

COMPONENT COMPOSITION OF ESSENTIAL OIL FROM *Artemisia abrotanum* AND *A. dracunculus*

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In continuation of research on sages, which grow naturally or are cultivated in Crimea [1], we determined and studied in detail the qualitative composition, quantitative content of components, and mass fraction of essential oil from *Artemisia abrotanum* L. and *A. dracunculus* L. during all vegetative phases of these plants, namely, during spring emergence of runners (I), budding (II), mass flowering (III), and seed ripening (IV). Tables 1 and 2 list the results.

Our goal was to report results from the first full-scale biochemical investigation of essential oils from the aforementioned *Artemisia* species, which are of great value in medicine, agriculture, and the food industry, that were growing in brown soils of Crimea, in particular, its southern shore.

According to the literature, the mass fraction of essential oil in *A. abrotanum* is 0.32–0.62%. The oil components include camphor (14.2%), eugenol (0.2%), thymol (0.1%), α -pinene (11.4%), β -pinene (2.4%), camphene (19.3%), sabinene (2.4%), α -terpinene (0.9%), 1,8-cineol (26.6%), *p*-cymol (1.2%), pulegone (6.2%), verbenone (2%), verbenol (1.8%), α -santalol (1.2%), and β -santalol (1.5%) [2]. Essential oil of *A. dracunculus* contains methylhavicol as the main component (up to 91%) and its derivatives. Methyleugenol is present in some samples. The mass fraction of essential oil is 0.22–0.61% [3].

The component composition of essential oils obtained by us from representative plants was found by the literature method [1]. *A. abrotanum* and *A. dracunculus* were collected near Nikita in AR Crimea. The mass fractions of essential oil in *A. abrotanum* calculated for raw and dry weight according to vegetative phases were I, 0.12% (0.28%); II, 0.16 (0.34); III, 0.17 (0.38); and IV, 0.10 (0.24). The mass fractions of essential oil of *A. dracunculus* calculated for raw and dry weight by vegetative phases were I, 0.10% (0.28); II, 0.13 (0.34); III 0.15 (0.47); and IV, 0.06 (0.09), respectively.

The investigations found that essential oil of *A. abrotanum* contained 63 components. They all, except 1-octen-3-ol; 2,2,3-trimethyl-3-cyclopenten-1-acetaldehyde; 1,4-dimethyl-4-propyl-2-on-1(2)-cyclohexene; and elemicine were mono- and sesquiterpenes. The dominant components were the oxide-1,8-cineol and ketone-camphor. The concentration of the main components varied over the whole vegetation as a function of phase. Thus, the content of 1,8-cineol predominated at the start and end of vegetation (during phase I, 33.19%; IV, 26.31%) and was much lower during phases II (15.46) and III (19.54). However, the quantitative camphor content was lower at the start of vegetation (phase I, 20.33%) and then increased by more than twice and remained stable at a high level up to the end of vegetation (phase II, 44.15; III, 44.63; IV, 43.76). Compounds for which the content was from 2 to 10% (average values) that were present during the whole vegetation (camphene, borneol, terpinen-4-ol) or were absent in some of its phases (verbenol and α -bisabolol) were also observed in the essential oil (Table 1). Also, minor components that were always present in essential oil, for which the quantitative content was <2%, and sporadically appearing minor components were found. The first group included α - and β -pinenes, sabinene, 1-octen-3-ol, α - and γ -terpinenes, *trans*-sabinenhydrate, etc.; the second group, tricyclene, myrcene, *trans*-ocimene, linalool, sabinoketone, etc. (Table 1).

Essential oil of *A. dracunculus* contained 51 components (Table 2), the main ones of which were sabinene and elemicine. Methyleugenol was added to the list of dominant components during phase III. Each of the predominant components had its own accumulation dynamics in essential oil. The content of sabinene at the start and finish of vegetation was at approximately the same level (phase I, 27.80%; II, 29.65; IV, 30.10). However, during flowering its concentration decreased by more than twice to 13.50. The content of elemicine for the whole vegetation cycle remained at about the same level (phase I, 30.11%; II, 33.84; III, 28.57; IV, 27.33).

