Comparison of the Volatile Leaf Oils of Juniperus chinensis L., J. chinensis var. kaizuca Hort. and cv. pyramidalis from China

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ABSTRACT: The volatile leaf oils of *Juniperus chinensis* (sensu stricto) are found to be polymorphic for cedrene, thujopsene, and cedrol as well as aromatic compounds derived from the phenyl propanoid pathway. Reports on the oil of putative *J. chinensis* in the literature did not correspond to the oil from China which suggests that the cultivated *J. chinensis* may be a selection from the species and not typical. The oil of cultivar *pyramidalis* possessed some similarities to the oil of one of the *J. chinensis* samples, whereas the oil of var. *kaizuca* was very different, supporting the continued recognition of the variety status.

KEY WORD INDEX: *Juniperus chinensis*, var. *kaizuca*, cv. *pyramidalis*, Cupressaceae, essential oil composition, terpenes, taxonomy.

INTRODUCTION: *Juniperus chinensis* L. in China is a 6-12 m tree called yuan-bai, with both scale and acicular leaves, a gland in the middle of leaf, female cones globose, 6-8 mm diam., with white bloom on the surface, usually with 2-3 seeds. *J. chinensis* ranges in nature from central, eastern and northern China to Korea and Japan.

Many cultivars have been introduced into horticulture, in fact J. chinensis cultivars are perhaps the most widely planted landscape species in the world. The volatile leaf oils of many cultivars have already been reported (1-10). However, many of these studies only reported on the monoterpenes or failed to present a full analysis of the oils. Chavchanidze and Kharababa (11) reported on the leaf oil of J. chinensis, cultivated at the botanic garden, Tbilisi, Georgia, CIS. They found the oil to be dominated by sabinyl acetate (38.4%) with moderate amounts of limonene (11.2%), sabinene (11.0%),

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Table I. Comparison of volatile leaf oils of Juniperus chinensis, J. chinensis cv. pyramidalis and J. chinensis var. kaizuca from China

RT	Compound	Percent total oil					
		J. chinensis			J. chinensis cv. pyramidalis	<i>J. chinensis</i> var. <i>kaizuca</i>	
		6765	6766	6767	6764	6793-94	
177	ethyl acetate	20.6	12.5	19.6	13.2	-	
301	tricyclene	t	t	0.1	0.1	0.4	
307	α-thujene	0.5	0.4	0.4	1.3	0.5	
319	α -pinene	11.1	10.6	22.6	1.6	18.6	
340	camphene	t	0.1	0.2	0.1	0.7	
379	sabinene	18.6	13.1	16.7	43.0	15.7	
386	β-pinene	0.2	0.3	0.4	0.2	2.4	
408	myrcene	2.5	2.8	3.1	4.4	8.6	
414	1,3,5-trimethyl benzene	t	0.1	0.1	-	-	
427	δ-2-carene	-	0.1	t	t	-	
457	lpha-terpinene	0.1	0.5	0.3	1.0	0.6	
471	p-cymene	0.2	0.1	0.1	0.1	t	
481	limonene	13.4	14.3	12.1	1.6	3.0	
482	β-phellandrene	-	-	-	t	0.8	
519	(E)-β-ocimene	0.1	0.2	0.1	0.6	-	
545	γ-terpinene	0.4	0.8	0.5	1.8	0.9	
560	trans-sabinene hydrate	0.3	0.6	0.3	0.9	0.6	
608	terpinolene	0.4	8.0	0.4	1.0	0.6	
629	cis-sabinene hydrate	0.3	0.5	0.3	0.6	0.3	
632	linalool	0.3	1.3	0.6	-	2.7	
683	cis-pinene hydrate	0.1	0.2	t	0.2	0.2	
725	trans-pinene hydrate	-	0.1	-	t	0.1	
734	camphor	-	-	-	-	0.3	
735	trans-verbenol	t	0.1	t	-	-	
746	camphene hydrate	-	-	-	t	0.2	
789	borneol	-	-	-	-	0.3	
820	terpin-4-ol	1.0	2.8	1.5	4.4	2.5	
852	α -terpineol	t	0.1	t	0.1	0.1	
869	methyl chavicol	-	0.2	0.3	0.1	-	
896	trans-piperitol	-	-	-	t	-	
950	citronellol	-	-	-	-	0.2	
1035	methyl citronellate	t	0.1	-	t	-	
1094	(E)-anethole	-	-	t	-	-	
1099	bornyl acetate	0.2	t	t	4.0	15.8	
1101	safrole	-	6.3	8.6	0.7	-	
1371	β-cubebene	-	-	-	t	-	
1401	methyl eugenol	-	4.4	5.3	0.4	-	
1421	α -cedrene	-	t	-	-	-	
1422	1,7-di-epi-β-cedrene	0.2	0.1	-	-	-	
1441	β-cedrene	0.2	-	0.1	-	-	

Table I. (cont.)

