Physicochemical characterization of *Crithmum maritimum* L. and *Daucus carota* subsp. *gummifer* (Syme) Hook.fil. and their antimicrobial activity against apple tree and grapevine phytopathogens

Eva Sánchez-Hernández, Laura Buzón-Durán, Celia Andrés-Juan, Belén Lorenzo-Vidal, Jesús Martín-Gil and Pablo Martín-Ramos

SUPPORTING INFORMATION

1. Elemental analysis of the biomass from *Crithmum maritimum* and *Daucus carota* subsp. *gummifer*

Table S1. Elemental (CHNSO) composition (wt%) of *C. maritimum* and *D. carota* fractions

		C	H	N	S	O	C/N ratio
C. maritimum	flowers	40.43%	6.2%	1.61%	0.06%	51.7%	23.1
	leaves	36.63%	6.3%	1.47%	0.10%	55.5%	24.9
	stems	40.02%	6.2%	0.73%	0.05%	53.0%	55.1
D. carota	flowers	42.18%	6.3%	2.51%	0.07%	48.9%	16.8
	leaves	39.86%	6.4%	1.95%	0.31%	51.4%	20.4
	stems	42.78%	6.3%	0.62%	0.01%	50.3%	70.9
	roots	39.74%	6.4%	0.57%	0.00%	53.3%	70.1

Table S2. Elemental composition (wt%) of *C. maritimum* and *D. carota* flowering aerial parts concentrate hydromethanolic extracts

	C	H	N	S	O	C/N ratio
C. maritimum	40.01%	6.3%	1.56%	0.08%	52.05%	25.7
D. carota	41.58%	6.4%	2.23%	0.10%	49.69%	18.6

1.1. *Calorific values calculation*

The calculation of calorific values from elemental analysis data was carried out according Equation: HHV = (0.341×%C) + (1.322×%H) - 0.12 (%O+%N), where HHV is the heating value for the dry material, expressed in $kJ \cdot kg^{-1}$, and %C, %H, %O and %N are the mass fractions, expressed in wt% of dry material. This formula gives acceptable results for biomass, according to the UK's Combined Heat and Power Quality Assurance program.

The calculated higher heating values (HHV) for *C. maritimum* flowers, leaves and stems were 15.39, 13.97 and 13.39 $kJ \cdot g^{-1}$, respectively, with a mean value of 14.9 $kJ \cdot g^{-1}$. The HHV for *D. carota* were 16.55 $kJ \cdot g^{-1}$ (flowers), 15.66 $kJ \cdot g^{-1}$ (leaves), 16.81 $kJ \cdot g^{-1}$ (stems) and 15.53 $kJ \cdot g^{-1}$ (roots), with a mean value of 16.1 $kJ \cdot g^{-1}$.

