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Thujone-Rich Essential Oils of *Artemisia rutifolia* Stephan ex Spreng. Growing Wild in Tajikistan

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Abstract: The essential oil from the aerial parts of *Artemisia rutifolia* Stephan ex Spreng., collected from two different regions of Tajikistan, were obtained by hydrodistillation and analyzed by GC-MS. A total of 77 compounds were identified in the oils, accounting for 98.6 % and 99.2 % of the two oils. Both essential oils were dominated by α-thujone (20.9 % and 36.6 %) and β-thujone (47.3 % and 36.1 %) with lesser amounts of 1,8-cineole (3.2 % and 11.7 %) and germacrene D (2.8 % and 1.8 %).

Key words: *Artemisia rutifolia*, essential oil composition, thujone, Tajikistan.

Introduction: *Artemisia rutifolia* Stephan ex Spreng. is a member of the Asteraceae (Compositae) and is distributed in Afghanistan, China, India, Kazakhstan, Kyrgyzstan, Mongolia, Nepal, Pakistan, Russian Federation and Tajikistan [1]. The plant is an important traditional medicine. An infusion of the herb is taken to relieve painful urination; the fresh herb is used as an analgesic for toothache; the dried herb is used to treat excessive sweating; a decoction of the herb is gargled for treatment of angina, stomach problems, and heart problems. *A. rutifolia* essential oil has antibacterial, antifungal and anthelmintic activity [2].

The essential oil of *A. rutifolia* growing in the Pamirs had been previously investigated by Goryaev in 1962, who reported the main constituents to be 1,8-cineole, α- and β-thujone, camphor, α- and β-pinene, camphene, and limonene [3]. Shavarda examined *A. rutifolia* oil from the Mongolian People's Republic and identified 15 components: 1,8-cineole (35.0 %), camphor (18.0 %), α- and β-thujone (11.0 %), terpinen-4-ol (7.0 %), α-terpineol (5.0 %), α-pinene, β-pinene, camphene, limonene, β-phellandrene, p-cymene, 4-phenylbutan-2-one, 4-phenyl-butan-2-ol, and 4-phenylbut-2-yl acetate [4].

Experimental

Plant material: Aerial parts of *Artemisia rutifolia* were collected from two regions of Tajikistan: Sample #1, the Khonaobod village, Muminobod region (38.107547 N, 69.966431 E, 1200 m above sea level), on 2 May 2010; Sample #2, the Chormaghzak village, Yovon region, (38.417502 N, 69.172175 E, 1300 m above sea level), on 25 July 2010. The plant was identified by V.A. Sulaimanova,

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and a voucher specimen (TJ2010-040) has been deposited in the herbarium of the Chemistry Institute of the Tajikistan Academy of Sciences. The air-dried samples (300 g each) were crushed and hydrodistilled using a Clevenger apparatus for 3 h to give the yellow essential oils, which were stored at 4°C until analysis.

Gas chromatographic-Mass spectral analysis: The essential oils of *Artemisia rutifolia* were analyzed by GC-MS using an Agilent 6890 GC with Agilent 5973 mass selective detector [MSD, operated in the EI mode (electron energy = 70 eV), scan range = 45-400 amu, and scan rate = 3.99 scans/sec], and an Agilent ChemStation data system. The GC column was an HP-5ms fused silica capillary with a (5 % phenyl)-polymethylsiloxane stationary phase, film thickness of 0.25 μm, a length of 30 m, and an internal diameter of 0.25 mm. The carrier gas was helium with a column head pressure of 48.7 kPa and a flow rate of 1.0 mL/min. Injector temperature was 200°C and detector temperature was 280°C. The GC oven temperature program was used as follows: 40°C initial temperature, hold for 10 min; increased at 3°C/min to 200°C; increased 2°/min to 220°C. A 1 % w/v solution of the sample in CH_2Cl_2 was prepared and 1 μL was injected using a splitless injection technique.

Identification of the oil components was based on their retention indices determined by reference to a homologous series of *n*-alkanes, and by comparison of their mass spectral fragmentation patterns with those reported in the literature [5] and stored on the MS library [NIST database (G1036A, revision D.01.00)/ChemStation data system (G1701CA, version C.00.01.080)]. The percentages of each component are reported as raw percentages based on total ion current without standardization. The essential oil composition of *A. rutifolia* is summarized in Table 1.

Results and discussion: The yellow essential oils of *Artemisia rutifolia* were obtained in 0.5 % yield for sample #1 (Muminobod region) and 0.8 % yield for sample #2 (Yovon region). A total of 77 compounds were identified in the *A. rutifolia* essential oils accounting for 98.6 % and 99.2 % of the compositions, respectively. The essential oils were dominated by oxygenated monoterpenoids, chiefly α-thujone (20.9 % and 36.6 %, respectively, for the Muminobod sample and the Yovon sample) and β-thujone (47.3 % and 36.1%, respectively). Other notable components included 1,8-cineole (3.2 % and 11.7 %, respectively) and germacrene D (2.8% and 1.8 %, respectively).

