ACTA SOCIETATIS
BOTANICORUM POLONIAE
Vol. 52, nr 1: 23-34
1983

Sesquiterpene lactones. XXIII. Isolation of sesquiterpene lactones from *Centaurea* L. species

BARBARA GEPPERT *, BOHDAN DROŻDŻ *, MICHAŁ KIEŁCZEWSKI **, MIROSŁAW HOLUB ***

*Department of Medicinal Plants, Institute of Drugs, Medical Academy, Mazowiecka 33, 61-123 Poznań, Poland
**Department of Natural Products, Institute of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
***Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Flemingowo nam. 2, Praha, Czechoslovakia

(Received: February 15, 1982)

Abstract

Sesquiterpene lactones were isolated from 18 species or subspecies of the genus *Centaurea* L.: salonitenolide (I) was found in *C. crithmifolia* Vis., *C. friderici* Vis., *C. paniculata* L., *C. calcitrapa* L., *C. pontica* Prodan et E. I. Nyarady, *C. eriophora* L., *C. alba* L. subsp. *deusta* (Ten.) Nyman, *C. alba* L. subsp. *caliacrae* (Prodan) Dostal and *C. weldeniana* Reichenb.; cnicin (II) was found in: *C. vallesiaca* (DC). Jordan, *C. calcitrapa* L., *C. aspera* L. subsp. *aspera*, *C. sphaerocephala* L. subsp. *lusitanica* (Boiss. et Reuter) Nyman, *C. sulphurea* Willd., *C. eriophora* L. and *C. rocheliana* (Heuffel) Dostal; cynaropicrin (III) was detected in *C. debeauxii* Gren. et Gordon subsp. *thuillieri* Dostal; acroptillin (V), repin (VI) and janerin (VII) in *C. bella* Trautv. Other unidentified sesquiterpene lactones were also found to be present in the examined plants.

INTRODUCTION

There are serious obstacles in establishing the correct taxonomy of the genus *Centaurea* L. (*Compositae*). It is, namely, difficult to ascertain the range of the genus and its internal divisions into subgenera and sections as well as species and subspecies. It is so because the taxonomy was based on variable morphological traits, mainly the varying structure of the perianthemum leaves and calyx pappus as well as the high facility of inter-species hybrid formation and the but little known evolutional pathway and relations between the taxonomic groups. The-

refore, numerous synonymic names appear in the literature and various suggestions for the division of the subtribe *Centaureinae* and genus *Centaurea*.

There are two tendencies in the taxonomy of *Centaurea*. One group of taxonomists considers the genus *Centaurea* in a wide sense and includes into it groups of plants treated by the adherents of the second tendency as independent genera. Extreme opinions were represented by Cassini (1817-1830), who established a suprageneric taxon *Centaurieae* grouping 70 genera and De Candolle (1837) and Hoffmann (1894) who returned to the concept of Linneus, adopting the genus *Centaurea* in a wide sense and they used the names of the genera sensu Cassini for the sections into which they divided the genus *Centaurea*.

The successive proposals concerned the division of *Centaurea* into subgenera and sections, and species and subspecies and the exclusion of groups of plants from the genus *Centaurea* sensu Hoffmann with establishment of independent genera. This opinion is presented in contemporary elaborations. Wagenitz in Flora of Turkey (1975) and in Flora Iranica (1980) excluded from *Centaurea* L. the genera: *Acroptilon* Cass., *Callicephalus* C. A. Meyer, *Amberboa* (Pers.) Less., *Rhaponticum* Hill., *Mantisalca* Cass., *Oligochaeta* (DC.) C. Koch.

The authors of the Flora USSR (1961) went still further and so did Dostal (1969) when elaborating the genus *Centaurea* L. in Flora Europaea (1976). They adopted as independent genera also *Grossheimia* Sosn. et Takht., *Cheirolepis* Boiss., *Tomenthea* DC. and a dozen or so others.

