenoids have pronounced bitter sensory qualities and are therefore believed to contribute to the plants' defence against herbivores (Rees and Harborne, 1985). In Cichorieae used as foods, the sesquiterpene lactones are the main ingredients

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Table 1
Deviations from Bremer's (1984) system and generic nomenclature of the Cichorieae

Genus according to Bremer	Generic concept used in this review	Reference
Calycocorsus	*Willemetia*	Kirschnerová and Kirschner (1996)
Leontodon s.l. (incl. *Scorzoneroides*)	two separate genera *Leontodon* and *Scorzoneroides* (=former subgenus Oporinia of the genus *Leontodon* s.l.)	Samuel et al. (2006)
Mulgedium	*Lactuca* s.l.	Greuter (2003) and Kilian et al. (2008)
Prenanthes s.l.	Members of *Prenanthes* s.l. were re-assigned to a number of genera, including *Prenanthes* s.str., which just contains *P. purpurea* L. *P. acerifolia* Maxim. is now member of the genus *Nabalus*	Kilian et al. (2008)
Pterocypsela	*Lactuca* s.l.	Kilian et al. (2008)

responsible for the characteristic bitter taste, e.g. in radicchio (*Cichorium intybus*) and lettuce (*Lactuca sativa*) (Sessa et al., 2000). As sesquiterpenoids exhibit a wide range of bioactivities which include toxicity for certain cancer cell lines and induction of detoxifying enzymes, the sesquiterpene content of salads and vegetables from the Cichorieae might contribute to the health promoting properties of these groceries (Zidorn et al., 1999c; Im et al., 2007).

2. Summary of literature data

The literature data on sesquiterpenoids from the Cichorieae tribe were retrieved with the help of the SciFinder database. Entries until the end of 2007 were considered. A total of 360 sesquiterpene lactones and related compounds from 139 taxa belonging to 31 different genera of the Cichorieae have been reported. Excluded from the reports considered here are reports solely based on compounds found in tissue culture or as artificially induced phytoalexins. Scheme 1 permits a fast and simple classification of the known sesquiterpenoids into 30 subgroups. Using this scheme assignments are made based on the basic carbon skeletons (eudesmane, germacrane, and guaiane) and further features such as double bonds within the ring system, symmetry of these double bonds, presence and absence and, if applicable, the position of the lactone ring. In Figs. 1–30 the chemical structures of the compounds belonging to the 30 subgroups of sesquiterpenoids are displayed. A list of trivial names of these compounds is available as Supplementary material (Table S1).

Guaianolides are the most diverse class of sesquiterpenoids within the Cichorieae. The guaianolides represent not only most of the compounds reported up to now but also contribute 13 of the 30 major compound classes as shown by the classification key (Scheme 1). Fig. 31 shows the structures of the substituents abbreviated in Figs. 1–30.

The three compound classes encompassing the largest number of compounds are also guaianolides: costus lactone type guaianolides with 92, lactucin type guaianolides with 75, and hieracin type guaianolides with 29 representatives.

As mentioned in Section 1, literature coverage of the various genera of the Cichorieae is quite different and presently there are no reports of sesquiterpene lactones from the following 65 genera of the Cichorieae (the numbers in brackets indicate the number of species assigned to these genera according to Bremer, 1994):

Acanthocephalus (2 species), *Actites* (1 species), *Aetheorrhiza* [1 species, recently transferred to the genus *Sonchus* (Greuter, 2003)], *Agoseris* (17 species), *Anisocoma* (1 species), *Aposeris* (1 species), *Arnoseris* (1 species), *Atrichoseris* (1 species), *Babcockia* (1 species), *Calycoseris* (2 species), *Catananche* (5 species), *Cephalorrhynchus* (15 species), *Chaetadelpha* (1 species), *Chaetoseris* (18 species), *Chorisis* (1 species), *Dianthoseris* (1 species), *Dubyaea* (10 species), *Embergeria* (1 species), *Epilasia* (3 species), *Garhadiolus* (4 species), *Geropogon* (1 species), *Glyptopleura* (2 species), *Heteracia* (2 species), *Heteroderis* (1 species), *Hispidiella* (1 species), *Hololeion* (3 species), *Hymenonema* (2 species), *Hyoseris* (5 species), *Ixeridium* (ca. 15 species), *Kirkianella* (1 species), *Koelpinia* (5 species), *Krigia* (7 species), *Lactucella* (1 species), *Lactucosonchus* (1 species), *Lagedium* (1 species), *Lygodesmia* (1 species), *Malacothrix* (16 species), *Microseris* (15 species), *Munzothamnus* (1 species), *Nothocalais* (4 species), *Paraprenanthes* (11 species), *Phalacroseris* (1 species), *Picrosia* (2 species), *Pilosella* (depending on the species concept this genus encompasses around 20 or more than 200 species), *Pinaropappus* (10 species), *Prenanthella* (1 species), *Pterachaenia* (1 species), *Pyrrhopappus* (3 species), *Rafinesquia* (3 species), *Rhagadiolus* (2 species), *Rothmaleria* (1 species), *Scariola* (10 species), *Scolymus* (3 species), *Shinnersoseris* (1 species), *Spiroseris* (1 species), *Stebbinsoseris* (2 species), *Stephanomeria* (17 species), *Steptorrhampus* (7 species), *Sventenia* (1 species), *Syncalathium* (4 species), *Thamnoseris* (1 species), *Tolpis* (20 species), *Tourneuxia* (1 species), *Tragopogon* (110 species), and *Uropappus* (1 species).

Two genera, *Gundelia* and *Warionia*, which until now have never been included in the Cichorieae tribe, have very recently been transferred to the Cichorieae by Kilian et al. (2008) based on molecular data. The genus *Gundelia*, which encompasses two species and was placed into the Arctoteae tribe by Bremer (1994), has so far yielded no sesquiterpene lactones. The monotypic genus *Warionia* was included in the Cichorioideae subfamily of Asteraceae by Bremer but was not assigned to any of its tribes. This genus yielded sesquiterpene lactones and is therefore included in this review. In the following paragraphs the sesquiterpene lactones reported so far for each genus are summarized. As the classification of genera into subtribal groups is currently under revision (Kilian et al., 2008), genera are treated in alphabetic rather than in systematic order. Immediately after the name of the species the following details – if available – are summarized in abbreviated form and printed in square brackets: (1) country of origin of the plant material (if plants were cultivated, this is stated and the country of origin of the seeds is additionally indicated if this information is available); (2) plant parts used for the phytochemical investigation; and (3) the solvent(s) used for the extraction of the plant material. Whether the study was just aimed at major compounds or was comprehensive is indirectly deducible from the number of sesquiterpenoids reported. The employed methodology of the studies is usually correlated with the publication year of the studies. In the exceptional cases where the employed methodology seems to be problematic, e.g. because the temperatures acting upon the investigated extracts were too high, this fact is also stated. In cases where later more appropriately performed studies confirmed all the initial findings from methodologically problematic studies, these hints are omitted. Problematic techniques like extraction with hot organic solvents or (worse) hot water, which might induce artifact formation, are not always discussed as being problematic in detail but are marked by an exclamation mark in brackets (!).

Andryala (20 species) – *Andryala integrifolia* L. [Spain/whole plants/hot (!) EtOH] yielded costus lactone type guaianolides

1(!)	Ring system eudesmane	2
1*	Ring system germacrane	8
1**	Ring system guaiane	...13
2	13-Nor-derivatives	Group 1
2*	C_{15} Eudesmane-derivatives	3
3	Lactones	4
3*	Non-lactonized compounds	7
4	12,6-Lactones	5
4*	12,8-Lactones	Group 6
5	No double bond in the ring system	Group 2
5*	One double bond in the ring system	6
6(!)	Double bond in position 1(2)	Group 3
6*	Double bond in position 3	Group 4
6**	Double bond in position 4	Group 5
7(!)	No double bond	Group 7
7*	One double bond in position 1	Group 8
7**	One double bond in position 3	Group 9
7***	Two double bonds	Group 10
8	One intracyclic double bond in position 4	Group 11
8*	Two intracyclic double bonds	9
9	Double bonds in positions 1(10) and 4	...10
9*	Double bonds in positions 4 and 9	Group 17
10(!)	Costunolides [germacra-1(10)-*trans*-4-*trans*-dienolides]	...11
10*	Melampolides [germacra-1(10)-*cis*-4-*trans*-dienolides]	...12
10**	Germacra-1(10)-cis-4-cis-dienolides	Group 16
11	12,6-Lactones	Group 12
11*	12,8-Lactones	Group 13
12	No additional ring	Group 14
12*	Additional ring from C 14 to an O in position 8	Group 15
13	Lactones	...14
13*	Non-lactonized compounds	Group 30
14(!)	12,5-Lactones	Group 18
14*	12,6-Lactones	...15
14**	12,8-Lactones	Group 29
15	Epoxy-derivatives	Group 28
15*	Other compounds	...16
16(!)	No double bond in each ring system	Group 19
16*	One double bond in each ring system	...17
16**	Two double bonds in each ring system	...18
16***	Three double bonds in each ring system	Group 27
17(!)	Double bond in position 1(10)	Group 20
17*	Double bond in position 1(2)	Group 21
17**	Double bond in position 3	Group 22
17***	Double bond in position 4	Group 23
17****	Double bond in position 8	Group 24
18	Monomers	Group 25
18*	Dimers linked via an oxygen in position 8/8'	Group 26

Scheme 1. Key for the classification of compounds **1**–**360** into major groups.

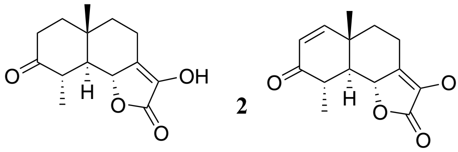
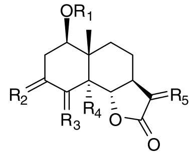


Fig. 1. *Group 1*: 13-*Nor*-12,6-eudesmanolides.



Nr.	R_1	R_2	R_3	R_4	R_5	Common name
3	H	H, H	CH_2	H	CH_2	reynosin
4	Glc	H, H	CH_2	H	CH_2	sonchuside D
5	H	H, H	CH_2	OH	CH_2	tanacetin
6	HPL	H, H	CHOGlc*	H	CH_2	ixerisoside M
7	H	H, H	α CH_3 ,β H	H	CH_2	
8	H	H, H	α CH_3 ,β H	H	α CH_3, β H	
9	H	H, H	α CH_2OH, β H	H	CH_2	15-hydroxy-4β,15-dihydroreynosin
10	Glc	H, H	α CH_2OH, β H	H	CH_2	sonchuside F
11	HPL	H, H	α CH_2OGlc, β H	H	CH_2	ixerisoside G
12	HPLHMB	H, H	α CH_2OGlc, β H	H	CH_2	ixerisoside H
13	H	H, H	α CH_2OH, β H	H	α CH_3, β H	15-hydroxytetrahydroreynosin
14	H	H, H	α CH_2OGlc, β H	H	α CH_3, β H	sonchuside I
15	Glc	H, H	α CH_2OH, β H	H	α CH_3, β H	sonchuside H
16	Ac	H, H	α CH_2O-Ac, β H	H	α CH_3, β H	
17	H	H, H	α CHO, β H	H	CH_2	sonchucarpolide
18	Glc	H, H	α CHO, β H	H	CH_2	sonchuside E
19	H	H, H	α CHO, β H	H	α CH_3, β H	11β,13-dihydrosonchucarpolide
20	Glc	H, H	α CHO, β H	H	α CH_3, β H	sonchuside G
21	H	H, H	α CH_3 ,β OH	H	α CH_3, β H	dendroserin
22	H	H, H	α CH_2OGlc, β OH	H	CH_2	ixerisoside I
23	H	α OH, β H	CH_2	H	α CH_3, β H	1-epierivanin
24	Glc	α H, β OH	α H, β CH_3	H	CH_2	
25	H	α H, β OH	α H, β CH_3	H	α CH_3, β H	4α,15,11β,13-tetrahydroridentin B
26	Glc	α H, β OH	α H, β CH_3	H	α CH_3, β H	
27	H	O	α CH_3, β H	H	α CH_3, β H	taraxacolide-*O*-β-D-glucopyranoside

* Double bond from C-4 to C-15!

Fig. 2. *Group 2*: 12,6-Eudesmanolides, reynosin type.

172, 174, 189, 190, **201**, **211**, and **220** (Massanet et al., 1984, 1993). Without any reference to the work by Massanet et al. (1993), compounds**172, 174, 189, 190**, and **201** were also reported by Marco et al. in 1994 [Spain/aerial parts/MeOH]. Moreover, these authors isolated **193** from a methanolic extract, to which at one stage of the isolation process high temperatures were applied ("resuspended in hot MeOH").

A. pinnatifida Ait. [Canary Islands/roots/Et_2O:petrol 1:2] yielded 8β-hydroxydehydrozaluzanin C **211** (Bohlmann and Gupta, 1982).

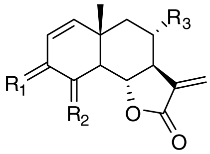
A. ragusina L. [Spain/aerial parts/MeOH] yielded integrifolin-3β-D-glucopyranoside **174** (Marco et al., 1994). At one stage of the isolation process high temperatures were applied ("resuspended in hot MeOH").

Calycocorsus – see *Willemetia* (Greuter, 2003).

Chondrilla (25 species) – *Chondrilla juncea* L. [Italy/subaerial parts/MeOH] yielded ixerin F **159** (Zidorn et al., 2006).

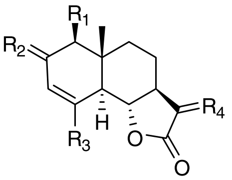
Cicerbita (35 species) – *C. alpina* Wallr. [Italy/roots and leaves/EtOH] yielded lactucin derivatives **309** and **316** (Appendino et al., 1991), [Montenegro/roots/EtOH] lactucin derivatives **301, 302, 309, 316**, and **317** (Djordjević et al., 2004), and [Austria/subaerial parts/MeOH] a germacranolide **83** and a lactucin derivative **309** (Zidorn et al., 2005a), respectively.

Cichorium (6 species) – Sesquiterpenoids reported from *Cichorium intybus* L. (chicory) prior to 2000 have been revised and summarized by Kisiel and Zielińska (2001a). These authors verified the



Nr.	R_1	R_2	R_3	Common name
28	α OGlc, β H	CH_2	H	ixerin W
29	α H, β OGlc	CH_2	H	
30	α H, β OGlc	α CH_3, β H	H	
31	O	CH_2	H	
32	O	α CH_3, β H	H	tuberiferine
33	O	CH_2	O-Ac	

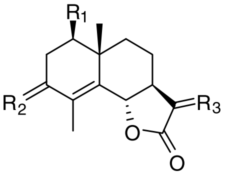
Fig. 3. *Group 3*: 12,6-Eudesmanolides, tuberiferine type [one intracyclic double bond, 1(2)].



Nr.	R_1	R_2	R_3	R_4	Common name
34	OH	H, H	CH_3	CH_2	santamarin
35	OH	H, H	CH_3	α CH_3, β H	dihydrosantamarin
36	OGlc	H, H	CH_3	α CH_3, β H	
37	OH	H, H	CH_2OH	CH_2	
38	OH	H, H	CH_2OGlc	CH_2	ixerisoside E
39	OH	H, H	CH_2O-PPA	CH_2	
40	OGlc	H, H	CH_2O-PPA	CH_2	
41	OGlc	H, H	CH_2O-PMP	CH_2	
42	O-PPA	H, H	CH_2OGlc	CH_2	lactuside D
43	OGlc-6′-*O*-PPA	H, H	CH_2O-PPA	CH_2	
44	OH	H, H	CH_2OH	α CH_3, β H	
45	OGlc	α H, β OH	CH_3	CH_2	
46	OH	O	CH_3	α CH_3, β H	

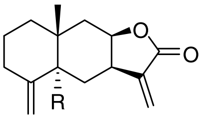
Fig. 4. *Group 4*: 12,6-Eudesmanolides, santamarin type (one intracyclic double bond in position 3).

presence [Poland, cultivated plants/leaves and roots/EtOH] of four eudesmane derivatives magnolialide **48**, its β-D-glucoside **49**, artesin **50**, and its β-D-glucoside **51**, one germacranolide **83**, and 11 guaiane derivatives, one of those of the costus lactone type **134**, eight of the lactucin type **291**, **297**, **298**, **301**, **305**, **316**, **319**, and **321**, one picridin type guaianolide **224**, and the methyl ester of the ring opened form of lactucopicrin **358**. Moreover, a guaianolide, whose production was induced by fungal infection [unavailable, probably Japan and cultivated plants/leaves/$(CH_3)_2CO$], cichoralexin **254**, was reported by Monde et al. (1990). The NMR data reported for the presumed **254** are identical with those reported for a substance **237**, isolated earlier from *Hypochaeris oligocephala* (Svent. & Bramw.) Lack (Bohlmann et al., 1982). As Monde et al. (1990) used NOE experiments to verify their proposed structure, a technique not yet available to Bohlmann et al. (1982), the structure of the compound isolated from *H. oligocephala* is also tentatively reassigned to **254** (Monde et al., 1990). Additionally, Sessa



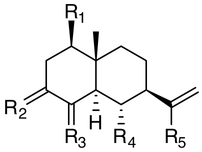
Nr.	R_1	R_2	R_3	Common name
47	H	α H, β OGlc	α CH_3, β H	sonchuside C
48	OH	H, H	CH_2	magnolialide
49	OGlc	H, H	CH_2	
50	OH	H, H	α CH_3, β H	artesin
51	OGlc	H, H	α CH_3, β H	
52	OH	H, H	α H, β CH_3	11-epiartesin
53	OH	α OH, β H	α CH_3, β H	epialkhanol

Fig. 5. *Group 5*: 12,6-Eudesmanolides, magnolialide type eudesmanolides (one intracyclic double bond in position 4).



