AN INVESTIGATION OF THE COMPONENT COMPOSITION OF THE ESSENTIAL OIL OF Monarda fistulosa

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The composition of the essential oil of wild bergamot bee balm introduced into the Krasnodarsk Krai has been analyzed by chromatomass spectrometry. The essential oil contains 34 components of which the main ones are α-pinene (3.5%), β-pinene (2.9%), α-terpinene (1.7%), p-cymene (32.5), an aliphatic aldehyde (6.3%), sabinene hydrate (1.9%), β-caryophyllene (1.1%), the methyl ether of carvacrol (5.5%), citronellyl acetate (1.6%), thymol (12.6%), and carvacrol (24.0%). The compounds were identified on the basis of their mass-spectrometric characteristics and arithmetical retention indices.

The perennial plant Monarda fistulosa L. (wild bergamot bee balm) is found growing wild on the heights of the eastern part of North America [1, 2]. Bee balms are widely used as decorative plants in parks and are good sources of honey [3]. The essential oil (EO) of bee balms is used as a perfume material and for medical purposes [4, 5].

With the aim of finding new promising biologically active compounds from plant raw material, we have investigated the composition of the EO of Monarda fistulosa L., family Laminaceae, introduced into the North Caucasian Zonal Experimental Station of the All-Union Scientific-Research Institute of Medicinal and Aromatic Plants in Krasnodarsk Krai.

The amount of EO in the herbage of wild bergamot bee balm was 0.6-0.9%.

The identification and quantitative determination of the components of the EO was carried out by the chromato-mass spectrometric (CMS) method, as we have described previously [6]. Mass spectra were intrepreted by comparison of the results obtained from the CMS experiment with the mass spectra given in catalogs and the literature [7, 8] and those that we had obtained in the investigation of other EOs [9, 10]. The mass-spectrometric structural assignment of the components was supplemented and checked by the chromatographic results, for which we selected the arithmetic retention indices [11]. The retention indices obtained from the CMS results were also compared with literature figures [11, 12]. Thus, a double check was made on the correctness of the assignment of the experimental results to concrete terpenoids.

The chromatogram of Fig. 1 shows the presence of 34 compounds with concentrations greater than 0.01%. We unambiguously identified 31 compounds by a known procedure [6] (Table 1). It was shown that the EO of wild bergamot bee balm grown under the conditions of Krasnodarsk Krai contains mono- and sesquiterpene hydrocarbons, and alcohols, ethers, and ketones of the terpene series. The main components of the EO studied were phenolic compounds: p-cymene, thymol, and carvacrol. Component 32 was assigned to the sesquiterpene hydrocarbons on the basis of the laws of fragmentation of compounds of this class [13].

An analysis of the mass spectrum of component 26 permitted the proposal for it of the structure of the methyl ether of carvacrol. The assignment made was based on the following facts. Since we had not literature information on component 26 nor a standard sample of it we were forced to carry out the methylation of a sample of the EO with a repeat of the CMS study. The disappearance of the chromatographic peak of carvacrol (compound 34) and an increase in the integral intensity of the chromatographic peak of component 26 with no change in its mass spectrum confirmed the correctness of the hypothesis made. The formation of methyl esters was observed universally for all the identified alcohols in the methylated EO.

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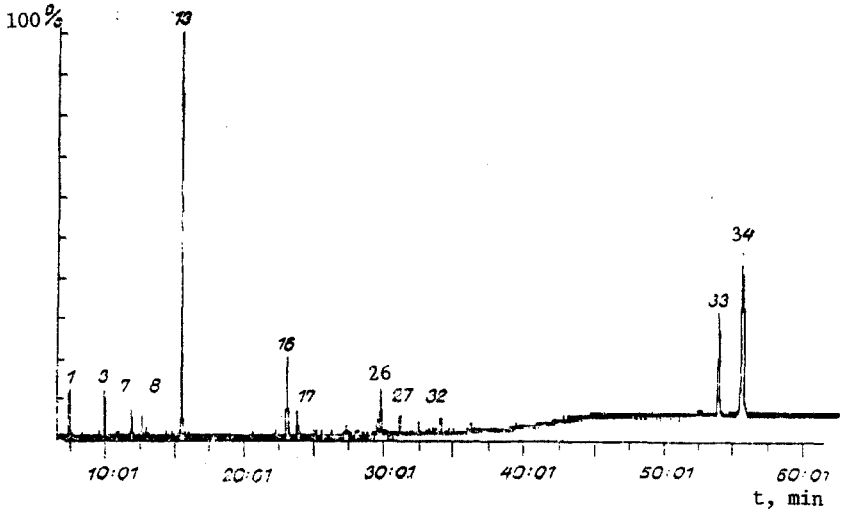

