

COMPOSITION OF THE ESSENTIAL OILS OF *Juniperus oxycedrus* SUBSP. *macrocarpa* FROM TURKEY

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Juniperus L. is represented in Turkey by eight taxa. *Juniperus oxycedrus* has two subspecies – subsp. *oxycedrus* and subsp. *macrocarpa* – in Turkey [1]. *J. oxycedrus* L. subsp. *macrocarpa* (Sibth. et Sm.) Ball. is called “Buyuk Kozalakli Katran Ardici” [2]. Leaf oil contents and compositions of *Juniperus oxycedrus* subsp. *macrocarpa* from countries like Italy [3], Colombia [4], Greece [5], and Spain [6] have been reported. The isolation and structure elucidation of junicedranol, a sesquiterpene with a novel carbon skeleton, from the leaf oil of *Juniperus oxycedrus* subsp. *macrocarpa* was reported in [7].

Juniperus oxycedrus subsp. *macrocarpa* leaves were collected in May, August, and October 1998 – in order to determine seasonal differences, from Altin Kum Beach of Ciftlik Village in Cesme - Izmir and distilled for 3 hours using a Clevenger Apparatus. Voucher specimens are kept at the Herbarium of the Faculty of Pharmacy of Gazi University. (GUEF98-444). The oils were analyzed by GC/MS using a Hewlett Packard GCD system. An HP-Innowax FSC column (60 m × 0.25 mm dia., with 0.25 mm film thickness) was used with helium as carrier gas (1 ml/min.). GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, then kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min. Split ratio was adjusted at 50:1. The injector temperature was at 250°C. MS were taken at 70 eV. Mass range was from 35 to 425 *m/z*.

The components were identified by comparison of their mass spectra with Wiley GC/MS Library, MassFinder and in-house Baser Library of Essential Oil Constituents. Relative percentage amounts of the separated compounds were calculated automatically from peak areas of the total ion chromatogram. Alkanes were used as reference points in the calculation of relative retention indices (RRI). The compounds identified in the oil can be seen in Table 1.

Oil contents varied between 0.03% and 0.13%. The highest yield was attained with the August samples. In the May, August, and October samples, 106, 83, and 94 components were characterized representing 84.6%, 95.2%, and 90.1% of the oils, respectively. The main components found in the oils are shown in Table 1. Manoyl oxide (7.7–21.9%), α -pinene (7.2–11.1%), α -cedrol (2.3–9.7%), widdrene (2.1–5.7%), α -muurolene (4.1–4.8%), *trans*-verbenol (1.7–4.3%), germacrene D (1.5–4.1%), δ -cadinene (3.2–3.8%), α -campholene aldehyde (1.7–3.2%), *trans*-pinocarveol (1.5–3.0%), cubebol (1.4–2.4%), caryophyllene oxide (1.5–1.9%), δ -cadinene (1.0–1.8%), β -caryophyllene (0.7–1.8%), and epi-cubebol (1.0–1.4%) were the main constituents of the oils. Manoyl oxide (21.9%), a diterpene, was the main component in the August sample. It was followed by α -cedrol (9.7%), α -pinene (7.2%), and widdrene (5.7%). The main components in the October sample were α -pinene (11.1%), manoyl oxide (9.1%), α -muurolene (4.8%), *trans*-verbenol (4.0%), and α -cedrol (3.4%). Manoyl oxide (7.7%), α -pinene (7.6%), *trans*-verbenol (4.3%), and α -muurolene (4.1%) were predominant in the May sample.

In previous studies, α -pinene (14.5% and 22.6%) and sabinene (24.6% and 26.5%) were reported as the main constituents in the oils of Colombia [4] and Spain [6], respectively. α -Pinene (26.9% and α -cedrol (13.9%) were the main constituents of the oil from Greece [5]. In the Italian oil [3], only the components detected were indicated without percentage amounts.