Nr.	R	Common name
54	H	isoalantolactone
55	OH	telekin

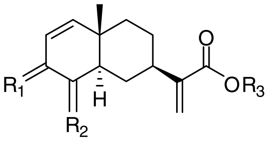
Fig. 6. *Group 6*: 12,8-Eudesmanolides.



Nr.	R_1	R_2	R_3	R_4	R_5	Common name
56	H	α OGlc, β H	CH_2	H	COOH	youngiajaponicoside D
57	OGlc	H, H	CH_2	H	COOH	hypochoeroside J
58	OH	H, H	CH_2	OH	COOH	1β,6α-dihydroxycostic acid
59	O-HMB	H, H	CHOGlc*	OH	$COOCH_3$	ixerisoside N
60	OH	H, H	α CH_2OH, β H	OH	$COOCH_3$	
61	O-HMB	H, H	α CH_2OGlc, β OH	OH	$COOCH_3$	ixerisoside J
62	O-HPL	H, H	α CH_2OGlc, β OH	OH	$COOCH_3$	ixerisoside K
63	O-HPL-HMB	H, H	α CH_2OGlc, β OH	OH	$COOCH_3$	ixerisoside L
64	OH	α H, β OGlc	CH_2	H	CH_3	hypochoeroside K
65	OH	O	CH_2	H	CH_3	

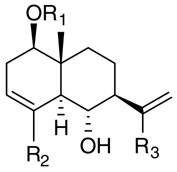
* Double bond from C-4 to C-15!

Fig. 7. *Group 7*: Non-lactonized eudesmane derivatives with no intracyclic double bond.



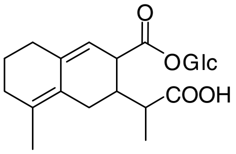
Nr.	R_1	R_2	R_3
66	α H, β OGlc	CH_2	CH_3
67	α H, β OGlc	α CH_3, β H	CH_3
68	O	CH_2	CH_3
69	O	CH_2	Glc
70	O	α CH_3, β H	CH_3

Fig. 8. *Group 8*: Non-lactonized eudesmane derivatives with one intracyclic double bond in position 1(2).



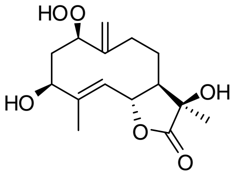
Nr.	R_1	R_2	R_3	Common name
71	HPL	CH_2OGlc	$COOCH_3$	ixerisoside F
72	Glc	COOH	CH_3	hypochoeroside L

Fig. 9. *Group 9*: Non-lactonized eudesmane derivatives with one intracyclic double bond in position 3.



73 napiferoside

Fig. 10. *Group 10*: Non-lactonized eudesmane derivatives with two double bonds.



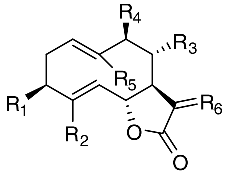
74

Fig. 11. *Group 11*: Germacranolides with one intracyclic double bond in position 4.

et al. (2000) [Great Britain, cultivated plants/latex/MeOH] reported the 15-oxalates of 8-deoxylactucin **296**, lactucin **303**, and lactucopicrin **307** from *C. intybus*. The latter highly significant paper implies that sesquiterpenoid oxalates, which are instable and therefore probably usually decompose in the course of isolation, are potentially widespread in the tribe Cichorieae. The authors also report isolation of novel sesquiterpenoid sulfates (from *Lactuca sativa* but not from *Cichorium intybus*), which are easily missed using traditional phytochemical techniques and therefore might also be more widespread than currently known.

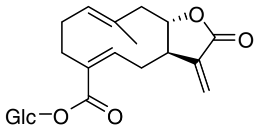
Moreover, two lactucin type aldehydes **327** and **328** and an isomer of lactucin with the lactone ring closed from C12 to *O*-8 instead of *O*-6, intybulide **350**, were reported from *C. intybus* [USA/whole plants/MeOH] by Deng et al. (2001).

Two guaia-4-enolides were reported from *C. pumilum* Jacq. [Egypt/roots/Et_2O:petrol 1:1] by El-Masry et al. (1984). However, according to Park et al. (2000) and Kisiel and Zielińska (2001a,



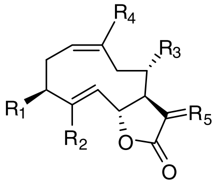
Nr.	R_1	R_2	R_3	R_4	R_5	R_6	Common name
75	H	CH_3	H	H	COOGlc	CH_2	taraxinic acid-1’-*O*-β-D-glucopyranoside
76	H	CH_3	H	H	COOGlc	α CH_3, β H	11β,13-dihydro-taraxinic acid-1’-*O*-β-D-glucopyranoside
77	H	CH_2OGlc	H	H	CH_3	CH_2	picriside B
78	H	CH_2OGlc	H	H	CH_3	α CH_3, β H	ixerin H
79	H	CH_2OGlc	H	H	CH_2O-PPA	CH_2	ixerin I
80	H	CH_2OGlc	O-PPA-Glc(1'''→4')	H	CH_3	CH_2	
81	OGlc	CH_3	H	H	CH_3	CH_2	picriside C
82	OH	CH_3	H	H	CH_3	α CH_3, β H	11β,13-dihydrohanphyllin
83	OGlc	CH_3	H	H	CH_3	α CH_3, β H	sonchuside A
84	OH	CH_3	H	H	CH_3	α CH_3, β OH	
85	OH	CH_3	H	H	CH_2OH	α CH_3, β H	3β,14-dihydroxy-11β,13-dihydro-costunolide
86	OGlc	CH_3	H	H	CH_2OH	α CH_3, β H	
87	OGlc	CH_3	H	H	CH_2OH	α CH_3, β OH	tataroside
88	OGlc	CH_3	H	O-PMP	CH_3	CH_2	sonchuside B
89	OH	CH_3	OH	H	CH_3	α CH_3, β H	
90	OH	CH_3	OGlc	H	CH_3	α CH_3, β H	hypochoeroside A
91	OGlc	CH_3	OH	H	CH_3	α CH_3, β H	cichorioside C

Fig. 12. *Group 12*: Costunolide type 12,6-germacranolides.



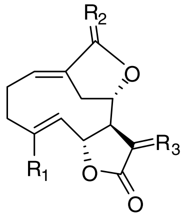
92

Fig. 13. *Group 13*: Costunolide type 12,8-germacranolides.



Nr.	R_1	R_2	R_3	R_4	R_5	Common name
93	H	CH_2OH	H	CH_2OH	α CH_3, β H	ixerin K
94	H	CH_2OH	H	CH_2OH	α H, β CH_3	ixerin L
95	H	CH_2OH	H	CHO	CH_2	8-desoxyurospermal A
96	H	CH_2OGlc	H	CHO	CH_2	ixerin B
97	H	CH_2OGlc-2'-*O*-PPA	H	CHO	CH_2	ixerin G
98	H	CH_2OGlc-6'-*O*-PPA	H	CHO	CH_2	ixerin C
99	H	CH_2OH	H	CHO	α CH_3, β H	ixerin A
100	H	CH_2OGlc	H	CHO	α CH_3, β H	ixerin J
101	H	CH_2OH	OH	CHO	CH_2	urospermal A
102	H	CH_2OGlc	OH	CHO	CH_2	
103	H	CH_2OGlc-3'-*O*-PPA	OH	CHO	CH_2	
104	H	CH_2OGlc-6'-*O*-PPA	OH	CHO	CH_2	
105	H	CH_2OH	OH	CHO	α CH_3, β H	11β,13-dihydrourospermal A
106	H	CH_2OGlc	OH	CHO	α CH_3, β H	15-*O*-β-D-glucopyranosyl-11β,13-dihydrourospermal A
107	H	CH_2OH	OH	CHO	α H, β CH_3	
108	OH	CH_3	H	CH_2OH	α CH_3, β H	
109	OGlc	CH_3	H	CH_2OH	α CH_3, β H	lactuside B
110	OH	CH_3	H	CHO	α CH_3, β H	lactulide A
111	OGlc	CH_3	H	CHO	α CH_3, β H	lactuside A

Fig. 14. *Group 14*: Melampolides.



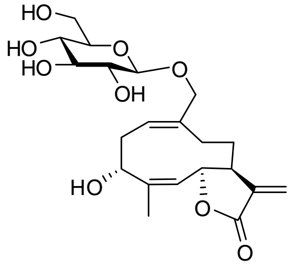
Nr.	R_1	R_2	R_3
112	CH_2OGlc-6'-*O*-PPA	OCH_3, H	
113	CH_2OGlc	O	CH_2
114	CH_2OGlc-6'-*O*-PPA	O	CH_2
115	CH_2OH	O	α CH_3, β H

Fig. 15. *Group 15*: Three ring melampolides.

2003), the structures of the compounds isolated from *C. pumilum* have to be revised to magnolialide **48** and artesin **50**. *C. pumilum* [Poland, cultivated plants/root/EtOH] also yielded eudesmane derivatives santamarin **34** and epiartesin **52**, and guaiane derivatives 8-deoxylactucin **291**, jacquinelin **297**, crepidiaside B **298**, lactucin **301**, lactucopicrin **305**, 11β,13-dihydrolactucin **316**, 11β,13-dihydrolactucopicrin **319**, intybulide **350**, and the methyl ester of the ring open form of lactucopicrin **358** (Kisiel and Zielińska, 2003).

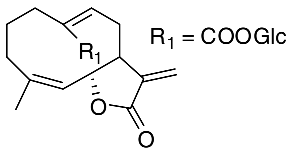
Cichorium spinosum L. [Poland, cultivated plants; seed origin: Sicily/aerial parts/EtOH] yielded eudesmanolide tanacetin **5** and lactucin type guaianolides **275**, **301**, and **316** (Michalska and Kisiel, 2007a).

Crepidiastrum (15 species) – *Crepidiastrum keiskeanum* Nakai [Japan/whole plants/MeOH under reflux (!)] yielded lactucin type



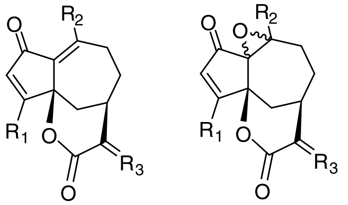
116

Fig. 16. *Group 16*: Germacra-1(10)-*cis*-4-*cis*-dienolides.



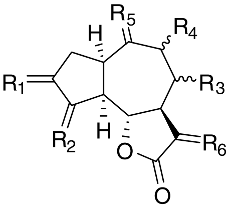
117: ainslioside

Fig. 17. *Group 17*: Ainslioside type germacranolides.



Nr.	R_1	R_2	R_3	Common name
Hypocretenolides				
118	CH_3	CH_3	CH_2	hypocretenolide
119	CH_3	CH_2OH	CH_2	14-hydroxyhypocretenolide
120	CH_3	CH_2OGlc	CH_2	14-hydroxyhypocretenolide-β-D-glucopyranoside
121	CH_3	CH_2OGlc-4'-*O*-Hyp	CH_2	
122	CH_3	CH_2OH	α H, β CH_3	11,13α-dihydro-14-hydroxyhypocretenolide
123	CH_3	CH_2OGlc	α H, β CH_3	11,13α-dihydro-14-hydroxyhypocretenolide-β-D-glucopyranoside
124	CH_2OH	CH_3	CH_2	15-hydroxyhypocretenolide
125	CH_2OGlc	CH_3	CH_2	15-hydroxyhypocretenolide-β-glucopyranoside
126	CH_2OH	CH_3	α CH_3, β H	11β,13-dihydro-15-hydroxyhypocretenolide
127	CH_2OGlc	CH_3	α CH_3, β H	11β,13-dihydro-15-hydroxy-hypocretenolide-β-glucopyranoside
1,10-Epoxyhypocretenolides				
128	CH_3	CH_2OGlc	CH_2	1,10-epoxy-14-hydroxyhypocretenolide-β-D-glucopyranoside
129	CH_3	CH_2OGlc-6'-*O*-PPA	CH_2	1,10-epoxy-14-hydroxyhypocretenolide-β-D-glucopyranoside-6'-*O*-*p*-hydroxyphenyl-acetic acid ester

Fig. 18. *Group 18*: Hypocretenolides.



Nr.	R_1	R_2	R_3	R_4	R_5	R_6	Common name
130	H, H	CH_2	H	H	CH_2	CH_2	dehydrocostuslactone
131	H, H	CH_2	H	H	α OGlc, β CH_3	CH_2	brachynereolide
132	H, H	CH_2	H	H	α OGlc, β CH_3	α H, β CH_3	ixerin V
133	H, H	CH_2	H	α OH	CH_2	CH_2	9α-hydroxy-3-deoxyzaluzanin C
134	H, H	CH_2	H	α OGlc	CH_2	CH_2	ixerisoside D
135	H, H	CH_2	H	α OH	CH_2	α CH_3, β H	annuolide D
136	H, H	CH_2	H	α OGlc	CH_2	α CH_3, β H	scorzoside
137	α H, β OH	CH_2	H	H	CH_2	CH_2	zaluzanin C
138	α H, β OGlc	CH_2	H	H	CH_2	CH_2	glucozaluzanin C
139	α H, β OGlc-3'-*O*-PPA	CH_2	H	H	CH_2	CH_2	youngiajaponicoside B
140	α H, β OGlc-4'-*O*-PPA	CH_2	H	H	CH_2	CH_2	crepiside B
141	α H, β OGlc-6'-*O*-PPA	CH_2	H	H	CH_2	CH_2	crepiside A
142	α H, β OH	CH_2	H	H	CH_2	α CH_3, β H	11β,13-dihydrozaluzanin C
143	α H, β OGlc	CH_2	H	H	CH_2	α CH_3, β H	11β,13-dihydro-glucozaluzanin C
144	α H, β OGlc	CH_2	H	H	CH_2	α CH_3, β OH	ixerisoside C
145	α H, β OH	CH_2	H	H	CH_2	α OH, β CH_2Cl	13-chlorosolstitialin
146	α H, β OGlc	CH_2	H	H	CH_2	α OH, β CH_2Cl	
147	α H, β OH	CH_2	H	H	α OH, β CH_3	CH_2	
148	α H, β OGlc	CH_2	H	H	α OH, β CH_3	CH_2	ixerin D
149	α H, β OGlc-6'-*O*-CAF	CH_2	H	H	α OH, β CH_3	CH_2	ixerin U
150	α H, β OGlc-6'-*O*-PPA	CH_2	H	H	α OH, β CH_3	CH_2	prenantheside B
151	α H, β O-Glc-2'-*O*-6'-*O*-diPPA	CH_2	H	H	α OH, β CH_3	CH_2	chinensiolide E
152	α H, β OH	CH_2	H	H	α OH, β CH_3	α CH_3, β H	
153	α H, β OGlc	CH_2	H	H	α OH, β CH_3	α CH_3, β H	ixerin E
154	α H, β OH	CH_2	H	α OH	CH_2	CH_2	9α-hydroxyzaluzanin C
155	α H, β OGlc	CH_2	H	α OH	CH_2	CH_2	macrocliniside A
156	α H, β OH	CH_2	H	α OH	CH_2	α CH_3, β H	9α-hydroxy-11β,13-dihydrozaluzanin C
157	α H, β OH	CH_2	H	α OGlc	CH_2	α CH_3, β H	salignoside
158	α H, β OAllo	CH_2	H	α OH	CH_2	α CH_3, β H	
159	α H, β OGlc	CH_2	H	α OH	CH_2	α CH_3, β H	ixerin F
160	α H, β OH	CH_2	H	β OH	CH_2	CH_2	
161	α H, β OGlc	CH_2	H	β OH	CH_2	CH_2	diaspanoside A
162	α H, β OGlc	CH_2	H	β OH	CH_2	α H, β CH_3	dentatin C
163	α H, β OH	CH_2	α OH	H	CH_2	CH_2	8-desacylcynaropicrin
164	α H, β OGlc	CH_2	α OH	H	CH_2	CH_2	crepiside E
165	α H, β OGlc	CH_2	α O-PPA	H	CH_2	CH_2	crepiside G
166	α H, β OGlc-3'-*O*-PPA	CH_2	α OH	H	CH_2	CH_2	youngiajaponicoside A
167	α H, β OGlc-6'-*O*-PPA	CH_2	α OH	H	CH_2	CH_2	crepiside H

Fig. 19. *Group 19*: Costus lactone type guaianolides.