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TABLE 1. Qualitative Composition and Quantitative Content of Essential Oil Components of *A. abrotanum* L. During Phases I-IV

Component	I		II		III		IV	
	w, %	t, min	w, %	t, min	w, %	t, min	w, %	t, min
Tricyclen	0.09	6.63	–	–	–	–	0.20	6.66
α -Pinene	0.63	7.00	0.43	7.00	0.27	7.02	1.54	7.03
Camphene	2.42	7.48	5.18	7.49	2.51	7.50	7.20	7.52
Sabinene	3.58	8.34	0.43	8.34	0.39	8.35	0.34	8.36
β -Pinene	0.55	8.44	0.40	8.44	0.26	8.46	0.97	8.47
1-Octen-3-ol	0.49	8.58	0.30	8.59	0.43	8.59	0.73	8.62
Myrcene	–	–	–	–	–	–	0.33	9.01
α -Terpinene	0.50	9.93	0.40	9.94	0.27	9.96	0.32	9.96
<i>p</i> -Cymene	0.31	10.27	–	–	0.52	10.28	1.69	10.29
Limonene	–	–	0.27	10.42	0.16	10.45	0.48	10.46
1,8-Cineol	33.19	10.61	15.46	10.56	19.54	10.59	26.31	10.64
<i>trans</i> -Ocimene	0.13	10.81	–	–	–	–	0.29	10.85
γ -Terpinene	1.06	11.63	0.73	11.64	0.72	11.66	0.85	11.68
<i>trans</i> -Sabinenehydrate	1.15	12.01	0.66	12.04	0.80	12.04	0.24	12.08
Terpinolene	0.24	12.87	–	–	0.21	12.90	0.26	12.91
<i>cis</i> -Sabinenehydrate	0.97	13.32	0.44	13.37	0.60	13.36	0.14	13.42
Linalool	–	–	–	–	0.20	13.48	–	–
<i>p</i> -Menth-2-en-1-ol	0.28	14.33	–	–	0.32	14.39	0.16	14.46
2,2,3-Trimethyl-3-cyclopenten-1-acetaldehyde	0.23	14.54	–	–	0.20	14.55	0.24	14.58
Camphor	20.33	15.38	44.15	15.44	44.63	15.47	43.76	15.53
Sabinoketone	0.24	15.94	–	–	–	–	–	–
2(10)-Pinen-3-one	–	–	–	–	3.75	16.22	–	–
Verbenol	2.83	16.18	3.22	16.21	–	–	2.96	16.25
Borneol	2.08	16.26	3.29	16.31	2.16	16.31	2.60	16.35
<i>p</i> -Menth-1-en-8-ol	–	–	–	–	2.16	16.31	–	–
Pinocarvone	–	–	1.26	16.65	–	–	–	–
Terpinen-4-ol	3.22	16.79	2.27	16.82	3.72	16.83	2.51	16.87
α -Thujenal	0.26	17.07	–	–	–	–	–	–
α -Terpineol	1.43	17.38	0.91	17.43	–	–	0.22	17.46
Menth-1,5-dien-7-ol	0.54	17.53	–	–	–	–	–	–
Myrtenol	–	–	0.13	17.66	0.39	17.64	0.09	17.66
Myrtenal	–	–	0.12	17.66	–	–	0.08	17.66
3(10)-Caren-2-ol	1.19	18.25	1.10	18.29	–	–	–	–
1,4-Dimethyl-4-propyl-2-on-1(2)-cyclohexene	–	–	–	–	0.39	17.64	0.54	18.32
<i>cis</i> -Carvone	0.13	18.63	–	–	–	–	–	–
<i>trans</i> -Carveol	0.23	19.15	0.33	19.19	0.31	19.18	0.23	19.22
Verbenolacetate	0.20	20.48	0.38	20.52	0.39	20.54	0.44	20.57
α -Terpenylacetate	0.31	24.29	0.28	24.34	0.29	24.36	0.13	24.38
Eugenol	0.16	24.63	–	–	–	–	–	–
<i>trans</i> -Carveylacetate	0.12	24.89	0.49	24.94	0.37	24.95	0.21	24.97
β -Burbonene	–	–	–	–	–	–	0.24	25.86
<i>cis</i> -Jasmone	0.31	26.39	0.45	26.46	0.28	26.46	–	–
Methyleugenol	1.58	26.68	–	–	0.30	26.73	–	–
Caryophyllene	–	–	–	–	–	–	0.15	27.23
Geranylisobutyrate	0.17	29.14	0.79	29.20	0.72	29.22	0.34	29.24
Germacrene D	1.18	29.69	1.43	29.74	1.27	29.77	0.68	29.77
Bicyclogermacrene	0.23	30.31	0.26	30.37	–	–	–	–
Elemicine	0.12	32.79	–	–	0.26	32.87	–	–
Nerolidol	0.28	33.01	–	–	–	–	–	–
Spatulenol	0.21	33.49	–	–	0.17	33.49	–	–
Caryophyllene oxide	0.11	33.69	–	–	0.19	33.77	–	–
Eudesma-5-en-11-ol	0.14	34.73	0.33	34.72	0.37	34.72	–	–
Agarospinol	1.01	35.46	2.03	35.54	2.40	35.56	0.19	35.56
Guaiol	0.72	35.53	1.19	35.61	–	–	–	–
Cadinol	–	–	–	–	1.09	35.62	–	–
<i>trans</i> - α -Bisabolene epoxide	0.35	35.71	0.29	35.79	–	–	–	–
β -Eudesmol	0.12	36.22	0.26	36.30	0.23	36.30	–	–
α -Eudesmol	4.18	36.36	4.85	36.43	1.87	36.42	0.19	36.44
α -Bisabolol	3.89	37.52	3.52	37.58	4.64	37.58	–	–

