

## SUPPLEMENTARY MATERIAL

### Comparison Of Essential Oils From *Cistus* Species Growing In Sardinia

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#### Abstract

*Cistus* genus is present in Sardinia with large populations of *C. monspeliensis*, *C. salvifolius*, *C. creticus* subsp. *eriocephalus* and few stations of *C. albidus*, *C. creticus* subsp. *creticus* and *C. creticus* subsp. *corsicus*. No chemical studies are currently being carried on *Cistus* species of Sardinia. The essential oils have shown six different profiles. *C. creticus* subsp. *eriocephalus* showed a high amount of manoyl oxide and its isomer (70%). *C. salvifolius* has pointed out the group of labdane, (20%); another consistent percentage is made of perfumed molecules as ionone and its derivate. Several linear hydrocarbons were produced by *C. monspeliensis*, and the heneicosane was the most represented element. In *C. albidus* no labdane-type diterpenes were identified. Analysis of *C. creticus* subsp. *creticus* revealed several oxygenated sesquiterpenes and labdane-type diterpenes, especially manoyl oxide. *C. creticus* subsp. *corsicus* was qualitatively very similar to *C. creticus* subsp. *creticus*, notably concerning the labdane-type compounds.

**Keywords:** *Cistus*, essential oil, labdane, manoyl oxide

RI	Components	<i>C. albidus</i>	<i>C. creticus</i> subsp. <i>corsicus</i>	<i>C. creticus</i> subsp. <i>creticus</i>	<i>C. creticus</i> subsp. <i>eriocephalus</i>	<i>C. monspeliensis</i>	<i>C. salvifolius</i>	ID <sup>a</sup>	References
<b>LINEAR HYDROCARBONS</b>									
2021	3-methyl eicosane					8.11	4.67	RI, MS	
2100	heneicosane					25.20	0.38	Std	
2400	tetracosane					2.42	0.99	Std	
2700	heptacosane					4.07		Std	
<b>NO TERPENIC CARBONYL COMPOUNDS</b>									
1101	nonanal				0.12		0.13	Std	
1320	5,9-dimethyl-5,8-decadien-2-one						0.70	RI, MS	
1327	undecanal					0.35		Std	
1333	2,6,6-trimethyl 1-cyclohexene-1-acetaldehyde						0.24	RI; MS	
1348	6-methyl-5-(1-methylethylidene)-6,8-nonadien-2-one						1.41	RI, MS	
1401	4-(4-methyl phenyl)-pentanal						1.98	RI, MS	
1409	dodecanal					0.32		Std	
1826	hexahydrofarnesyl acetone [(+/-)-phytone]					6.55	0.51	RI, MS	

1828	<i>cis,cis,cis</i> -7,10,13-hexadecatrienal	0.39			RI, MS	
1843	15-methyl-( <i>Z</i> )-11-hexadecenal	0.51		0.26	RI, MS	
<b>FATTY ACIDS</b>						
1566	lauric acid		0.81		Std	
1753	miristic acid		1.09		Std	
1963	palmitic acid		1.45		Std	
<b>ALIPHATIC ESTERS</b>						
1317	methoxyacetic acid-2-ethylcyclohexyl ester			0.48	RI, MS	
<b>AROMATIC ESTERS</b>						
1567	(3 <i>Z</i> )-2-hexenyl benzoate		2.80	0.45	RI, MS	Hazzit, Baaliouamer, et al., 2006
1588	(2 <i>E</i> )-2-hexenyl benzoate		0.38		RI, MS	Campeol, Flamini, et al., 2001
1760	benzyl benzoate		0.95		Std	Su, Ho, et al., 2006
1845	benzyl oleate		0.32	0.27	Std	
<b>MONOTERPENE HYDROCARBONS</b>						
939	$\alpha$ -pinene		0.36		Std	
954	camphene		0.16		Std	
979	$\beta$ -pinene		0.21		Std	
1029	limonene		0.12		Std	
<b>OXIGENATED MONOTERPENES</b>						
1169	borneol		0.49		Std	
1177	terpinen-4-ol		0.26		Std	