Nr.	R_1	R_2	R_3	R_4	R_5	R_6	Common name
168	α H, β OGlc	CH_2	α OH	H	CH_2	α CH_3, β H	
169	α H, β OGlc-2'-*O*-CAF	CH_2	α OH	H	CH_2	α CH_3, β H	prenantheside C
170	α H, β O-ANG	CH_2	α OGlc	H	CH_2	α CH_3, β H	
171	α H, β OH	CH_2	α OH	H	α OH, β CH_3	CH_2	
172	α H, β OH	CH_2	β OH	H	CH_2	CH_2	integrifolin
173	α H , β OH	CH_2	β O-PPA	H	CH_2	CH_2	ixerochinolide
174	α H, β OGlc	CH_2	β OH	H	CH_2	CH_2	integrifolin-3β-D-glucopyranoside
175	α H, β OGlc	CH_2	β O-Ac	H	CH_2	CH_2	
176	α H, β OGlc	CH_2	β O-HEOB	H	CH_2	CH_2	
177	α H, β OGlc	CH_2	β O-HMB	H	CH_2	CH_2	ixerin M
178	α H, β OGlc	CH_2	β O-HMOB	H	CH_2	CH_2	
179	α H, β OGlc	CH_2	β O-HMV	H	CH_2	CH_2	ixerin N
180	α H, β OGlc	CH_2	β O-HPL	H	CH_2	CH_2	tectoroside
181	α H, β OGlc	CH_2	β O-PPA	H	CH_2	CH_2	ixerisoside A
182	α H, β OGlc	CH_2	β O-PMP	H	CH_2	CH_2	
183	α H, β OGlc-6'-*O*-PPA	CH_2	β OH	H	CH_2	CH_2	crepiside I
184	α H, β OGlc-4'-*O*-PPA	CH_2	β O-HMB	H	CH_2	CH_2	ixerin O
185	α H, β OGlc-4'-*O*-PPA	CH_2	β O-HMV	H	CH_2	CH_2	ixerin Q
186	α H, β OGlc-6'-*O*-PPA	CH_2	β O-HMB	H	CH_2	CH_2	ixerin P
187	α H, β OGlc-6'-*O*-PPA	CH_2	β O-HMV	H	CH_2	CH_2	ixerin R
188	α H, β OGlc-6'-*O*-PPA	CH_2	β O-PPA	H	CH_2	CH_2	ixerochinoside
189	α H, β OH	CH_2	β OH	H	CH_2	α CH_3, β H	11βH-11,13-dihydrointegrifolin
190	α H, β OGlc	CH_2	β OH	H	CH_2	α CH_3, β H	11βH-11,13-dihydrointegrifolin-3β-D-glucopyranoside
191	α H, β OH	CH_2	β OH	H	CH_2	α H, β CH_3	
192	α H, β OGlc	CH_2	β OH	H	CH_2	α H, β CH_3	dentatin B
193	α H, β OGlc	CH_2	β OH	H	CH_2	α CH_2OCH_3, β H	
194	α H, β OGlc	α CH_3, β H	H	H	CH_2	α CH_3, β H	
195	α H, β OH	α CH_3, β H	H	α OH	CH_2	CH_2	aglycone of ixerin F
196	α H, β OH	α CH_3, β H	H	α OH	CH_2	α CH_3, β H	
197	α H, β OH	α CH_3, β H	α OH	H	CH_2	α CH_3, β H	isolipidiol
198	α H, β OH	α CH_3, β H	β OH	H	CH_2	CH_2	8β-hydroxy-4β,15-dihydrozaluzanin C
199	α H, β OGlc	α CH_3, β H	β OH	H	CH_2	CH_2	
200	α H, β OGlc	α CH_3, β H	β O-HPL	H	CH_2	CH_2	ixerisoside B
201	α H, β OH	α CH_3, β H	β OH	H	CH_2	α CH_3, β H	8-epiisolipidiol
202	α H, β OGlc	α CH_3, β H	β OH	H	CH_2	α CH_3, β H	8-epiisolipidiol-3-*O*-β-D-glucopyranoside
203	α H, β OH	α H, β CH_3	H	H	CH_2	α OH, β CH_3	

Fig. 19 *(continued)*

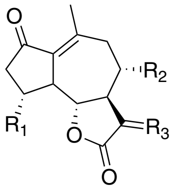
guaianolides crepidiaside E **268**, crepidiaside C **270**, crepidiaside D **271**, crepidiaside A **293**, and crepidiaside B **298** (Adegawa et al., 1985).

Crepidiastrum lanceolatum Nakai [Japan/aerial parts/MeOH] yielded 11 guaianolides, one of the hieracin type **256** and 10 of the lactucin type: **260**, **263**, **264**, **265**, **266**, **267**, **269**, **272**, **295**, and **299** (Takeda et al., 2002, 2005).

Crepis (ca. 200 species) – *Crepis aspera* L. [Egypt/aerial parts/MeOH:CH_2Cl_2 1:1] yielded costus lactone type guaianolide **201** (Ahmed et al., 2000).

Nr.	R_1	R_2	R_3	R_4	R_5	R_6	Common name
204	α H, β OH	α H, β CH_3	H	α OH	CH_2	α CH_3, β H	
205	α H, β OH	α H, β CH_3	α OH	H	CH_2	α CH_3, β H	8α-hydroxy-4α(13), 11β(15)-tetrahydro-zaluzanin C
206	α H, β OGlc	α H, β CH_3	β OH	H	CH_2	CH_2	
207	α H, β OGlc	α H, β CH_3	β OH	H	CH_2	α CH_3, β H	
208	α H, β OH	α H, β CH_3	β OH	H	CH_2	α H, β CH_3	dentalactone
209	α H, β OGlc	α H, β CH_3	β OH	H	CH_2	α H, β CH_3	dentatin A
210	O	CH_2	H	H	α OH, β CH_3	CH_2	chinensiolide A
211	O	CH_2	β OH	H	CH_2	CH_2	8β-hydroxy-dehydrozaluzanin C
212	O	α CH_3, β H	H	H	CH_2	CH_2	
213	O	α CH_3, β H	H	H	α OH, β CH_3	CH_2	chinensiolide B, prenanthelide A
214	O	α CH_3, β H	H	H	α OH, β CH_3	α CH_3, β H	
215	O	α CH_3, β H	H	α OH	CH_2	α CH_3, β H	
216	O	α CH_3, β H	α OH	H	CH_2	CH_2	
217	O	α CH_3, β H	α O-PPA	H	CH_2	CH_2	youngiajaponicol A
218	O	α CH_3, β H	α OH	H	CH_2	α CH_3, β H	isoamberboin
219	O	α CH_3, β H	β OH	H	CH_2	CH_2	8-epigrosheimin
220	O	α CH_3, β H	β OH	H	CH_2	α CH_3, β H	8-epiisoamberboin
221	O	α H, β CH_3	H	H	α OH, β CH_3	CH_2	chinensiolide D

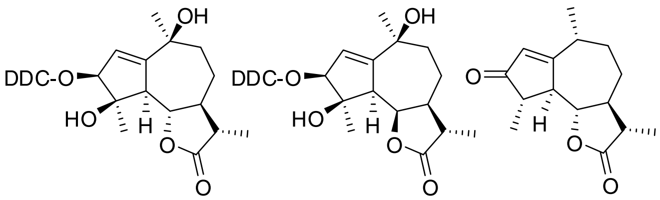
Fig. 19 *(continued)*



Nr.	R_1	R_2	R_3	Common name
222	CH_2OH	H	CH_2	picridin
223	CH_2OH	H	α CH_3, β H	dihydropicridin
224	CHO	O-PPA	CH_2	3,4β-dihydro-15-dehydrolactucopicrin

Fig. 20. *Group 20:* Picridin type guaianolides.

Crepis aurea (L.) Cass. [Poland, cultivated plants/roots/unavailable] yielded hypocretenolides **119**, **120**, and **123** (Kisiel, 1994).



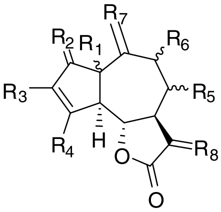
225 **226** **227**

Fig. 21. *Group 21:* Hypochaerin type guaianolides.

Crepis biennis L. [Poland/roots/EtOH] yielded guaianolide ixerin F **159** (Kisiel and Kohlmünzer, 1987).

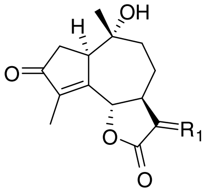
Crepis cameroonica Babcock ex Hutchinson & Dalziel [Cameroon/aerial parts/MeOH] yielded guaianolides **160**, **163**, and **205** (Ndom et al., 2006).

Crepis capillaris (L.) Wallr. (syn.: *C. virens* L.) [Italy/flowers/H_2O] yielded costus lactone guaianolide **219** (Barbetti et al., 1979). A more detailed investigation [Poland/aerial parts and roots/EtOH] yielded costus lactone type guaianolides **172**, **174**, **176**, **178**, **201**, **202**, and **220** (Kisiel, 1983a,b, 1984).



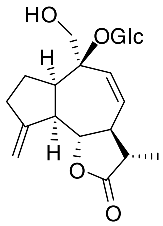
Nr.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Common name
228	α H	H, H	OGlc	CH_3	H	H	α OH, β CH_3	CH_2	prenantheside A
229	α H	H, H	OGlc	CH_3	α OH	H	CH_2	CH_2	crepiside D
230	α H	H, H	OGlc	CH_3	α O-PPA	H	CH_2	CH_2	crepiside F
231	α H	H, H	OGlc	CH_3	β OH	H	CH_2	CH_2	crepiside C
232	α H	H, H	OGlc	CH_3	β O-Ac	H	CH_2	CH_2	
233	α H	H, H	OGlc	CH_3	β O-HPL	H	CH_2	CH_2	
234	α H	H, H	OGlc	CH_3	β O-HMB	H	CH_2	CH_2	ixerin S
235	α H	H, H	OGlc	CH_3	β O-HMV	H	CH_2	CH_2	ixerin T
236	α H	α H, β OH	H	CH_3	H	H	CH_2	CH_2	
237	α H	O	H	CH_3	H	H	α CH_3, β H	α CH_3, β H	
238	α H	O	H	CH_3	H	α OGlc	α H , β CH_3	CH_2	ixerinoside
239	α H	O	H	CH_3	α O-Ac	H	α H , β CH_3	CH_2	montanone
240	α H	O	H	CH_3	α OGlc	H	α CH_3, β OH	α CH_3, β H	
241	α H	O	H	CH_2OH	H	H	α CH_3, β OH	CH_2	hieracin II
242	α H	O	H	CH_2OH	H	H	α CH_3, β OH	α CH_3, β H	hieracin I
243	α H	O	H	CH_2OGlc	H	H	α H, β CH_3	CH_2	
244	α H	O	H	CH_2OH	H	H	α H, β CH_3	α CH_3, β H	
245	α H	O	H	CH_2OGlc	H	H	α H, β CH_3	α CH_3, β H	
246	α H	O	H	CH_2OH	α O-CAM	H	α H, β CH_3	CH_2	hyporadiolide-8-*O*-cinnamate
247	α H	O	H	CH_2OH	α O-IPG	H	α H, β CH_3	CH_2	
248	α H	O	H	CH_2OH	α O-MAC	H	α H, β CH_3	CH_2	hyporadiolide-8-*O*-[2-methylacrylate]
249	α H	O	H	CH_2OGlc	α O-CAM	H	α H, β CH_3	CH_2	hypochoeroside F
250	α H	O	H	CH_2OGlc	α O-MAC	H	α H, β CH_3	CH_2	hypochoeroside E
251	α H	O	H	CH_2OH	α O-MAC	H	α H, β CH_3	α CH_3, β H	11,13-dihydrohyporadiolide-8-*O*-[2-methylacrylate]
252	α H	O	H	CH_2OGlc	α O-MAC	H	α H, β CH_3	α CH_3, β H	hypochoeroside G
253	α H	O	OH	CH_3	H	H	α CH_3, β OGlc	CH_2	
254	β H	O	H	CH_3	H	H	α H, β CH_3	α CH_3, β H	cichoralexin
255	β H	O	H	CH_2OGlc	H	H	α H, β CH_3	CH_2	
256	α/β OH	O	H	CH_2OGlc-6'-*O*-PPA	H	H	α H, β CH_3	CH_2	lanceocrepidiaside F

Fig. 22. *Group 22:* Hieracin type guaianolides.



257: R = CH$_2$; chinensiolide C
258: R = α CH$_3$, β H

Fig. 23. *Group 23:* Chinensiolide C type guaianolides.



259

Fig. 24. *Group 24*: Guai-8-enolides.

Crepis conyzifolia (Gouan) Kern. [Poland, cultivated plants, seed origin: Poland/roots/EtOH] yielded guaianolides **194**, **198**, **201**, and **202** (Kisiel and Michalska, 2001).

Crepis crocea (Lam.) Babcock [Mongolia/aerial parts/ MeOH:Et$_2$O:petrol 1:1:1] yielded costus lactone type guaianolides **172**, **189**, and **220** (Kisiel et al., 1994).

Crepis foetida L. [Poland, cultivated plants/roots/EtOH] yielded five costus lactone type guaianolides: **143**, **156**, **159**, **196**, and **204** (Kisiel and Barszcz, 1999).

Crepis japonica (L.) Benth. (Miyase et al., 1985) is currently assigned to genus *Youngia* and its current name is *Youngia japonica* (L.) DC.

Crepis micrantha Czerep. [Egypt/aerial parts/EtOH] yielded costus lactone type guaianolides **163**, **189**, and **201** (Kassem, 2007).

Crepis mollis Aschers. [Poland, cultivated plants/roots/EtOH] yielded germacranolide picriside B **77** and 11 guaianolides **142**, **159**, **174**, **176**, **178**, **190**, **193**, **201**, **202**, **215**, and **219** (Kisiel et al., 2000).

Crepis multicaulis Ledeb. [Kazakhstan/aerial parts/CHCl$_3$] yielded lactucin type guaianolide crepidiaside A **293** (Fazylova et al., 2000).

Crepis napifera (Franch.) Babcock (syn.: *Lactuca napifera* Franch.) [China/roots/not available] yielded eudesmane derivative **73** (Zhao et al., 2000) and germacranolides taraxinic acid-1′-*O*-β-D-glucopyranoside **75** and 11β,13-dihydrotaraxinic acid-1′-*O*-β-D-glucopyranoside **76** (Wu et al., 2002).

Crepis pulchra L. [Poland, cultivated plants/roots/EtOH] yielded four costus lactone type guaianolides **138, 155, 161**, and **220** (Kisiel and Gromek, 1994).

Crepis pygmaea L. [Italy/whole plants/(CH$_3$)$_2$CO] yielded 13-nor-12,6-eudesmanolides **1** and **2** (Casinovi et al., 1982; Rossi et al., 1985).

Crepis pyrenaica (L.) Greuter [Poland, cultivated plants/roots/ EtOH] yielded seven costus lactone type guaianolides **155**, **159**, **174**, **176**, **178**, **199**, and **202** (Kisiel and Barszcz, 1995a).

Crepis rhoeadifolia M.Bieb. [Poland, cultivated plants/roots/ EtOH] yielded four costus lactone type guaianolides **143**, **159**, **196**, and **204** (Kisiel and Barszcz, 1996).

Crepis setosa Haller f. [Poland, cultivated plants/roots/EtOH] yielded four costus lactone type guaianolides **143**, **156**, **159**, and **168** (Kisiel and Kohlmünzer, 1990).

Crepis sibirica L. [Poland, cultivated plants/roots/not available] yielded costus lactone type guaianolides **138**, **174**, and **220** (Kisiel, 1995a).

Crepis tectorum L. [Poland, cultivated plants/roots/EtOH] yielded nine costus lactone type guaianolides **138**, **159**, **172**, **176**, **178, 180**, **197**, **201**, and **202** (Kisiel and Kohlmünzer, 1989a,b; Adekenov et al., 1991; Fazylova et al., 2000).

Crepis tingitana Ball [Spain/subaerial parts/CH$_2$Cl$_2$] yielded costus lactone type guaianolides **174** and **181** (Zidorn et al., 1999b).

Crepis zacintha (L.) Loisel. [Poland, cultivated plants/roots/EtOH] yielded germacranolide picriside B **77** and 12 costus lactone type guaianolides **143**, **159**, **174**, **177**, **195**, **196**, **198, 199**, **202**, **204**, **206**, and **207** (Kisiel et al., 2002).

