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Sesquiterpene lactones. XXXII. Guaianolides in species from the genus *Chartolepis* Cass.

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Abstract

Differences in the composition of the "lactone fraction" of 4 species from the genus *Chartolepis* Cass. were observed. Cynaropicrin was isolated from the above-ground parts of *Chartolepis intermedia* Boiss. and the occurrence there of grossheimin was confirmed. The following compounds were isolated from the above-ground parts of *Chartolepis glastifolia* (L.) Cass.: centaurepensin, repin, cebellin C, acroptillin, cebellin D, cynaropicrin, cebellin F and janerin. Centaurepensin, repin, cebellin C, acroptillin, cynaropicrin, janerin and a new guaianolide, pterocaulin were isolated from the herb *Chartolepis biebersteinii* Jaub. et Spach. In addition to the lactones found in *Chartolepis biebersteinii*, *Chartolepis pterocaula* (Trautv.) Czer. also accumulated grossheimin.

Key words: sesquiterpene lactones, Chartolepis, Centaureinae, Compositae, chemotaxonomy

INTRODUCTION

Plants belonging to the genus *Chartolepis* Cass., subtribe *Centaureinae*, tribe *Cynarae*, family *Compositae*, are found mainly in the Caucasus region of the USSR and are also encountered in Iran and Turkey.

Some taxonomists set *Chartolepis* Cass. apart from the genus *Centaurea* L. as a section (Flora Iranica 1980, Flora of Turkey 1975). There is also a lack of agreement among botanists on the choice of the morphological traits of plants which should be decisive in differentiating some of the

* This compound is probably identical with a 8-desacetylcentaurepension-8-0(4-hydroxytiglate) isolated from *Centaurea imperialis* (Rustaiyan A., Sharif Z., Tajarodi A., Ziesche J., Bohlmann F., 1984. Neue Guaianolide aus *Centaurea imperialis*. Planta Medica 2: 193-194).

species grouped together in this taxonomic unit. And so, in Flora Europea (1976) one representatie of the genus *Chartolepis* Cass. is given — *Chartolepis glastifolia* (L.) Cass. with its synonym, *Chartolepis intermedia* Boiss. Whereas the authors of Flora USSR (1961) treat *Chartolepis glastifolia* (L.) Cass. and *Chartolepis intermedia* Boiss. as two separate species, differentiated on the basis of the morphology of the bracts and appendages. Similar divergencies are found in the case of *Chartolepis biebersteinii* Jaub. et Spach. and *Chartolepis pterocaula* (Trautv.) Czer. listed separately in Flora USSR (1961) on the basis of leaf width and structure of bracts and appendages, while the authors of Flora of Turkey (1975) and Flora Iranica (1980) consider these differences to be indistinct and treat both as synonyms.

In light of these differences in the proposed classifiation of *Chartolepis* Cass. species, it seemed purposeful to study the chemical composition of their sesquiterpene lactones, in the hope that this might facilitate their proper taxonomical arrangement.

MATERIAL AND METHODS

Four (of the seven) spcies from the genus *Chartolepis* Cass., cultivated in the Garden of the Chair of Medicinal Plants in Poznań (Poland) from seeds obtained from botanical gardens in Mainz (FRG) and Yerevan (USSR), were used in this study. "Lactone fractions" were isolated by the method of Drożdż and Piotrowski (1973) from the above-ground parts of *Chartolepis intermedia* Boiss., *Ch. pterocaula* (Trautv.) Czer., *Ch. glastifolia* (L.) Cass., and *Ch. biebersteinii* Jaub. et Spach.

Chromatographic analysis. The composition of the "lactone fraction" was controlled by TLC on silica gel plates, in comparison with known sesquiterpene lactones present in the subtribe *Centaureinae*. The final results are presented on the chromatogram (Fig. 1) on which the varied composition of the lactone fractions in the studied species is visible. The most differing in its "lactone fraction" is *Chartolepis intermedia*, where the dominant spot of cynaropicrin is evident, as is the clearly weaker grossheimin spot. A greater number of lactones was found in the remaining species.

