GEOGRAPHIC VARIATION AND SYSTEMATICS OF *JUNIPERUS PHOENICEA* L. FROM MADEIRA AND THE CANARY ISLANDS: ANALYSES OF LEAF VOLATILE OILS

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ABSTRACT

All of the oils of *J. phoenicea* from the Canary Islands and Madeira were very similar. The volatile leaf oils were dominated by α-pinene (57.3 - 76%) as was the oil from Morocco (65.4%). This is higher than in *J. p.* var. *phoenicea*, Spain (41.2%) or var. *turbinata*, Spain, (25.8%). The Madeira and Canary Island oils had moderate amounts of β-phellandrene (0.5 - 8.0%), myrcene (2.3 - 3.3%), α-terpinyl acetate (trace - 5.0%), (E)-caryophyllene (0.4 - 1.4%), and trans-totarol (0.1 - 2.1%). There is some differentiation in the oils from Madeira and the Canary Islands from populations in Spain and Morocco, but not enough to justify the recognition of *J. p.* subsp. *canariensis* at this time. *Phytologia 91(1):40-53 (April, 2009*).

KEY WORDS: *Juniperus phoenicea,* Cupressaceae, Madeira Island, Canary Islands, leaf essential oils, α-pinene, myrcene, β-phellandrene.

Juniperus phoenicea L. of the Mediterranean has red seed cones (berries) and is the only serrate leaf margined juniper in section Sabina in the eastern hemisphere (Adams, 2008). Gaussen (1968) discussed several other infraspecific taxa: var. *canariensis* (Guyot & Mathou) Rivas-Martinez et al., of the Canary Islands, var. *lycia* (L.) Gaussen, France littoral zone, var. *mollis* M & W, Morocco, and var. *megalocarpa* Maire, dunes near Mogador, Morocco. Adams et al. (1996) examined leaf terpenoids of *J. phoenicea* var. *phoenicea*, Greece and Spain, *J. p.* var. *turbinata* (Guss.) Parl. (=var. *oophora* Kunze), Tarifa Sand Dunes, Spain and *J. p.* subsp. *eu-mediterranea*, west of Setubal, Portugal. Adams et al. (1996) concluded that *J. p.* var. *turbinata* is conspecific with *J. p.* subsp. *eu-mediterranea*. There are a number of older literature reports on analyses of the leaf volatile oil of *J. phoenicea* and these are reviewed in Adams et al. (1996). The Adams et al. (1996) study was followed up using RAPDs (Adams et al., 2002). Figure 1 shows the PCO based on 119 RAPD bands. Note that *eu-mediterranea* and v. *turbinata* form a cluster (lower left). However, the plants from Tenerife, Canary Islands (cf. v. *canariensis*, fig. 1) cluster closely with plants from Nea Epidavios, Greece! This study confirmed the previous terpene analyses (Adams, et al., 1996) that subsp. *eu-mediterranea* and v. *turbinata* are conspecific. The plants from Corsica Island and Delphi Greece formed a separate group.

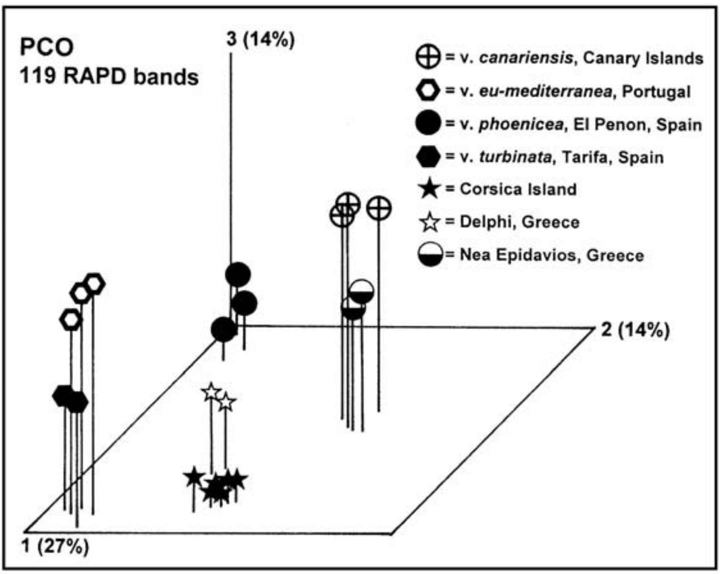

Figure 1. PCO based on 119 RAPD bands ordinating various taxa of *J. phoenicea*.