Dendroseris (11 species) – *Dendroseris neriifolia* Hook. & Arn. [Chile/aerial parts/MeOH] yielded the new eudesmanolide dendroserin **21** and lactucin type guaianolide **282** (Campos et al., 1989a,b). Kilian et al. (2008) included *Dendroseris* into the genus *Sonchus* s.l.

Hedypnois (2 species) – *Hedypnois cretica* Willd. [Egypt/aerial parts/EtOH] yielded four 14-hydroxyhypocretenolides **119**, **120**, **122**, and **123** (Harraz et al., 1988).

Helminthotheca (6 species) – *Helminthotheca aculeata* (Vahl) Lack (syn.: *Picris aculeata* Vahl) [Sicily/aerial parts/CHCl$_3$] yielded the eudesmanolides 1-epierivanin **23** and 1-epialkhanol **53** (Bruno and Herz, 1988).

H. echioides (L.) Holub (syn.: *Picris echioides* L.) [unavailable/aerial parts/Et$_2$O:petrol 1:2] yielded the eudesmanolide telekin **55**, the germacrane derivative 11β,13-dihydrohanphyllin **82**, and the lactucin derivatives 8-deoxylactucin **291**, jacquinelin **297**, and 11-epi-jacquinelin **300** (Bohlmann et al., 1981b). Furthermore, Marco et al. (1992a) [Spain/aerial parts/hexane:Et$_2$O:MeOH 1:1:1] reported a new germacranolide **89** and two guaianolides **241** and **242**. Milovanović et al. (2000) [Serbia/aerial parts/petrol:Et$_2$O:MeOH 1:1:1] additionally isolated the guaianolide achillin **277** from *H. echioides*.

H. spinifera (Franco) Zidorn (syn.: *Picris spinifera* Franco) [Portugal/aerial parts/CHCl$_3$] yielded eudesmanolide 2-oxo-11β,13-dihydrosantamarin **46** (Kijjoa et al., 1992).

***Hieracium* s.str.** (i.e. excluding Pilosella) (ca. 90 species, when using a narrow species concept – as usually employed in Central Europe – this number increases to more than 1000 species) – *Hieracium intybaceum* All. [Austria/subaerial parts/CH$_2$Cl$_2$] yielded four eudesmanolides **29**, **30**, **31**, and **32**, the corresponding eudesmanic acid methyl esters **66**, **67**, **68**, and **70**, and the costus lactone type guaianolide **130** (Grass et al., 2004). Kilian et al. (2008) recently reinstated the monotypic genus *Schlagintweitia*, which only encompasses *H. intybaceum* (*Schlagintweitia intybacea* Griseb.).

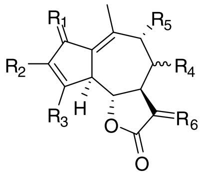
H. irasuense Benth. ex Oerst. (erroneously named *H. irazuensis* L. in the original paper) [Costa Rica/whole plants/CH$_2$Cl$_2$] yielded eudesmanolide irazunolide **33** (Hasbun et al., 1982).

H. murorum L. [Germany/subaerial parts/MeOH] yielded 12,8-germacranolide **92** (Zidorn et al., 2001c).

Hypochaeris (ca. 60 species) – *Hypochaeris achyrophorus* L. [Italy/whole plants/MeOH] yielded the unusual guaianolide **354** and its precursor acid **360** (Zidorn et al., 2007d).

H. cretensis Benth. & Hook.f. [Germany, cultivated plants, seed origin: France/whole plants/Et$_2$O:petrol 1:2] yielded eudesmanolide isoalantolactone **54**, hypocretenolide **118**, and its precursor hypocretenoic acid **357** (Bohlmann and Singh, 1982).

H. glabra L. [Germany, cultivated plants/roots and aerial parts/ Et$_2$O:petrol 1:2] yielded two related guaianolide-15-ols, both esterified with a sesquiterpenic acid **304** and **318** (Bohlmann et al., 1981a).



Nr.	R_1	R_2	R_3	R_4	R_5	R_6	Common name
260	H, H	H	CH_2OGlc	H	OH	CH_2	youngiaside A
261	H, H	H	CH_2OGlc-3'-*O*-PPA	H	OH	CH_2	youngiaside B
262	H, H	H	CH_2OGlc-4'-*O*-PPA	H	OH	CH_2	youngiaside C
263	H, H	H	CH_2OGlc-6'-*O*-PPA	H	OH	CH_2	youngiaside D
264	H, H	H	CH_2OGlc	H	OH	α CH_3, β H	lanceocrepidiaside A
265	H, H	H	CH_2OGlc-6'-*O*-PPA	H	OH	α CH_3, β H	lanceocrepidiaside B
266	H, H	H	CH_2OGlc	α OH	H	CH_2	ixerin Y
267	H, H	H	CH_2OGlc	α O-PPA	H	CH_2	lanceocrepidiaside C
268	H, H	H	CH_2OGlc-2'-*O*-PPA	α OH	H	CH_2	crepidiaside E
269	H, H	H	CH_2OGlc-6'-*O*-PPA	α OH	H	CH_2	crepidialanceoside A
270	H, H	H	CH_2OGlc	α OH	H	α CH_3, β H	crepidiaside C
271	H, H	H	CH_2OGlc-2'-*O*-PPA	α OH	H	α CH_3, β H	crepidiaside D
272	H, H	H	CH_2OGlc-6'-*O*-PPA	α OH	H	α CH_3, β H	crepidialanceoside B
273	H, H	H	CH_2OGlc	β OH	H	CH_2	ixerin X
274	O	H	CH_3	H	H	CH_2	11,13-dehydroleucodin
275	O	H	CH_3	H	H	α CH_3, β H	desacetoxymatricarin, leucodin
276	O	H	CH_3	H	H	α CH_3, β OGlc	11β-hydroxyleucodin-11-*O*-β-D-glucopyranoside
277	O	H	CH_3	H	H	α H, β CH_3	achillin
278	O	H	CH_3	H	α OGlc	α CH_3, β H	lactuside C
279	O	H	CH_3	α OH	H	CH_2	15-deoxylactucin
280	O	H	CH_3	α OSO_3H	H	CH_2	15-deoxylactucin-8-sulfate
281	O	H	CH_3	α OGlc	H	CH_2	15-deoxylactucin-8-glucoside
282	O	H	CH_3	α OH	H	α CH_3, β H	desacetylmatricarin
283	O	H	CH_3	α OGlc	H	α CH_3, β H	notoserolide A
284	O	H	CH_3	α OSO_3H	H	α CH_3, β H	8-deacetylmatricarin-8-*O*-sulfate
285	O	H	CH_3	α OSO_3Na	H	α CH_3, β H	
286	O	H	CH_3	α O-Ac	H	α CH_3, β H	matricarin
287	O	H	CH_3	α O-HPP-Glc (1''→4')	H	α CH_3, β H	scorzonerin
288	O	H	CH_3	α O-SEN	H	α CH_3, β H	notoserolide B
289	O	H	CH_3	α OGlc	H	α CH_3, β OH	11β-hydroxydeacetylmatricarin-8-*O*-β-D-glucopyranoside

Fig. 25. *Group 25*: Lactucin type guaianolides.

Hypochaeris oligocephala (Svent. et Bramwell) Lack [Canary Islands/roots/Et_2O:petrol 1:2] yielded hieracin derivatives **237** and **247**, lactucin derivative **275**, and the lactucin derivative precursor **355** (Bohlmann et al., 1982).

H. radicata L. [Germany, cultivated plants/roots/Et_2O:petrol 1:2] yielded hieracin type guaianolides **246**, **248**, and **251** (Bohlmann and Bohlmann, 1980). An extensive study conducted on Japanese plant material [Japan/whole plants/MeOH, under reflux (!)] yielded a large number of sesquiterpenoids, mostly guaiane derivatives **148**, **159**, **249**, **250**, **252**, **310**, **311**, **316**, **321**, **324**, **351**, and **359**, but also some germacranolides **77**, **83**, **90**, and **91**, and eudesmane derivatives **57**, **64**, and **72** (Ohmura et al., 1989). Extraction of the

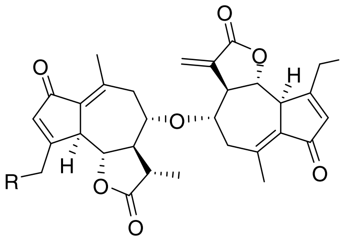
Nr.	R_1	R_2	R_3	R_4	R_5	R_6	Common name
290	O	H	CH_3	β OGlc	H	α CH_3, β OH	taraxafolide
291	O	H	CH_2OH	H	H	CH_2	8-deoxylactucin
292	O	H	CH_2O-HMPS	H	H	CH_2	8-deoxy-15-(3'-hydroxy-2'-methyl-propanoyl)-lactucin 3'-sulfate
293	O	H	CH_2OGlc	H	H	CH_2	crepidiaside A
294	O	H	CH_2OGlc-3'-*O*-PPA	H	H	CH_2	
295	O	H	CH_2O-Glc-6'-*O*-PPA	H	H	CH_2	lanceocrepidiaside D
296	O	H	CH_2O-Ac	H	H	CH_2	8-deoxylactucin-15-oxalate
297	O	H	CH_2OH	H	H	α CH_3, β H	jacquinelin
298	O	H	CH_2OGlc	H	H	α CH_3, β H	crepidiaside B
299	O	H	CH_2OGlc-6'-*O*-PPA	H	H	α CH_3, β H	lanceocrepidiaside E
300	O	H	CH_2OH	H	H	α H, β CH_3	11-epi-jacquinelin
301	O	H	CH_2OH	α OH	H	CH_2	lactucin
302	O	H	CH_2OH	α O-Ac	H	CH_2	8-acetyl-lactucin
303	O	H	CH_2O-Ac	α OH	H	CH_2	lactucin-15-oxalate
304	O	H	CH_2OH	α O-HPG	H	CH_2	lactucin-8-*O*-hypoglabrate
305	O	H	CH_2OH	α O-PPA	H	CH_2	lactucopicrin
306	O	H	CH_2OH	α O-PMP	H	CH_2	
307	O	H	CH_2O-Ac	α O-PPA	H	CH_2	lactucopicrin-15-oxalate
308	O	H	CH_2OGlc	α OH	H	CH_2	picriside A
309	O	H	CH_2OGlc	α O-Ac	H	CH_2	8-acetyl-15-β-D-glucopyranosyllactucin
310	O	H	CH_2OGlc	α O-CAM	H	CH_2	hypochoeroside D
311	O	H	CH_2OGlc	α O-MAC	H	CH_2	hypochoeroside C
312	O	H	CH_2OGlc	α O-PIC	H	CH_2	picrioside A
313	O	H	CH_2OGlc	α O-PPA	H	CH_2	
314	O	H	CH_2O-PPA	α OH	H	CH_2	15-*p*-hydroxyphenylacetyllactucin
315	O	H	CH_2O-PPA	α OSO_3H	H	CH_2	15-*p*-hydroxyphenylacetyl-lactucin-8-sulfate
316	O	H	CH_2OH	α OH	H	α CH_3, β H	11β,13-dihydrolactucin
317	O	H	CH_2OH	α O-Ac	H	α CH_3, β H	8-acetyl-11β,13-dihydrolactucin
318	O	H	CH_2OH	α O-HPG	H	α CH_3, β H	8α-hypoglabroyloxyjacquinelin
319	O	H	CH_2OH	α O-PPA	H	α CH_3, β H	11β,13-dihydrolactucopicrin
320	O	H	CH_2OH	α O-PMP	H	α CH_3, β H	11β,13-dihydrolactucin-8-*O*-*p*-methoxyphenylacetate
321	O	H	CH_2OGlc	α OH	H	α CH_3, β H	cichorioside B
322	O	H	CH_2OGlc	α O-ANG	H	α CH_3, β H	notoserolide C
323	O	H	CH_2OH	α O-MAC	H	α CH_3, β H	11β,13-dihydrolactucopicrin-8-*O*-methacrylate
324	O	H	CH_2OGlc	α O-MAC	H	α CH_3, β H	hypochoeroside B
325	O	H	CH_2OGlc	α O-PIC	H	α CH_3, β H	picrioside B
326	O	H	CHO	α O-MAC	H	CH_2	15-dehydrolactucin-8-*O*-methacrylate
327	O	H	CHO	α O-PPA	H	CH_2	15-dehydrolactucopicrin

Fig. 25 (*continued*)

plant material was performed with hot MeOH under reflux in this study. Therefore, it is possible that some of the nineteen sesquiterpenoids reported were artifacts and not genuine natural products. A second study conducted on Japanese plant material [Japan/leave exudates/EtOAc] was focused on phytoalexins and yielded **65** and **356** (Maruta et al., 1995). It is stated in the latter report that these compounds also occur in non-infected plants irradiated with UV-radiation. Therefore, and in contrast to other

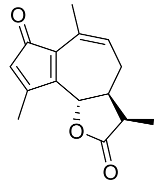
Nr.	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	Common name
328	O	H	CHO	α O-PPA	H	α CH$_3$, β H	15-dehydro-11β,13-dihydrolactucopicrin
329	O	H	COOH	H	H	α CH$_3$, β H	notoserolide D
330	O	OGlc	CH$_3$	H	H	CH$_2$	ixerin Z
331	O	OGlc-6'-*O*-PMP	CH$_3$	H	H	CH$_2$	ixerin Z$_A$
332	O	OGlc-6'-*O*-PPA	CH$_3$	H	H	CH$_2$	ixerin Z-6'-*p*-hydroxyphenylacetate
333	O	OH	CH$_3$	H	H	α CH$_3$, β H	8-desoxyartelin
334	O	OGlc	CH$_3$	H	H	α CH$_3$, β H	11,13β-dihydroixerin Z

Fig. 25 (*continued*)



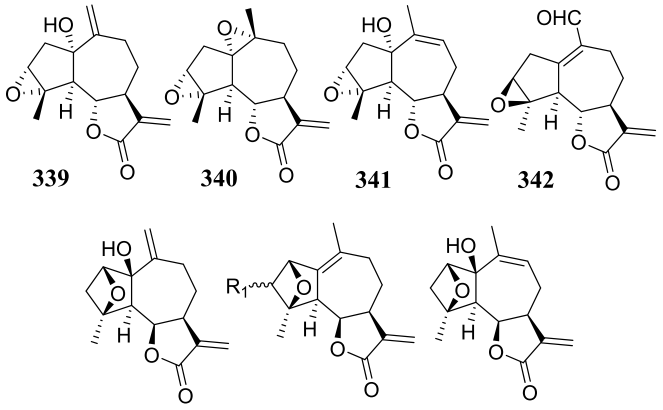
335: lactucain A; R = H
336: lactucain B; R = OH
337: lactucain C; R = OPPA

Fig. 26. *Group 26:* Dimeric lactucin type guaianolides.



338: notoserolide E

Fig. 27. *Group 27*: Guaiane derivatives with three intra-cyclic double bonds.



344: R$_1$ = α OH
345: R$_1$ = β OH
346: R$_1$ = β O-MBU

Fig. 28. *Group 28*: Epoxyguaian-12,6-olides.

phytoalexins, these two substances are considered in the chemosystematic data interpretation section of this article.

H. setosus Rusby [Venezuela/whole plant/EtOH, Soxhlet] yielded four guaianolides **227**, **275**, **277**, and **297** and one eudesmanolide **50** (Gonzaléz et al., 1976, 1977). The stereochemistry of the 1-hydroxy group of **50** is not indicated in the reference by Gonzaléz et al. (1976). However, because OH-1 is β-oriented in the compound isolated from other sources of the Cichorieae (e.g. in the genus *Cichorium*) and in all similar compounds (**47-53**), β-orientation is here also assumed for the compound isolated from *H. setosus*.

H. uniflora Vill. [Germany, cultivated plants/roots/Et$_2$O:petrol 1:2] yielded a guaianolide-15-aldehyde **326** (Bohlmann et al., 1981a).

Ixeris (ca. 20 species) – *Ixeris chinensis* Nakai [not available, probably Taiwan/whole plants/EtOH, under reflux (!)] yielded **148**, **174**, and **181** (Lee et al., 1994). In this paper the then already known compound **181** (Warashina et al., 1990) is presented as a new compound; moreover, the structure of ixerin D (**148**) is misprinted (erroneously drawn with an additional OH-group in position 8β). A study with material from mainland China [China/whole plants/MeOH] yielded **210**, **213**, and **257** (Zhang et al., 2002). A second more comprehensive Taiwanese study [not available, probably Taiwan/whole plants/(CH$_3$)$_2$CO] yielded **171**, **173**, **188**, **211**, and **301** and confirmed the occurrence of **181** (Khalil et al., 2005). A second Chinese study [China/whole plants/MeOH] confirmed the presence of **188** and additionally yielded **151**, **214**, **221**, **258**, and **291** (Zhang et al., 2006).