The quoted examples indicate that the elaboration of a natural phylogenetic system for the genus *Centaurea* still remains an open problem. It is therefore, suggested to utilise in studies aiming at ordering of the taxonomy of the subtribe *Centaureinae* and the genus *Centaurea* more extensively other traits than those routinely quoted. Wagenitz (1955) demonstrated the high utility for taxonomic purposes of the differences in pollen grain structure and Dittrich (1966) those in the fruit structure. It would seem that chemotaxonomic characters, the different structure of the chemical compounds synthesised by plants classified to the genus *Centaurea* L. and related ones should be taken into account. It is obvious that evolution was accompanied by changes both in the morphological structure of the plants and in their enzymatic composition, appearing in the production of various metabolites.

To the chemical compounds which may constitute a chemotaxonomic trait in the family *Compositae* belong sesquiterpene lactones (Hegnauer 1964, Herout and Sorm 1969).

It results from the investigations carried out to date that within the genus *Centaurea* L. there also exist plant species synthesising sesqui-

terpene lactones differing in their chemical structure (Gonzales et al. 1977). Studies on the usefulness of sesquiterpene lactones for taxonomic purposes should be preceded by investigations on the composition of sesquiterpenes in a great number of species and indication of plants which do not produce them.

The present study was undertaken to check 18 species or subspecies (considered by other authors as independent species) of *Centaurea* L. for the presence of sesquiterpene lactones, to isolate and identify them.

MATERIAL AND METHODS

Plants with a particularly bitter taste were chosen for investigation. According to observations to date it could be expected that they contain sesquiterpene lactones (Drożdż 1968). The studies included 18 species and subspecies of *Centaurea* L. representing seven subgenera. The names of the plants and their appurtenance to the subspecies and sections are given after Flora Europea (1976). *Centaurea bella* Trautv. not listed in Flora Europea was identified from the description in Flora USSR (1961) and, according to the attached recommendation, classified to the subgenus *Hyalinella* in the section *Hyalinella* (Table 1). The following species had been the only ones studied earlier.: *C. calcitrapa* L. (Drożdż 1967) and *C. alba* L. (Gonzales et al. 1977). In both these species the germacranolide cnicin (II) was revealed.

The above ground parts of the plants collected in the phase of flowering were dried at 40°C. Seeds for sowing on the experimental plots in the Department of Medicinal Plants of the Medical Academy in Poznań were received from various botanical gardens, but most were collected from wild plants. In two cases — *C. calcitrapa* L. and *C. alba* L. subsp. *caliacrae* (Prodan) Dostal — plants were taken from a natural site in the environs of Burgas (Bulgaria). Information on the investigated plants is compiled in Table 1.

ISOLATION OF LACTONE FRACTIONS

Lactone fractions were obtained by the method earlier described (Błoszyk and Drożdż 1978) (Fig. 1). The powdered raw material was extracted at room temperature with methanol. The extract was concentrated under reduced pressure, diluted with distilled water, lead acetate solution was added and the sediment was centrifuged off. The purified aqueous solution was extracted with chloroform. The chloroform solution concentrated under reduced pressure and containing sesquiterpene lactones constituted the "lactone fraction".

Table 1

Information about investigated species
Entries from 1 to 17 are classified according to Flora Europaea (1976) and entry 18 according to Flora USSR (1961)