The *A. rutifolia* essential oils from Tajikistan, as revealed in this study, clearly belong to a thujone-rich chemotype, and differ markedly from the cineole/camphor-rich chemotype previously reported from Mongolia [4].

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Table 1. Chemical compositions of the essential oils of *Artemisia rutifolia* Stephan ex Spreng. from Tajikistan

RI[a]	Compound	Percent #1[b]	Composition #2[c]
852	(2E)-Hexenal	-	0.1
919	Santolina triene	0.1	-
935	α-Thujene	0.1	-
941	α-Pinene	0.2	tr
953	Camphene	0.1	-
976	Sabinene	0.3	0.4
978	β-Pinene	0.1	0.1
981	1-Octen-3-ol	0.1	-
993	Myrcene	2.8	0.3
1004	α-Phellandrene	0.5	0.1
1016	α-Terpinene	0.2	0.2
1024	p-Cymene	1.8	0.9
1031	1,8-Cineole	3.2	11.7
1037	Santolina alcohol	0.4	-
1048	(E)-β-Ocimene	tr	-
1058	γ-Terpinene	0.5	0.4
1088	Terpinolene	-	0.1
1106	α-Thujone	20.9	36.6
1119	β-Thujone	47.3	36.1
1130	Chrystanthenone	0.1	0.8
1137	*iso*-3-Thujanol	0.3	0.1
1141	*trans*-p-Menth-2-en-1-ol	0.9	0.5
1145	Camphor	0.9	0.2
1151	p-Menth-3-en-8-ol	0.1	0.2
1154	Menthone	0.9	-
1158	Sabina ketone	0.2	0.3
1162	Pinocarvone	0.1	0.2
1165	Borneol	0.2	0.4
1174	*cis*-Pinocamphone	-	0.1
1177	Terpinen-4-ol	0.6	1.2
1184	Thuj-3-en-10-al	0.2	-
1185	p-Cymen-8-ol	-	0.1
1190	α-Terpineol	0.1	0.3
1194	*cis*-Piperitol	0.4	-
1195	Myrtenol	-	0.3
1203	γ-Terpineol	tr	-
1206	*trans*-Piperitol	0.5	0.2
1226	*m*-Cumenol	0.1	0.1
1228	*nor*-Davanone	-	0.1
1236	Pulegone	1.0	0.3
1243	Carvone	0.9	0.1
1246	Carvotanacetone	0.1	0.1
1255	*cis*-Piperitone epoxide	2.0	0.9
1261	*cis*-Chrysanthenyl acetate	0.2	tr

table 1. (continued).

RI[a]	Compound	Percent #1[b]	Composition #2[c]
1265	*iso*-3-Thujanol acetate	0.1	0.1
1279	*neoiso*-3-Thujanol acetate	-	0.1
1283	1-Phenyl-2,4-pentadiyne	-	0.1
1285	Bornyl acetate	-	tr
1289	p-Cymen-7-ol	0.1	tr
1292	Thymol	0.7	0.2
1301	Carvacrol	0.9	0.4
1317	(Z)-Patchenol	-	0.2
1336	*cis*-Piperitol acetate	0.1	0.1
1343	Piperitenone	0.1	0.1
1366	Piperitenone oxide	1.4	tr
1375	α-Copaene	0.1	tr
1399	(Z)-Jasmone	0.1	0.3
1418	(E)-Caryophyllene	0.4	0.1
1458	(E)-β-Farnesene	0.2	0.1
1467	(2E)-Dodecenal	0.2	-
1476	β-Chamigrene	0.1	-
1482	Germacrene-D	2.8	1.8
1487	(E)-®-Ionone	0.1	tr
1497	Bicyclogermacrene	0.5	0.8
1509	β-Bisabolene	0.2	-
1514	Davana ether	-	0.1
1524	δ-Cadinene	0.1	tr
1578	Spathulenol	0.7	0.2
1583	Caryophyllene oxide	0.2	0.1
1589	Davanone	-	1.3
1592	Viridiflorol	0.4	-
1603	Ledol	0.1	-
1640	Germacrene-D 1,10-epoxide	0.3	-
1654	α-Cadinol	0.1	-
1670	Phloroacetophenone 2,4-dimethylether	0.3	-
1685	Germacra-4(15),5,10(14)-trien-1α-ol	0.1	0.1
1694	4-Cuprenen-1-ol	-	tr
	Compounds Identified	98.6	99.2
	Monoterpene hydrocarbons	6.5	2.3
	Oxygenated monoterpenoids	85.0	91.9
	Sesquiterpene hydrocarbons	4.4	2.8
	Oxygenated sesquiterpenoids	1.9	1.8
	Miscellaneous compounds	0.8	0.5

[a] RI = Retention Index, determined with reference to a homologous series of normal alkanes on an HP-5ms column
[b] Sample # 1: collected from Muminobod region
[c] Sample # 2: collected from Yovon region