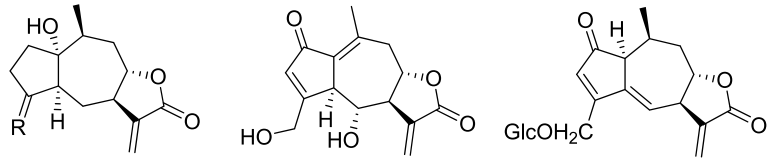
Ixeris debilis A.Gray [Japan/whole plants/MeOH, under reflux (!)] yielded 11 sesquiterpenoids: 10 costus lactone type guaianolides **138**, **148**, **155**, **174**, **177**, **179**, **180**, **181**, **186**, and **187** and one hieracin type guaianolide **235** (Warashina et al., 1990).

Ixeris dentata Nakai [Japan/whole plants/hot (!) H$_2$O (!)] yielded eudesmanolide ixerin W **28**, germacranolides **77** and **78** as well as the costus lactone type guaianolides **132**, **138**, **143**, **147**, **148**, **149**, **172**, and **174** (Seto et al., 1986). A second set of investigations on plants from Korean [Korea/whole plants/MeOH] origin yielded **162**, **192**, **208**, and **209** (Chung et al., 1994a,b). A further investigation of Korean plants [Korea/roots/MeOH:H$_2$O 4:1] yielded **133**, **137**, **164**, and **199** (Bang et al., 2004).

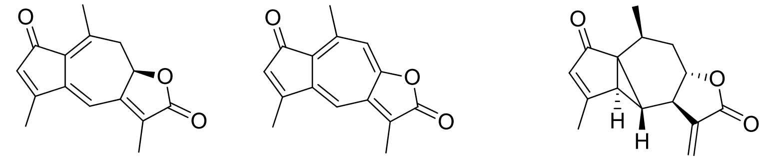
Ixeris denticulata (Houtt.) Nakai ex Stebbins is currently assigned to the genus *Youngia* and its phytochemistry is discussed under *Y. denticulata* (Houtt.) Kitam.

Ixeris polycephala Cass. yielded two norsesquiterpenoids containing 13 carbon atoms, which are neither sesquiterpene lactones nor immediate precursors to sesquiterpene lactones and are therefore omitted in the account at hand (Han et al., 2006).

Ixeris repens A.Gray [Japan/whole plants/MeOH, under reflux (!)] yielded a total of 20 sesquiterpenoids: 10 eudesmane derivatives **6**, **11**, **12**, **22**, **38**, **59**, **61**, **62**, **63**, and **71**, germacranolide **77**,

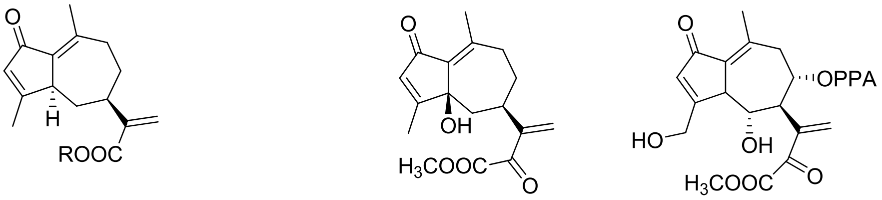


348: R = CH_2
349: R = αOH, βCH_3
350: intybulide
351: hypochoeroside I

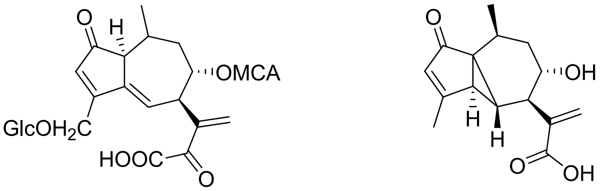


352: taraxacin
353
354

Fig. 29. *Group 29*: 12,8-Guaianolides.



355: R = H; isohypoglabric acid
356: R = CH_3; isohypoglabric acid methylester
357: methyl hypocretenoate
358: methyl lactucopicrinoate



359: hypochoeroside H
360

Fig. 30. *Group 30*: Guaianic acid derivatives.

and nine costus lactone type guaianolides **134**, **138**, **144**, **148**, **155**, **174**, **177**, **180**, and **200** (Warashina et al., 1990).

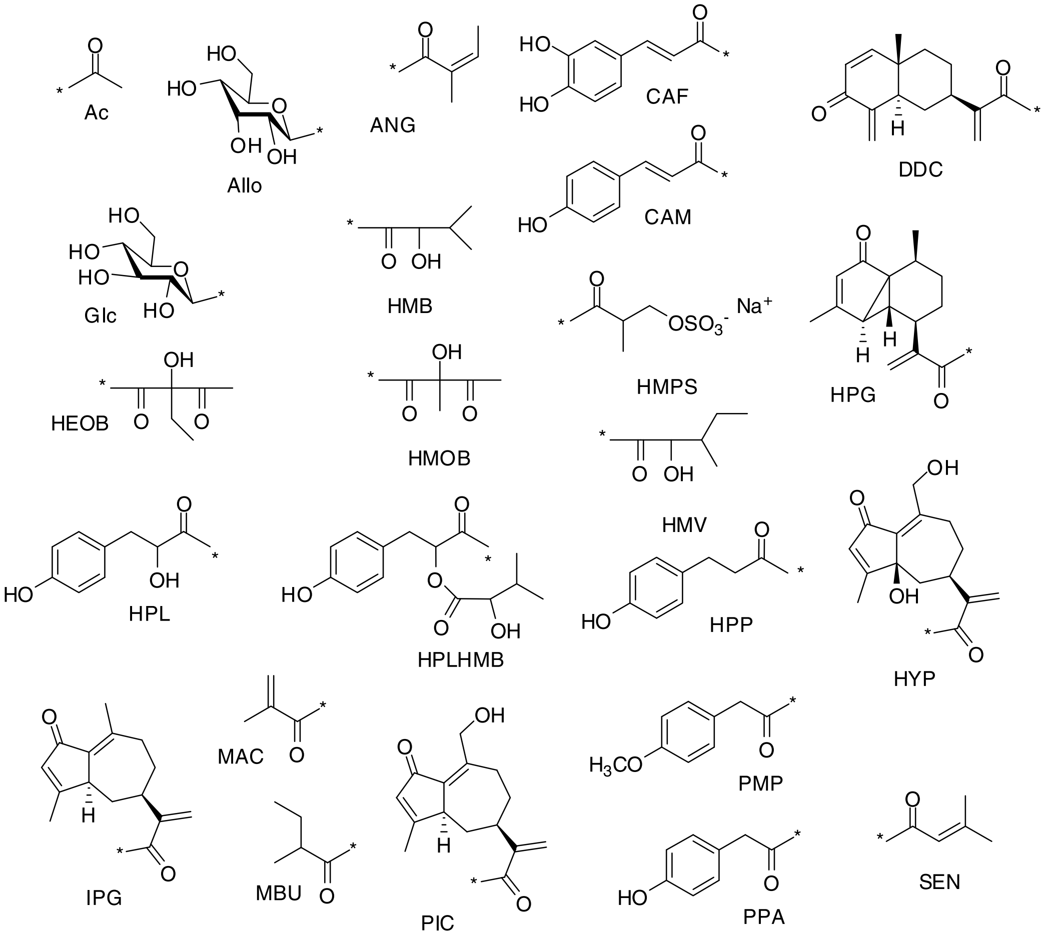
Ixeris sonchifolia Hance was studied by various research groups and yielded santamarin type eudesmanolides **35** and **38**, germacranolides **78** and **82**, the unusual germacranolide **116**, costus lactone type guaianolides **138**, **154**, **155**, and **174** and hieracin type guaianolides **238** and **253**, and six lactucin type guaianolides **293**, **330**, **331**, **332**, **333**, and **334** (Ma et al., 1998, 1999a; Feng et al., 1999, 2001; Suh et al., 2002; Jo et al., 2005; Ye et al., 2005, 2007; He et al., 2006; Na et al., 2007). In detail, commercially available plants from China [China/whole plants/hot (!) EtOH] yielded **154**, **330**, and **333** (Ma et al., 1998, 1999a). Chinese plants [China/whole plants/unavailable] also yielded **331**, **332**, and **333** (Feng et al., 1999, 2001; He et al., 2006). Moreover, plants collected in China [China/whole plants/$(CH_3)_2CO$:H_2O 7:3] yielded **35**, **38**, **82**, **116**, **174**, and **333** (Ye et al., 2005, 2007). Korean plants [Korea/leaves/MeOH, under reflux (!)] yielded **253**, **330**, **332**, and **334** (Suh et al., 2002) as well as [Korea/roots/MeOH, under reflux (!)] **78**, **138**, and **155** (Jo et al., 2005). Korean plants [Korea/whole plants/MeOH and EtOAc] were also the source of **238**, **293**, **330**, and **334** (Na et al., 2007).

Ixeris stolonifera A.Gray [unavailable/whole plants/MeOH, under reflux (!)] yielded eight costus lactone type guaianolides **155**, **174**, **177**, **179**, **184**, **185**, **186**, and **187** as well as two hieracin type guaianolides **234** and **235** (Nishimura et al., 1985).

Ixeris tamagawaensis Kitam. [Japan/whole plants/MeOH, under reflux (!)] yielded germacranolides **78** and **79**, melampolides **93**, **94**, **95**, **96**, **97**, **98**, **99**, and **100**, and costus lactone type guaianolides **148**, **153**, and **159** (Asada et al., 1984a,b,c).

Lactuca (ca. 75 species) – *Lactuca floridana* Gaertn. [Germany, cultivated plants/roots/Et_2O:petrol 1:2] yielded lactucin type guaianolides **301**, **302**, **305**, and **317** (Bohlmann et al., 1981a). An investigation on North American plants [USA/roots/CH_2Cl_2] additionally yielded **291** and confirmed the occurrence of **305** and **317** (Song et al., 1995).

Lactuca indica L. (syn.: *Pterocypsela indica* (L.) C.Shih) from Taiwan [Taiwan/whole plants/$(CH_3)_2CO$:H_2O 7:3] yielded two



Abbreviations: Ac acetyl; Allo allosyl; ANG angeloyl; CAF caffeoyl; CAM cinnamoyl; DDC 1,2-didehydro-3-oxo-costoyl; Glc glucopyranosyl; HEOB 2-hydroxy-2-ethyl-3-oxo-butyryl; HMB 2-hydroxy-3-methylbutyryl; HMOB 2-hydroxy-2-methyl-3-oxo-butyryl; HMPS 3-hydroxy-2-methyl-propanoyl 3-sulfate; HMV α-hydroxy-β-methyl-n-valeroyl; HPG hypoglabroyl; HPL *p*-hydroxyphenyllactyl; HPLHMB *p*-hydroxyphenyllactyl-α-hydroxymethylbutyryl; HPP *p*-hydroxyphenylpropanoyl; HYP hypocretenoyl; IPG isohypoglabroyl; MAC methacryloyl; MBU 2-methylbutyryl; PIC picriosyl; PMP *para*-methoxyphenylacetic acid; PPA *para*-hydroxyphenylacetyl; SEN senecioyl.

Fig. 31. Explanation of abbreviations used in Figs. 1–30.

lactucin derivatives **316** and **321** and three dimeric lactucin derivatives **335**, **336**, and **337** (Hou et al., 2003). In a minor study, plant material of unknown but presumably Chinese origin [unavailable, probably China/unavailable, probably whole plants/EtOH:H_2O 7:3] and of undocumented (no reference to a voucher) and therefore non-confirmable identity yielded the eudesmanolide **42** (Fan et al., 2006).

Lactuca laciniata Roth [Japan/roots/H_2O] yielded eudesmanolide **35**, melampolides **109**, **110**, and **111**, costus lactone type guaianolides **138**, **143**, **154**, **155**, and **156**, and lactucin type guaianolides **313** and **316** (Nishimura et al., 1986b).

Lactuca perennis L. [Poland, cultivated plants/aerial parts/EtOH] yielded a melampolide **111**, two costus lactone type guaianolides **136** and **143**, and a lactucin derivative **298** (Kisiel and Zielińska, 2000).

Lactuca quercina L. [Poland, cultivated plants/roots/boiling (!) EtOH] yielded one germacranolide **77**, two melampolides **110** and **111**, five costus lactone type guaianolides **143**, **154**, **155**, **156**, and **159**, and five lactucin type guaianolides **291**, **297**, **301**, **316**, and **319** (Kisiel and Szneler, 1998).

Lactuca saligna L. [Egypt/aerial parts/EtOH] collected in Egypt yielded **301**, **305**, and **319** (Khalil et al., 1991). Cultivated plants from Poland [Poland, cultivated plants/roots/EtOH] yielded melampolide **111**, costus lactone type guaianolides **155**, **157**, and **159**, and lactucin type guaianolides **291**, **297**, and **298**; moreover, occurrence of **301**, **305**, and **319** was confirmed (Kisiel and Gromek, 1993a,b). In samples cultivated in the US [USA, cultivated plants; seed origin: Portugal/leaves/MeOH] **291**, **301**, and **305** were confirmed as the main sesquiterpene lactones of *L. saligna* (Tamaki et al., 1995).

Lactuca sativa L. infected with *Pseudomonas cichorii* yielded two phytoalexins (+)-costunolide and lettucenin A (Takasugi et al., 1985). Both have so far not been found in uninfected samples of *L. sativa* and are therefore not considered in the chemosystematic part of this article. Aerial parts of *L. sativa* from Egypt [Egypt/aerial parts/Et2O:petrol 1:2] yielded germacranolide **85**, melampolide **110**, and three lactucin derivatives **301**, **305**, and **316** (Mahmoud et al., 1986). Japanese plants [Japan/roots/hot (!) water] yielded melampolide **111**, costus lactone type guaianolide **155**, and lactucin derivative **278** (Ishihara et al., 1987). In addition to these compounds isolated in conventional studies, Sessa et al. (2000) [Great Britain, cultivated plants/latex/MeOH] found a number of sesquiterpenoid oxalates **296**, **303**, and **307** and sulfates **280** and **315** by direct HPLC-MS of latex obtained from *L. sativa*. These compounds are the main constituents in the latex of the living plant but decompose rapidly when subjected to standard phytochemical purification techniques. As already stated under *Cichorium intybus* the paper by Sessa et al. (2000) implies that these sulfate and oxalate sesquiterpenoids might be much more widespread in the plant kingdom than currently realized.

Lactuca serriola L. [Poland/roots/MeOH] yielded lactucin derivatives **291**, **297**, **301**, and **305** (Pyrek, 1977); as well as [Spain/aerial parts/MeOH] melampolide **111**, two further lactucin type guaianolides **275** and **316**, and sesquiterpenic acid ester **358** (Marco et al., 1992b). Moreover, the latter study confirmed the presence of the lactucin derivatives **291**, **297**, **301**, and **305** in plants collected in Spain.

Lactuca tatarica C.A.Mey. [USSR/aerial parts/unavailable] yielded **301** and **305** (Akyev et al., 1990). A detailed study on plants cultivated in Poland [Poland/roots/EtOH] yielded four germacranolides **77**, **81**, **83**, and **87**, three costus lactone type guaianolides **143**, **155**, and **159**, and five lactucin type guaianolides **297**, **298**, **301**, **320**, and **321** (Kisiel et al., 1997; Kisiel and Barszcz, 1998).

Chinese plants [China/whole plants/EtOH] yielded lactucin derivatives **301**, **305**, **316**, and **319** (Ren et al., 2005); moreover, plants of Chinese origin [China/whole plants/MeOH] yielded **74**, **84**, and **306** (Wang et al., 2006).

Lactuca virosa L. [Poland/whole plants/EtOH] yielded melampolide **111** and lactucin derivatives **291**, **297**, **301**, **305**, and **316** (Gromek, 1989, 1991). In samples cultivated in the US [USA, cultivated plants/leaves/MeOH] **291**, **301**, and **305** were confirmed to be the main sesquiterpenoids of *L. virosa* (Tamaki et al., 1995). A detailed investigation of minor constituents of the roots [Poland, cultivated plants/roots/EtOH] additionally yielded two germacranolides **77** and **86**, five costus lactone derivatives **143**, **154**, **155**, **156**, and **159**, and four lactucin type sesquiterpene lactones **298**, **319**, **321**, and **323** (Kisiel and Barszcz, 1997). In order not to distort chemosystematic evaluations of the data set, compounds only produced in tissue culture (Stojakowska et al., 1993, 1994, 1995, 1997, 1999; Kisiel et al., 1995; Malarz and Kisiel, 1999, 2000) are not included in this review.

Lapsana (ca. 10 species) – *Lapsana communis* L. [France/stem latex/$(CH_3)_2CO$] yielded three costus lactone type guaianolides **164**, **175**, and **180** and two hieracin type guaianolides **232** and **233** (Fontanel et al., 1999). This is a remarkably elegant study, only 670 mg of latex were the source of five compounds including three new compounds.