No.	Species	Subgenus	Section	Catalogue number	Origin of seeds	Date of collection	Lactone found
1	*Centaurea crithmifolia* Vis.	*Acrolophus* (Cass.) Dobrocz.	*Panophyllum* Hayek	38/78	Italy (Trieste)	1978	salonitenolide (I)
2	*Centaurea friderici* Vis.	*Acrolophus* (Cass.) Dobrocz.	*Panophyllum* Hayek	28/77	Italy (Trieste)	1977	salonitenolide (I)
3	*Centaurea vallesiaca* (DC.) Jordan	*Acrolophus* (Cass.) Dobrocz.	*Maculosae* (Hayek) Dostal	44/77	Italy (Trieste)	1977	cnicin (II)
4	*Centaurea paniculata* L.	*Acrolophus* (Cass.) Dobrocz.	*Paniculatae* (Hayek) Dostal	67/77-N	France (Bordeaux)	1977	salonitenolide (I)
5a	*Centaurea calcitrapa* L.	*Calcitrapa* (Heister ex Fabr.) Hayek	,,	186/77	Rumania (Cluj)	1977	salonitenolide (I)
5b	*Centaurea calcitrapa* L.	*Calcitrapa* (Heister ex Fabr.) Hayek	,,	17/78-P	Bulgaria (Burgas)	1978	cnicin (II)
6	*Centaurea pontica* Prodan et E. I. Nyarady	*Calcitrapa* (Heister ex Fabr.) Hayek	,,	74/77-N	Rumania (Bucuresti)	1977	salonitenolide (I)
7	*Centaurea aspera* L. subsp. *aspera*	*Seridia* (Juss.) Czerep.	,,	179/77	France (Paris)	1977	cnicin (II)
8	*Centaurea sphaerocephala* L. subsp. *lusitanica* (Boiss. et Reuter) Nyman syn. *C. lusitanica* Boiss. et Reuter	*Seridia* (Juss.) Czerp.	,,	12/78-N	Portugal (Coimbra)	1978	cnicin (II) and unknown lactone
9	*Centaurea sulphurea* Willd.	*Solstitiaria* (Hill) Dobrocz.	,,	92/77	Belgium (Anvers)	1977	cnicin (II)

No.	Species	Subgenus	Section	Cataloque number	Origin of seeds	Date of collection	Lactone found
10a	*Centaurea eriophora* L	*Solstitiaria* (Hill) Dobrocz.	,,	51/76	France (Dijon)	1976	cnicin (II)
10b	*Centaurea eriophora* L.	*Solstitiaria* (Hill.) Dobrocz.	,,	289/78	Poland (Poznań)	1978	salonitenolide (I)
11	*Centaurea nicaensis* All.	*Solstitiaria* (Hill.) Dobrocz.	,,	942/76-N	Italy (Palermo)	1977	unknown lactone
12	*Centaurea alba* L. subsp. *deusta* (Ten.) Nyman syn. *C. deusta* Ten.	*Phalolepis* (Cass.) Dobrocz.	*Phalolepis*	2/74-N	Italy (Pisa)	1877	salonitenolide (I)
13	*Centaurea alba* L. subsp. *caliacrae* (Prodan) Dostal syn. *C. caliacrae* Prodan	*Phalolepis* (Cass.) Dobrocz.	*Phalolepis*	12/77-P	Bulgaria (Warna)	1977	salonitenolide
14	*Centaurea rocheliana* (Heuffel) Dostal syn. *C. jacea* subsp. *banatica* Hayek	*Jacea* (Miller) Hayek	*Jacea*	715/15	Czechoslovakia	1977	cnicin (II)
15	*Centaurea weldeniana* Reichenb.	*Jacea* (Miller) Hayek	*Jacea*	242/75-N	Italy (Trieste)	1977	salonitenolide (I)
16	*Centaurea phrygia* L. subsp. *pseudophrygia* (C. A. Meyer) Gugler syn. *C. pseudophrygia* C. A. Meyer	*Jacea* (Miller) Hayek	*Lepterantus* (DC.) Dumort	626/76-N	GDR (Dresden)	1977	unknown lactone
17	*Centaurea debeauxii* Gren. et Gordon subsp. *thuillieri* Dostal syn. *C. pratensis* Thuill. non Salisb.	*Jacea* (Miller) Hayek	*Lepterantus* (DC.) Dumort	625/76-N	France (Paris)	1977	cynaropicrin (III)
18	*Centaurea bella* Trautv.	*Hyalinella* (Tzvel.) Tzvel.	*Hyalinella*	65/73	FRG (Giessen)	1978 1980	acroptillin (V) repin (VI) janerin (VII)

Abbreviations: N — seeds collected from wild plants, P — plant material from wild stands

