Chemistry of Natural Compounds, Vol. 35, No. 1, 1999

CHROMATOGRAPHIC STUDY OF THE COMPOSITION OF THE ESSENTIAL OIL OF *Ziziphora clinopodioides*, A VICARIOUS FORM OF *Origanum vulgare*

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UDC 615.332.544

The chemical composition of the essential oil of Ziziphora clinopodioides *has been studied by GLC. A similarity of the qualitative compositions of the terpenoids of the essential oils of* Z. clinopodioides *and other species of this genus has been shown.*

Various species of *Ziziphora* are used in folk medicine for the treatment of cardiovascular and gastrointestinal diseases [1]. *Ziziphora* is one of the genera of oil-bearing plants of the Labiatae family that are widely distributed in the territory of Kazakhstan. The chemical composition of a *Ziziphora* herb includes an essential oil, tanning substances, ascorbic acid, and flavonoids [2]. It is just the present of the essential oil that is responsible for its pharmacological action. The main components of *Ziziphora* essential oil are α-pinene, β-pinene, limonene, menthone, isomenthone, pulegone, and thymol [2].

The chemical compositions of the essential oils of some *Ziziphora* species have been studied previously [3]. In the present paper we give the results of a study of the composition of the essential oil of *Z. clinopodioides* Lam. illustr. — one of 26 vicarious species growing on the territory of Kazakhstan — which it has been proposed to include in the National Pharmacopeia of the Republic of Kazakhstan, now being drawn up. *Ziziphora clinopodioides* is a substitute form of *Origanum vulgare* L. (common origanum or wild marjoram), which, as is well known, is included in GF XI [State Pharmacopeia of the USSR, XIth ed.] [4].

The herb *Ziziphora clinopodioides* was gathered in 1997 in the flowering phase in the valley of the R. Chubai-Nura (Karagandinskaya oblast). The essential oil was obtained from the herb and the components were determined quantitatively by chromatography. Table 1 gives the chemical composition of the essential oil. Previous experimental results [3] are also given here for comparison. Of the 34 compounds, 26 have been identified. As can be seen from Table 1, in the qualitative composition of its terpenoids the essential oil of *Ziziphora clinopodioides* does not differ from other species of *Ziziphora* (it also contains the main compounds of the *para*-menthane series: menthone, isomenthone, menthol, neoisomenthone, limonene, γ-terpinene, pulegone, thymol, carvacrol, and others), regardless of their geographical growth site. At the same time, there are substantial differences in the relative amounts of some components. Thus, the essential oil of *Ziziphora clinopodioides* has higher levels of camphene, isomenthol, neoisomenthol, nerol, and piperitone and lower levels of other compounds (α-pinene, sabinene, *p*-cymene). The amounts of the major component — pulegone — are very close for the *Ziziphora* species given in Table 1 that grow in Kazakhstan territory: mean concentration 62%, mean square deviation 4.3%, concentration in the essential oil of *Ziziphora clinopodioides* 62.4%.

Thus, it is possible to draw the conclusion that, in spite of the closeness of the quantitative levels of the main components of the essential oils of *Ziziphora clinopodioides* and other species of *Ziziphora*, each species is individual with respect both to its qualitative composition and to the quantitative levels of its components.

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Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 66—68, January-February, 1999. Original article submitted May 25, 1998.

0009-3130/99/3501-0052$22.00

TABLE 1. Chemical Compositions of the Essential Oils of *Ziziphora* Species Growing in Kazakhastan

Component	*Ziziphora*			
	pakhuchkovidnaya (*clinopodioides*)	vykhodnevskaya	tsvetonozhechnaya	persidskaya (*persica*)
1. α-Pinene	0.1	0.8	0.8	0.3
2. Camphene	0.9	0.2	0.1	0.1
3. Sabinene	0.1	0.3	0.4	0.3
4. β-Pinene	0.1	0.8	1.0	0.2
5. Myrcene	Tr.	-	-	-
6. α-Terpinene	0.2	0.2	0.3	0.4
7. *p*-Cymene	0.1	0.3	2.2	2.1
8. Limonene + β-phellandrene	0.5	1.5	1.0	3.4
9. 1,8-Cineole	0.1	0.1	0.1	0.2
10. γ-Terpinene	0.1	0.1	0.1	4.8
11. Terpinolene	Tr.	-	-	-
12. Linaeol	0.2	Tr.	0.1	0.3
13. Not ident.	0.1	-	-	-
14. Menthone	2.0	2.3	5.5	1.4
15. Isomenthone	9.0	15.7	11.5	5.1
16. Menthol	5.1	1.6	9.2	2.8
17. Isomenthol	2.4	0.1	Tr.	0.8
18. Neoisomenthol	3.6	0.9	1.2	3.0
19. Nerol	1.4	0.6	0.5	0.3
20. Not ident.	2.1	-	-	-
21. Not ident.	5.9	-	-	-
22. Pulegone	62.4	66.0	62.0	57.5
23. Carvone	0.2	0.3	0.6	0.5
24. Piperitone	1.9	1.1	0.6	4.1
25. Geraniol	0.1	0.1	0.3	0.9
26. Not ident.	0.4	-	-	-
27. Thymol	0.2	1.1	Tr.	0.5
28. Carvacrol	0.1	0.2	Tr.	0.6
29. Not ident.	0.3	-	-	-
30. Not ident.	Tr.	-	-	-
31. Not ident.	Tr.	-	-	-
32. Piperitone oxide	0.2	1.0	0.2	0.8
33. Not ident.	0.1	-	-	-
34. γ-Cadinene	0.1	0.8	Tr.	0.2

EXPERIMENTAL

The distillation of the essential oil was performed by the method of GF X [State Pharmacopeia of the USSR, Xth ed.] [5] in a 2-liter flask with a charge of 30 g of raw material and 1200 ml of water for 4 h. The quantitative determination of the essential oil content was made by the method of GF X [5].

The gas-chromatographic analysis of the essential oil was conducted on a model 3700 chromatograph with a flame-ionization detector. A 2 mm × 3 m stainless column was used. The stationary phase was the silicone elastomer SE-30 deposited in an amount of 5 wt-% on a solid support — Chromaton N Super (particle size 0.125—0.160 cm). Chromatographic analysis was conducted in the regime of linear programming of temperature: from 60 to 220°C at the rate of 4°C/min and in the isothermal regime at 220°C for 5 min. Temperature of the evaporator: 220°C; mobile phase: inert argon at 20 ml/min. Ratio of the rates of flow of hydrogen and air: 1:10. Specimen injected: 1 μl of a 2% solution of the essential oil in acetone.

The components were identified from their characteristic retention times through the introduction of individual components. In a number of cases, pure specimens — chromatographic standards — were isolated from various plants in which they were present in large amount. In individual cases, identification was made on the basis of handbook figures for retention times [6]. Quantitative calculations were performed by the internal normalization method [7]. The essential oil content of *Ziziphora clinopodioides* was 1.2%.

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