w, content (%); t, retention time (min).

TABLE 2. Qualitative Composition and Quantitative Content of Essential Oil Components of *A. dracunculus* L. During Phases I-IV

Component	I		II		III		IV	
	w, %	t, min	w, %	t, min	w, %	t, min	w, %	t, min
2-Methyl-3-buten-2-ol	–	–	–	–	0.10	1.91	–	–
3-Cyclohepten-1-one	0.05	4.19	–	–	–	–	–	–
3-Hexen-1-ol	0.02	4.90	–	–	–	–	–	–
1,3,5-Octatriene	0.02	5.41	–	–	–	–	–	–
α -Thujene	0.12	6.80	–	–	–	–	–	–
α -Pinene	0.16	7.01	0.13	7.02	0.11	7.02	0.19	6.92
Sabinene	27.80	8.44	29.65	8.43	13.50	8.40	30.10	8.33
β -Pinene	0.23	8.50	–	–	–	–	0.21	8.90
Myrcene	1.37	8.99	1.09	9.00	0.40	9.00	0.86	8.90
3-Hexen-1-ol acetate	0.30	9.62	0.28	9.63	0.09	9.64	–	–
α -Terpinene	0.83	9.94	0.69	9.96	0.32	9.96	0.97	9.85
<i>p</i> -Cymene	–	–	0.18	10.27	0.63	10.27	–	–
Limonene	0.48	10.42	0.46	10.43	0.70	10.43	0.84	10.33
<i>trans</i> -Ocimene	4.24	10.84	8.03	10.86	0.72	10.83	2.99	10.74
<i>cis</i> -Ocimene	5.87	11.27	5.54	11.28	1.29	11.26	2.65	11.15
γ -Terpinene	1.31	11.65	1.20	11.67	0.46	11.67	1.85	11.56
Artemisia ketone	–	–	–	–	–	–	2.54	11.72
<i>trans</i> -Sabinenehydrate	0.26	12.02	0.32	12.04	0.30	12.04	0.67	12.03
Terpinolene	0.50	12.88	0.63	12.90	0.21	12.90	0.67	12.79
<i>cis</i> -Sabinenehydrate	0.14	13.33	0.19	13.35	0.20	13.35	–	–
Linalool	0.59	13.43	0.84	13.45	0.42	13.44	0.64	13.42
Nonanal	–	–	–	–	–	–	0.26	13.55
<i>cis</i> -Menth-2-en-1-ol	0.17	14.33	0.18	14.35	0.20	14.35	0.39	14.33
<i>allo</i> -Ocimene	0.04	14.67	–	–	–	–	–	–
<i>trans</i> -Menth-2-en-1-ol	0.10	15.12	0.10	15.14	0.12	15.14	0.23	15.14
Camphor	–	–	–	–	–	–	0.92	15.25
Citronellal	0.40	15.73	0.36	15.76	–	–	–	–
Terpinen-4-ol	2.93	16.79	3.00	16.82	3.41	16.83	7.15	16.82
α -Terpineol	0.21	17.39	0.22	17.41	0.17	17.41	0.26	17.42
Methylsalicylate	0.04	17.58	0.19	17.54	–	–	–	–
<i>trans</i> -Piperitol	0.04	17.58	–	–	–	–	–	–
Methylhavicol	0.64	17.71	1.02	17.75	1.10	17.75	2.74	17.67
<i>cis</i> -Piperitol	0.04	18.13	–	–	–	–	–	–
Citronellol	0.17	19.09	0.23	19.12	0.14	19.12	0.40	19.14
Linalylacetate	–	–	–	–	0.14	20.33	–	–
Bornylacetate	0.04	21.55	–	–	–	–	0.29	21.50
Thymol	0.02	21.97	0.15	21.98	0.13	21.99	0.24	22.13
Carvacrol	0.02	22.36	0.20	22.38	4.31	22.42	–	–
Methylgeranate	0.03	23.23	–	–	–	–	–	–
Citronellylacetate	1.87	24.51	2.49	24.58	1.86	24.58	2.77	24.47
Nerylacetate	–	–	–	–	0.25	25.05	–	–
Geranylacetate	1.77	25.81	1.36	25.87	0.61	25.87	0.84	25.76
Methyleugenol	6.06	26.74	6.40	26.80	38.16	26.96	7.62	26.73
Germacrene D	0.16	29.69	0.16	29.77	0.26	29.78	0.36	29.62
Germacrene B	–	–	–	–	–	–	0.17	30.25
Bicyclgermacrene	0.17	30.31	0.16	30.39	0.12	30.40	–	–
Elemicine	30.11	33.00	33.84	33.07	28.57	33.07	27.33	32.95
Nerolidol	–	–	–	–	0.28	33.14	–	–
Diethylphthalate	0.09	34.24	–	–	–	–	–	–
γ -Cadinol	0.08	35.91	–	–	–	–	–	–
<i>trans</i> -Isoelemicine	10.11	36.47	0.17	36.47	0.10	36.47	0.65	36.45