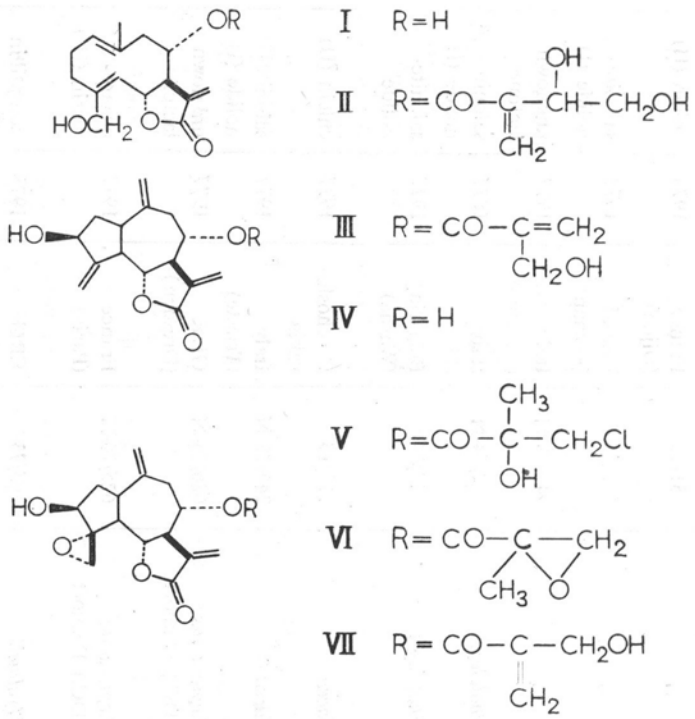

Fig. 1. Sesquiterpene lactones found in the studied *Centaurea* L. species: salonitenolide (I), cnicin (II), cynaropicrin (III), deacylcynaropicrin (IV) (hydrolysis product of cynaropicrin), acroptilin (V), repin (VI), janerin (VII)

Chromatographic analysis

The composition of the lactone fractions was examined by means of thin-layer chromatography on glass plates coated with silica gel with gypsum added (D r o ż d ż and B ł o s z y k 1978). As standard substances served some sesquiterpene lactones previously detected in species of *Centaurea* L. such as salonitenolide (I), cnicin (II) and cynaropicrin (III).

The results obtained indicate that salonitenolide can be isolated from nine, cnicin from seven and cynaropicrin from two species or subspecies of *Centaurea* L. Moreover, chromatographic analysis pointed to the presence in all the tested extracts of other unknown sesquiterpene lactones.

Salonitenolide (I) isolation

Chloroform extracts from plants ("lactone fractions") in which thin-layer chromatography revealed the presence of salonitenolide (nos. 1, 2, 4, 5a, 6, 10b, 12, 13, 15 — Table 1) after dehydration with anhydrous

sodium sulphate were left to stand for several days at -5°C. The appearing crystalline sediment was filtered off and the filtrate was placed on a column filled with silica gel and eluted with a chloroform-acetone mixture (5 : 1 v/v). Fractions showing in the control chromatograms the presence of salonitenolide were combined, the solvent was distilled off under reduced pressure and the fraction was crystallised from chloroform. The crystals were combined with earlier obtained ones and purified by repeated crystallisation from chloroform.

From all the nine analysed plants crystals (needles) were obtained with m.p. 137°-138°C and R_f values identical with that of the standard substance, salonitenolide, isolated from *Centaurea salonitana* Vis. (S u c h y et al. 1967). The identity of the crystals was confirmed by comparing their spectra with the corresponding ones obtained by the method of spectroscopy in infrared (IR), the method of nuclear magnetic resonance (^{1}H-NMR), the method of mass spectrometry (MS) and of circular dichroism (CD) for the standard salonitenolide.

Cnicin (II) isolation

From the lactone fraction of seven species or subspecies of *Centaurea* L. (nos 3, 5b, 7, 8, 9, 10a, 14 — Table 1) which on control chromatograms exhibited a spot corresponding to standard cnicin, this germacranolide was isolated by the earlier developed method (D r o ż d ż 1966).

Each time, as the result of crystallisation from ethyl ether the characteristic needles with m.p. 142°-145°C and R_f values were identical to those obtained for the standard substance — cnicin extracted from *Cnicus benedictus* L. (S a m e k et al. 1969).

The crystals were idendified by comparison of the IR, ^{1}H-NMR, MS and CD spectra with those of the standard substance.

