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

Present work. The residue (44 g) obtained from the $CHCl_3$ 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 C_6H_6, C_6H_6–EtAc and MeOH.

p-Coumaric esters (712 mg), eluted with 5% EtAc in C_6H_6; IR(KBr) ν_{max} 3380, 3010, 2925, 1685, 1470, 1265, 1165, 975, 860, 715 cm^{-1}; UV(MeOH) λ_{max} 230, 315 nm; PMR, ($CDCl_3$) 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 α-CH_2 group), 6·00 (1 H, exc. with D_2O, phenolic OH), 6·91, 7·47 (4 H, AA′BB′ system, $J \simeq 9$ Hz, aromatic protons), 6·33, 7·70 (2 H, AM system, $J \simeq 16$ Hz, olefinic protons); M^+ at *m/e* 402 + 14*n*, $n = 0$–10, corresponding to molecular formula $C_9H_7O_3(CH_2)_nMe$, $n = 17$–27; *p*-coumaric esters (500 mg) were saponified [2] to give (a) *p*-coumaric acid (37 mg), mp 205°, $C_9H_8O_3$ (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 CH_2N_2 soln); GLC–MS [3] analysis of these (OV −1, 3%, Chromosorb W, 80–100, 6 m × 1 mm, 100–330°, 8°/min) showed the alcohol fraction (b) to consist of eleven straight chain primary aliphatic alcohols (C_{18}–C_{28}, Table 1).

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

Carbon	% of Total Alcohol	
	Esters	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 C_6H_6 (after *p*-coumaric esters), IR(KBr) ν_{max} 3640, 1470, 1050 cm^{-1}; identified as mixture of nine straight chain aliphatic alcohols (C_{18}–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 collected in the mountainous areas near Sendai, Japan.

Present work. Al_2O_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.

of the dried total herb (5·8 kg), followed by SiO_2 chromatography, preparative TLC, yielded a series of kaurenoids as well as phytol, phytosterols, friedelin and taraxasterol. (−)-*Kaur*-16-*en*-19-*al*: needles, after recrystallization of the petrol–Et_2O (10:1) eluate from Al_2O_3, from EtOH, mp 110–114°, $[\alpha]_D^{20}$ −100°, $C_{20}H_{30}O$; IR (KBr) ν_{max} cm^{-1}: 2715 and 1718 (CHO), 880 (end methylene); NMR ($CDCl_3$) δ ppm: 0·89 (3H, *s*), 0·97 (3H, *s*), 4·68 and 4·73 (2H, unresolved, end methylene), 9·74 with a shoulder (1H, CHO) [1, 2]. An authentic sample for comparison (TLC, IR, NMR) was prepared form (−)-kaur-16-en-19-ol by CrO_3 oxidation. *Friedelin*: needles after recrystallization of the eluate following (−)-kaur-16-en-19-al, from EtOAc, mp 254–257°; identified by comparison (TLC, IR, NMR) with an authentic specimen. *Taraxasterol*: needles after recrystallization of the petrol–Et_2O (3:2) eluate on Al_2O_3 from EtOH, mp 221–222°, IR (KBr) ν_{max} cm^{-1}: 3450 (OH), 880 (end methylene), identified by comparison with an authentic specimen (TLC, IR, NMR). *Phytol*: distilled from the mother liquor of taraxasterol, bp_{10mm} 160°, IR (CCl_4) ν_{max} cm^{-1}: 3600 (OH), MS (*m/e*): 278 ($M^+ - H_2O$), identified by comparison with an authentic specimen (TLC, IR, NMR). (−)-*Kauran*-16α-*ol*: needles, after recrystallization of the eluate following taraxasterol and phytol, from EtOAc, mp 207–210°, $[\alpha]_D^{20}$ −84°, $C_{20}H_{34}O$; MS: 290 (M^+); IR (KBr) ν_{max} cm^{-1}: 3340 (OH); NMR ($CDCl_3$) δ ppm: 0·80, 0·83, 1·02 and 1·34 (3H each, *s*), these properties are identical with the reported data for (−)-kauran-16α-ol [3]. Dehydration of this compound with $POCl_3$ in pyridine provided two olefins, one of which was identified as kaurene by comparison with an authentic specimen (TLC, IR, NMR). (−)-*Kaur*-16-*en*-19-*ol* [14]: preparative TLC of the residue after removal of (−)-kauran-16α-ol afforded needles after recrystallization from n-hexane, mp 142–144°; $[\alpha]_D^{20}$ −128°, $C_{20}H_{32}O$; IR (KBr) ν_{max} cm^{-1}: 3345 (OH), 880 (end methylene); NMR ($CDCl_3$) δ ppm: 0·95 and 1·02 (3H each, *s*), 3·45 and 3·77 (2H, a pair of doublets, *J* 11 Hz, CH_2OH on C_4), 4·8 (2H, end methylene). An authentic sample for comparison was prepared through $LiAlH_4$ reduction of the methyl ester of (−)-kaur-16-en-19-oic acid. *Phytosterols*: plates after recrystallization of the eluate with petrol–Et_2O (1:1) on the Al_2O_3 chromatography from EtOH, mp 137–140°; IR (KBr) ν_{max} cm^{-1}: 3440 (OH); MS: 414 (M^+ for $C_{29}H_{50}O$), 412 (M^+ for $C_{29}H_{48}O$), 410 (M^+ for $C_{28}H_{48}O$), presumably a mixture of sitosterol, stigmasterol, and campesterol. (−)-*Kaur*-16-*en*-19-*oic acid*: EtOAc eluate on Al_2O_3, was subjected to SiO_2 chromatography and Et_2O–C_6H_6 (1:1) gave prisms, after recrystallization from EtOH, mp 174–177°; $[\alpha]_D^{20}$ −115°; $C_{20}H_{30}O_2$; methyl ester, mp 81–84°; $C_{21}H_{32}O_2$; MS: 316 (M^+); IR (KBr) ν_{max} cm^{-1}: 1720 (C=O), 880 (end methylene); NMR ($CDCl_3$) δ ppm: 0·88 and 1·09 (3H each, *s*), 3·58 (3H, *s*, OMe), 4·70 (2H, br end methylene). The acid was identified as (−)-kaur-16-en-19-oic acid by comparison with an authentic specimen (TLC, IR, NMR).

Comment. Cacalia bulbifera is significantly different from several other *Cacalia* species in the chemical constitution, because it contains kaurenoids while the others have cacalol, its related sesquiterpenes [7–10] and bakenoide [9]. The relatively high yield (0·2%) of (−)-kaur-16-en-19-oic acid appears to make *C. bulbifera* a promising source of this compound.

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