Fig. 1. Chromatogram of the essential oil of wild bergamot bee balm.

TABLE 1. Composition of the Essential Oil of Wild Bergamot Bee Balm

Compound	Retention index	Amount, %	Molecular mass
1. α-Pinene	1024	3.50	136
2. Camphene	1067	0,01	136
3. β-Pinene	1108	2,90	136
4. Sabinene	1118	0,25	136
5. Myrcene	1144	0,20	136
6. Δ^3-Carene	1158	0,01	136
7. α-Terpinene	1177	1,72	136
8. Limonene	1198	1,05	136
9. β-Phellandrene	1212	0,58	136
10. 1,8-Cineole	1214	0,01	154
11. γ-Terpinene	1246	0.24	136
12. Octan-3-one	1254	0.22	128
13. p-Cymene	1272	32,52	134
14. Terpinolene	1284	0,01	136
15. Octan-3-ol	1399	0,35	130
16. Aliphatic aldehyde	1442	6,33	
17. Sabinene hydrate	1456	1.86	154
18. Menthone	1480	0.47	154
19. α-Cubebene	1488	0,01	204
20. Phenol	1514	0.24	154
21. Linalool	1538	0,27	154
22. Isomer of sabinene hydrate	1543	0.32	154
23. Bornyl acetate	1577	0,01	196
24. β-Caryophyllene	1593	1,10	204
25. Terpinen-4-ol	1595	0.24	154
26. Methyl ether of carvacrol	1598	5.50	164
27. Citronellyl acetate	1638	1.64	198
28. Neral	1678	0,16	152
29. Humulene	1684	0,21	204
30. α-Terpineol	1689	0,33	154
31. Borneol	1698	0,23	154
32. Sesquiterpene hydrocarbon	1712	1,05	204
33. Thymol	2146	12,61	150
34. Carvacrol	2180	23.90	150

We were unable to make a correct structural assignment for component 16 solely on the basis of the CMS results. By using a standard procedure for obtaining a hydrazone by reaction with 2,4-dinitrophenylhydrazine [14] we recorded for this derivative a peak $[M]^+$ with m/z 372, which corresponds to a molecular mass of 192 a.m.u. for component 16.

EXPERIMENTAL

The amount of EO was determined by steam distillation using Ginzburg's procedure [15].

The chromato-mass spectrometric investigation was performed on a Finnigan-MAT ITD 700 instrument (ion trap). The recording conditions were the standard ones: energy of the ionizing electrons 70 eV, temperature of the source 230°C. The components of the EO were separated in a capillary column with the grafted phase Carbowax-20 M (0.25 mm × 60 m). The initial temperature of the chromatograph thermostat was 60°C, with programming of the temperature at the rate of 3°C per minute to a final temperature of 180°C, and then isothermal conditions; the rate of flow of the carrier gas (He) was 1 ml/min, and the temperature of the injector and the line connecting the chromatograph with the mass spectrum was 200°C.

The methylation of the EO of wild bergamot bee balm was performed by the procedure of [16].

SUMMARY

The composition of the EO of wild bergamot bee balm has been studied with the aid of chromato-mass spectrometry, 32 compounds being identified. The main components of the EO were p-cymene, thymol, and carvacrol, which are responsible for the biological activity of the EO as an antihelminthic agent. Thymol can be used as an antiseptic epicutaneously and for the disinfection of the mucous membranes of the mouth and throat.

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