Most recently, Adams et al. (2006) analyzed RAPDs from *J. phoenicea* from sand and rock areas in Morocco and compared these populations with plants from Tenerife, Canary Islands and var. *turbinata*, Tarifa sand dunes, Spain. PCO ordination (fig. 2) shows that 41% of the variance in the RAPDs was due to the differences between var. *phoenicea* (Spain) and the Morocco, Tenerife and var. *turbinata* populations.

The Tenerife population accounted for about 14% of the variance (fig. 2). Although, the Canary Island plants are loosely associated with var. *turbinata*, they generally have large, round berries (seed cones), not turbinate shaped.

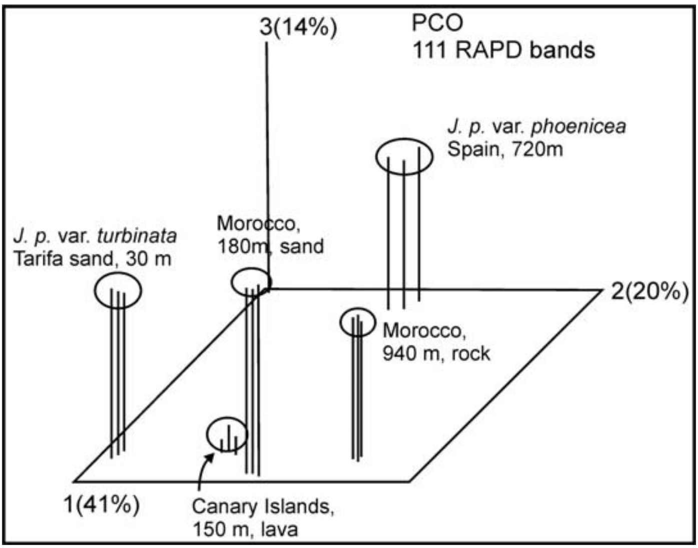

Figure 2. PCO ordination of *J. phoenicea* populations based on 111 RAPD bands.

The purpose of this study was to report on the volatile leaf oil compositions of populations of *J. phoenicea* from several islands in the Canary archipelago and Madeira, and to contrast these oils with *J. p.* var. *phoenicea* (Iberian Peninsula, Spain) and var. *turbinata* (Tarifa sand dunes, Iberian Peninsula, Spain) oils. The distribution of *J. phoenicea* in Madeira and the Canary Islands is shown in figure 3.

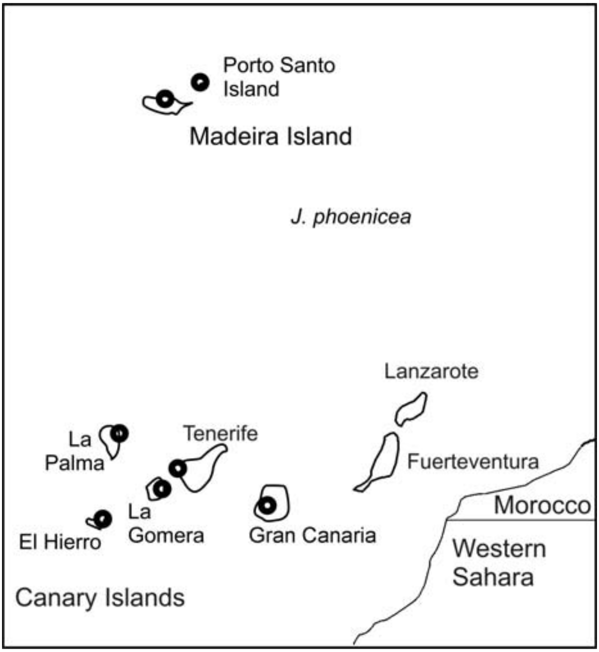

Figure 3. Distribution of *J. phoenicea* in Madeira and Canary Islands.