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TABLE 1. The Composition of the Leaf Essential Oils of *Juniperus oxycedrus* subsp. *macrocarpa*

RRI	Compound	%			RRI	Compound	%		
		A	B	C			A	B	C
1032	α -Pinene	7.6	7.2	11.1	1726	Germacrene D	2.9	1.5	4.1
1076	Camphene	0.1	0.1	0.1	1729	<i>cis</i> -Muurolo-4(15),5-diene*	0.6	0.7	0.4
1118	β -Pinene	0.3	0.2	0.4	1740	<i>p</i> -Menth-1,5-dien-8-ol	1.6	0.9	1.6
1132	Sabinene	0.1	Tr.	0.1	1740	α -Muurolole	4.1	4.3	4.8
1159	δ -3-Carene	0.4	1.1	1.5	1751	Carvone	0.2	0.1	0.3
1174	Myrcene	1.1	0.3	1.3	1758	α -Cuprenene	0.1	0.6	0.2
1203	Limonene	0.6	0.4	0.7	1758	(<i>E,E</i>)- α -Farnesene	-	-	0.2
1218	β -Phellandrene	0.7	0.1	1.3	1765	Naphthalene	0.2	-	0.2
1266	(<i>E</i>)- β -Ocimene	0.1	0.1	0.5	1766	Decanol	0.3	-	-
1280	<i>p</i> -Cymene	0.5	0.3	0.5	1772	δ -Cadinene	3.3	3.8	3.2
1290	Terpinolene	0.3	0.2	0.6	1776	γ -Cadinene	1.8	1.0	1.8
1400	Nonanal	0.2	Tr.	0.2	1786	ar-Curcumene	-	0.1	-
1435	γ -Campholene aldehyde	0.5	0.2	0.3	1797	<i>p</i> -Methylacetophenone	0.1	-	Tr.
1444	α,p -Dimethylstyrene	0.2	0.1	0.2	1798	Cubenene	0.5	-	-
1466	α -Cubebene	0.4	0.3	0.4	1803	β -Cuprenene	-	0.6	-
1500	α -Campholene aldehyde	3.2	1.7	2.2	1804	Myrtenol	1.0	0.5	0.7
1529	α -Bourbonene	Tr.	0.6	-	1811	3,7-Guaiadiene	0.1	0.1	0.1
1535	Pinocamphone	0.9	0.3	0.4	1827	(<i>E,E</i>)-2,4-Decadienal	0.2	Tr.	0.2
1535	β -Bourbonene	-	-	0.3	1845	<i>trans</i> -Carveol	1.4	-	1.4
1542	Benzaldehyde	0.1	Tr.	Tr.	1849	Cuparene	-	2.2	0.2
1547	β -Cubebene	0.3	0.4	0.5	1849	Calamenene	0.6	0.7	0.2
1553	Linalool	0.4	0.1	-	1864	<i>p</i> -Cymen-8-ol	0.2	0.1	0.3
1562	Isopinocamphone	-	0.2	-	1868	(<i>E</i>)-Geranylacetone	1.2	0.1	Tr.
1562	Octanol	0.8	-	0.3	1900	<i>epi</i> -Cubebol	1.1	1.0	1.4
1568	<i>trans</i> - α -Bergamotene	0.1	0.2	-	1921	β -Calacorene	Tr.	Tr.	Tr.
1571	<i>trans-p</i> -Menth-2-en-1-ol	0.1	-	Tr.	1941	α -Calacorene	0.4	0.4	0.2
1577	α -Cedrene	-	0.5	-	1957	Cubebol	1.9	1.4	2.4
1586	Pinocarvone	1.2	0.4	1.0	1973	Dodecanol	0.1	-	Tr.
1594	β -Funebrene	0.2	0.6	0.3	1984	γ -Calacorene	0.2	0.1	0.1
1597	Bornyl acetate	0.4	0.4	0.4	2008	Caryophyllene oxide	1.9	1.5	1.8
1600	β -Elemene	-	-	0.3	2043	Salvial-4(14)-en-1-on	0.4	0.2	0.4
1604	Methyl thymol	0.4	-	0.4	2045	Humulene epoxide I	0.1	-	-
1612	β -Caryophyllene	1.5	0.7	1.8	2050	(<i>E</i>)-Nerolidol	Tr.	0.2	0.1
1614	Methyl carvacrol	0.1	-	0.3	2051	Gleenol	0.1	0.2	0.2
1645	Widderene	2.1	5.7	2.4	2070	Cinnamaldehyde	0.8	-	-
1648	Myrtenal	1.0	0.9	1.0	2071	Humulene epoxide II	0.7	0.9	1.1
1655	(<i>E</i>)-2-Decenal	0.1	-	0.1	2080	Cubenol	0.3	0.3	0.4
1668	<i>cis</i> -Verbenol	0.8	0.4	0.7	2084	Octanoic acid	0.2	-	-
1671	<i>trans</i> -Pinocarveol	3.0	1.5	2.1	2088	1- <i>epi</i> -Cubenol	1.5	1.3	1.4
1674	<i>p</i> -Mentha-1,5-dien-8-ol	0.6	0.5	0.4	2096	(<i>E</i>)-Methyl cinnamate	0.1	-	-
1678	<i>epi</i> -Zonarene	0.6	0.9	0.6	2131	Hexahydrofarnesylacetone	0.3	-	0.2
1684	<i>trans</i> -Verbenol	4.3	1.7	4.0	2149	α -Cedrol	2.3	9.7	3.4
1698	Myrtenyl acetate	0.4	-	-	2179	Widdrol	0.3	0.8	0.4
1700	γ -Muurolole	0.4	0.2	-	2187	T-Cadinol	0.6	0.6	1.0
1707	α -Terpineol	0.7	0.4	1.2	2205	Thymol	0.4	-	-
1709	α -Terpinyl acetate	0.5	0.7	0.5	2209	T-muurolol	0.3	0.2	0.3
1719	Borneol	0.1	0.1	0.1	2219	δ -Cadinol	0.3	0.2	0.3
1725	Verbenone	0.7	0.3	0.7	2246	Carvacrol	0.3	0.2	0.3

