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## LOLIOLIDE FROM *ARNICA MONTANA*\*

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**Key Word Index**—*Arnica montana*; Compositae; terpenoid; loliolide.

**Plant.** *Arnica montana* L. **Source.** Leaves collected in the Šumava Mountains (Specimen No 236/69 deposited in the Herbarium of our Institute in Průhonice). **Previous work.** Isolation of loliolide from *Fumaria officinalis* L. [1]; from the leaves of *Digitalis lanata* Ehrh. [2]; from the pasture [3]; from *Lolium perenne* L. [4]; from the leaves of *Digitalis purpurea* L. [5]; its structure [4–6]; stereostructure [4, 7]; synthesis of racemic loliolide [8].

**Present work.** Dry, ground leaves were extracted with petrol [9] and then with  $\text{CHCl}_3$ . The residue of the  $\text{CHCl}_3$  extract was worked up as described earlier [10]. Repeated chromatography on Si gel yielded loliolide, mp 151–152°,  $[\alpha]_D^{20} -9.0^\circ$  (MeOH),  $\text{C}_{11}\text{H}_{16}\text{O}_3$  ( $\text{M}^+$  at  $m/e$  196).

(Found: C, 67.54; H, 8.07; H act., 0.56. Calc: C, 67.33; H, 8.22%; H act. 0.51), IR ( $\text{CHCl}_3$ ): 3460, 3615, 1738, 1626  $\text{cm}^{-1}$ ), identical (mp, mmp, IR,  $[\alpha]_D$ , MS and PMR) with the authentic loliolide.

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## *p*-COUMARIC ESTERS AND FATTY ALCOHOLS FROM *ARTEMISIA CAMPESTRIS*

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**Key Word Index**—*Artemisia campestris*; Compositae; *p*-coumaric esters; fatty alcohols.

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**Plant.** *Artemisia campestris* L., identified and collected by Ž. Joksimović (Botanic Garden,

Faculty of Sciences, Belgrade). *Source*. Deliblatska peščara, Yugoslavia. *Previous work*. On roots [1].

*Present work*. The residue (44 g) obtained from the  $\text{CHCl}_3$  extract of dried powdered *A. campestris* L. (whole plant, 3 kg) was extracted with MeOH. The solvent was evaporated to give residue (20 g) which was chromatographed on Si gel column by successive elution with  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_6$ -EtAc and MeOH.

*p*-Coumaric esters (712 mg), eluted with 5% EtAc in  $\text{C}_6\text{H}_6$ ; IR(KBr)  $\nu_{\text{max}}$  3380, 3010, 2925, 1685, 1470, 1265, 1165, 975, 860, 715  $\text{cm}^{-1}$ ; UV(MeOH)  $\lambda_{\text{max}}$  230, 315 nm; PMR, ( $\text{CDCl}_3$ ) 0.80–1.00 (ca 3 H, *m*, Me-group), 1.27 (ca 40 H, *s*, aliphatic straight chain), 4.22 (2 H, *t*, *J* 6.5 Hz, ester  $\alpha$ - $\text{CH}_2$  group), 6.00 (1 H, exc. with  $\text{D}_2\text{O}$ , phenolic OH), 6.91, 7.47 (4 H, AA'BB' system, *J*  $\approx$  9 Hz, aromatic protons), 6.33, 7.70 (2 H, AM system, *J*  $\approx$  16 Hz, olefinic protons);  $\text{M}^+$  at *m/e* 402 + 14*n*, *n* = 0–10, corresponding to molecular formula  $\text{C}_9\text{H}_7\text{O}_3(\text{CH}_2)_n\text{Me}$ , *n* = 17–27; *p*-coumaric esters (500 mg) were saponified [2] to give (a) *p*-coumaric acid (37 mg), mp 205°,  $\text{C}_9\text{H}_8\text{O}_3$  ( $\text{M}^+$  164) and (b) alcohol fraction (220 mg) which was converted into a mixture of methyl esters by oxidation (Jones reagent) and subsequent esterification (etheral  $\text{CH}_2\text{N}_2$  soln); GLC-MS [3] analysis of these (OV –1, 3%, Chromosorb W, 80–100, 6 m  $\times$  1 mm, 100–330°, 8°/min) showed the alcohol fraction (b) to consist of eleven straight chain primary aliphatic alcohols ( $\text{C}_{18}$ – $\text{C}_{28}$ , Table 1).

Table 1. Composition of alcohols from *Artemisia campestris* as *p*-coumaric esters, or as free alcohols

Carbon	Esters	% of Total Alcohol Free
18	9.5	0.9
19	1.4	0.9
20	52.0	2.8
21	1.2	0.8
22	27.2	41.0
23	0.3	3.0
24	5.1	42.1
25	0.2	2.6
26	2.1	5.9
27	0.2	
28	0.8	

Fatty alcohols (80 mg), waxy solid, eluted with 5% EtAc in  $\text{C}_6\text{H}_6$  (after *p*-coumaric esters), IR(KBr)  $\nu_{\text{max}}$  3640, 1470, 1050  $\text{cm}^{-1}$ ; identified as mixture of nine straight chain aliphatic alcohols ( $\text{C}_{18}$ – $\text{C}_{26}$ , Table 1) by GLC-MS analysis of methyl esters (conditions of chromatography as in above).

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### KAURENOIDS FROM *CACALIA BULBIFERA*\*

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**Key Word Index**—*Cacalia bulbifera*; Compositae; kaurenoids; phytol; phytosterols; friedelin; taraxasterol.

*Plant and source*, *Cacalia bulbifera* (Maxim.) Kitam. (Compositae). The plant material was col-

lected in the mountainous areas near Sendai, Japan.

*Present work*.  $\text{Al}_2\text{O}_3$  chromatography of the petrol soluble portion (30 g), of the MeOH extract

\* Part 2 in the series "Constituents of *Cacalia* spp." For Part 1 see Ref. 10.