MATERIALS AND METHODS

Plant material - J. phoenicea Madeira Island: 32º 48.822'N, 16º 52.627'W, ca 100 m, *R. P. Adams 11502, 11503,* cultivated at Botanic Garden in Funchal, ex Porto de la Cruz, 32º 39.08'N, 16º 47.14'W, ca 100 m, *R. P. Adams 11504*; Canary Islands: Tenerife, volcanic rock, ca. 150 m, *R. P. Adams 8147-8149*, La Palma Island, Santa Lucia, loose volcanic pumice, 28º 44.250'N, 17º 44.198'W, 283 m, *R. P. Adams 11514-11516*, La Gomera Island, volcanic rock, 28º 11.358'N, 17º 12.320'W, 370 m, *R. P. Adams 11528-115230;* Spain, limestone soil, 25 km e. Guadahortuna, 720 m, El Penon, *R. P. Adams, 7077-7079*; Morocco, red clay, 20 km sse Marrakech, 31º 21.033'N, 07º 45.893'W, 940 m, *R. P. Adams 9408-9410;* Spain, *J. phoenicea* var. *turbinata*:

Tarifa sand dunes, 15 km w. of Tarifa, 30 m, 36º 04.996'N, 5º 42.104' W, *R. P. Adams, 7202-7204*. Voucher specimens are deposited at the Herbarium, Baylor University (BAYLU).

Isolation of Oils - Fresh leaves (200 g) were steam distilled for 2 h using a circulatory Clevenger-type apparatus (Adams, 1991). The oil samples were concentrated (ether trap removed) with nitrogen and the samples stored at -20ºC until analyzed. The extracted leaves were oven dried (100ºC, 48 h) for determination of oil yields.

Chemical Analyses - Oils from 10-15 trees of each of the taxa were analyzed and average values are reported. The oils were analyzed on a HP5971 MSD mass spectrometer, scan time 1/ sec., directly coupled to a HP 5890 gas chromatograph, using a J & W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column (see 5 for operating details). Identifications were made by library searches of our volatile oil library (Adams, 2006), using the HP Chemstation library search routines, coupled with retention time data of authentic reference compounds. Quantitation was by FID on an HP 5890 gas chromatograph using a J & W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column using the HP Chemstation software.

Data Analysis - Terpenoids (as per cent total oil) were coded and compared among the species by the Gower metric (1971). Principal coordinate analysis was performed by factoring the associational matrix using the formulation of Gower (1966) and Veldman (1967).

RESULTS AND DISCUSSION

All of the oils from the Canary Islands and Madeira were very similar (table 1). The volatile leaf oils were dominated by α-pinene (57.3 - 76%) as was the oil from Morocco (65.4%). α-pinene was higher in concentration in than in *J. p.* var. *phoenicea*, Spain (41.2%) or var. *turbinata*, Spain, (25.8%). The Madeira and Canary Island oils had moderate amounts of β-phellandrene (0.5 - 8.0%), myrcene (2.3 - 3.3%), α-terpinyl acetate (trace - 5.0%), (E)-caryophyllene (0.4 - 1.4%), and trans-totarol (0.1 - 2.1%).

The oil from Morocco was the only oil with camphor (1.3%, table 1). The oil of *J. p.* var. *phoenicea*, Spain, contained a large concentration of manoyl oxide (22.0%). The oil of *J. p.* var. *turbinata*, Spain, contained large amounts of β-phellandrene (31.5%) and α-terpinyl acetate (13.1%) along with the smallest amount of α-pinene (25.8%).

Only two compounds seem to separate the oils of Madeira and Canary Islands from continental oils: (E)-2-hexenal and (Z)-3-hexenol (table 1). However, these very volatile components are easily lost during transport and distillation, so the lack of these compounds in the oils from Morocco and Spain (table 1) may not be so significant.

The *J. phoenicea* oil from Madeira shows differentiation from the Canary Islands in having higher concentrations of β-phellandrene (8.0%), linalool (1.0%), α-terpinyl acetate (5.0%) and α-eudesmol (0.9%, vs. absent in the Canary Island oils, table 1). In general, these compounds point to a similarity to the oil of *J. p.* var. *phoenicea* from Spain.