1189	$\alpha$ -terpineol			0.42		0.40			Std	
<del>1233</del>	<del><math>\beta</math>-cyclocitral</del>								<del>0.31</del>	
1237	ascaridole								0.29	RI, MS
1388	10-(acetyl methyl)-3-carene								0.79	RI, MS
	<b>SESQUITERPENE HYDROCARBONS</b>									
1351	$\alpha$ -cubebene	0.1	0.49		0.17					Std
1377	$\alpha$ -copaene								0.45	Std
1388	(-)- $\beta$ -bourbonene	4.88	0.93	1.38	0.64					Std
1413	cis- $\alpha$ -bergamotene	0.61	0.33							RI, MS
<del>1418</del>	<del><i>E</i>-<math>\alpha</math>-ionene</del>								<del>0.73</del>	
1419	<i>E</i> - $\beta$ -caryophyllene	4.54	0.92	1.18	0.22					Std
1432	$\beta$ -copaene	0.77	0.32							RI, MS
1440	$\alpha$ -guaiene					0.27		0.47		RI, MS
1441	aromadendrene	0.98						0.09		Std
1443	$\beta$ -Z- farnesene	1.79				0.46				Std
1455	$\alpha$ -humulene	1.04								Std
1457	$\beta$ - <i>E</i> -farnesene					0.43				Std
1457	muurolo-4,11-diene	2.54								RI, MS
										Weyerstahl, Marschall, et al., 1999
1467	<i>cis</i> -muurolo-4(14)5-diene							0.17		RI, MS
1460	alloaromadendrene	5.32			0.22			1.97		Std
1481	$\alpha$ -curcumene (= ar curcumene)	16.01						0.72		Std
1485	D-germacrene	3.57	0.64		0.27		2.33			Std
1494	$\alpha$ -zingiberene	3.53								RI, MS

1498	$\alpha$ -selinene			2.09	0.50			RI, MS	
1498	viridiflorene	0.90					0.36	RI, MS	
1480	$\gamma$ -muurolene		0.97	0.96	0.46			RI, MS	
1500	$\alpha$ -muurolene	2.04	1.39	1.80	1.15	1.92	0.38	RI, MS	
1502	$\gamma$ -patchoulene			0.77				RI, MS	
1505	$\beta$ -himachalene						0.66	RI, MS	
1514	$\gamma$ -cadinene	2.45	1.98	1.17	0.71			RI, MS	
1515	$\gamma$ -bisabolene	1.25						RI, MS	
1523	$\delta$ -cadinene	6.70	7.67	2.18	2.51		0.12	RI, MS	
1528	cada-1,4-diene		1.02		0.85			RI, MS	Hamm, Bleton, et al., 2005
1539	$\alpha$ -cadinene	1.67						RI, MS	
1566	$\beta$ -calacorene	0.71	0.47		0.26	0.50		RI, MS	
1677	cadalene		0.33		0.28	1.07		RI, MS	
	<b>OXYGENATED SESQUITERPENES</b>								
<del>1177</del>	<del>terpinen-4-ol</del>				0.26				
<del>1189</del>	<del><math>\alpha</math>-terpineol</del>				0.42	0.40			
1498	6-epi-shyobunone	1.13						RI, MS	
1510	shyobunone	1.43						RI, MS	
1566	<i>cis</i> -( <i>Z</i> )- $\alpha$ -bisabolene epoxide		0.80					RI, MS	
1567	isoaromadendrene epoxide	4.86				0.53		RI, MS	
1578	spathulenol	0.65	0.31		0.36	0.42	0.18	RI, MS	
1580	<i>trans</i> -( <i>Z</i> )- $\alpha$ -bisabolene epoxide					0.41	0.14	RI, MS	
1583	caryophyllene oxide	0.80	0.40		0.24	0.53	0.21	Std	