Identification of the isolated compounds. The known guaianolides which were obtained were identified on the basis of their color reaction with selectively staining developers (Drożdż and Błoszyk 1978), R_f values and IR spectra compared with standards. The structure of the new sesquiterpene lactone was determined in cooperation with the Institute of Chemistry and Biochemistry of the Czechoslovak Academy of Sciences on the basis of ^{1}H-NMR 200 MHz, MS and CD spectra.

Guaianolides of *Chartolepis pterocaula* (Trautv.) Czer. The chloroform extract ("lactone fraction") obtained from dired and fragmented above-ground

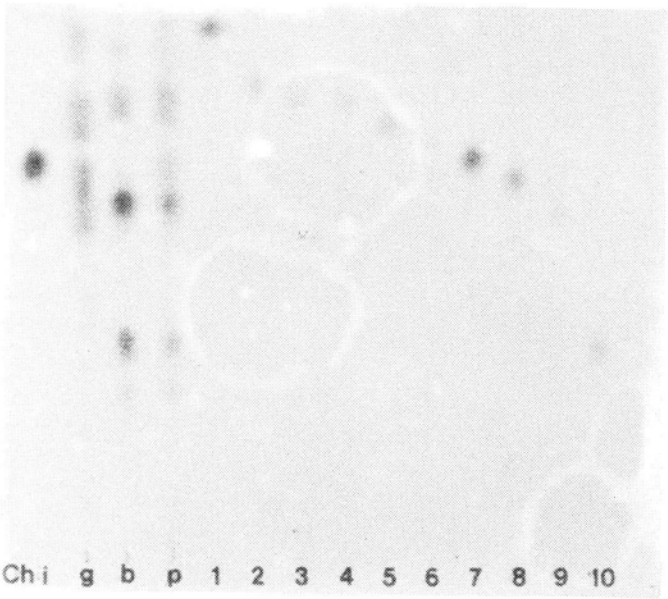

Fig. 1. Chromatography of "lactone fractions" from species from the genus *Chartolepis* Cass. and of isolated lactones. Ch. i. — "lactone fraction" from *Chartolepis intermedia*, g — "lactone fraction" from *Chartolepis glastifolia*, b — "lactone fraction" from *Chartolepis biebersteinii*, p — "lactone fraction" from *Chartolepis pterocaula*, 1 — centaurepensin, 2 — repin, 3 — cebellin C, 4 — acroptillin, 5 — cebellin D, 6 — grossheimin, 7 — cynaropicrin, 8 — cebellin, F, 9 — janerin, 10 — pterocaulin

parts was applied to a 100 cm long column filled with silica gel (120 g) suspended in chloroform. The compounds were eluted with chloroform-acetone 7:1 (v/v), gradually increasing the polarity of the system.

Isolation of centaurepensin (I). Fraction 1 crystallized after condensation to a small volume (3 cm^3). The substance was separated from the liquid, rinsed with chloroform and dried. White crystals (95 mg) with a melting point of 216-218°C were obtained and identified as centaurepensin (I).

Isolation of grossheimin (IX) and repin (IV). Fraction 2 crystallized in the eluent. The crystalline substance was filtered off and rinsed with chloroform. Forty-thre mg of a compound identified as grossheimin (IX) were obtained. The filtrate remaining after removing grossheimin was condensed and dissolved in 1cm^3 of chloroform. A two-fold volume of ethyl ether was added and the mixture chilled. Twenty-three mg of a substance with a m.p. of 154-156°C were obtained and identified as repin (IV).