Launaea (ca. 50 species) – *Launaea mucronata* Muschl. [unavailable/roots/EtOH] yielded four lactucin type guaianolides **301**, **302**, **316**, and **317** (Sarg et al., 1982).

L. spinosa Sch.Bip. [Egypt/aerial parts/*n*-hexane:Et_2O:$CHCl_3$ 5:1:1] yielded lactucin type guaianolide **293** (Sokkar et al., 1993).

L. tenuiloba Muschl. [Egypt/aerial parts and roots/EtOH] yielded the lactucin type guaianolides **291**, **297**, and **301** (Salam et al., 1986).

Leontodon (ca. 25 species) – In this account the genus *Leontodon* encompasses only *Leontodon* subgenus Leontodon *sensu* Widder (1975). Thus, section Oporinia is, following Samuel et al. (2006), regarded as a separate genus, *Scorzoneroides*.

L. hispidus L. [Austria/whole plants/CH_2Cl_2] yielded hypocretenolides **119**, **120**, **121**, **122**, and **123** (Zidorn, 1998; Zidorn et al., 1998, 1999c; Zidorn and Stuppner, 2001).

L. rigens (Dryander in Aiton) Paiva et Ormonde [Austria, cultivated plants; origin of species: Azores; origin of seeds: Germany/roots/MeOH] yielded two 1,10-epoxyhypocretenolides **128** and **129** (Zidorn et al., 2005b).

L. rosani Fiori [Italy/roots/MeOH] yielded hypocretenolides **124**, **125**, **126**, and **127** (Zidorn et al., 2007b).

L. tuberosus L. [Italy/subaerial parts/MeOH] yielded the eudesmane derivative **69** (Spitaler et al., 2004).

Mulgedium (ca. 15 species) – The genus *Mulgedium* is lumped with *Lactuca* by both Greuter (2003) and Kilian et al. (2008). This approach is also followed here; data for *Mulgedium tartaricum* DC. are therefore to be found under *Lactuca tatarica* C.A.Mey.

Mycelis (1 species) – *Mycelis* is lumped with *Lactuca* s.l. by Greuter (2003) and with *Cicerbita* by Kilian et al. (2008). Due to this unclear situation, *Mycelis* is retained in generic rank here. *Mycelis muralis* Dumort. [Poland, cultivated plants/roots/EtOH] yielded melampolide **111**, costus lactone derivatives **138**, **142**, **154**, **156**, and **159**, and lactucin derivatives **291**, **297**, and **298** (Kisiel and Barszcz, 1995b).

Nabalus (ca. 15 species) – *Nabalus acerifolius* Maxim. (syn.: *Prenanthes acerifolia* Benth.) [Japan/whole plants/hot (!) H_2O] yielded six costus lactone type guaianolides **148**, **150**, **164**, **169**, **174**, and **213** and one hieracin type guaianolide **228** (Miyase et al., 1987).

Notoseris (12 species) – *Notoseris gracilipes* C.Shih [China/whole plants/unavailable] yielded melampolide **109**, costus lactone type guaianolides **134** and **136**, and lactucin derivatives **282**, **283**, **293**, **297**, and **298** (Ye et al., 2001c).

N. henryi (Dunn) C.Shih [China/whole plants/EtOH] yielded lactucin derivatives **282**, **283**, **288**, **293**, **297**, and **298** as well as notoserolide E **338**, which belongs to a new subclass of guaiane type sesquiterpenoids (Liao et al., 2002a).

N. porphyrolepis C.Shih [China/aerial parts/unavailable] yielded two eudesmanolides **48** and **50** and five lactucin type guaianolides **283**, **288**, **291**, **297**, and **298** (Xu et al., 2000).

N. psilolepis C.Shih [China/whole plants/MeOH] yielded melampolide **109**, costus lactone type guaianolide **136**, and lactucin derivatives **282**, **283**, **293**, **297**, **298**, and **322** (Ye et al., 2000, 2001b).

N. rhombiformis C.Shih [China/whole plants/unavailable] yielded melampolide **108** and lactucin derivatives **282**, **283**, **297**, and **329** (Liao et al., 2002b).

N. triflora (Hemsl.) C.Shih [China/whole plants/MeOH] yielded eudesmanolide **35**, germacranolide **83**, costus lactone type guaianolides **134** and **135**, hieracin type guaianolides **248**, **250**, **251**, and **252**, and lactucin derivatives **282**, **293**, **297**, **298**, **316**, and **321** (Ye et al., 2001a).

Picris (ca. 40 species) – *Picris altissima* Delile [Poland, cultivated plants/aerial parts/EtOH] yielded 12,6-guaianolides **130**, **147**, **152**, and **214** (Kisiel, 1992a).

P. cyanocarpa Boiss. [Egypt/aerial parts/Et_2O:petrol:MeOH 1:1:1] yielded lactucin type guaianolides **291**, **294**, and **297** (Hafez et al., 1988).

P. evae Lack [Poland, cultivated plants, seed origin: Germany, origin of species: Australia/aerial parts and roots/EtOH] yielded costus lactone type guaianolides **133**, **134**, **135**, **136**, **156**, **159**, **196**, and lactucin type guaianolide **297** (Kisiel and Zielińska, 2001b).

P. hieracioides L. s.str. [Poland, cultivated plants/aerial parts (**297**) and roots (**143**)/EtOH] yielded costus lactone type guaianolide **143** and lactucin type guaianolide **297** (Kisiel, 1992b).

Picris hieracioides L. var. *japonica* Regel [Japan/whole plants/MeOH, under reflux (!)] yielded two germacranolides **77** and **81**, two costus lactone type guaianolides **141** and **159**, and five lactucin derivatives **301**, **308**, **312**, **316**, and **325** (Nishimura et al., 1986a; Uchiyama et al., 1990). *Picris hieracioides* L. var. *japonica* Regel [Japan/flowers/MeOH] flowers additionally yielded two hieracin, derivatives **241** and **242** and two lactucin derivatives **291** and **297** (Kanayama and Tada, 1988).

P. kamtschatika Ledeb. [Poland, cultivated plants, seed origin: Russia/roots/EtOH], which is regarded as a variety of *P. hieracioides* by some authors, yielded germacranolide **77**, eight costus lactone type guaianolides **133**, **135**, **136**, **142**, **143**, **156**, **158**, and **159**, the unusual guaianolide **259**; aerial parts from the same plants [Poland, cultivated plants, seed origin: Russia/aerial parts/EtOH] yielded lactucin derivatives **291** and **297** (Kisiel and Michalska, 2002).

Picris koreana (Kitam.) Vorosch. [Poland, cultivated plants, seed origin: plants cultivated in Russia/roots/EtOH] yielded two eudesmanolides **34** and **48**, germacranolide **83**, four costus lactone derivatives **133**, **143**, **156**, and **159**, and four lactucin derivatives **274**, **275**, **282**, and **316** (Michalska et al., 2007).

P. pauciflora Willd. [Poland, cultivated plants/aerial parts/EtOH] yielded costus lactone type guaianolides **143** and **159** and lactucin derivative **316** (Kisiel, 1995b).

P. radicata Less. [Qatar/aerial parts/CH_2Cl_2:MeOH 1:1] yielded 12,8-guaianolides **348** and **349** (Al-Easa et al., 1996).

Prenanthes (ca. 30 species) – Species of *Prenanthes* s.l. have recently been scattered among a number of genera including a very narrow *Prenanthes* s.str., *Nabalus*, and *Notoseris* (Kilian et al., 2008). This treatment is followed here and records for *P. acerifolia* Matsum. are accordingly listed under *Nabalus acerifolius* Maxim. *Prenanthes* s.str., which is probably monotypic and solely comprises *P. purpurea* L., has yielded no sesquiterpene lactones so far.

Pterocypsela (11 species) – This genus is integrated into *Lactuca* s.l. by most authors including Kilian et al. (2008). This approach is followed here and data for *Pterocypsela indica* (L.) C.Shih are listed under *Lactuca indica* L.

Reichardia (8 species) – *Reichardia crystallina* (Sch.Bip. ex Webb & Berthault) Bramwell (syn.: *Picridium crystallinum* Sch.Bip.) [Canary Islands/aerial parts/hot (!) EtOH] yielded picridin type guaianolides **222** and **223** and lactucin derivative **282** (Gonzaléz et al., 1974). The isolation procedure included the dissolution in hot EtOH and also the application of hot (!) aqueous solutions.

R. gaditana (Willk.) Coutinho [Spain/roots/MeOH] yielded lactucin derivative **292** (Zidorn et al., 2007c).

R. tingitana (L.) Roth [Poland, cultivated plants/aerial parts/CH_2Cl_2] yielded lactucin derivatives **279** and **282** (Daniewski et al., 1989). *R. tingitana* (L.) Roth var. *orientalis* (L.) Asch. & Schweinf. [Egypt/roots (**301**) and aerial parts (**279**)/EtOH] yielded lactucin derivatives **279** and **301** (El-Masry et al., 1980). Furthermore, this taxon [Egypt/whole plants/petrol:Et_2O:MeOH 1:1:1] yielded lactucin derivatives **281**, **282**, and **314**. The compound designated as **314** is most probably identical with **305** according to the text of the references and therefore as such in the chemosystematic data evaluation part of this review (Abdel-Mogib et al., 1993).

Scorzonera (ca. 175 species) – *Scorzonera austriaca* Willd. [not available, probably China/roots/$(CH_3)_2CO$] yielded costus lactone type guaianolide **203** (Li et al., 2004).

S. hispanica L. [Belgium, cultivated plants/subaerial parts/MeOH] yielded two costus lactone type guaianolides **134** and **170** (Zidorn et al., 2000a). The costus lactone derivative scorzoside **136** was first isolated from tissue cultures of *S. hispanica* (Bryanskii et al., 1992). However, it was never reported from "normal plants" of *S. hispanica*, and therefore the occurrence of scorzoside in *S. hispanica* is not used in the section devoted to the chemosystematic analysis of data.

Scorzonera pseudodivaricata Lipsch. [Mongolia/aerial parts/MeOH] yielded lactucin type guaianolide **287** (Tsevegsuren et al., 2007).

Scorzoneroides (ca. 25 species) – The circumscription of the genus *Scorzoneroides* is identical with that of subgenus Oporinia of genus *Leontodon*. Based on molecular evidence this taxon was reinstated as a separate genus (Samuel et al., 2006). For priority reasons the correct name at the generic level for this taxon is *Scorzoneroides* (Samuel et al., 2006). The necessary new combinations were published by Greuter et al. (2006). In the following paragraph we follow the nomenclature provided by these authors, which however differs in all cases from the old nomenclature used by the authors of the corresponding phytochemical papers. Therefore, the nomenclature given in the original articles is indicated in brackets.

Scorzoneroides autumnalis (L.) Moench (syn.: *Leontodon autumnalis* L.) [Poland/flowers and whole plants/CH_2Cl_2:MeOH] yielded lactucin derivatives **291** and **297** (Pyrek, 1985). A second investigation of subaerial parts [Austria, Belgium, France, Germany, Romania, and Switzerland/subaerial parts/MeOH] yielded hieracin derivatives **243**, **244**, **245**, and **255** and lactucin derivatives **293** and **298** (Zidorn et al., 2000b).

S. cichoracea (Ten.) Greuter (syn.: *L. cichoraceus* Boiss.) [Italy/subaerial parts/MeOH] yielded germacrane derivative **80** and costus lactone type guaianolide **138** (Zidorn et al., 2001a,b).

S. muelleri (Sch.Bip.) Greuter & Talavera [syn.: *L. muelleri* (Sch.Bip.) Fiori] – not *S. palisiae* (Izuzquiza) Greuter & Talavera (*L. palisiae* Izuzquiza) [Spain/whole plants/MeOH] as erroneously stated in the original publication – yielded costus lactone type guaianolides **145**, **146**, **147**, and **181** and lactucin derivative **291** (Zidorn et al., 2004, 2007a).

A comparative HPLC investigation revealed that guaianolides isolated from *S. autumnalis* also occur in a number of other representatives of the genus *Scorzoneroides*: *S. crocea* (Haenke) Holub (syn.: *L. croceus* Haenke) [Austria and Romania/subaerial parts/MeOH] contained **243**, **244**, **245**, **293**, and **298**; *S. duboisii* (Greuter) Sennen (syn.: *L. duboisii* Sennen ex Widder) [Spain/subaerial parts/MeOH] **243**, **244**, **245**, **255**, **293**, and **298**; *S. helvetica* (Mérat) Holub (syn.: *L. helveticus* Mérat emend. Widder) [Austria and Italy/subaerial parts/MeOH] **243**, **244**, **245**, **255**, **293**, and **298**; *S. montana* (Lam.) Holub (syn.: *L. montanus* Lam.) [Austria and Switzerland/subaerial parts/MeOH] **293** and **298**; *S. montaniformis* (Widder) Gutermann (syn.: *L. montaniformis* Widder) [Austria/subaerial parts/MeOH] **293** and **298**; *S. pyrenaica* (Gouan) Holub (syn.: *L. pyrenaicus* Gouan) [Spain/subaerial parts/MeOH] **243**, **244**, **245**, **255**, **293**, and **298**; and *S. rilaensis* (Hayek) Holub (syn.: *L. rilaensis* Hayek) [Romania/subaerial parts/MeOH] **243**, **244**, **245**, **255**, **293**, and **298** (Zidorn et al., 2000b).

Sonchus (ca. 60 species) – *Sonchus asper* (L.) Hill [Pakistan/whole plants/MeOH, under reflux (!)] from Pakistan yielded eudesmanolides **4**, **10**, **14**, **15**, **18**, and **20** (Shimizu et al., 1989). Interestingly the same species collected in Egypt [Egypt/roots/MeOH] yielded a totally different set of secondary metabolites: melampolides **102**, **104**, **105**, **106**, and **112** (Helal et al., 2000). Within the Cichorieae, compounds of this type had so far been only reported from the genus *Urospermum*.

Sonchus hierrensis (Pit.) Boulos [Canary Islands/tubers/$CHCl_3$] yielded eudesmanolide **35** and lactucin derivative **297** (Bermejo Barrera et al., 1968b).

Sonchus jacquinii DC. [Canary Islands/stems/$CHCl_3$] was the first source of and gave the name to the lactucin derivative jacquinelin **297** (Bermejo Barrera et al., 1966).

Sonchus macrocarpus Boulos & C.Jeffrey [Egypt/aerial parts/Et_2O:petrol 2:1] yielded six reynosin type eudesmanolides **7**, **8**, **9**, **13**, **17**, and **19** and the precursor compound **60** (Mahmoud et al., 1983, 1984). Moreover, Mahmoud et al. (1984) reported two cichopumilide type guaianolides from *S. macrocarpus*. However, their structures have to be revised as the structure of compounds isolated by the same group from *Cichorium pumilum* Jacq. were revised to the magnolialide type eudesmanolides **48** and **50** (Park et al., 2000; Kisiel and Zielińska, 2003).

Sonchus nymani Tineo & Guss. [Jordan/herb/EtOH] yielded eudesmanolides **13** and **16** (Mahmoud and Al-Kofahi, 1992).

Sonchus oleraceus L. [unavailable, probably Japan/whole plants/MeOH, under reflux (!)] yielded eudesmanolides **4** and **47**, germacranolides **77**, **81**, **83**, and **88**, costus lactone type guaianolides **138** and **155**, and lactucin derivative **292** (Miyase and Fukushima, 1987). Aerial parts of Egyptian plants [Egypt/aerial parts/$(CH_3)_2CO$] yielded eudesmanolide **9** and hieracin type guaianolide **239** (El-Seedi, 2003).

Sonchus pinnatus Ait. [Canary Islands/stems/$CHCl_3$] yielded lactucin derivative **297** (Bermejo Barrera et al., 1966).

Sonchus radicatus Ait. [Canary Islands/stems/$CHCl_3$] yielded lactucin derivative **297** (Bermejo Barrera et al., 1966).

Sonchus transcaspicus Nevski [China/whole plants/MeOH] yielded santamarin type eudesmanolides **36**, **40**, **41**, and **43** (Han et al., 2005a,b).

Sonchus tuberifer Svent. [unavailable, probably Canary Islands/roots/unavailable] yielded and gave the name to eudesmanolide tuberiferine **32** (Bermejo Barrera et al., 1967, 1968a).

Sonchus uliginosus M.Bieb. [China/whole plants/MeOH] yielded santamarin type eudesmanolides **37**, **39**, **40**, **43**, and **44** (Zhang et al., 2006).

Soroseris (8 species) – *Soroseris hookeriana* Stebbins subsp. *erysimoides* (Hand.-Mazz.) Stebbins [China/aerial parts/petroleum:Et_2O:MeOH 1:1:1] yielded six costus lactone type guaianolides **138**, **147**, **172**, **174**, **191**, and **208** (Meng et al., 2000).

