THE ESSENTIAL OIL OF Dracocephalum foetidum

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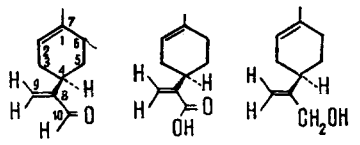
Dracocephalum foetidum Bge. (family Labiatae) has a limited area and is established in the waste stony and sandy steppes of south eastern Altai, Tuva, and Mongolia [1]. To investigate the essential oil, the flowering plants were collected in the environs of the town of Kyzyl. The essential oil (yield 0.7-1.0%), obtained by steam distillation immediately after collection from the epigeal part of the plant, possesses a very sharp smell and a high antimicrobial activity.

Analysis of the essential oil by gas-liquid chromatography (GLC) under the conditions described previously [2] showed that it included 37 components, but only three of them were present in considerable amounts. Of the minor components we identified α-pinene, thujene, camphene, β-pinene, Δ^3-carene, myrcene, β-phellandrene, γ-terpinene, terpinolene, and p-cymene.

The main components were isolated by preparative GLC and thin-layer chromatography. The first compound (22%) was identified by GLC and IR and NMR spectroscopy as d-limonene. The two other compounds – an aldehyde (67%) and an alcohol (6%) – proved to be derivatives of limonene.

The aldehyde, $C_{10}H_{14}O$, has n_D^{20} 1.4998; $[\alpha]_D^{20}+70°$ (c 0.087; CH_3OH); M^+ 150; semicarbazone with mp 117-118°C (ethanol); 2,4-dinitrophenylhydrazone with mp 178-179°C (ethyl acetate). The IR spectrum of the aldehyde has the absorption bands of a trisubstituted double bond (800, 3012 cm^{-1}) and of the fragment $CH_2=\overset{|}{C}-C\overset{O}{\underset{H}{\diagdown\!\!\diagup}}$ (943, 1630, 1700, 2705, 3090 cm^{-1}). The two absorption maxima in the UV spectrum ($\lambda_{max}^{CH_3OH}$ 218, 329 nm, log ε 4.10, 2.6) correspond to this fragment. In the NMR spectrum, signals at 1.65 and 5.33 ppm are assigned to the $CH_3-\overset{|}{C}=\overset{|}{C}-H$, group and four one-proton signals at 2.66, 5.89, 6.14, and 9.48 ppm to the $CH_2=\underset{\underset{>C-H}{|}}{C}-C\overset{O}{\underset{H}{\diagdown\!\!\diagup}}$ group. The aldehyde was reduced with lithium tetrahydroaluminate in ethanol to give an alcohol identical with that isolated from the essential oil. On the basis of the above facts, the structure of p-mentha-1,8-dien-10-al (I) is proposed for the aldehyde.



I II III

On oxidation with silver oxide [3], the p-mentha-1,8-dien-10-al was converted into an acid (II) with the composition $C_{10}H_{14}O_2$, mp 80-81°C (ethanol); $[\alpha]_D^{20}+86.2°$ (c 0.145; CH_3OH) M^+ 166; IR spectrum: 957, 1632, 1700 cm^{-1} $\left(CH_2=\overset{|}{C}-C\overset{O}{\underset{OH}{\diagdown\!\!\diagup}}\right)$; NMR spectrum 1.62, 5.25 ppm $\left(CH_3-\overset{|}{C}=\overset{|}{C}-H\right)$; 2.57, 5.62, 6.32, 12.38 ppm $\left(CH_2=\underset{\underset{>C-H}{|}}{C}-C\overset{O}{\underset{OH}{\diagdown\!\!\diagup}}\right)$.

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The third main component of the essential oil is present in considerably smaller amounts than the d-limonene and the p-mentha-1,8-dien-10-al. Its properties ($[\alpha]_D^{20}$ + 107° (c 0.15; CH_3OH); 3,5-dinitrobenzoate with mp 71-72°C) and spectral characteristics [IR spectrum: 3628, 3345 cm^{-1} (OH); 3095, 1655, 905 cm^{-1} ($CH_2=C<$); NMR spectrum: 1.62, 5.30 ppm ($CH_3-\overset{|}{C}=\overset{|}{C}-H$); 4.0 ppm ($-CH_2-O-$); and 4.78 and 4.92 ppm ($CH_2=C<$)] coincide with those for synthetic p-mentha-1,8-dien-10-ol (III) [4].

The d-limonene, the aldehyde (I), the alcohol (II), and the acid (III) give similar positive smooth optical rotatory dispersion curves, and therefore the last three compounds, like the d-limonene, have the R configuration of the asymmetric centers [5]. p-Mentha-1,8-dien-10-al has not been found previously in plant material, while p-mentha-1,8-dien-10-ol has been isolated only in the form of the acetate [6].

The species Dracocephalum foetidum is very close to Dracocephalum moldavica. Some workers [7] have considered it as a variety of the latter. Other systematists [8] distinguish Dracocephalum foetidum as an independent species on the basis of stable morphological characteristics. The latter point of view is confirmed by the study of the chemical composition of the essential oils. Thus, the essential oil of Dracocephalum moldavica consists mainly of the acyclic monoterpenoids geraniol, nerol, and citral [9], while the essential oil of Dracocephalum foetidum consists of the monocyclic compounds limonene, p-mentha-1,8-dien-10-al, and p-mentha-1,8-dien-10-ol.

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