To better understand the similarities among the oils, similarity measures were computed and the matrix of associations was factored. Eigenroots were extracted and accounted for 31.08, 19.50, 18.77, and 13.0% of the variance among the seven samples. The eigenroots appeared to asymptote after the fourth eigenroot, implying that five groups may be present. Principal Coordinate Ordination (PCO) of the samples (Fig. 3) shows that the oils from the Canary Islands (La Gomera, La Palma and Tenerife) are very similar (0.77 - 0.84). The next most similar oil is from Madeira (0.73 to La Palma). The Canary Islands oils are then linked to Morocco (0.70). *Juniperus phoenicea* var. *turbinata* (Tarifa sand dunes, Spain) are the least similar and link to Madeira (0.60) just smaller than the link of *J. p.* var. *phoenicea*, Spain to Madeira (0.64). There is certainly considerable variation in the volatile leaf oil compositions from various populations of *J. phoenicea* from the populations sampled in this study. It is not clear if there is sufficient differentiation in the Canary Islands to support the recognition of *J. phoenicea* subsp. *canariensis* at this time.

Geographic variation among the samples was further analyzed by plotting a minimum spanning network onto a geographic map. The

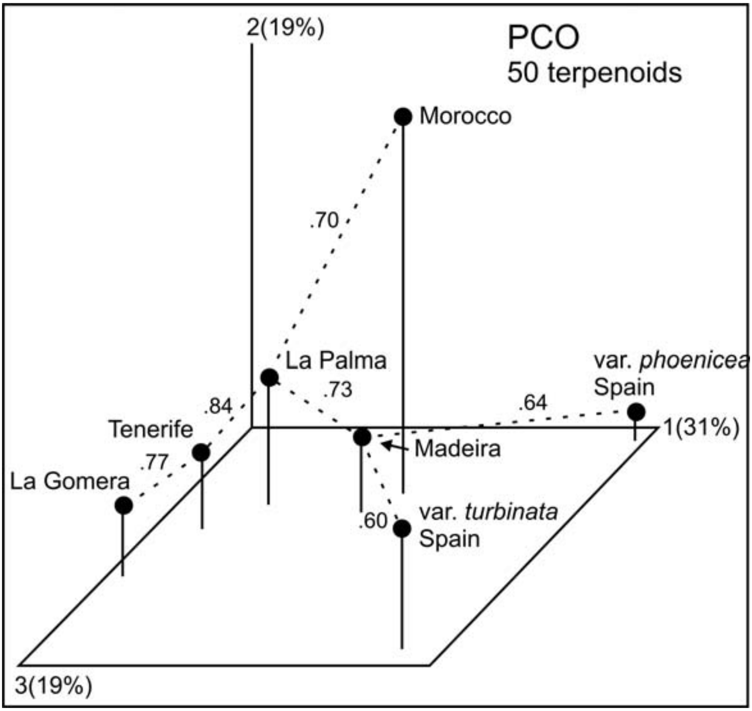

Figure 4. PCO ordination based on 50 terpenoids with the minimum spanning network super-imposed.

samples from the Canary Islands are, geographically, the nearest neighbors and their oils high similarities reflect the co-differentiation and genetic isolation of the Canary Islands from Africa and Madeira (fig. 5).

However, the linkage of the Canary Islands populations to Madeira is larger than its linkage to Africa (fig. 5). This may reflect more gene flow from north - south bird migrations (and seed cone dispersal) than from the east-west bird migrations to Morocco.

Alternatively, the linkage to Madeira may reflect co-evolution in similar climates of the Canary Islands and Madeira.

