COMPOSITION OF THE ESSENTIAL OIL OF *Salvia garedzhii*. TERPENOIDS AND SESQUITERPENE HYDROCARBONS

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The composition of the terpenoid and sesquiterpene hydrocarbon fraction of *Salvia garedzhii* has been studied by chromato-mass spectrometry. A total of 19 compounds have been identified and a provisional assignment of another 6 components has been made.

Among representatives of the genus *Salvia* (family Lamiaceae), many species of plants deserve attention as essential-oil producers. In the Caucasus, 37 species of the genus *Salvia* are known [1], the majority of which are xerophytes and grow on dry slopes. During prospecting expeditions in the Gardabani region of Georgia an essential-oil-bearing plant with a specific odor, *Salvia garedzhii* N. A.-Tr. was collected. This semibrush plant with large pink flowers belongs to the endemic species of the central belt of Central Caucasus [2].

To determine the desirability of cultivating *S. garedzhii* as a crop, we have made an analysis of the essential oil (EO) in the green mass of the plant. The amount of EO varied according to the phases of development from the beginning of flowering to the ripening of the seeds from 0.20 to 0.29%. The yield of green mass on cultivation amounted to 8 tons/ha, and the yield of EO was 17 kg.

Thus, *Salvia garedzhii* may be considered as a promising essential-oil crop. The composition of the EO of this species of sage has not previously been studied. The necessity for studying its component composition was dictated by the high perfume score of this EO (3.5-4.2 points) and also by the possible introduction of this crop into agricultural production.

The component composition of the EO was established by the method of chromato-mass spectrometry. We have shown previously [3] that a comparison of the experimental and published mass spectra permits a reliable identification of terpenoids to be made in the majority of cases. A detailed procedure for determining the components of a EO by this method was subsequently developed [4]. Identification was performed on the basis of the results of a comparison of the mass spectra in relation to the intensities of the characteristic peaks of ions specific for a concrete class of compounds, and the mass spectrum of a standard. The correctness of the structure assignment of a component was checked from the Kovats chromatographic indices.

It was established that the EO of *S. garedzhii* contained terpene hydrocarbon derivatives and sesquiterpene hydrocarbons and alcohols. The quantitative ratio within the class of terpenoids and sesquiterpene hydrocarbons varied only slightly, while the percentages of the sesquiterpene alcohols varied substantially, and qualitative changes were also observed for them according to the growth conditions of the oil-bearing plant. In the present communication we give an interpretation of the composition of the terpenoid and sesquiterpene hydrocarbon fraction. The identification of the sesquiterpene alcohols requires further investigations.

Information on the identification of the components of the *S. garedzhii* EO fraction studied and their quantitative characteristics are given in Table 1. As follows from Table 1, in the fraction studied 19 compounds, together making up 90.3% of the total, were unambiguously identified. We first determined the structure of terpinyl acetate (content, 1.7%), since its mass spectrum contains the peaks of characteristic ions the ratio of the intensities of which exceed the experimental error with respect to reproducibility. Components 23 and 24 were assigned to the class of carbonyl terpene compounds, and component 13 was a sesquiterpene

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TABLE 1. Qualitative and Quantitative Compositions of the EO of *Salvia garedzhii* (without taking the amount of sesquiterpene alcohols into account)

Compound	Mol. wt.	Kovats index	Content, %	Literature
1. 1,8-Cineole	154	1186	2.0	5
2. Octan-3-ol	130	1362	2,3	6
3. Menthone	154	1432	0.3	7
4. Isomethone	154	1451	1.7	7
5. Camphor	152	1455	25,7	8
6. β-Bourbonene	204	1499	1.0	9
7. Linalool	154	1548	4.0	5
8. Linalyl acetate	196	1563	1.0	5
9. Terpinen-4-ol	154	1557	2.0	5
10. Humulene	204	1667	0.7	10
11. Isobornyl propionate	210	1617	6,9	5
12. Terpinyl acetate	196	1622	1,7	11
13. A sesquiterpene hydrocarbon	202	1640	1,7	
14. Structure not established		1650	1,0	
15. Borneol	154	1674	1,7	12
16. α-Terpineol	154	1679	3,0	12
17. Isobornyl butyrate	224	1704	10.0	12
18. Isobornyl valerate	238	1707	17.8	12
19. α-Curcumene	202	1762	1,3	13
20. Citronellol	156	1770	5.9	12
21. Structure not established		1789	0.7	
22. Nerol	154	1800	0.7	12
23. A terpene aldehyde	152	1820	0.6	
24. A monoterpenoid	150	1830	0,7	
25. Geraniol	154	1848	2.3	12

