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TERPENOIDS OF *Mentha piperita* OF THE VARIETIES KRASNODARSKAYA 2, PRILUKSKAYA 6, KUBANSKAYA 6, SELENA, AND SEREBRISTAYA

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Three varieties of *Mentha piperita* (peppermint) are cultivated on the territory of Krasnodar Krai: Krasnodarskaya 2, Prilukskaya 6 and Kubanskaya 6. The last was isolated in the North Caucasus ZOS of VILR in cooperation with the Institute of Cytology and Genetics, Siberian Branch, Academy of Sciences of the USSR [1]. In 1986, another two varieties of peppermint bred by the North Caucasus ZOS VILR were passed to Gossortset' [State Variety Inspectorate for Grain and Oilseed Crops] Serebristaya (hybrid 36-77-1) and Selena (hybrid 24-77-1). They were obtained with the inclusion of wild species of mint [2] and have been studied for the essential oil and menthol that they contain.

Hybrid 24-77-1 was obtained on crossing with the species *M. spicata* L.; it contains a 4.6-5% of essential oil with up to 69% of menthol. From a total of two cuttings it gives about 2100 kg/ha of leaves and up to 83 kg/ha of essential oil.

Hybrid 36-77-1 is similar in its morphological characteristics of the wild species *M. crispa* L. It contains 4.3-4.9% of essential oil with more than 60% of menthol. A total of two cuttings gives about 2300 kg/ha of leaves and up to 100 kg/ha of essential oil.

We investigated the amounts of the 15 main terpenoids of the essential oil of mint of the given varieties by gas—liquid chromatography (Tsvet-4). Conditions of performing the analysis: carrier gas argon at a rate of flow of 32 ml/min; Chromaton NAW; liquid phase PEGS, 15%; 3-m stainless-steel column at a temperature of 220°C; thermostat temperature 150°C. The terpenoids were identified by the addition of markers and from their relative retention times, and their amounts from the areas of the peaks. The results are given in Table 1.

TABLE 1

Compound	Amounts for the following varieties, %				
	arskaya 6	Priluk-skaya 6	Kuban-skaya 6	Selena (hybrid 24-77-1)	Serebristaya (hybrid 36-77-1)
Piperitone	2,61	2,78	2,18	0,87	2,36
Pulegone	6,22	0,9	1,64	0,35	—
Menyl acetate	0,69	0,45	0.55	—	0,42
Methol	36.25	35,67	45,83	61,26	56,47
Neomenthol	10,80	7,13	21,27	5,57	6,96
Isomenthol	10,11	12,49	11,45	17.05	6,46
Menthone	24,05	24,97	13,64	12.80	22,59
Menthofuran	0,17	0,06	Tr.	Tr.	0,05
Linalool	—	0,03	Tr.	—	—
p-Cymene	0 34	0,03	Tr.	0 09	0,26
Cineole	5,32	2,67	Tr.	0,7	1,84
Limonene	1,66	10,93	1,64	1,04	1,94
β-Pinene	1,13	1,56	1,64	0,02	0,53
Camphene	0 04	0,01	Tr.	Tr.	—
α-Pinene	0,22	0,33	0,14	Tr.	0,13

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STRUCTURE-SELECTIVE STEREOSPECIFIC CYLCIZATION OF E,E-FARNESOL AND ITS ACETATE BY FLUOROSULFONIC ACID

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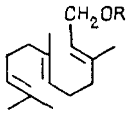
UDC 547.597+542.91

Information on the acid cyclization of farnesol (I) and its acetate (II) is sparse. Under the action of formic acid, depending on the conditions, farnesol is converted into a mixture of bisabolenes or α-cadinene [1], and on interaction with the complex of mercury trifluoromethanesulfonate and N,N-dimethylaniline followed by the reduction of the reaction product with sodium tetrahydroboride it is converted into drimenol (III) (yield 51%) [2]. The cyclization of E,E-farnesyl acid (II) with the mercury trifluoromethanesulfonate—2,6-di-tert-butylpyridine complex takes place structure-specifically and stereospecifically and leads after the reduction of the product with sodium tetrahydroborate to a mixture of a monoacetate of driman-8α,11-diol (IV) (44%) and the acetates of drimenol (V) and of 9-epidrimenol (VI) (23%) [2].

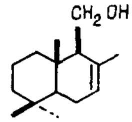
We have investigated the cyclization of E,E-farnesol (I) and its acetate (II) with fluorosulfonic acid in 1-nitropropane. The main product of the reaction of E,E-farnesol (I) proved to be (±)-drimenol (III) (71%). In addition to this, a small amount of hydrocarbons (12%) and of a polymeric substance was formed. The optimum reaction conditions were the following: ratio of substrate to cyclizing agent 1:1; −80 to −85°C; 1 h. Triethylamine was added to the reaction mixture which was then worked up in the usual way, and the product was chromatographed on a column of silica gel impregnated with silver nitrate.

On cyclization with fluorosulfonic acid, E,E-farnesyl acetate (I) gave (±)-drimane-8α,11-diol 11-monoacetate (IV) and a small amount of hydrocarbons. The greatest yield of the hydroxy acetate (IV) (77%) was achieved under the following conditions: ratio of substrate to fluorosulfonic acid 1:10; −80 to −85°C; 5 min. The yield of the hydrocarbon fraction under these conditions was 13%.

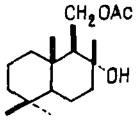
Compounds (III) and (IV) were identified by a spectral comparison with optically active forms of them.



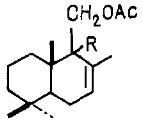
I. R=H
II. R=Ac



III



IV



V. R=αH
VI. R=βH

Thus, fluorosulfonic acid is a highly effective cyclizing agent converting E,E-farnesol (I) and its acetate (II) structure-selectively and stereospecifically into drimane sesquiterpenoids.

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