Cynaropicrin (III) isolation

Lactone fractions from *Centaurea phrygia* subsp. *pseudophrygia* (C. A. Meyer) Gugler and *C. debeauxii* Gren. et Gordon subsp. *thuillieri* Dostal (nos 16 and 17 — Table 1) which showed on the control chromatograms the presence of cynaropicrin in them were separated on columns filled with silica gel until a chromatographically homogenous substance was obtained.

An amorphous compound with $(\alpha)^{20}_D + 109°$ was isolated from *Centaurea debeauxii* subsp. *thuillieri*. The IR, ^{1}H-NMR, MS and CD spectra as well as the R_f were identical with those of standard cynaropicrin obtained from *Cynara scolymus* L. (S a m e k et al. 1971). Alkaline

hydrolysis of the isolated sesquiterpene lactone yielded a compound with m.p. 149°-150°C identical with deacylcynaropicrine (IV) obtained by hydrolysis of cynaropicrin from *Cynara scolymus* L. (S a m e k et al. 1971).

The amorphous chromatographically homogeneous compound isolated from *Centaurea phrygia* subsp. *pseudophrygia* was not, however, identical with cynaropicrin. Although it has similar R_f and $(\alpha)^{20}_D$ values, comparison of the IR, ^{1}H-NMR and CD indicated differences in structure.

Acroptillin (V), repin (VI) and janerin (VII) isolation

Chromatographic control of the lactone fraction isolated from the green parts of *Centaurea bella* Trautv. (no. 18 — Table 1) pointed to the presence of at least eight compounds. Chromatographic separation with the use of chloroform with acetone added on silica gel columns yielded three homogeneous compounds — two crystalline ones and an amorphous one. The compound with m.p. 195°-198°C was recognised as acroptillin (V) (= chlorohyssopifolin C), the compound with m.p. 163°-165°C as repin (VI) and the amorphous compound as janerin (VII).

Isolation of unidentified sesquiterpene lactones

Chromatographic separation of the lactone fraction isolated from *Centaurea nicaensis* All. (no. 11 — Table 1) and *C. sphaerocephala* L. subsp. *lusitanica* (Boiss et Reuter) Nyman (no. 8 — Table 1) led to two crystalline unknown sesquiterpene lactones. Elution with a chloroform--acetone mixture (5 : 1 v/v) of the fractions on a silica gel column yielded in the first case a compound with m.p. 126°-128°C and in the second with m.p. 179°C.

Both these compounds exhibit absorption bands for γ-lactones characteristic in the IR spectra.

RESULTS AND DISCUSSION

The present investigations supplied new information on the occurrence of sesquiterpene lactones in species of the genus *Centaurea* L.

It was found that **salonitenolide (I)** — a sesquiterpene lactone of the germacranolide group appears only in *Centaurea salonitana* Vis. from the subspecies *Lopholoma* (Cass.) Dobrocz. (S u c h y et al. 1967) as well as in representatives of other subspecies of *Centaurea* L. Salonitenolide (I) was isolated from the green parts of *C. crithmifolia* Vis., *C. friderici* Vis. and *C. paniculata* L. of the subgenus *Acrolophus* (Cass.)

Dobrocz., from *C. calcitrapa* L. (Heister ex Fabr.) Hayek, from *Centaurea eriophora* L. of the subgenus *Solstitiaria* (Hill.) Dobrocz., from *C. alba* L. subsp. *deusta* (Ten.) Nyman and *C. alba* L. subsp. *caliacrae* (Prodan) Dostal from the subgenus *Phalolepis* (Cass.) Dobrocz. and from *Centaurea weldeniana* Reichenb. from the subgenus *Jacea* (Miller) Hayek (Table 1).

Cnicin (II) — a germacranolide with a structure similar to that of salonitenolide was found in *Centaurea vallesiaca* (DC.) Jordan, subgenus *Acrolophus* (Cass.) Dobrocz., *C. sphaerocephala* L. subsp. *lusitanica* (Boiss. et Reuter) Nyman and in *C. aspera* L. subsp. *aspera* from the subgenus *Seridia* (Juss.) Czerep., *C. eriophora* L. and *C. sulphurea* Willd. from the subgenus *Solstitiaria* (Hill.) Dobrocz. and *C. rocheliana* (Heuffel) Dostal from the subgenus *Jacea* (Miller) Hayek.