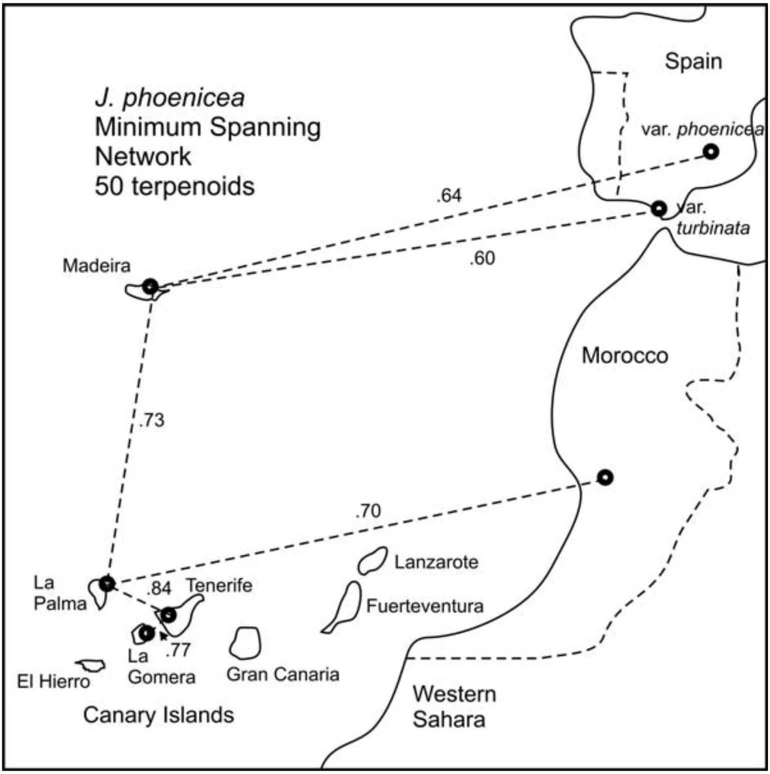

Figure 5. Minimum spanning network based on 50 terpenoids.

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Table 1. Composition of the leaf oils of *J. phoenicea* from Madeira and the Canary Islands: Tenerife, La Palma and La Gomera compared with *J. phoenicea* from Morocco and Spain and *J. phoenicea* var. *turbinata*, Tarifa, Spain.

AI	Compound	Madeira	Tenerife	La Palma	La Gomera	Morocco	Spain	*turbinata*
844	(E)-2-hexenal	0.2	t	t	0.3	-	-	-
850	(Z)-3-hexenol	-	0.1	0.2	0.3	-	-	-
921	tricyclene	0.1	0.2	0.2	0.1	0.3	0.1	0.1
932	**α-pinene***	**57.8**	**67.9**	**76.0**	**57.3**	**65.4**	**41.2**	**25.8**
945	α-fenchene	0.1	0.1	0.1	t	0.2	0.1	t
946	camphene	0.3	0.4	0.5	0.5	0.6	0.1	0.2
953	thuja-2,4-diene*	0.2	0.1	0.1	0.2	0.5	0.1	-
961	verbenene	-	-	-	-	-	0.3	0.1
969	sabinene	0.2	0.4	t	t	0.2	0.1	t
974	β-pinene*	1.2	1.6	1.4	1.5	0.8	2.1	1.3
988	**myrcene***	**3.3**	**2.7**	**2.8**	**2.3**	**1.7**	**3.2**	**6.6**
1001	δ-2-carene	0.1	t	0.1	t	0.2	0.1	0.5
1002	**α-phellandrene***	**1.1**	**-**	**-**	**-**	**-**	**0.7**	**4.4**
1008	**δ-3-carene***	**-**	**0.3**	**t**	**t**	**2.3**	**1.5**	**-**
1014	α-terpinene*	0.1	0.1	t	t	0.1	0.1	0.3
1020	p-cymene*	0.5	0.1	0.3	0.3	0.6	0.4	1.3
1024	limonene*	0.9	1.9	1.9	0.6	0.9	0.6	t
1025	**β-phellandrene***	**8.0**	**1.2**	**1.3**	**0.5**	**0.6**	**4.9**	**31.5**
1044	(E)-β-ocimene	0.3	0.2	0.1	0.1	-	-	t
1054	γ-terpinene	0.3	0.3	0.5	0.3	0.4	0.2	0.3
1083	fenchone*	t	t	t	-	1.0	-	-
1086	terpinolene*	1.0	0.6	0.6	0.6	-	0.7	1.8
1095	linalool*	1.0	0.4	t	t	0.3	1.0	0.1

