COMPONENTS OF Matricaria discoidea – GERANYL ISOVALERATE, trans-β-FARNESENE, AND HERNIARIN

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In a study of the components of the Matricaria discoidea DC. growing in Estonia, three individual compounds have been isolated from the essential oil. On the basis of spectral characteristics, their structures have been shown as geranyl isovalerate, trans-β-farnesene, and herniarin.

According to the literature [1-3], the composition of the essential oil of the pineapple weed Matricaria discoidea DC. [Matricaria matricarioides] greatly depends on its growth site. To character the chemotype of pineapple weed growing in Estonia, in the present work we have used three components. Component (I) was isolated as the result of chromatography of the essential oil on a column of silica gel with elution by the solvent mixture benzene–ethyl acetate (10:1). By the rechromatography of certain fractions of the primary separation, with the solvent mixture petroleum ether–diethyl ether (10:1), we isolated component (II) and, with the solvent mixture benzene–ethyl acetate (2:3), component (III). Their structures were determined by the methods of NMR and IR spectroscopy.

Component (I), consisting of a colorless oily aromatic liquid with a purity of 98% according to GLC was geranyl isovalerate (3,7-dimethylocta-2E,6-dienyl 3-methylbutanoate). IR spectrum: $\lambda_{\max}^{\mathrm{KBr}}$ 3030 (=CH–); 1675, 840 $\left(\mathrm{>C{=}C\!<}_{\mathrm{H}}\right)$; 1740 (C=O); 1185, 1120 (C–O–C); 1170, 1095 $\left(\mathrm{>C\!<}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\right)$; 2960, 2930, 2870, 1460, 1380 cm^{-1} (doublet) ($-CH_3$ and $-CH_2-$). An unambiguous proof of the structure and configuration of (I) followed from a comparison with the chemical shifts of its ^{13}C nuclei with those in geranyl acetate [4] and in butyl isovalerate [5]. The E-configuration of the unsymmetrical double bond followed from the chemical shift of C-10 in (I), since in the Z-isomer (the nerol ester), the methyl group would give a signal at about 23.5 ppm instead of 16.4 ppm [4].

Component (II) was isolated in the form of an oily mobile aromatic liquid with a purity of 95% according to GLC, and it consisted of E-β-farnesene (7,11-dimethyl-3-methylenedodeca-1,6E,10-triene). IR spectrum: $\lambda_{\max}^{\mathrm{KBr}}$ 3090 ($=CH_2$); 3030 (=CH–), 1810 (overtone), 1640, 994, 895 $\left(\mathrm{\diagdown CH{=}CH_2}\right)$; 1675, 840 $\left(\mathrm{>C{=}C\!<}_{\mathrm{H}}\right)$; 1640, 1605 (C=C–C=C); 2960, 2925, 2860, 1465, 1385

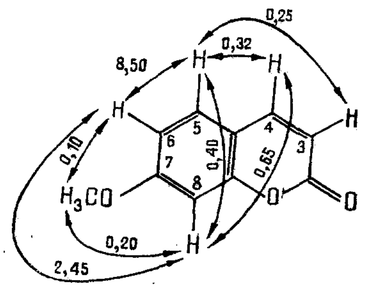

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TABLE 1. Chemical Shifts of the ^{13}C and ^{1}H Nuclei of Geranyl Isovalerate (I) and of E-β-farnesene (II) and of the ^{1}H Nuclei of Herniarin (III)

Atom	Chemical shifts				
	I		II		III
	$\delta^{13}C$	$\delta^{1}H$	$\delta^{13}C$	$\delta^{1}H$	$\delta^{1}H$
1	25,64	1,670	25,63	1,615	—
2	131,76	—	131,08	—	—
3	123,72	5,065	124,06	5,097	6 277
4	26 25	2,082	26,64	2,002	7,659
5	39,48	2,030	39,73	1,926	7,394
6	142,08	—	135.25	—	6,870
7	118,40	5,321	124,40	5,035	—
8	61,03	4,583	26.74	2,136	6,847
9	17.64	1,592	17,61	1,538	—
10	16,40	1 696	15,96	,535	—
11	173,14	—	31,45	2,166	3,899
12	43,45	2,168	146,08	—	—
13	25,72	2,090	139,02	6,300	—
14	22,35	0,946	112,88	5,174[a] 4,979	
15	22,35	0,946	115,61	4,923[a] 4,939	

Trans to H-13.

cm^{-1} ($-CH_3$ and $-CH_2-$). Maxima at 990 and 910 cm^{-1} are characteristic for the α- and β-isomers of farnesene, but that at 890 cm^{-1} only for β-farnesene [6]. The practical coincidence of the C-1...C-6, C-9, and C-10 chemical shifts with those in (I), allowance for the effect of the ester group through the allyl carbon atom on the double bond, the presence of two unsaturated methylene carbon atoms, and the presence of a fragment of 2-substituted buta-1,3-diene according to the characteristic spin-spin interaction between the ^{1}H nuclei [7] and unambiguously determined not only the structure but also the configuration of the double bond.

Component III — a white crystalline powder having fluorescence in UV light, with a degree of purity of 95% according to GLC — was herniarin (7-methoxycoumarin). IR spectrum: λ_{max}^{KBr} 2840, 1465, 1350, ($-CH_3$); 3020, 2940, 1625, 1580, 760 (aromatic ring); 1760 ($>C{=}O$); 1290, 1230, 1120, 1035, (C—O—C, ether and lactone); 1625 cm^{-1} ($\diagup CH{=}CH \diagdown$). The structure of (III) was confirmed by ^{1}H NMR spectrum in which it was possible to see the signal of a methoxy group and the characteristic chemical shifts and $^{3}J_{H,H}$ between the H-3 and H-4 atoms of the coumarin ring [8]. Allowance for long-range spin-spin interactions unambiguously showed that this substance was 7-methoxycoumarin.

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