1585	globulol	2.22		0.86	0.95	3.80	0.13	Std	
1593	viridiflorol	2.51			0.43	1.56	0.74	Std	
1594	aromadendrene oxide-(2)		0.58					Std	
1595	cubedol		0.30		0.28	0.88		RI, MS	
1601	guaiol	1.26	2.49	8.80		0.36		Std	
1624	$\delta$ -cadinol	3.02	6.47	4.86	2.82	2.23	0.64	RI, MS	
1630	$\tau$ -muurolol		1.81	0.93	0.92	0.68		RI, MS	
1637	<i>cis</i> -cadin-4-en-7-ol	7.43				5.03		RI, MS	Su, Ho, et al., 2006
1640	$\tau$ -cadinol	6.22	13.63		3.47	3.37		RI, MS	
1644	selina-3,11-dien-6- $\alpha$ -ol		4.23	18.04				RI, MS	
1660	selin-11-en-4- $\alpha$ -ol			15.55	0.69	1.55		RI, MS	
1664	7- <i>epi</i> - $\alpha$ -eudesmol	2.73						RI, MS	
1686	$\alpha$ -bisabolol	3.59				1.07		Std	
1761	ambroxide				0.23		0.75	Std	
1833	alloaromadendrol						0.57	RI, MS	
<b>NORISOPRENOIDS</b>									
1233	$\beta$ -cyclocitral						0.31	Std	
1334	dehydro-ar-ionene						0.50	RI, MS	
1385	( <i>E</i> )- $\beta$ -damascenone						0.13	Std	
1414	dihydro- $\alpha$ -ionone						0.75	RI, MS	
1417	$\beta$ -iso-ionone						2.47	RI, MS	
1418	$\alpha$ -ionene						0.73	RI, MS	
1430	$\alpha$ -ionone						1.32	Std	
1439	7,8-dihydro- $\beta$ -ionone						3.89	RI, MS	

1489	<i>trans</i> - $\beta$ -ionone					0.27	Std	
	<b>DITERPENE</b>							
	<b>HYDROCARBONS</b>							
1962	geranyl- $\alpha$ -terpinene					2.13	RI, MS	Paolini et al.,2008
1965	geranyl-p-cymene					9.61	RI, MS	Paolini et al.,2008
1969	cembrene A (3 <i>Z</i> )					1.42	RI, MS	Rahimi-Nasrabadi, Gholivand, et al., 2009
1972	cembrene A (3 <i>E</i> )					8.55	RI, MS	Rahimi-Nasrabadi, Gholivand, et al., 2009
2017	kaur-16-ene					1.30	RI, MS	Demetzos et al., 2002
	<b>OSSIGENATE</b>							
	<b>DITERPENES</b>							
2049	phytol					4.01	Std	
	<b>LABDANE TYPE</b>							
	<b>DITERPENES</b>							
1998	manoyl oxide	0.18	2.47	8.17	64.00	11.98	RI, MS	Demetzos et al., 2002
1985	manoyl oxide isomer				4.40	2.10	RI, MS	Demetzos et al., 2002
2017	13- <i>epi</i> -manoyl oxide		2.46				RI, MS	Demetzos et al., 2002
2097	dihydromanoyl oxide				0.77		RI, MS	
	<b>LABDANES</b>							
1825	sclareol oxide ( <i>trans</i> -A/B)		1.06				RI, MS	Wulfson et al., 1966
1846	sclareol oxide ( <i>cis</i> -A/B)		0.40	2.07	1.10	6.07	RI, MS	Wulfson et al., 1966 Hutschenreuther et

al., 2010

	labdane unidentified (MW 281)	1.24						
	labdane unidentified (MW 281)	1.21			1.24	1.50		
	labdane unidentified (MW 281)					1.77	RI, MS	
1967	Sclareol oxide ( <i>cis</i> B/C)					1.47	RI, MS	Hutschenreuther et al., 2010
1983	13-oxo-15,16-bis-nor-ent-labd-8(17)-ene	11.66	1.46	0.36			RI, MS	
1996	13-oxo-15,16-bis-nor-ent-labd-7(8)-ene	1.78	5.95				RI, MS	
2057	manool	21.07	20.26	2.82			RI, MS	
2223	sclareol	3.70	0.78				Std	
<b>OTHERS</b>								
1381	1,1-dimethyl-2-(2-methyl-1-propenyl)-cyclopropane	0.49						
1702	hexadecanol				1.56		Std	
	cistodiol					1.42	RI, MS	
		99.43	97.6	99.26	94.15	92.15	81.27	

**Table S1.** Chemical composition of the essential oils of *Cistus* species growing wild in Sardinia

<sup>a</sup>Identification methods: MS by comparison of the Mass spectrum with those of the computer mass libraries Adams, Nist 11 and by interpretation of the mass spectra fragmentations. RI by comparison of retention index with those reported in literature. Std by comparison of the retention time and mass spectrum of available authentic standards.



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