Isolation of acroptillin (V) and cebellin C (II). As shown by control chromatography, fraction 4 contained, after crystallization, two compounds. The crystals were filtered off and thouroughly washed with chloroform. Sevety-two mg of a chromatographically homogenous compound with a m.p. of 195-196°C were obtained and identified as acroptillin (V). The second compound (remaining in the filtrate) was purified from traces of acroptillin by preparative chromatography on silica gel in a system of ethyl ether--benzene 5:1 (v/v). A substance with a m.p. of 181-183°C crystallized from ethyl ether and was shown to be identical with cebellin C (II).

Isolation of cynaropicrin (VII). A colorless, syrupy liquid was obtained from fraction 7 in the amount of 79 mg. This compound was identified as cynaropicrin (VII).

Isolation of janerin (VI). Fraction 9, which was chromatographically homogenous, contained 86 mg of an amorphous lactone which was identified as janerin (VI).

Isolation of petrocaulin (X). Fraction 12 contained a substance which crystallized in chloroform-ethyl ether and exhibited a m.p. of 157-158°C. This was the new guaianolide, pterocaulin (X). Details of its structure are presented in a separate paper (Budějšínský et al. 1986).

Guaianolides in *Chartolepis glastifolia* (L.) *Cass.* The compounds contained in the "lactone fraction" obtained from 630 g of dried plant parts were prepared identically as in the case of *Ch. pterocaula*. The following compounds were obtained: centaurepensin (I) — 39 mg, repin (IV) — 26 mg, acroptillin (V) — 87 mg, cebellin C (II) — 12 mg, cynaropicrin (VII) — 45 mg, janerin (VI) — 98 mg and two compounds which do not occur in *Ch. pterocaula*.

Isolation of cebellin D (III). Fraction 4 was rechromatographed on a 25 cm long column filled with 18 g of silica gel suspended in chloroform. The dominant compound in this fraction was purified in a hexane-chloroform-

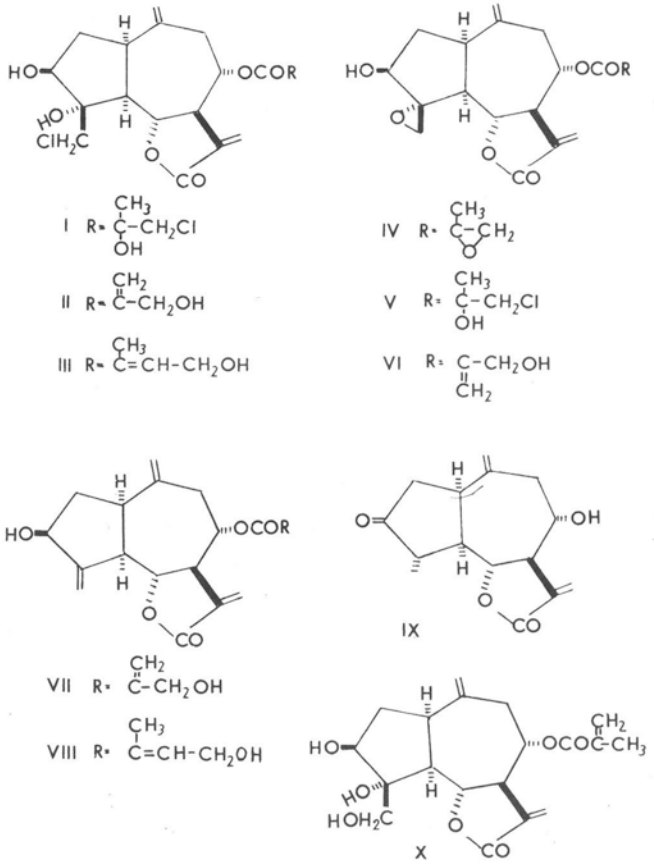

Fig. 2. Sesquiterpene lactones present in species from the genus *Chartolepis* Cass. I — centaurepensin, II — cebellin C, III — cebellin D, IV — repin, V — acroptillin, VI — janerin, VII — cynaropicrin, VIII — cebellin F, IX — grossheimin, X — pterocaulin

-ethyl acetate 1:1:1 (v/v/v) system. A chromatographically homogenous compound identified as cebellin D (III) was obtained.

