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Sesquiterpene lactones. XXX. Cynaropicrin in species of the subtribe *Centaureinae* Dumort.

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Abstract

The presence of cynaropicrin was determined in 13 species of the subtribe *Centaureinae* Dumort.: *Centaurea declinata* M. B., *C. leucophylla* M. B., *C. dealbata* Willd., *C. zangezuri* (Sosn.) Sosn., *C. carthalinica* (Sosn.) Sosn., *C. thracica* (Janka) Hayek, *C. exarata* Boiss. ex Cosson, *C. phaeopappoides* Bordz., *Chartolepis intermedia* Bioss., *Ch. glastifolia* (L.) Cass., *Rhaponticum carthamoides* (Willd.) Iljin, *Rh. serratuloides* (Georgi) Bobr., *Leuzea rhapontica* (L.) Holub.

Key words: distribution of cynaropicrin, Centaureinae, sesquiterpene lactones, chemotaxonomy

INTRODUCTION

The working out of a natural system within the subtribe *Centaureinae* Dumort., tribe *Cynarae*, family *Compositae*, presents many difficulties. The reason for this is the lack of distinct traits which could serve as the basis for a division not arousing any doubts. Different authors propose often very differing classifications of the plants grouped here into genera, subgenera, sections, species and subspecies. Knowledge about the chemical compounds found in the genera of subtribe *Centaureinae* Dumort. may facilitate the work of taxonomists, show the relationships among the plants grouped together here.

It can be seen from the studies done until now that within *Centaureinae* Dumort., systematic units of plants can be found which are characterized by the ability to synthesize the same sesquiterpene lactones. Cnicin — a germacranolide — was found in the genus *Cnicus* L. (Samek et al. 1969), in most of the tested species of the subgenus *Acrolophus* (Cass.) Dobrocz. (Nowak et al. 1984) and the subgenus *Calcitrapa* (Heister ex Fabr.) Hayek of the genus *Centaurea* L. (Drożdż 1967). Another germacranolide, 9 α-hydroxyparthenolide, was found in a representative of the genus *Zoega* L. (Budějšinsky et al. 1984). Whereas, different guaianolides were found in species of the genera *Acroptilon* Cass. (Evstratova et al. 1967), *Grossheimia* Sosn. et Takht. (Daniewski et al. 1982), *Volutaria* Cass. (Gonzales et al. 1977) and others.

The objective of the present study was to examine representatives of the subtribe *Centaureinae* Dumort. for the guaianolide, cynaropicrin (Fig. 1),

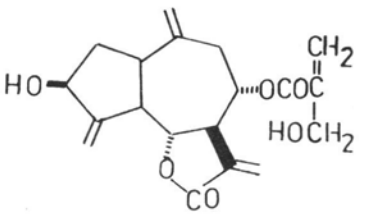

Fig. 1. Cynaropicrin

first discovered in the genus *Cynara* L. of the subtribe *Carduinae*, tribe *Cynareae* (Samek et al. 1971) and later demonstrated in several other genera belonging to the subtribe *Centaureinae* Dumort. such as *Centaurea* L., *Grossheimia* Sosn. et Takht., *Amberboa* (Pers.) Less. and *Tricholepis* DC. (Seaman 1982).

MATERIAL AND METHODS

The plants used in this study came from the Garden of the Chair of Medicinal Plants of the Poznań (Poland) Medical Academy. They were identified on the basis of Flora USSR (1961) and Flora Europea (1976).

The "lactone fraction" was isolated using the method of Drożdż and Piotrowski (1973) from dried, crumbled, above-ground plant parts. The chemical composition of the chloroform extracts was controlled by thin-layer chromatography on silica gel plates using standard cynaropicrin and other sesquiterpene lactones found in the subtribe *Centaureinae* Dumort. The chromatograms were developed with selectively staining reagents (Drożdż and Błoszyk 1978). Lactone fractions from 13 species belonging to the subtribe *Centaureinae* Dumort. which, on control chromatograms, exhibited

Table 1

The presence of cynaropicrin in the subtribe *Centaureinae* Dumort.

