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SESQUITERPENE LACTONES FROM *CENTAUREA* SPECIES

ANTONIO G. GONZÁLEZ, JAIME BERMEJO BARRERA, TOMÁS ZARAGOZA GARCÍA and FRANCISCO ESTÉVEZ ROSAS

Instituto de Química Orgánica, Universidad de La Laguna; Instituto de Productos Naturales Orgánicos, CSIC, La Laguna, Tenerife, Canary Islands, Spain

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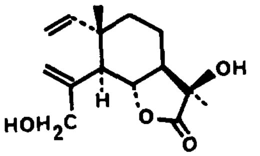
Key Word Index—*Centaurea castellana*; *C. sulphurea*; *C. sonchifolia*; *C. tagananensis*; Compositae; sesquiterpene lactones; eudesmanolides; germacranolides; guaianolides; elemanolides.

Abstract—The investigation of further *Centaurea* species gave, in addition to known compounds, one new sesquiterpene lactone, 11β,15-dihydroxysaussurea lactone, of the elemanolide type.

In continuation of our investigations of the genus *Centaurea*, we have studied the constituents of a species from the Canary Islands and three species from the Iberian Peninsula. The aerial parts of *Centaurea castellana* Boiss afforded artemissifolin [1], dehydromelitensin [2] and the elemanolide (**1**).

The structure of **1** followed from the ^{1}H NMR spectrum (Table 1) which was similar to that of 8-deoxymelitensin (**2**) [3] except that the C-11 methyl signal was shifted slightly downfield in the spectrum of **1** compared with the corresponding shift in the spectrum of **2**. The stereochemistry of the hydroxyl at C-11 is probably β, judging by the downfield chemical shift of the H-6 signal.

The aerial parts of *Centaurea sulphurea* Willd afforded cnicin [4] and the flavone pectolinarigenin [5].



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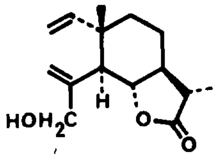

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Table 1. Comparison of the ^{1}H NMR spectral data of compounds **1** and **2** [chemical shift, δ in $CDCl_3$; coupling constants (in parentheses) in Hz; TMS as internal standard]

	1*	**2†**
H-1	5.86 *q* (17.11)	5.78 *q* (17.5, 10.0)
H-2	4.95 *s*	4.94 *dd* (17.5, 1.00)
		4.98 *dd* (10.0, 1.00)
H-3	5.42 *s*	5.36 *m*
	4.95 *s*	4.95 *m*
H-5	2.33 *d* (11.5)	2.35 *d* (12.0)
H-6	4.30 *t* (10)	4.14 *dd* (12.0, 10.0)
H-13	1.28 *s*	1.23 *d* (6.8)
H-14	4.02 *s*	4.01 *m*
H-15	1.10 *s*	1.10 *s*

*90 MHz ^{1}H NMR data.
†100 MHz ^{1}H NMR data.

The aerial parts of *Centaurea sonchifolia* L. afforded acetyl-artemisiifolin [6] and artemisiifolin [1].

The aerial parts of *Centaurea tagananensis* Svent afforded cynaropicrin [7], onopordopicrin [8], dehydromelitensin-8-(*O*)-4(4′-hydroxymethacrylate) [9], melitensin [10] and deacylcynaropicrin [8].

EXPERIMENTAL

The air-dried, finely cut aerial part of the plant was extracted with EtOH in a Soxhlet. After concentrating, the residue was dissolved in hot EtOH. Pb $(OAc)_2$ in hot H_2O was added and the soln was left overnight. It was filtered, concd until the EtOH was eliminated, and extracted with EtOAc. Evapn of the solvent gave a residue which was separated by CC (silica gel) and further TLC (silica gel). Known compounds were identified by comparing ^{1}H NMR spectra with those of authentic material.

Centaurea castellana was collected in June 1977 in Tarrajón (Guadalajara). 10 kg afforded 20 mg artemisiifolin, 16 mg dehydromelitensin and 12 mg **1** (C_6H_6–EtOAc, 3:2).

Centaurea sulphurea was collected in May 1977 in Pantano de los Bermejales (Granada). 3 kg afforded 500 mg cnicin and 60 mg pectolinarigenin.

Centaurea sonchifolia was collected in May 1978 in Totana (Murcia). 3 kg afforded 50 mg acetyl-artemisiifolin and 25 mg artemisiifolin.