TABLE 1. (continued)

RRI	Compound	%			RRI	Compound	%		
		A	B	C			A	B	C
2256	Cadalene	0.2	0.2	0.2	2419	4-Isopropyl-6-methyl-1-tetralone	Tr.	0.1	Tr.
2264	4,7-Dimethyl-1-tetralone	0.1	0.1	Tr.	2489	8,13-Abietadiene	1.1	1.4	1.0
2287	Sandaracopimaradiene	0.2	0.1	Tr.	2503	Dodecanoic acid	2.2	-	0.9
2300	Decanoic acid	0.3	-	0.2	2524	Abietatriene	0.6	1.1	0.5
2349	Cadina-4,10(15)-dien-3-one	0.1	-	0.1	2554	Nootkatone	Tr.	-	0.1
2376	Manoyl oxide	7.7	21.9	9.1	2713	Tetradecanoic acid	0.2	-	0.1
2386	Farnesyl acetone	0.2	-	-	2931	Hexadecanoic acid	0.1	-	0.1
2396	8 α -13-oxy-14-en-epiladane	-	0.3	0.3		Number of components	106	83	94
2419	4-Isopropyl-6-methyl-1-tetralone	Tr.	0.1	Tr.		Total, %	84.6	95.2	90.1

A: Collected in May; B: collected in August; C: collected in October.

RRI: Relative retention indices calculated against *n*-alkanes calculated TIC data.

*Tentative identification from Mass Finder.

Tr.: trace < 0.1%.

REFERENCES

1. M. J. E. Coode and J. Cullen, *Cupressaceae*; P. H. Davis, *Flora of Turkey and the East Aegean Islands*, The University Press, Edinburgh, 1965, 76 pp.
2. S. Muderrisoglu, *J. Turkish Forest Res. Inst.*, **17**, 1 (1971).
3. V. Picci, A. Manunta, A. D. Atzei, G. Pirisimo, *Riv. Ital. Essenze*, **56**, 305 (1974).
4. T. A. Fretz, T. D. Syndor, and M. R. Cobbs, *Sci. Hortic.*, **5**, 85 (1976).
5. V. Stassi, E. Verykokidou, A. Loukis, A. Harvala, and S. Philianos, *J. Essent. Oil Res.*, **7**, 675 (1995).
6. R. P. Adams, J. Altarejos, C. Fernandez, and A. Camacho, *J. Essent. Oil Res.*, **11**, 167 (1999).
7. A. F. Barrero, E. Alvarez-Manzaneda, and A. Larn, *Tetrahedron Lett.*, **36**, 6347 (1995).