Taeckholmia (8 species) – Four species of the genus *Taeckholmia*, which some authors tend to (re-)unite with the genus *Sonchus* (Greuter, 2003; Kilian et al., 2008), have been investigated for the occurrence of sesquiterpene lactones. In contrast to the predominant occurrence of eudesmanolides in *Sonchus*, only costus lactone type guaianolides have been found in *Taeckholmia*. *T. arborea* (DC.) Boulos [Canary Islands/aerial parts/EtOH] yielded **147**, **163**, and **171**; *T. capillaris* (Svent.) Boulos [Canary Islands/aerial parts/EtOH] yielded **147** and **163**; *T. microcarpa* Boulos [Canary Islands/aerial parts/EtOH] yielded **147**, **163**, and **171**; and *T. pinnata* (L.fil.) Boulos [Canary Islands/aerial parts/EtOH] yielded **147**, **163**, and **171** (Gonzaléz et al., 1985).

Taraxacum (60 to ≫500 species, depending on the species concept) – *Taraxacum alpinum* (Hoppe) Hegetschw. [Poland, cultivated plants, seed origin: plants cultivated in Romania/roots/EtOH] yielded germacranolide **83**, costus lactone type guaianolides **133** and **135**, and lactucin derivatives **276**, **282**, **283**, **284**, and **285** (Michalska and Kisiel, 2007b).

Taraxacum bessarabicum (Hornem.) Hand.-Mazz. [Poland, cultivated plants, seed origin: Russia/roots/EtOH] yielded germacranolides **83** and **91**, costus lactone type guaianolides **133**, **135**, and **148**, hieracin derivative **240**, and lactucin derivatives **282**, **283**, and **286** (Kisiel and Michalska, 2006).

Taraxacum bicorne Dahlst. [Poland, cultivated plants/roots/EtOH] yielded germacranolides **75** and **76**, ainslioside type germacranolide **117**, and costus lactone type guaianolide **138** (Michalska and Kisiel, 2001).

Taraxacum formosanum Kitam. [Taiwan, commercially obtained/roots/MeOH, under reflux (!)] yielded lactucin derivative **290** (Leu et al., 2005).

Taraxacum hallaisanense Nakai [Korea/roots/hot (!) MeOH] yielded reynosin type eudesmanolides **24**, **25**, and **26** (Yang et al., 1996).

Taraxacum hondoense Nakai ex Koidz. [Poland, cultivated plants, seed origin: Japan/roots/EtOH] yielded germacranolides **75**, **76**, **77**, and **83**, ainslioside type germacranolide **117**, costus lactone type guaianolides **138** and **143**, and lactucin derivatives **276**, **282**, **283**, and **289** (Kisiel and Michalska, 2005).

Taraxacum linearisquameum Soest [Austria/subaerial parts/MeOH] yielded reynosin type eudesmanolide **24**, santamarin type eudesmanolide **45**, and germacranolide **75** (Zidorn et al., 1999a).

Taraxacum mongolicum Hand.-Mazz. is extensively used as a medicinal plant in China. On September 13, 2007 the search phrase *Taraxacum mongolicum* yielded 612 hits in the SciFinder database. However, only in one review written in Chinese sesquiterpene lactones are mentioned and the English summary of this review provides no clues, which sesquiterpene lactones were reported from *T. mongolicum* (Meng and Xu, 1997).

Taraxacum obovatum DC. [Poland, cultivated plants, seed origin: Sicily/roots/EtOH] yielded germacranolides **75**, **76**, and **83** and lactucin derivatives **276**, **282**, and **283** (Michalska and Kisiel, 2003).

Taraxacum officinale agg. (currently usually correctly named *Taraxacum* sectio Ruderalia, however not yet so in the Pharmacopoeias and in the phytochemical literature) [unavailable, commercially obtained/roots/MeOH:H_2O 4:1] yielded eudesmanolides **25** and **27** and germacranolides **75** and **76** (Hänsel et al., 1980). *Taraxacum officinale* [Poland/roots/EtOH] also yielded germacranolides **75** and **76**; additionally ainslioside **117**, costus lactone type guaianolide **148**, and lactucin derivative **316** were isolated (Kisiel and Barszcz, 2000). A bioactivity guided fractionation confirmed the presence of **75** and **76** in *T. officinale* roots [unavailable/roots/MeOH] (Kashiwada et al., 2001).

Taraxacum platycarpum Dahlst. [Korea/whole herb/MeOH, under reflux (!)] yielded lactucin derivative **282** (Ho et al., 1998).

Taraxacum rubicundum (Dahlst.) Dahlst. [Poland, cultivated plants, seed origin: France/roots/EtOH] yielded germacranolides **75** and **76** (Michalska and Kisiel, 2005).

Taraxacum wallichii DC. [Pakistan/whole plants/MeOH] yielded 12,8-guaianolides **352** and **353** (Ahmad et al., 2000).

Urospermum (2 species) – *Urospermum dalechampii* (L.) F.W.Schmidt [Spain/aerial parts/MeOH] yielded melampolides **101**, **104**, and **105** and guaianolide zaluzanin C **137** (Marco et al., 1994). In this study, the isolation procedure included re-suspension of the extract in hot MeOH. Roots of *Urospermum dalechampii* (L.) F.W.Schmidt [unavailable/roots/Et_2O and $(CH_3)_2CO$] were the first source of urospermal A **101** (Bentley et al., 1970); **101** and **105** were also reported from aerial parts [unavailable/aerial parts/unavailable] by Rychlewska et al. (1986).

U. picroides (L.) F.W.Schmidt is also characterized by the occurrence of melampolides: **101**, **102**, **103**, **104**, **105**, **107**, **113**, **114**, and **115** (Salam et al., 1982; Amer et al., 1984; Marco et al., 1994; Balboul et al., 1997). Moreover, compounds **106** and **112** ascribed to *Sonchus asper* by Helal et al. (2000) may also have to be regarded as natural products of *U. picroides*.

In detail, aerial parts from plants of unspecified origin [unavailable/aerial parts/EtOH] yielded **101** and **104** (Salam et al., 1982); roots from the same accession [unavailable/roots/MeOH] yielded **102** and **104** (Amer et al., 1984). Aerial parts collected in Spain [Spain/aerial parts/MeOH] yielded melampolides **101**, **102**, **104**, and **105** (Marco et al., 1994). The latter study also included re-suspension of the extract in hot (!) MeOH. Whole plants collected in Egypt [Egypt/whole plants/$CHCl_3$:MeOH 1:1] yielded in addition to known melampolides **101**, **102**, **104**, and **105** five new melampolide derivatives: **103**, **107**, **113**, **114**, and **115** (Balboul et al., 1997).

Warionia (monotypic) – *Warionia saharae* Benth. & Coss. [Morocco/leaves/CH_2Cl_2] yielded eudesmanolides **3** and **58**, hypochaerin type guaianolides **225** and **226**, hieracin derivative **236**, lactucin derivative **274**, and a number of unique epoxyguaianolides **339**, **340**, **341**, **342**, **343**, **344**, **345**, **346**, and **347** (Hilmi et al., 2002, 2003a,b).

Willemetia (2 species) – *Willemetia stipitata* (Jacq.) Dalla Torre [Austria/subaerial parts/CH_2Cl_2], also known as *Calycocorsus stipitatus* (Jacq.) Rauschert (Kirschnerová and Kirschner, 1996), yielded costus lactone type guaianolide **182** (Zidorn et al., 1999b).

Youngia (ca. 40 species) – *Y. denticulata* (Houtt.) Kitam. [Japan/whole plants/MeOH, under reflux (!)] yielded germacranolide **81** and lactucin derivatives **260**, **261**, **262**, **263**, and **293** (Adegawa et al., 1986). Moreover, *Y. denticulata* [as *Ixeris denticulata* (Houtt.) Nakai ex Stebbins] [China/whole plants/hot (!) H_2O] yielded lactucin type guaianolides **266** and **273** (Ma et al., 1999a,b).

Y. japonica (L.) DC. [syn.: *Crepis japonica* (L.) Benth.] yielded in a number of studies eudesmanolide **56**, costus lactone type guaianolides **137**, **138**, **139**, **140**, **141**, **164**, **165**, **166**, **167**, **183**, **197**, **212**, **216**, **217**, and **218**, and hieracin derivatives **229**, **230**, and **231** (Miyase et al., 1985; Jang et al., 2000; Chen et al., 2006). In detail, *Y. japonica* of unknown origin [probably Japan/whole plants/MeOH, under reflux (!)] yielded **138**, **140**, **141**, **164**, **165**, **167**, **183**, **229**, **230**, and **231** (Miyase et al., 1985). Whole plants from Korea [Korea/whole plants/MeOH] yielded **197** and **218** (Jang et al., 2000). Chinese plant material [China/whole plants/EtOH] yielded nine sesquiterpenoids **56**, **137**, **138**, **139**, **165**, **166**, **212**, **216**, and **217** (Chen et al., 2006).

Y. koidzumiana Kitam. [Korea/whole plants/MeOH] yielded costus lactone type guaianolide **131** and lactucin derivatives **266** and **270** (Dat et al., 2002, 2005).

3. Chemosystematic analysis of the literature data on sesquiterpenoids

3.1. General trends in the summarized phytochemical data

As discussed elsewhere (Zidorn, 2006), one of the main problems in interpreting phytochemical data is that most compounds reported in the literature are new compounds and that known compounds isolated from new sources are often not reported at all. In the case of the Cichorieae there are a total of 838 chemosystematic reports (compound/taxon) for 360 different compounds found in 139 different source taxa.

A chemosystematic report is defined here as the report of one particular compound for one particular species. Thus, if the same compound is reported from two different species in the same genus, these are two chemosystematic reports. On the other hand, if four compounds are reported from one species, this is to be considered as four chemosystematic reports.

The histogram in Fig. 32 displays the distribution of the 360 sesquiterpene lactones and precursors covered in this review among frequency classes of the numbers of sources for these compounds. Each compound has been found on average in 2.3 different taxa of the Cichorieae. The compound most frequently reported is the lactucin derivative jacquinelin **297**, which has been reported from 27 different sources. It is evident that most compounds were reported only once and that there are many more compounds with few reported sources than compounds with many reported sources. As new compound reports are easier to publish than new source reports of known compounds, this distribution might to some extent be an artifact.

Fig. 33 shows a histogram which groups the analyzed species according to the number of isolated sesquiterpenoids. There are many species with only one reported sesquiterpenoid. The average of reported sesquiterpenoids per investigated taxon is 6.0 and the median is 4. The maximum is 24 sesquiterpenoids reported for *Hypochaeris radicata*. Again the observed distribution pattern among frequency classes might to some extent be an artifact as the invested man power, time, and expenses disproportionately increase when minor compounds are encompassed in isolation and structure elucidation attempts.

Though predictions are hard to make, it is to be expected that the distributions of reports per compound and number of compounds reported per species found in the Cichorieae are in accordance with universal trends, which will also be found in other systematic groups and for other compound classes. Trend 1: There are many rare and only few ubiquitous plant secondary metabolites. Trend 2: There are many species with only a few reported secondary metabolites. In fact for the majority of taxa from the Cichorieae and from the plant kingdom in general so far no secondary metabolites have been reported at all. There are only a few well-investigated species with a large number of reported secondary metabolites. All higher plant species so far investigated in detail contain numerous plant secondary metabolites and it is currently unknown how many compounds on average each taxon of higher plants contains.

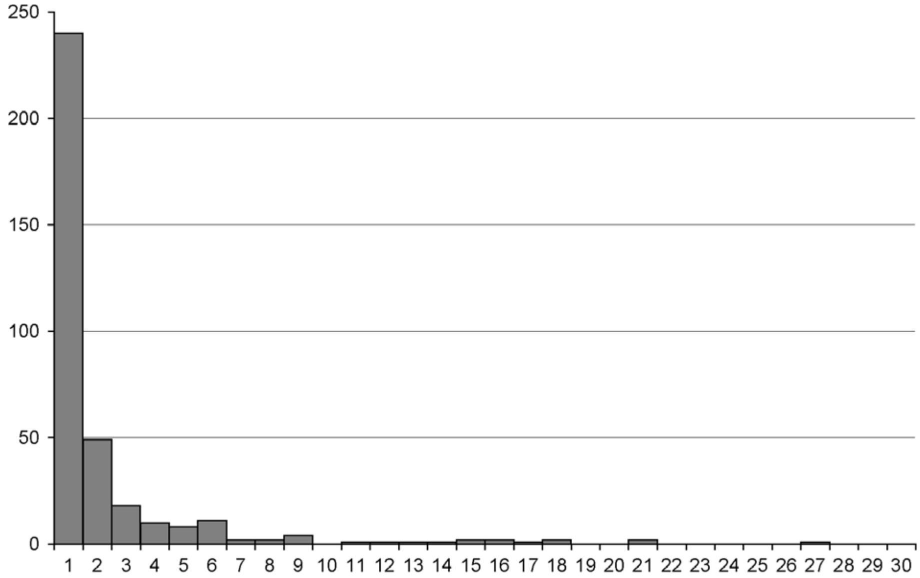


Fig. 32. Number of reports per sesquiterpenoid (*n* = 359, compounds **1**–**360**, except **314**).

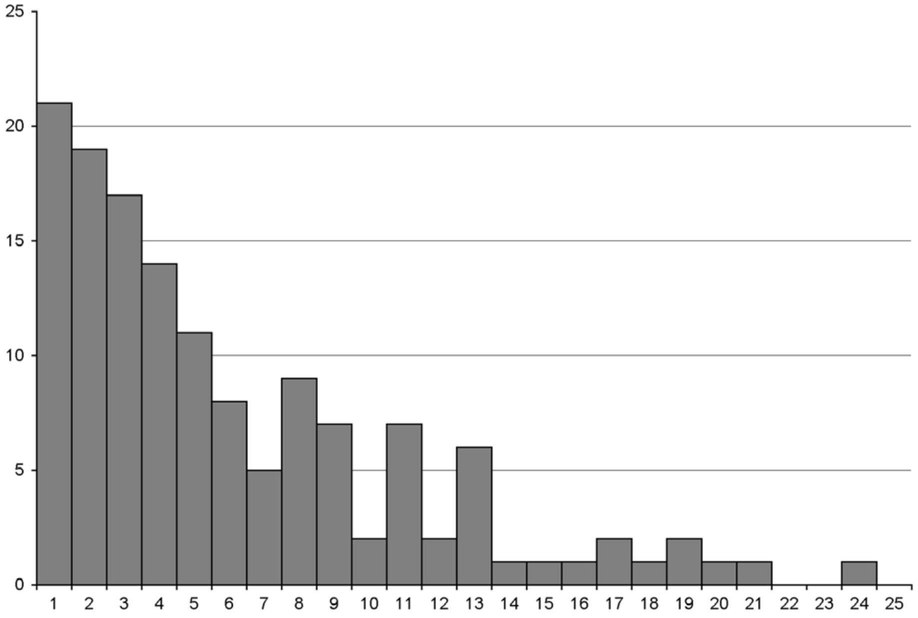


Fig. 33. Number of reported sesquiterpenoids per taxon ($n = 139$).

3.2. Distribution of sesquiterpenoid subtypes in the genera of the Cichorieae

Table 2 gives an overview about the total number of sesquiterpenoid reports (reported sesquiterpenoids per species) per genus and the relative share of the 30 sesquiterpenoid classes contributing to this number. Generic comparisons of the data compiled in Table 2 are hard to perform because of the vastly varying numbers of chemosystematic reports per genus. Chemosystematic reports for each genus range from 1 for *Chondrilla* and *Willemetia* to more than 100 for *Ixeris* ($n = 106$) and *Lactuca* ($n = 105$). However, apart from these differences, which distort the figures given in Table 2, the following conclusions can be drawn:

Guaianolides are the prevalent group of sesquiterpenoids in the Cichorieae (76.6% of all chemosystematic reports). Many compounds are substituted with glucose moieties (177 compounds/49.2% of all sesquiterpenoids). Another common feature in Cichorieae sesquiterpenoids is the substitution of hydroxy groups with carbonic acids, mainly acetic acid and various aromatic acids like hydroxyphenylacetic acid, caffeic acid, and hydroxphenyllactic acid.

The most important subgroups of sesquiterpenoids within the Cichorieae are costus lactone type guaianolides (G19) and lactucin derivatives (G25). These compound classes contribute the major share of all chemosystematic reports (34.2% and 29.2%, respectively) and they also contribute large numbers to the total of 360 different sesquiterpene lactones and precursors reported in the Cichorieae up to the present day (92 and 75 different compounds, respectively).

A well-established approach to analyze phytochemical data is to perform a hierarchical cluster analysis (Zidorn, 2006, 2008). The dendrogram resulting from such a hierarchical cluster analysis employing the Minitab 13.31 software package and using Euclidean distance and average linkage is depicted in Fig. 34. The 31 genera from which sesquiterpene lactones have been reported are grouped, based on the similarity of their sesquiterpenoid profiles, into seven main clusters, each with a similarity index of at least 50% (Fig. 34). These seven groups and their characteristics are discussed in the following paragraphs.