Species	Catalog number	Subgenus	Accompanying guaianolides and other sesquiterpene lactones	Comments
Centaurea exarata Boiss. ex Cosson	18/82	*Acrolophus* (Cass.) Dobrocz.	cnicin^{+}	own studies
Centaurea africana Lam.		*Centaurea* L.	cnicin^{+}	(Gonzalez et al. 1977)
Centaurea canariensis Brouss. var. *subexpinnata* Burch.		*Cheirolophus* Cass.	8α-hydroxy-11β13 H dehydrocostus lactone, 3-desoxycinaropicrin, 8αmethary-loxy dehydrocostus lactone, 8αhydro-xydehydrocostus lactone	(Bohlmann, Gupta 1981)
Centaurea taganananensis Svent.		,,	onopordopicrin^{+}, dehydromelitensin-8--(0)-4 (4 hydroxymethacrylate)$^{++}$, melitensin^{++}, desacilcinaropicrin	(Gonzalez et al. 1984)
Centaurea debeauxii Gren. et Gordon subsp. *thuillieri* Dostal		*Jacea* (Miller) Hayek		(Geppert et al. 1983)
Centaurea hyssopifolia Vahl.		,,	centaurepensin, chlorohyssopifolin B, acroptilin, aguerin B, vahlenin^{+++}	(Gonzalez et al. 1977)
Centaurea linifolia L.		,,	centaurepensin, acroptilin, chlorohyssopifolin B, D, E, linichlorin A, B, C, aguerin B, desacilcinaropicrin, desacillinichlorin C, vahlenin^{+++}	,,
Centaurea clementei Boiss. ex DC.		*Lopholoma* (Cass.) Dobrocz.	desacilcinaropicrin	
Centaurea thracica (Janka) Hayek	567/81	*Microlophus* (Cass.) DC.		own studies
Centaurea behen L. syn.		*Microlophus* (Cass.) DC.	desacilcinaropicrin, aguerin B, grossheimin	(Rustaiyan et al. 1981)
Centaurea alata Lam.				
Centaurea phaeopappoides Bordz.	458/83	*Odontolophopsis* Tzvel.	janerin, $C_{15}H_{17}O_4Cl$	own studies
Centaurea americana Nutt.		*Plecteocephalus* D. Don.		(Ohno et al. 1973)
Centaurea dealbata Willd. syn.	29/74	*Psephellus* Cass.	centaurepensin, acroptilin, linichlorin B, 15 desoxyrepin, repin, janerin	own studies
Psephellus dealbatus Willd.				
Centaurea declinata M.B. syn.	190/77	,,	15-desoxyrepin, linichlorin B,	,,
Psephellus declinatus M.B.				

Table 1 continued

Species	Catalog number	Subgenus	Accompanying guaianolides and other sesquiterpene lactones	Comments
Centaurea carthalinica (Sosn.) Sosn. syn. *Psephellus carthalinicus* Sosn.	39/76	"	centaurepensin, acroptilin, linichlorin B, 15-desoxyrepin, repin, janerin	"
Centaurea leucophylla M.B. syn. *Psephellus leucophyllus* M.B.	190a/77	"	15-desoxyrepin, linichlorin B	"
Centaurea zangezuri (Sosn.) Sosn. syn. *Psephellus zangezuri* Sosn.	32/77	"	centaurepensin, acroptilin, linichlorin B, 15-desoxyrepin, repin, janerin	"
Acroptilon repens (L.) DC. syn. *Centaurea repens* L.			repin, janerin, aguerin B, repidiol, epoxyrepidiolid	(Stevens 1982)
Amberboa muricata (L.) DC. syn. *Centaurea muricata* (L.) Dostal			isolipidiol, muricatin	(Gonzalez et al. 1977)
Chartolepis glastifolia (L.) Cass. syn. *Chartolepis tournefortii* Jaub et Spach.. *Centaurea glastifolia* L.	40/78		centaurepensin, grossheimin, acroptilin, cebelin C, repin, janerin	own studies
Chartolepis intermedia Boiss. syn. *Centaurea glastifolia* var. *intermedia* (Boiss.) Gugler, *Chartolepis bieberstei-inii* Jaub et Spach.	205/74		grossheimin	own studies (Mukhamethanov et al. 1969)
Grossheimia macrocephala (Muss.-Puschk.) Sosn. et Takht. syn. *Centaurea macrocephala* Muss.-Puschk.			grossheimin, isolipidiol	(Daniewski et al. 1982)
Leuzea rhapontica (L.) Holub syn. *Centaurea rhapontica* L.	584/81	*Rhaponticinum* Holub		own studies
Rhaponticum carthamoides (Willd.) Iljin syn. *Centaurea carthamoides* Benth. in Benth. et Hook.	580/81			"
Rhaponticum serratuloides (Georgi) Bobr. syn *Centaurea serratuloides* Georgi	483/82			"
Tricholepis glaberrima DC.			desacilcinaropicrin	(Singhal et al. 1982)

+ — garmacranolide, ++ — eudesmanolide, +++ — elemanolide.