hydrocarbon with an aromatic ring in the structure of the molecule. The assignment of these three compounds with a total proportion in the fraction of 3.0% was made on the basis of general laws of the fragmentation of the molecular ions (M^+) of compounds of the terpene series [14].

The EO of *S. garedzhii* did not contain monoterpene hydrocarbons. Sesquiterpene hydrocarbons were represented by β-bourbonene, humulene, α-curcumene, and an unidentified hydrocarbon with M^+ 202 a.m.u. The greatest contribution to the composition of the EO was made by ketones of the terpene series (mainly camphor), and alcohols and their esters. The considerable amount of the latter (37.4% of the fraction) substantially distinguished the EO investigated from the oils of other species of sage.

EXPERIMENTAL

The essential oil was isolated from the whole of the epigeal part of the plants by steam distillation. The composition of the EO was determined by Ginzburg's method. The EO was freed from sesquiterpene alcohols with the aid of preparative GLC on a column 1 m long and 10 mm in diameter with 5% of silicone SE-30 on Chromosorb W-GMDS as stationary phase at a thermostat temperature of 165°C. The mass spectrometric investigation was performed on a Varian MAT 311A instrument under standard conditions: accelerating voltage 3 kV; energy of the ionizing electrons 70 eV; cathodic emission current 1000 μA. The chromatography of the EO fraction under conditions of mass-spectrometric recording was performed on a Varian-3700 chromatograph using glass capillary columns 20 m long with the stationary phase PEG-20M (initial temperature 60°C, rate of programming 3°C/min, rate of flow of carrier gas (He), 1.5 ml/min). The temperature of the injector and of the separator was 230°C and that of the source of ions in the mass spectrometer 250°C. Quantitative determination was performed with the use of a digital integrator. The treatment of the mass spectra was carried out with the aid of spectrosystem SS-188.

SUMMARY

The composition of the terpenoid and sesquiterpenoid hydrocarbon fraction of *Salvia garedzhii* has been studied for the first time with the aid of chromato-mass spectrometry. A total of 19 compounds making up 90.3% of this fraction of the essential oil have been identified. A preliminary assignment of six other components has been made.

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CIRCULAR DICHROISM OF GUAIANOLIDES AND THE PRODUCTS OF THEIR AMINATION

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The presence of an α-oriented hydroxy group at C_8 in a guaianolide promotes the stereospecificity of the amination of an exomethylene bond linked with the γ-lactone grouping. The addition of morphiline and of piperidine to the exomethylene bond of the lactone ring of a guaianolide containing an α-oriented hydroxy group at C_8 takes place with the preferential formation of the 11S isomer.

Continuing a study of the stereospecificity of amination of an exomethylene bond conjugated with a γ-lactone grouping [1], we have investigated the addition of the cyclic secondary amines morphiline and piperidine to unsaturated lactones of the guaiane type: rupicolin A (I), rupicolin B (II) ajanin (III), ajadin (IV), and chrysartemin (V), and a eudesmanolide – artecalin (VI).

With this aim, the circular dichroism (CD) spectra of the lactones (I-VI) and their amination products have been recorded. The results obtained have enabled us to refine the conclusion drawn previously relative to the stereospecificity of the amination of unsaturated lactones [1].

As can be seen from Table 1, in the CD spectra of the lactones considered a negative Cotton effect (CE) is observed in the 250-270 nm region which is due to the n–π* transition in the α-methylene-γ-lactone chromophore, confirming the trans-linkage of rings B/C.

In ajanin and ajadin, the double bond in ring B causes an inversion of the CE in the 265 nm region. The presence of oxygen-containing substituents at C_4 may also change the sign of the lactone CE, as has been reported previously for the pseudoguanolides ambrosiol and anoludin [2].

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