Centaurea tagananensis was collected in March 1978 in La Laguna (Tenerife). 4 kg gave 15 mg cynaropicrin, 308 mg onopordopicrin, 16 mg dehydromelitensin-8-(*O*)-4(4′-hydroxymethacrylate), 43 mg melitensin and 10 mg desacylcynaropicrin.

11β,15-Dehydroxysaussurea lactone (**1**) was crystallized (EtOAc–hexane) to give colourless needles, mp 138–140°, $[\alpha]_D^{25}$ $+70°$ ($CHCl_3$; *c* 1.7). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 3540 (OH), 1770 (γ-lactone), 1630 (C=C). MS *m/z*: 266 $[M]^+$ $C_{15}H_{22}O_4$, 248 $[M-H_2O]^+$.

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FURANOHELIANGOLIDES AND FLAVONOIDS FROM *LOURTEIGIA BALLOTAEFOLIA*

JORGE TRIANA*

Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, Venezuela

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Key Word Index—*Lourteigia ballotaefolia*; Compositae; Eupatorieae; heliangolides; flavonoids.

Abstract—The aerial parts of *Lourteigia ballotaefolia* afforded, in addition to three known flavonoids, two furanoheliangolides. The structures and stereochemistries were determined by chemical and spectroscopic means and were established as the 8- and 9-acetylsarracinoyl esters of 1-keto-8β-9β-dihydroxygermacra-2,4,11(13)-trien-3, (10β)-oxo-6α,12-olide. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Lourteigia* contains seven species which are distributed in Colombia and Venezuela. This genus is placed in the *Gyptis* group (tribe Eupatorieae) [1], and to it belongs *Eupatorium ballotaefolium* H.B.K. which is now named *L. ballotaefolia* (H.B.K.) K. et R. [2]. No chemical investigations have been reported previously on these plants. We have investigated this species to determine if the chemistry might help in taxonomic revision within this diverse group. The aerial parts of this plant afforded several known flavonoids and two furanoheliangolides which are closely related to those isolated from other genera of this tribe.

RESULTS AND DISCUSSION

The aerial parts of *Lourteigia ballotaefolia* afforded the flavonoids hispidulin (**1**) [3], eupafolin (**2**) [4] and the 3-methyl ether of quercetin (**3**) [5], as well as two sesquiterpene lactones, **4** and **5**, which could only be separated with difficulty. The structure of **4** was identical to conoprasiolide 5′-*O*-acetate, isolated from *Conocliniopsis prasiifolia* [6], for which the stereochemistry was given, but the 8β-acyloxy group cannot be assigned with certainty. Acetylation of **4** using pyridine gave a mixture of several compounds. Acetylation using *p*-toluenesulfonic acid as a catalyst afforded the acetate **6**. Catalytic hydrogenation of **4** afforded **7**. The C-6 lactone closure was confirmed since the signal at δ5.15 in the ^{1}H NMR spectrum of **4** attributed to the C-6 allylic hydrogen of the lactone closure was shifted upfield to δ4.45 in **7** (Table 1). All the signals were clearly established by decoupling experiments. When **4** was hydrolysed with pyridine it afforded **8**. This reaction supports the stereochemistry at C-8 since the hydrolysis under these conditions occurs by an intramolecular catalysis, which is facilitated by the ester and the hydroxyl group in the *cis* position. The second sesquiterpene lactone was a furanoheliangolide isomer of **4**, in which the relative positions of the acetylsarracinate and the hydroxyl group were interchanged. The ^{1}H NMR spectral data (Table 1) and the obtainment of **8** by hydrolysis with pyridine showed that the structure was **5**. The free C-8 hydroxyl group caused a downfield shift of the H-6 signal, again supporting the stereochemistry at these centres. Compounds **4** and **5** were derivatives of atripliciolide, which is the 8-desacyl-9-desoxy derivative of **4** [7].

The sesquiterpene lactones isolated from *L. ballotaefolia* support the proposed relationship of this genus to the *Gyptis* group. Obviously more species of the genus *Lourteigia* need to be investigated but furanoheliangolides have been isolated in the tribe Eupatorieae only from the *Gyptis* group (*Conocliniopsis* [6], *Trichogonia* [8],

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*Present address: Departamento de Química Fundamental, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica, Las Palmas de Gran Canaria, Canary Islands, Spain.