AI	Compound	Madeira	Tenerife	La Palma	La Gomera	Morocco	Spain	*turbinata*
1095	linalool	1.0	0.4	t	t	0.3	1.0	0.1
1100	n-nonanal	t	0.1	t	-	-	-	-
1106	cis-rose oxide	-	t	t	-	0.1	-	-
1114	endo-fenchol	-	-	-	-	-	0.1	t
1118	cis-p-menth-2-en-1-ol*	-	-	-	-	-	0.2	0.6
1122	chrysanthenone	-	-	-	-	0.1	-	-
1122	α-campholenal*	0.7	0.1	0.4	0.3	0.5	0.2	0.1
1122	trans-rose oxide	-	-	-	-	t	-	-
1132	cis-limonene oxide (furanoid)	-	-	-	-	-	t	-
1135	trans-pinocarveol*	0.7	0.1	0.4	0.3	0.5	0.3	0.5
1137	cis-verbenol	t	-	-	0.1	0.2	t	-
1139	$C_{10}OH$, <u>41</u>,55,81,95,152*	-	-	-	-	-	1.4	-
1140	trans-verbenol*	0.1	0.1	0.4	0.8	0.6	-	-
1141	**camphor***	**-**	**-**	**-**	**-**	**1.3**	**-**	**-**
1148	citronellal	-	-	-	-	-	0.1	-
1155	iso-pulegol	-	-	-	-	-	0.1	-
1158	trans-pinocamphone*	t	-	t	0.1	0.2	0.1	-
1160	pinocarvone	t	t	0.1	t	0.2	-	-
1165	borneol*	-	-	-	-	-	0.6	-
1166	p-mentha-1,5-dien-8-ol	0.4	0.1	0.3	0.3	0.3	-	0.1
1172	cis-pinocamphone	-	-	-	-	0.2	0.2	-
1174	terpinen-4-ol	t	0.2	t	t	0.3	0.1	0.2
1178	naphthalene	t	0.2	t	0.2	-	t	-
1179	p-cymen-8-ol	0.1	t	0.1	t	-	0.1	0.4
1186	**α-terpineol***	**t**	**0.2**	**0.1**	**0.2**	**-**	**2.3**	**0.4**
1195	cis-piperitol	-	-	-	-	-	-	0.2
1195	myrtenal	-	t	0.1	0.1	t	-	-

AI	Compound	Madeira	Tenerife	La Palma	La Gomera	Morocco	Spain	*turbinata*
1195	myrtenol	0.1	-	0.1	0.1	t	0.1	-
1204	verbenone*	0.3	0.2	0.2	0.6	0.3	0.2	-
1207	trans-piperitol	-	-	-	-	-	-	0.3
1215	trans-carveol	0.1	-	0.1	0.1	0.2	0.1	t
1218	endo-fenchyl acetate	t	-	0.2	0.1	-	-	0.1
1223	citronellol	0.1	t	t	t	1.4	0.5	0.6
1232	thymol, methyl ether	-	0.2	t	t	-	-	-
1233	pulegone	-	-	-	-	-	0.1	-
1235	trans-chrysanthenyl acetate	-	-	-	-	-	-	0.1
1249	piperitone	-	-	-	-	-	0.2	0.3
1255	(4Z)-decenol*	0.7	0.6	t	t	0.5	0.2	0.5
1259	(4E)-decenol	-	-	-	-	0.1	-	-
1274	neo-isopulegyl acetate*	0.2	t	t	t	0.1	-	0.8
1287	bornyl acetate	0.4	0.4	0.4	0.3	0.1	-	0.2
1287	trans-linalool oxide acetate (pyranoid)	-	-	-	-	-	-	0.2
1292	(E,Z)-2,4-decadienal	-	-	-	-	-	-	-
1309	decadienol isomer	-	0.2	t	t	t	0.3	0.3
1315	(E,E)-2,4-decadienal	-	-	-	-	t	t	-
1335	δ-elemene	-	-	-	-	0.1	-	-
1341	$C_{15}OH$, <u>43</u>,134,59,91,115	-	-	-	-	-	-	0.8
1345	α-cubebene	-	0.1	t	0.1	0.2	-	-
1346	**α-terpinyl acetate***	**5.0**	**0.2**	**t**	**0.1**	**-**	**0.1**	**13.1**
1374	α-copaene	-	-	-	-	0.1	-	-
1387	β-bourbonene	-	-	-	-	0.1	-	-
1387	β-cubebene	-	t	t	t	-	-	-
1389	β-elemene	-	-	-	-	-	0.1	-