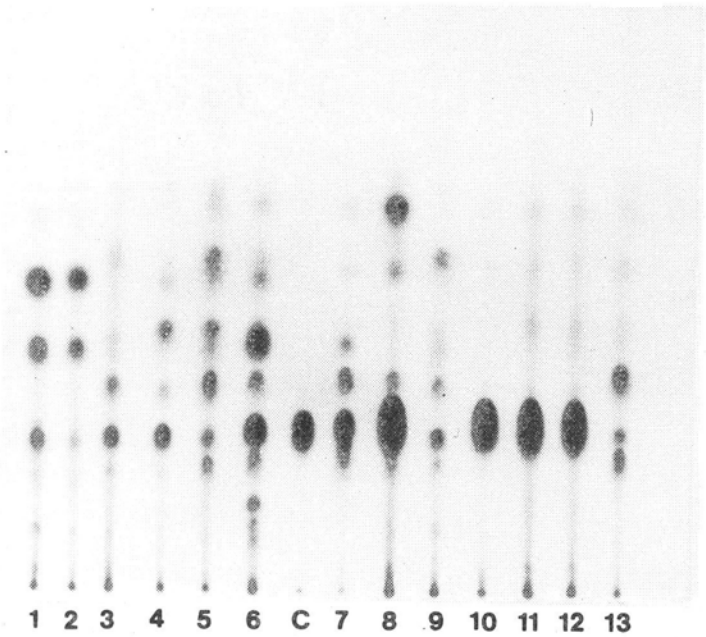

Fig. 2. Thin-layer chromatography of "lactone fractions" from the above-ground parts of plants belonging to the subtribe *Centaureinae* Dumort., in the presence of standard cynaropicrin in the solvent system chloroform: ethyl acetate (30:20 v/v). The chromatogram was sprayed with concentrated sulfuric acid and heated at 100°C for 3 min. The "lactone fractions" of: 1 — *Centaurea declinata*, 2 — *C. leucophylla*, 3 — *C. dealbata*, 4 — *C. zangezuri*, 5 — *C. carthalinica*, 6 — *C. exarata*, 7 — *C. phaeopappoides*, 8 — *C. thracica*, 9 — *Chartolepsis glastifolia*, 10 — *Ch. intermedia*, 11 — *Rhaponticum carthamoides*, 12 — *Rh. serratuloides*, 13 — *Leuzea rhapontica*, C — standard cynaropicrin

the presence of a compound with the same color and R_f as standard cynaropicrin (Fig. 2), were chosen for further detailed studies.

The compounds were isolated by column chromatography on silica gel. They were eluted with chloroform-ethyl acetate, chloroform-methanol. The amorphous substance so obtained was identified by comparison of its R_f value, color in selectively staining developers (Drożdż and Błoszyk 1978) and IR spectra with those of standard cynaropicrin. The substance obtained from *Rhaponticum carthamoides* was additionally identified on the basis of ^{1}H NMR 100MHz and MS spectra.

RESULTS AND DISCUSSION

On the basis of the results obtained in this study, the presence of cynaropicrin in 13 more species from the subtribe *Centaureinae* Dumort. was demonstrated. The chromatographic studies showed that among them, species were found in which cynaropicrin dominated (*Rhaponticum carthamoides* (Willd.) Iljin, *R. serratuloides* (Georgi) Bobr., *Chartolepis intermedia* Boiss., *Centaurea thracica* (Janka) Hayek) as well as species in which this guaianolide was present along with other sesquiterpene lactones (Fig. 2).

Table 1 presents a compilation of species in which, to date, cynaropicrin has been found. From our own studies and the reports of other authors, it can be seen that many species assigned to the subtribe *Centaureinae* Dumort. are characterized by the ability to synthesize cynaropicrin. Further studies of plants from the genus *Rhaponticum auct.*, which numbers about 10 species, will show if the accumulation of this compound can be considered a chemotaxonomic characteristic for this taxon.

Acknowledgment

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Laktony seskwiterpenowe. XXX. Cynaropikryna w gatunkach podplemienia Centaureinae Dumort.

Streszczenie

Stwierdzono obecność cynaropikryny w 13 gatunkach podplemienia *Centaureinae* Dumort.: *Centaurea declinata* M. B., *C. leucophylla* M. B., *C. dealbata* Willd., *C. zangezuri* (Sosn.) Sosn., *C. carthalinica* (Sosn.) Sosn., *C. thracica* (Janka) Hayek, *C. exarata* Boiss. ex Cosson, *C. phaeopappoides* Bordz., *Chartolepis intermedia* Boiss., *Ch. glastifolia* (L.) Cass., *Rhaponticum carthamoides* (Willd.) Iljin, *Rh. serratuloides* (Georgi) Bobr., *Leuzea rhapontica* (L.) Holub.