Group I comprises the genera *Andryala*, *Chondrilla*, *Soroseris*, *Taeckholmia*, *Willemetia*, *Crepis*, *Nabalus*, *Ixeris*, *Mycelis*, *Picris*, *Youngia*, *Scorzonera*, and *Lapsana.* Within this large cluster the genera *Andryala*, *Chondrilla*, *Soroseris*, *Taeckholmia*, and *Willemetia* have an identical sesquiterpenoid pattern (i.e. they contain only costus lactone type guaianolides). Moreover, *Crepis* and *Nabalus* have secondary metabolite patterns similar to these five genera, while the genera *Ixeris*, *Mycelis*, *Picris*, *Youngia*, and *Scorzonera* form another subgroup within the first cluster. *Lapsana* on the other hand is most dissimilar from the other genera within group 1. Group 1 is characterized by the prevalence of guaianolides, mainly of the costus lactone type.

Group II comprises the genera *Scorzoneroides*, *Notoseris*, *Lactuca*, *Cichorium*, *Launaea*, *Crepidiastrum*, *Reichardia*, *Cicerbita*, *Taraxacum*, *Helminthotheca*, and *Hypochaeris.* The cluster can be sub-divided into four subgroups: (a) *Scorzoneroides*; (b) *Notoseris*, *Lactuca*, and *Cichorium*; (c) *Launaea*, *Crepidiastrum*, *Reichardia*, and *Cicerbita*; and (d) *Taraxacum*, *Helminthotheca*, and *Hypochaeris*. Group 2 is also characterized by the prevalence of guaianolides. In contrast to group 1 most genera contain predominantly lactucin type compounds.

Group III only comprises the genus *Warionia*. *Warionia* is so far the only genus of the Cichorieae, which has yielded epoxyguaian-12,5-olides. These compounds also contribute the major share of all sesquiterpenoids found in *Warionia* so far.

Group IV comprises the genera *Dendroseris* and *Sonchus*. *Dendroseris* and *Sonchus* are both characterized by the fact that reynosin type eudesmanolides contribute a major share of the chemosystematic data. However, in *Dendroseris* this pattern is based only on two reported sesquiterpenoids.

Group V only comprises the genus *Hieracium*. *Hieracium* is characterized by the prevalence of eudesmanolides of the tuberiferine type and their non-lactonized precursor acids.

Group VI comprises the genera *Hedypnois* and *Leontodon* s.str. *Hedypnois* and *Leontodon* s.str. are characterized by the dominance of guaianolides of the hypocretenolide type.

Group VII only comprises the genus *Urospermum*. *Urospermum* is characterized by two characteristic groups of melampolides which are rarely found outside the genus *Urospermum*.

The groupings discussed above are based solely on the phenetic similarity of the sesquiterpenoid patterns (as far as they are known today) of the genera for which reports on sesquiterpenoids are available. Groupings are not or only partially in accord with

Table 2
Relative contributions (%) of different compound classes and sub-classes to the total number of sesquiterpenoids for each genus

Genus	n	Eudes	Germa	Guaia	G01	G02	G03	G04	G05	G06	G07	G08	G09	G10	G11	G12	G13	G14	G15	G16	G17	G18	G19	G20	G21	G22	G23	G24	G25	G26	G27	G28	G29	G30
Andryala	11	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chondrilla	1	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cicerbita	6	0.0	16.7	83.3	0.0	0.0	0.0	0.0	0.0	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	0.0	0.0	0.0	0.0	0.0	83.3	0.0	0.0	0.0	0.0	0.0
Cichorium	38	23.7	2.6	73.7	0.0	2.6	0.0	2.6	18.4	0.0	0.0	0.0	0.0	0.0	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0	2.6	2.6	0.0	2.6	0.0	0.0	60.5	0.0	0.0	0.0	2.6	2.6
Crepidiastrum	16	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.3	0.0	0.0	93.8	0.0	0.0	0.0	0.0	0.0
Crepis	95	3.2	4.2	92.6	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	4.2	0.0	0.0	0.0	0.0	0.0	3.2	88.4	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0
Dendroseris	2	50.0	0.0	50.0	0.0	50.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	50.0	0.0	0.0	0.0	0.0	0.0
Hedypnois	4	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Helminthotheca	12	33.3	16.7	50.0	0.0	8.3	0.0	8.3	8.3	8.3	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	0.0	0.0	16.7	0.0	0.0	33.3	0.0	0.0	0.0	0.0	0.0
Hieracium	11	81.8	9.1	9.1	0.0	0.0	45.5	0.0	0.0	0.0	0.0	36.4	0.0	0.0	0.0	0.0	9.1	0.0	0.0	0.0	0.0	0.0	9.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hypochaeris	41	14.6	9.8	75.6	0.0	0.0	0.0	0.0	2.4	2.4	7.3	0.0	2.4	0.0	0.0	9.8	0.0	0.0	0.0	0.0	0.0	2.4	4.9	0.0	2.4	19.5	0.0	0.0	29.3	0.0	0.0	0.0	4.9	12.2
Ixeris	106	12.3	15.1	72.6	0.0	3.8	0.9	2.8	0.0	0.0	3.8	0.0	0.9	0.0	0.0	6.6	0.0	7.5	0.0	0.9	0.0	0.0	58.5	0.0	0.0	4.7	1.9	0.0	7.5	0.0	0.0	0.0	0.0	0.0
Lactuca	105	1.9	20.0	78.1	0.0	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	1.0	8.6	0.0	10.5	0.0	0.0	0.0	0.0	22.9	0.0	0.0	0.0	0.0	0.0	51.4	2.9	0.0	0.0	0.0	1.0
Lapsana	5	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.0	0.0	0.0	40.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Launaea	8	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0
Leontodon	12	8.3	0.0	91.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	91.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mycelis	9	0.0	11.1	88.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.1	0.0	0.0	0.0	0.0	55.6	0.0	0.0	0.0	0.0	0.0	33.3	0.0	0.0	0.0	0.0	0.0
Nabalus	7	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	85.7	0.0	0.0	14.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Notoseris	49	6.1	8.2	85.7	0.0	0.0	0.0	2.0	4.1	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	6.1	0.0	0.0	0.0	0.0	10.2	0.0	0.0	8.2	0.0	0.0	65.3	0.0	2.0	0.0	0.0	0.0
Picris	58	3.4	6.9	89.7	0.0	0.0	0.0	1.7	1.7	0.0	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0	0.0	0.0	0.0	0.0	48.3	0.0	0.0	3.4	0.0	1.7	32.8	0.0	0.0	0.0	3.4	0.0
Reichardia	9	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	22.2	0.0	0.0	0.0	0.0	77.8	0.0	0.0	0.0	0.0	0.0
Scorzonera	4	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	75.0	0.0	0.0	0.0	0.0	0.0	25.0	0.0	0.0	0.0	0.0	0.0
Scorzoneroides	48	0.0	2.1	97.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0	0.0	10.4	0.0	0.0	47.9	0.0	0.0	39.6	0.0	0.0	0.0	0.0	0.0
Sonchus	48	64.6	18.8	16.7	0.0	33.3	2.1	20.8	6.3	0.0	2.1	0.0	0.0	0.0	0.0	8.3	0.0	8.3	2.1	0.0	0.0	0.0	4.2	0.0	0.0	2.1	0.0	0.0	10.4	0.0	0.0	0.0	0.0	0.0
Soroseris	6	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Taeckholmia	11	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Taraxacum	57	12.3	35.1	52.6	0.0	10.5	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29.8	0.0	0.0	0.0	0.0	5.3	0.0	15.8	0.0	0.0	1.8	0.0	0.0	31.6	0.0	0.0	0.0	3.5	0.0
Urospermum	13	0.0	92.3	7.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	69.2	23.1	0.0	0.0	0.0	7.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Warionia	15	13.3	0.0	86.7	0.0	6.7	0.0	0.0	0.0	0.0	6.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	13.3	6.7	0.0	0.0	6.7	0.0	0.0	60.0	0.0	0.0
Willemetia	1	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Youngia	30	3.3	3.3	93.3	0.0	0.0	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.0	0.0	53.3	0.0	0.0	10.0	0.0	0.0	30.0	0.0	0.0	0.0	0.0	0.0
Total	838	11.2	12.2	76.6	0.2	3.6	0.8	2.4	1.8	0.2	1.2	0.6	0.2	0.1	0.1	6.7	0.1	4.3	0.5	0.1	0.4	2.3	34.2	0.4	0.4	6.6	0.2	0.1	29.2	0.4	0.1	1.1	0.8	0.8

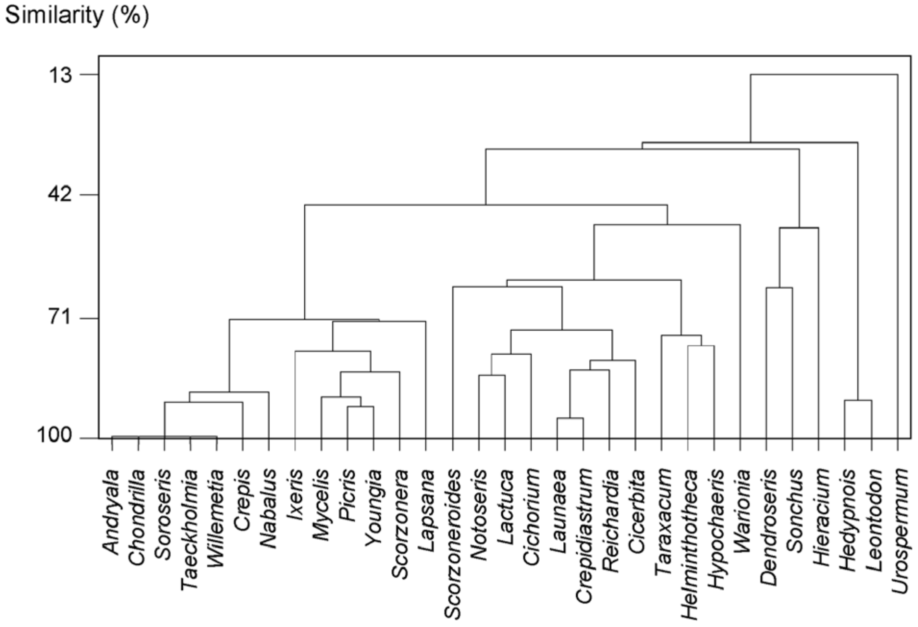


Fig. 34. Dendrogram resulting from a Hierarchical Cluster Analysis of the sesquiterpenoid data summarized in Table 2 (Average Linkage, Euclidean Distance, variables: percentages of main groups and groups).

relationships based on morphology and/or molecular methods. Comparison even with the clades of the highest order as defined by Kilian et al. (2008) are impossible as no sesquiterpene lactones are known from clade 3 (Scolyminae) and from clade 2 (Scorzonerinae) only *Scorzonera* yielded sesquiterpene lactones so far. Clade 1 (Warioniae) just encompasses *Warionia*; the larger clades 4 (Crepidinae, Chondrillinae, Hypochaeridinae, Hyoseridinae, and Lactucinae) and 5 (Cichoriinae, Microseridinae, and Hieraciinae) encompass 26 and three genera, respectively, from which sesquiterpene lactones have been reported. Thus, meaningful statistical comparisons are hampered by uneven data availability. The interested reader is referred to the original cladograms by Kilian et al. (2008); these are available online as Supplementary Figs. 1–3.

However, these phytochemical data are interesting in their own right as they might be used to phenetically define groupings that have emerged from molecular investigations. Moreover, some of the groupings are worth discussion in more detail. (a) *Hedypnois* and *Leontodon* s.str., though not very similar morphologically, are clustered together in recent molecular studies and they also share a very similar chemistry (Samuel et al., 2006). (b) *Dendroseris*, which was (re-)united with *Sonchus* by Kilian et al. (2008), also clusters with *Sonchus* based on chemical data. (c) In contrast, *Taeckholmia*, which was also reunited with *Sonchus* by Kilian et al. (2008), differs chemically from *Sonchus* s.str. (i.e. *Sonchus* excluding *Dendroseris* and *Taeckholmia*).

3.3. Problematic aspects of chemosystematic data in plant systematics

Poor and uneven coverage of taxa is one of the major obstacles for meaningful chemosystematic comparisons between taxa which have not been analyzed by the same research group within the same research project. Literature reports which contain chemosystematic data are often focused mainly on other aspects like bioactivity, pharmacology or biosynthesis. Therefore, pieces of chemosystematic information are scattered throughout the medical and scientific literature, while predominantly chemosystematic papers are rare. In contrast to other techniques used in systematic botany, the acquisition of chemosystematic data is rather expensive and time consuming. Moreover, chemosystematic research requires special expertise and equipment which is found in only few institutions predominantly focused on botanical research. On the other hand, institutions equipped with the necessary personnel and machinery are usually focused on other areas of research while chemosystematic data are merely by-products from other studies.

In addition to the problems highlighted above, comparative chemosystematic studies based on literature reports are hampered by the fact that formation of artifacts cannot be excluded in the case of some studies, either because of the chemical instability of the natural products found, e.g. peroxides, polyacetylenes, and esters, or because of the harsh methods used for natural product isolation, e.g. aqueous solvents and high temperatures.

Another important aspect covered elsewhere in more detail is the problematic coding of chemosystematic data (Zidorn, 2008). This problem is intricately related to the problem of detection limits of plant secondary metabolites (Waterman, 2007). A recent example is the detection of minute amounts of atropine in the genus *Lycium* (Adams et al., 2006).

Another point, which diminishes the impact of chemosystematic data on botanical systematics, is the prevailing ignorance among phytochemists regarding the importance of voucher specimens (Waterman, 2007). Missing or inaccessible vouchers make it impossible to verify the identity of the investigated plant material like e.g. in the case of *Urospermum* compounds in *Sonchus asper* (Helal et al., 2000) or in the recent report of taraxinic acid, so far restricted to the genus *Taraxacum*, from *Crepis* (Wu et al., 2002), a genus usually characterized by the occurrence of guaiane derivatives. On the other hand, well-preserved voucher specimens enable correct assignment or re-assignment of the taxon investigated, even in cases where initial determinations were erroneous (Zidorn et al., 2004, 2007a).

Infraspecific variation is another problem in the assessment of chemosystematic data and the extent of infraspecific phytochemical variation is generally unknown. Exceptions are plants varying in the composition of their volatile oils, in these cases infraspecific variations can usually be detected by the different smells of the particular chemotypes, or in medicinal plants, which are of pronounced commercial interest and have therefore been studied in more detail, e.g. *Uncaria tomentosa* (Mur et al., 2002).

Another obvious problem for comparative chemosystematic studies is the erroneous interpretation of spectral data and consequently the publication of wrong structural data. Examples for this kind of problem are the revised structures of various *Cichorium* sesquiterpenoids. More critical are however unnoticed mal-assignments. Candidates for such structures are compounds from group 23, chinensiolide C type compounds **257** and **258**. The structure assigned to these compounds, guaia-3-enolides, are similar to the original structure assignments for the cichoriopumilides from *Cichorium pumilum*. However, structures of the latter were later revised to more common magnolialide type eudesmanolides (Kisiel and Zielińska, 2001a, 2003). Accordingly presumed structures **257** and **258** might have to be revised to those of the corresponding eudesmanolides ludovicin C and dehydroerivanin, respectively (Miyashita et al., 1987).

4. Discussion

This review gives a summary of the sesquiterpenoids reported for the Cichorieae tribe of the Asteraceae. The provided classificatory key permits fast and unambiguous assignment of the amazing variety of sesquiterpenoids within this tribe. Moreover, the key will be helpful in future structure elucidation efforts of compounds either covered by this review or related to them. The main features of the classificatory key provided here are derived from classificatory keys used for plant determination (e.g. in Flora Europaea). Such keys might be helpful for the systematic classification of natural products.

The diversity of structures within the Cichorieae and their special features are highlighted. Though members of the Cichorieae contain a large number of different chemical compounds, the variation is based mainly on the substitution patterns of a few basic carbon skeletons. As in combinatorial chemistry the same or very similar building blocks (sesquiterpene lactone moieties, sugar moieties, phenolic acid moieties, sesquiterpenic acid moieties, acyl groups, etc.) are combined to produce the observed variety of natural products.

The present account also points out which genera have so far been neglected by phytochemists. Chemical variation within genera is usually smaller than chemical variation between genera. Investigations of unexplored genera are therefore more likely to yield new classes of compounds than investigations of additional representatives of genera, which have already been investigated to some extent.

Additionally, the present comprehensive review highlights possibilities and shortcomings of chemosystematic data in general. Overall bias towards describing new chemical compounds and unequal coverage of different genera by phytochemical reports make general predictions for the entire tribe Cichorieae impossible. These deficits can only be eliminated by concerted and systematic investigations of the genera omitted up to know. Most importantly, data acquired during such investigations have to be reported in freely accessible journals, regardless whether new compounds are discovered or not.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.phytochem.2008.06.013.

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