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GERMACRANOLIDES FROM *CENTAUREA MELITENSIS*

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Key Word Index—*Centaurea melitensis*; Compositae; germacranolides; elemanolides.

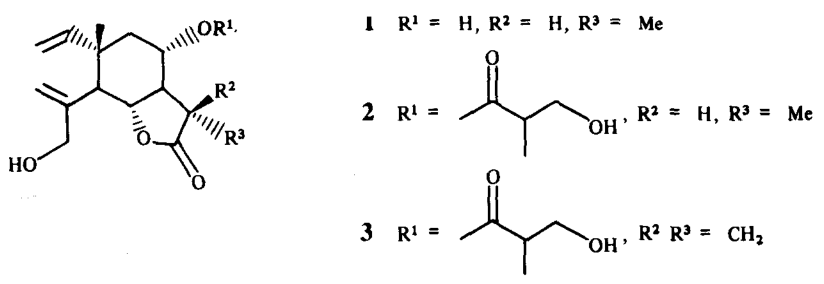
Abstract—The germacranolides salonitenolide, onopordopicrin and arctiopicrin have been isolated from the ether extract of *Centaurea melitensis*. No elemanolide has been found. These results are different from those previously reported.

As a part of our investigations of the synthesis of sesquiterpene lactones, we had to isolate the elemanolide melitensin (**1**), which has been described as a constituent of the ethanol extract of *Centaurea melitensis* L. together with the related compounds melitensin-β-hydroxyisobutyrate (**2**) and dehydromelitensin-β-hydroxyisobutyrate (**3**) [1, 2].

When the aerial parts of *C. melitensis* collected in Granada were extracted with ether, the germacranolides salonitenolide (**4**) (3% of the extract), onopordopicrin (**5**) (38%) and arctiopicrin (**6**) (8%), which were not described in the preceding papers, were obtained. The physical and spectroscopic properties of these compounds are identical to bibliographical values [3–5], and the ^{13}C NMR data confirm their structures (Table 1). We have not, however, detected any elemanolide in the extract.

These contradictory results could be attributed to the different extraction procedures used in this and previous studies. In ref. [1], the plant was extracted with refluxing ethanol and the extract defatted by treatment with lead acetate. A defatting step was not necessary in our work-up of the ether extract, since not many fats are extracted under these conditions. Thus, the high temperatures that could cause Cope rearrangements of the germacranolides into their corresponding elemanolides were avoided. These results are similar to those obtained in our study of *Centaurea malacitana* Boiss. [6].

We suggest that **1** is not a component of *C. melitensis* as was previously reported [1], but an artefact resulting from the extraction and manipulation process.



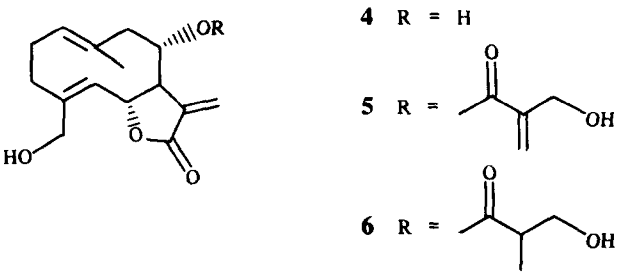


Table 1. ^{13}C NMR spectral data of compounds **5** and **6** (75 MHz, Me_2CO-d_6)

C	**5**	mult.	**6**	mult.
1	129.92	CH	130.11	CH
2	26.35	CH_2	26.81	CH_2
3	34.49	CH_2	34.92	CH_2
4	144.66	C	144.98	C
5	128.59	CH	128.63	CH
6	76.92	CH	77.08	CH
7	52.95	CH	52.91	CH
8	73.21	CH	73.14	CH
9	48.72	CH_2	49.21	CH_2
10	132.55	C	133.27	C
11	136.95	C	137.01	C
12	169.72	C	170.25	C
13	124.32	CH_2	128.82	CH_2
14	16.50	Me	16.77	Me
15	60.40*	CH_2	60.61	CH_2
1′	165.15	C	174.81	C
2′	141.48	C	43.40	CH
3′	60.75*	CH_2	64.34	CH_2
4′	123.72	CH_2	13.95	Me

*Interchangeable values.

EXPERIMENTAL

Plant material was collected in May at La Rabita, Granada, Spain, and identified by Professor F. Valle, Department of Botany, University of Granada. A voucher specimen is available for inspection at the herbarium of the Faculty of Sciences of the University of Granada. The plant, once air-dried (1 kg), was cut up and extracted with refluxing Et_2O (4 l). The Et_2O extract (22 g, 2.2% of the plant material) was chromatographed on a silica gel column with $CHCl_3$–Me_2CO mixtures giving salonitenolide (**4**) (0.6 g), onopordopicrin (**5**), (8.3 g) and arctiopicrin (**6**) (1.8 g).

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A DITERPENE, DISTANOL, FROM *SIDERITIS DISTANS*

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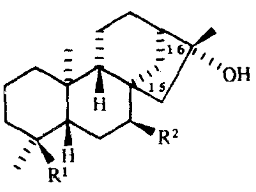
Key Word Index—*Sideritis distans*; Labiatae; *ent*-kauran-7α,16β,18-triol.

Abstract—A new diterpene, distanol, has been isolated from the petrol extract of the aerial part of *Sideritis distans* Wild. Its structure and stereochemistry has been assigned by spectroscopic methods.

From the aerial part of *Sideritis distans* Wild, a species growing in Greece, we have previously [1] isolated four tetracyclic isokaurene diterpenes: siderol (*ent*-7α-acetoxykaur-15-ene-18-ol) [2], sideridiol (*ent*-kaur-15-ene-7α,18-diol) [2], sideroxol (*ent*-15β,16β-epoxy-kaurane- 7α,18-diol) [3], epoxysiderol (ent-15β,16β-epoxykauran-7α-acetoxy-18-ol) [4].

Further investigation of the petrol extract of this plant led us to the isolation (trace amounts) of a new diterpenoid of the *ent*-kaurane series which was named distanol (**1**).

Distanol (**1**), mp 260–265° has molecular formula $C_{20}H_{34}O_3$ (*m/z* 322 M^+) determined by mass spec-



	R^1	R^2
1	CH_2OH	OH
2	CH_2OAc	OAc