w, content (%); t, retention time (min).

The concentration of methyleugenol at the start and finish of vegetation was about the same and in the range of medium values (from 2 to 10%). It was during phase I, 6.06; II, 6.40; IV, 7.62. However, during flowering it increased sharply (to 38.16) with a sharp decrease of sabinene content. Obviously there was an inverse biosynthetic correlation between methyleugenol and sabinene in plants of this species.

Essential oil of *A. dracunculus* contained groups of components, the contents of which were in the range of medium values (from 2 to 10%) over the whole vegetation, either in separate phases or in one of them. The first group included terpinen-4-ol (phase I, 2.93; II, 3.00; III, 3.41; IV, 7.15). It can be seen that this compound illustrates well the accumulation dynamics during the whole vegetation. The second group included *trans*- and *cis*-ocimene (contents in phase I, 4.24, 5.87; II, 8.03, 5.54; III, 0.72, 1.29; IV, 2.99, 2.65, respectively) and citronellylacetate (phase I, 1.87; II, 2.49; III, 1.86; IV, 2.77). The third group included artemisia ketone, methylhavicol, carvacrol, and *trans*-isoelemicine, the contents of which by phases were during phase I, not observed, 0.64%, 0.02, 10.11; II, not observed, 1.02, 0.20, 0.17; III, not observed, 1.10, 4.31, 0.10; IV, 2.54, 2.74, not observed, 0.65, respectively).

Most of the essential oil components of *A. dracunculus* were minor compounds that we divided into two groups, those always present and those sporadically appearing. In particular, the first group included, for example, α -pinene, myrcene, α - and β -terpinenes, limonene, etc.; the second, for example, 2-methyl-3-buten-2-ol, 3-cyclohepten-1-one, 3-hexen-1-ol, 1,3,5-octatriene, α -thujene, β -pinene, etc. (Table 2).

Discrepancies in the dominant components of essential oils between our results (predominance of sabinene, methyleugenol, and elimicine) and those in the literature (predominance of methylhavicol) [3] were obviously related to the different origins of the studied *A. dracunculus* (soil and climate conditions, intentional selection).

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