The presence of cnicin (II) was noted earlier in *Centaurea africana* Lam. from the subgenus *Centaurea* (Gonzalez et al. 1977). *C. calcitrapa* L. and *C. iberica* Trev. from the subgenus *Calcitrapa* (Heister ex Fabr.) Hayek, *C. diffusa* Lam., *C. ovina* Pallas ex Willd., *C. micranthos* I. F. Gmel. (Drożdż 1968), *C. stoebe* (L.) Sch. et Thell. (Suchy and Herout 1962), *C. squarrosa* Willd. (Tarasov et. al. 1973), *C. castellanii* Boiss. et Reut. (Gonzalez et al. 1977) from the subgenus *Acrolophus* (Cass.) Dobrocz., *C. alba* L. from the subgenus *Phalolepis* (Cass.) Dobrocz. (Gonzalez et al. 1977) and in *Cnicus benedictus* L. also belonging to the subgenus *Centaureinae* Dumort. (Samek et al. 1969). The results obtained indicate a frequent occurrence of this biologically active germacranolide in plants from various sugenera of *Centaurea* L.

The finding in *Centaurea debeauxii* Gren. et Gordon subsp. *thuillieri* Dostal from the subgenus *Jacea* (Miller) Hayek of **cynaropicrin (III)** confirms the earlier observations of occurrence of this guaianolide in various representatives of the subgenus *Centaureinae,* isolated for the first time from the green parts of *Cynara scolymus* L. of the subgenus *Carduinae* Dumort. (Suchy et al. 1960).

To date cynaropicrin (III) has been found in *Centaurea africana* Lam. from the subgenus *Lapholoma* (Cass.) Dobrocz. in *C. linifolia* L. from the subgenus *Jacea* (Miller) Hayek (Gonzalez et al. 1977), in *C. americana* Nutt. (Ohno et al. 1973) from the subgenus *Plectocephalus* (D. Don.) Hayek and in related genera such a *Cheirolophus* Cass. and *Cynopsis* Cass. (Gonzalez et al. 1977).

Interesting from the point of view of chemical plant taxonomy were the results of investigation of the composition of the lactone fraction of *Centaurea bella* Trautv. from the subgenus *Hyalinella* (Tzvel.) Tzvel.

The isolated guaianolides, **acroptilin (V), repin (VI)** and **janerin (VII),** previously revealed in *C. hyrcanica* Bornm. (Evstratova et al. 1967),

C. linifolia L., *C. hyssopifolia* Vahl. and *C. janeri* Graells (Gonzalez et al. 1977) as well as in *Acroptilon repens* (L.) DC. (syn. *Centaurea repens* L.) (Evstratova et al. 1967). Acroptilin (syn. chlorohyssopifolin C) belongs to the rare sesquiterpene lactones containing chlorine in the molecule.

During the investigations changes were observed in the composition of the "lactone fraction" isolated from some species of the genus *Centaurea* L. It was found that in leaves of *Centaurea bella* Trautv. collected in 1978 the content of acroptilin (V) was markedly higher than that of repin (VI), whereas, in leaves collected from the same plants in the same stage of development in 1980, the former substance was not found. Similarly in the above ground parts of *Centaurea eriophora* L. collected in 1976 the dominant compound was cnicin (II) and in 1978 salonitenolide (I). In the green parts of *Centaurea calcitrapa* L. collected in 1977 in Poznań salonitenolide (I) dominated, whereas in material from a natural site collected in 1978 in the environs of Burgas in Bulgaria cnicin (II) prevailed, in agreement with the earlier observations of Drożdż (1967). It should be mentioned here that in both cases the plants were collected in the same vegetation phase.