AI	Compound	Madeira	Tenerife	La Palma	La Gomera	Morocco	Spain	*turbinata*
1400	β-longipinene	-	-	-	-	0.1	0.2	-
1417	(E)-caryophyllene*	0.9	0.6	0.4	1.4	0.8	1.2	0.1
1429	cis-thujopsene	0.2	t	t	t	0.2	-	-
1448	cis-muurola-3,5-diene*	t	0.5	0.3	0.6	0.3	-	-
1452	α-humulene*	0.7	0.6	0.4	1.1	0.2	-	-
1475	trans-cadina-1(6),4-diene*	-	0.6	0.3	0.6	0.4	-	-
1478	γ-muurolene	0.1	-	0.1	-	0.5	-	-
1484	germacrene D*	-	-	-	-	-	0.5	0.2
1493	trans-muurola-4(14),5-diene	0.1	1.2	0.5	1.3	0.5	-	-
1493	epi-cubebol*	0.2	0.6	0.5	-	0.4	-	-
1495	γ-amorphene	-	-	-	-	-	-	0.1
1500	α-muurolene	0.2	0.3	0.1	0.4	0.3	-	0.1
1509	$C_{15}OH$,<u>41</u>,55,81,161,220	-	-	-	-	0.1	0.3	0.1
1513	cubebol*	0.3	1.2	1.1	1.9	0.4	-	-
1513	γ-cadinene*	0.5	1.6	-	1.6	-	0.1	0.1
1522	δ-cadinene*	-	-	0.8	-	1.1	0.2	0.4
1528	zonarene	-	-	t	-	0.2	-	-
1531	Z-nerolidol	-	0.4	-	0.5	-	-	-
1531	cis-calamenene	-	-	-	-	0.4	-	-
1533	trans-cadina-1,4-diene	-	0.2	0.2	0.2	-	-	-
1535	**$C_{15}OH$,<u>41</u>,69,105,161,204***	**-**	**-**	**-**	**-**	**-**	**1.0**	**0.1**
1548	**elemol***	**0.3**	**0.1**	**0.1**	**0.1**	**0.7**	**1.8**	**0.6**
1559	germacrene B*	-	-	-	-	-	0.6	0.2
1561	(E)-nerolidol*	-	-	-	-	0.9	t	-
1574	germacrene-D-4-ol*	0.5	0.2	0.3	0.6	0.1	0.2	0.2
1582	caryophyllene oxide*	0.4	0.5	0.4	1.4	0.6	1.0	0.1
1608	humulene epoxide II*	0.1	0.3	0.2	0.7	0.1	-	-

AI	Compound	Madeira	Tenerife	La Palma	La Gomera	Morocco	Spain	*turbinata*
1625	$C_{15}OH$, 43,119,161,204,220*	0.4	2.3	1.3	2.0	1.2	0.4	0.3
1630	γ-eudesmol	-	-	-	-	-	0.2	0.1
1638	epi-α-cadinol	0.2	0.5	0.3	0.6	0.2	0.2	0.1
1638	epi-α-muurolol	0.3	0.5	0.3	0.5	0.2	0.1	0.2
1645	cubenol	-	-	0.3	0.4	t	-	-
1649	β-eudesmol	0.2	-	0.2	-	0.2	0.4	0.2
1652	**α-eudesmol***	**0.9**	**-**	**-**	**-**	**0.2**	**0.3**	**0.2**
1652	**α-cadinol***	**-**	**1.0**	**0.8**	**1.4**	**0.2**	**0.3**	**0.3**
1670	bulnesol	-	-	t	0.1	t	0.1	-
1685	**germacra-4(15),5,10(14)-trien-1-al***	**0.6**	**0.7**	**0.6**	**t**	**t**	**0.1**	**-**
1688	shyobunol*	1.0	-	0.3	1.3	0.5	1.5	0.8
1715	(2Z,6E)-farnesol*	-	-	-	-	0.1	1.2	-
1968	sandaracopimara-8(14),15-diene	-	-	-	-	-	0.1	0.1
1978	**manoyl oxide***	**-**	**1.1**	**-**	**2.4**	**2.6**	**22.0**	**0.4**
2009	epi-13-manoyl oxide	-	-	-	-	0.1	0.1	-
2056	manool	-	-	-	-	0.1	-	-
2055	abietatriene	0.3	0.1	-	0.3	-	0.1	t
2087	abietadiene	0.4	t	-	0.4	-	0.1	0.1
2298	4-epi-abietal	0.4	0.2	0.2	0.4	0.1	0.2	-
2314	trans-totarol*	2.1	0.4	0.1	2.0	0.1	0.2	0.2
2331	trans-ferruginol	0.2	-	-	0.2	-	-	-

AI = Arithmetic Index on DB-5 column. *Used in numerical analyses. Compositional values less than 0.1% are denoted as traces (t). Unidentified components less than 0.5% are not reported. Those compounds that appear to distinguish taxa are in boldface.