RT	Compound	Percent total oil					
		J. chinensis			J. chinensis cv. pyramidalis	J. chinensis var. kaizuca	
		6765	6766	6767	6764	6793-94	
1442	β-caryophyllene	_	-	-	0.1	-	
1467	thujopsene	0.2	0.2	0.2	-	-	
1550	germacrene isomer #1	t	0.2	-	0.1	-	
1586	γ-muurolene	t	t	-	0.1	-	
1594	germacrene D	0.1	0.1	0.3	0.1	-	
1629	epi-cubebol	0.1	t	-	0.2	_	
1643	α-muurolene	0.1	t	-	0.3	_	
1675	α-alaskene	t	-	-	•	-	
1676	γ-cadinene	0.3	0.2	-	1.0	t	
1700	δ-cadinene	0.5	0.4	0.1	1.6	0.2	
1733	α -cadinene	t	-	-	0.1	-	
1759	elemol	-	-	-	-	10.8	
1772	elemicin	-	0.7	8.0	-	-	
1809	(Z)-hexenyl benzoate	0.3	-	0.5	0.1	-	
1821	germacrene D-4-ol	0.5	0.8	0.2	2.7	0.3	
1837	caryophyllene oxide	-	-	-	0.1	-	
1852	sesquiterpene alcohol?	-	0.9	0.7	0.9	_	
1876	cedrol	19.5	19. 1	0.9	-	-	
1898	β-oplopenone	0.9	0.6	0.3	1.3	-	
1951	α-acorenol	0.1	0.1	-	-	-	
1951	γ-eudesmol	-	-	-	-	0.9	
1973	epi-α-cadinol (=T-cadinol)	0.3	0.2	t	1.1	-	
1976	epi-α-muurolol (=T-muurolol)		0.3	t	2.1	-	
1984	torreyol	0.1	t	0.2	0.6	-	
1993	β-eudesmol	-	_	_	-	1.3	
2000	α-eudesmol	-	-	_	-	5.5	
2003	α-cadinol	1.4	1.1	0.5	5.8	-	
2034	bulnesol	-	-	-	-	1.6	
2183	oplopanone	1.2	0.1	t	t	-	
2306	8-α-acetoxyelemol		-	_	<u>.</u>	1.7	
2369	sesquiterpene alcohol	0.7	_	_	_	-	
2660	13-epi-manool	t	-	t	t	t	
2841	abietatriene	t	0.2	_	t	t	
2845	manool	_	-	_	-	0.8	
3253	cis-totarol	-	_	_	t	0.1	
3272	4-epi-abietal	0.1	0.3	0.2	ť	0.1	
3297	trans-totarol	t	t	-	t	-	

 α -pinene (5.6%) and myrcene (4.2%). The sesquiterpenes were not identified. However, on a recent visit to the botanic garden in Tbilisi, the senior author did not find J. chinensis, the tall, pyramidal tree, but rather shrubs of a cultivar of J. chinensis. It appears that Chavchanidze and Kharababa (11) reported on the oil of a cultivar of J. chinensis. Kuo and Chen (12) recently reported a new sesquiterpene from the roots of J. chinensis, cultivated in Taiwan.

All of these studies used putative *J. chinensis*, plants of unknown origin and cultivated in local gardens outside the natural range of the taxon. As far as can be determined, there is no report on the leaf oil of *J. chinensis* (*sensu stricto*) from within its natural range.

EXPERIMENTAL: Fresh foliage (10-12 terminal branches, 15-20 cm long) was collected and voucher specimens [*J. chinensis* L., Northwest Normal University, Lanzhou but originally from Shannxi Province where it is native. R. P. Adams, 6765-6767; *Juniperus chinensis* L. var. *kaizuca* Hort. (= *J. chinensis* cv. *torulosa*), Xian Botanic Garden, Xian, R. P. Adams, 6793-6794; *Juniperus chinensis* L. cv. *pyramidalis*, Northwest Normal University, Lanzhou, R. P. Adams, 6764] are deposited at BAYLU and NWTU.