The causes of these changes in the composition of the lactone fractions of *Centaurea bella* Trautv., *C. eriophora* L. and *C. calcitrapa* L. have not been so far elucidated. It is possible that the influence of climatic factors played a certain role here. Both in the case of *C. eriophora* L. and *C. calcitrapa* L. it was found that the cnicin (II) content was higher than that of salonitenolide (I) in plants exposed during vegetation to higher temperature. Neither can the influence of ontogenetic factors be ruled out. Therefore the sesquiterpene lactone composition should be checked in the course of the annual vegetation of the plants.

On the basis of information accumulated to date it is difficult to advance conclusions as to the significance of sesquiterpene lactones as a chemotaxonomic trait in the genus *Centaurea* L. The presence of various sesquiterpene lactones was revealed in as few as 1/10 of the species classified to this genus comprising numerous plants. A list of *Centaurea* L. species which do not produce sesquiterpene lactones is also lacking.

On the basis of the information collected so far it may be assumed that the ability of synthesising germacranolides — salonitenolide (I) or its ester, cnicin (II), is a characteristic trait of representatives of the subgenus *Acrolophus* (Cass.) Dobrocz., *Phalolepis* (Cass.) Dobrocz. and *Calcitrapa* (Heister ex Fabr.) Hayek. The presence of the above mentioned compounds was revelated in all the so far studied species belonging to the above mentioned subgenera.

Plants from the subgenus *Solstitiaria* (Hill.) Dobrocz. and *Seridia* (Juss.) Czerep. also frequently exhibit the ability of producing germa-

cranolides, mainly salonitenolide (I) and cnicin (II). There may, however, also be found species synthesising other types of sesquiterpene lactones as for instance in the subgenus *Solstitiaria, Centaurea solstitialis* L. producing guaianolides and *C. melitensis* L. producing elemanolides (Gonzalez et al. 1977).

Among the respentatives of the subgenus *Jacea* (Miller) Hayek the ability of synthesising various guaianolides prevails. Two species were, however, found in this subgenus — *Centaurea weldeniana* Reichenb. and *C. rocheliana* (Heuffel) Dostal producing germacranolides. Data concerning other subspecies are still too fragmentary to be included in the discussion.

Acknowledgments

Investigations under grant within problem PMR — I. 12. 1. 5. 2. 3.

REFERENCES

Błoszyk E., Drożdż B., 1978. Sesquiterpene Lactones in Species of the Genus *Chrysanthemum*. Acta Soc. Bot. Pol. 47: 3-12.

Cassini A., 1817-30. Dictionnaire des sciences naturelles. F. G. Levrault (ed.), Strassbourg-Paris.

De Candolle A. P., 1837. Prodromus systematis naturalis regni vegetabilis. Vol. 6. Fortin, Masson (eds.), Paris.

Dittrich M., 1966. Karpologische Untersuchungen zur Systematik von *Centaurea* und verwandeten Gattungen. Bot. Syst. 88: 70-162.

Dostal J., 1969. Taksonomicka studie o celedich *Lycopodiaceae* a *Asteraceae* a o rodech *Lycopodium* a *Centaurea*. Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. 31: 5-38.

Drożdż B., 1966. Wyodrębnienie knicyny z ziela *Centaurea diffusa* Lam. Dissert. Pharm. 18: 281-283.

Drożdż B., 1967. Obecność knicyny w zielu *Centaurea calcitrapa* L., *Centaurea iberica* Trev. i *Centaurea ovina* Pal. Dissert. Pharm. 19: 223-225.

Drożdż B., 1968. Gorzkie laktony seskwiterpenowe w gatunkach plemienia *Cynareae*. Dissert. Pharm. 20: 93-103.

Drożdż B., Błoszyk E., 1978. Selective Detection of Sesquiterpene Lactones by TLC. Planta Medica 33: 379-384.

Evstratova R. I., Mukamietshanov M. N., Sheitshenko V. I., Shreter A. I., Pakaln D. A., 1969. Isolation of Repin from *Centaurea hyrcanica*. Khim. Prir. Soedin. 3: 186.

Evstratova R. I., Rybalko K. S., Rzazade R. Y., 1967. Acroptilin — A New Sesquiterpene Lactone from *Acroptilon repens*. Khim. Prir. Soedin. 4: 284.