Isolation of cebellin F (VIII). Fraction 7 contained an amorphous compound of which 43 mg were obtained. It was identified as cebllin F (VIII).

Guaianolides in *Chartolepis biebersteinii* **Jaub. et Spach.** The "lactone fraction" obtained, as described earlier, from 450 g of dried plant parts was also separated as described previously. The following amounts were obtained: centaurepensin (I) — 21 mg, repin (IV) — 33 mg, acroptillin (V) — 29 mg, cebellin C (II) — 10 mg, cynaropicrin (VII) — 35 mg, janerin (VI) — 35 mg and pterocaulin (X) — 41 mg.

Guaianolides in *Chartolepis intermedia* **Boiss.** The two compounds seen on the chromatogram of the "lactone fraction" of *Ch. intermedia* (850 g of dried plant parts) were separated by column chromatography on silica gel in a chloroform-ethyl acetate 1:1 (v/v) system. Forty-five mg of grossheimin

were obtained, which confirmed the results of previous studies (Mukamietshanov et al. 1969). One and one-half g of cynaropicrin (VII) were also obtained.

DISCUSSION

Diversity was observed in the composition of the sesquiterpene lactones of the four studied species of the genus *Chartolepis* Cass. (Fig. 1). This is especially evident in the case of *Ch.* intermedia Boiss. which contains the highest amounts of cynaropicrin and grossheimin. *Ch. glastifolia* (L.) Cass., given in Flora Europea (1976) as a synonymous species, accumulated 8 sesquiterpene lactones, among which are 3 redently found in *Cenaturea bella* Trautv. (Nowak et al. 1986). These are cebellin C, D and F.

Similar guaianolides were found in two species which have been described separately only in Flora USSR (1961), *Ch. biebersteinii* Jaub. et Spach. and *Ch. pterocaula* (Trautv.) Czer., which, additionally, accumulates grossheimin. Also, the newly identified guaianolide, pterocaulin, was isolated from these species.

The following compounds were obtained from the above-ground parts of *Chartolepis pterocaula* (Trautv.) Czer.: centaurepesin I, repin IV, cebellin C II, acroptillin V, cynaropicrin VII, janerin VI, pterocaulin X and grossheimin IX (Fig. 2).

Chartolepis glastifolia (L.) Cass. accumulates: centaurepensin, repin, cebellin C, acroptillin, cebellin D III, cynaropicrin, cebellin F VIII and janerin.

Centaurepensin, repin, cebellin C, acroptillin, cynaropicrin, janerin and pterocaulin were obtained from *Chartolepis biebersteinii* Jaub. et Spach.

The presence of grossheimin in *Chartolepis intermedia* Boiss. (Mukamietshanov et al. 1969) was confirmed, and cynaropicrin was obtained from this plant.

Acknowledgment

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Laktony seskwiterpenowe. XXXII. Gwajanolidy w gatunkach rodzaju Chartolepis Cass.

Streszczenie

Zaobserwowano zmienny skład „frakcji laktonowych" u czterech gatunków z rodzaju *Chartolepis* Cass. Z części nadziemnych *Chartolepis intermedia* Boiss. wyizolowano cynaropikrynę i potwierdzono obecność grossheiminy. Z części nadziemnych *Chartolepis glastifolia* (L.) Cass. wyodrębniono centaurepensynę, repinę, cebellinę C, akroptylinę, cebellinę D, cynaropikrynę, cebellinę F i janerynę. Z ziela *Chartolepis biebersteinii* Jaub. et Spach. wyizolowano centaurepensynę, repinę, cebellinę C, akroptylinę, cynaropikrynę, janerynę i nowy gwajanolid — pterokaulinę. *Chartolepis pterocaula* (Trautv.) Czer. obok laktonów występujących w *Chartolepis biebersteinii* gromadzi jeszcze dodatkowo grossheiminę.