The volatile leaf oils were isolated by steam distillation (200 g foliage, FW) using a circulatory Clevenger apparatus (13) for 2 and 24 h to determine yields. The oil samples were concentrated (diethyl ether trap removed when collected in a Clevenger unit) with nitrogen and stored at $-20\,^{\circ}\text{C}$ until analyzed. Mass spectra were recorded with a Finnigan Ion Trap (ITD) mass spectrometer, model 700, directly coupled to a Varian 6500 gas chromatograph, using a J&W DB5, 30 m x 0.26 mm (0.25 μm film thickness) fused silica capillary column (see reference 14 for operating details). Identifications were made by library searches of our volatile oil library, LIBR(TP) (14) using the Finnigan library search routines based on fit. Additional searches were made of the EPA/NIH mass spectral data base (15). Mass spectra for unidentified constituents [ITMS, m/z (rel. int.)]: RT1852, 222 [M]+, 43(100), 55(27), 67(28), 79(27), 95(37), 105(21), 119(19), 137(7), 149(39), 161(14), 189(3), 207(6), sesquiterpene alcohol; RT2369, 220 [M]+, 43(100), 55(18), 67(14), 79(12), 93(23), 105(14), 119(19), 133(9), 145(12), 159(40), 187(20), 202(6), 220(4), sesquiterpene alcohol.

RESULTS AND DISCUSSION: Oil yields (2 h) ranged from 0.6% in J. chinensis to 1.2% cv. pyramidalis (oil wt/extracted, oven dried foliage weight). The leaf oil of J. chinensis was found to be polymorphic for cedrene/thujopsene/cedrol (typical Juniper wood oil components) (13,16) and also for phenolics such as methyl chavicol, safrole, methyl eugenol and elemicin, derived from the phenyl propanoid pathway. Therefore, individual plant oils are reported in Table I for J. chinensis. In spite of the polymorphisms, the J. chinensis oils do share many features: they are dominated by α -pinene, sabinene and limonene. Both samples 6765 and 6766, contained large amounts of cedrol (19.5% and 19.1%, respectively, Table I), whereas sample 6767 was low in cedrol (0.9%). Although the presence of the cedar wood oil components in the leaf oil is extremely rare in Juniperus sect. sabina in the western hemisphere, and when found, they are present only in trace amounts (13,16). That is not the case in the sabina junipers of the eastern hemisphere [cf. J. excelsa M.-Bieb. $(17); \textit{J. foetidissima} \ \textbf{Willd.} \ (18); \textit{J. saltuaria} \ \textbf{Rehd.} \ \& \ \textbf{Wils.} \ (19); \textit{J. przewalskii} \ \textbf{Kom. f. pendula}$ (Cheng & L.K. Fu) R. P. Adams & Chu Ge-lin (20); J. semiglobosa Regel (21)]. The polymorphism for the phenyl propanoid aromatic compounds has also been found in I. scopulorum and I. virginiana (22). Note that bornyl acetate is low in all three samples and elemol is absent in contrast to the report by Fournier et al. (3,4) who found 14.9% bornyl acetate and 12.4% elemol with no cedrene, thujopsene or cedrol.

The oil of J. chinensis cv. pyramidalis did not contain the cedrene/cedrol components and was similar to the J. chinensis 6767 sample (Table I), although there was a shift towards

more sabinene (43%). There is some agreement with Fournier et al. (3,4) although they reported 27.7% bornyl acetate, 0.5% elemol as well as a trace of sabinyl acetate in their study of ev. *pyramidalis*.

Juniperus chinensis var. kaizuca is also known as J. chinensis cv. torulosa and J. chinensis cv. kaizuka as well as the "Hollywood Juniper." It is characterized by limbs that curve counterclockwise about the trunk. No reports of its oil are known. Its oil is very different from that of J. chinensis (sensu stricto) and is dominated by α -pinene, sabinene, myrcene, bornyl acetate, elemol and the eudesmols. The oil is very simple without either the cedrene/cedrol series or the phenyl propanoid compounds. The divergence of the oil from that of J. chinensis supports the recognition of the variety ranking for var. kaizuca.

The previous reports (3-5) of the oil of J. chinensis are not comparable to our analyses and this suggests that material cultivated under the name of J. chinensis is not typical of the species. Overall, the oil of J. chinensis is very variable. Clearly, additional samples are needed from natural stands across the geographical range of the species. Unfortunately, that may not be possible because much of its natural range has been converted to agricultural use.

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