Flora Europaea, 1976. Vol. 4. Cambridge University Press, Cambridge.

Flora Iranica, 1980. No 139a. Akademische Druck und Verlaganstalt, Graz.

Flora of Turkey, 1975. Vol. 5. University Press, Edinburgh.

Flora USSR, 1961. Vol. 28. Izdatielstvo Nauka, Moskwa.

Gonzalez A. G., Bermejo J., Massanet G. M., 1977. Aportation al estudio quimiotaxonomico del genera *Centaurea*. Rev. Latinoamer. Quim. 8: 176-181.

Hegnauer R., 1964. Chemotaksonomie der Pflanzen. Band 3. Birkhaüser Verlag, Basel-Stuttgart.

Herout V., Sorm F., 1969. Sesquiterpenoids in the *Compositae*. In: Perspectives in Phytochemistry. J. Harborne and T. Swain (eds.). Academic Press, London--New York.

Hoffman O., 1894. *Compositae*. In. Die natürlichen Pflanzenfamilien. A. Engler and K. Prantl (eds.), Band IV/5. Engelmann, Leipzig.

Ohno N., Hirai H., Yoshioka H., Dominguez X. A., Mabry T. J., 1973. Cynaropicrin, a sesquiterpene lactone from *Centaurea americana*. Phytochem. 12: 221-222.

Samek Z., Holub M., Drożdż B., Jomni G., Corbella A., Gariboldi P., 1971. Sesquiterpenic Lactones of *Cynara scolymus* L. species. Tetrahedron Lett. pp. 4775-4778.

Samek Z., Holub M., Herout V., Sorm F., 1969. Revision of the structure of Cnicin. Tetrahedron Lett. pp. 2931-2933.

Suchy M., Herout V., 1962. Identity of the Bitter Principle from *Centaurea stoebe* (L.) Sch. et Thell. Coll. Czechoslov. Chem. Commun. 27: 1510-1512.

Suchy M., Herout V., Sorm F., 1960. Structure of Cynaropicrin. Coll. Czechoslov. Chem. Commun. 25: 2777-2782.

Suchy M., Samek Z., Herout V., Sorm F., 1967. The Structure of Salonitenolide, a sesquiterpenic lactone of germacrane type from *Centaurea salonitana* Vis. Coll. Czechoslov. Chem. Commun. 32: 2017-2021.

Tarasov V. A., Kasymov Sh. E., Sidiakin G. P., 1973. Isolation of the Cnicin from *Centaurea squarrosa*. Khim. Prir. Soedin. 3: 437.

Wagenitz G., 1955. Pollenmorphologie und Systematic in der Gattung *Centaurea* L. Flora. 142: 213-279.

Laktony seskwiterpenowe. XXIII. Izolacja laktonów seskwiterpenowych z gatunków Centaurea L.

Streszczenie

Z 18 gatunków lub podgatunków z rodzaju *Centaurea* L. wyodrębniono laktony seskwiterpenowe. Salonitenolid (I) znaleziono w: *Centaurea crithmifolia* Vis., *C. friderici* Vis., *C. paniculata* L., *C. calcitrapa* L., *C. pontica* Prodan et E. I. Nyarady, *C. eriophora* L., *C. alba* L. subsp. *deusta* (Ten). Nyman, *C. alba* L. subsp. *caliacrae* (Prodan) Dostal i *C. weldeniana* Reichenb. Knicynę (II) znaleziono w: *Centaurea vallesiaca* (DC.) Jordan, *C. calcitrapa* L., *C. aspera* L. subsp. *aspera*, *C. sphaerocephala* L. subsp. *lusitanica* (Boiss. et Reuter) Nyman, *C. sulphurea* Willd., *C. eriophora* L. i *C. rocheliana* (Heuffel) Dostal. Cynaropikrynę (III) znaleziono w: *Centaurea debeauxii* Gren. et Gordon subsp. *thuillieri* Dostal; acroptilinę (V), repinę (VI) i janerynę (VII) — w *Centaurea bella* Trautv. Stwierdzono, że w badanych roślinach występują jeszcze inne, niezidentyfikowane laktony seskwiterpenowe.