2. Thermal analysis of the biomass from *Crithmum maritimum* and *Daucus carota* subsp. *gummifer*

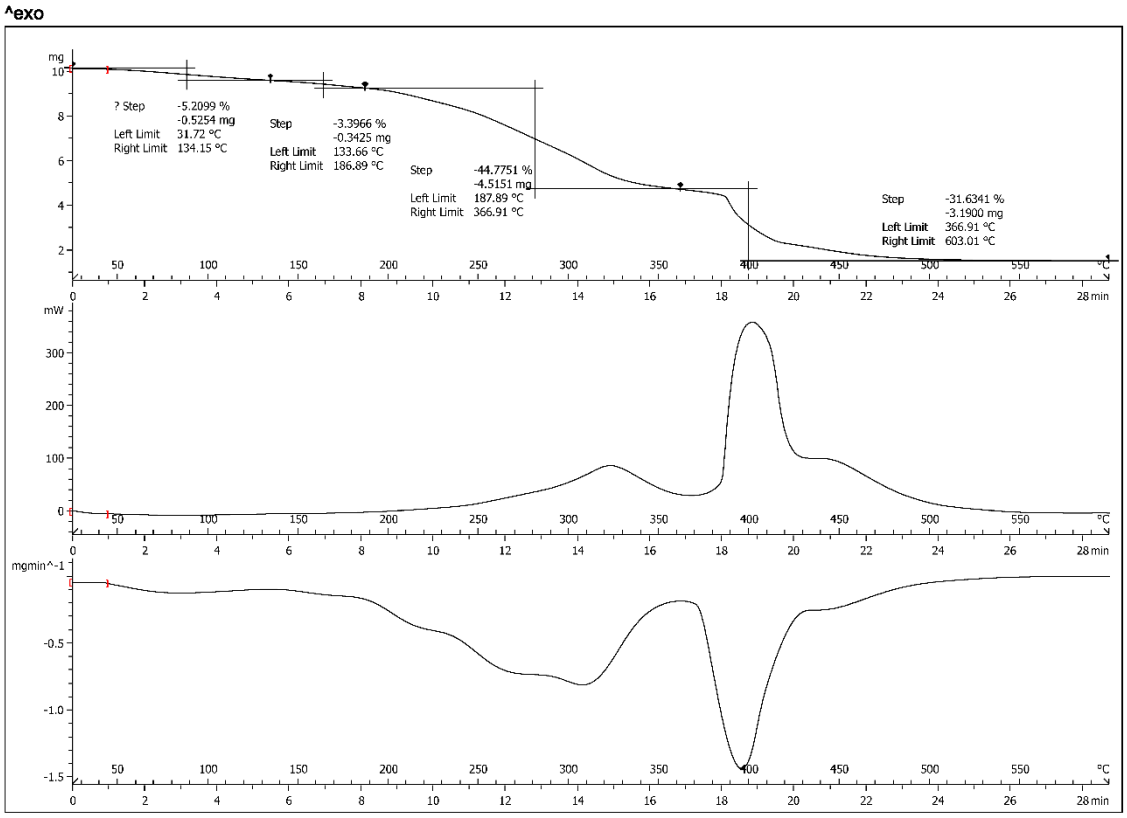

Figure S1. *From top to bottom*: TG, DSC and DTG curves for *C. maritimum*

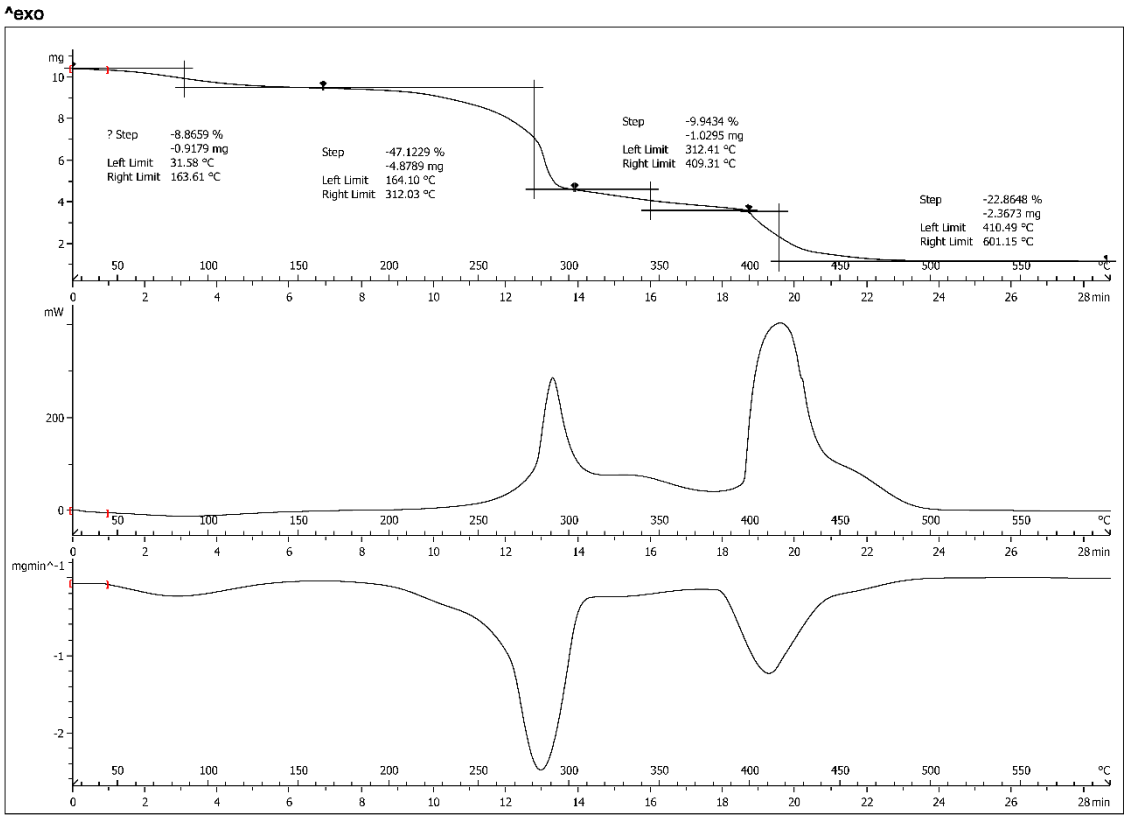

Figure S2. *From top to bottom*: TG, DSC and DTG curves for *D. carota* subsp. *gummifer*

3. Vibrational characterization of the biomass from *Crithmum maritimum* and *Daucus carota* subsp. *gummifer*

Table S3. Main bands in the ATR-FTIR spectra of various *C. maritimum* and *D. carota* subsp. *gummifer* fractions and their assignments.

C. maritimum				***D. carota***			**Assignment**
flowers	leaves	stems	umbel	leaves	stems	roots	
3381	3398	3366	3335	3277	3336	3307	Bonded O-H stretching (cellulose)
			3285		3293		
2916	2916	2916	2918	2918	2917	2919	$-CH_2$ asymmetric stretching of alkyls (cutine, wax, pectin)
2849	2848	2848	2851		2850	2850	$-CH_2$ symm stretching (cutine and wax); CH_2–(C6)– bend (cellulose)
		2359	2360		2360		C=N stretch (cyanogen glycosides)
		2158	2158		2157		CN stretching (HCN), suggesting anthocyanin
1732	1732	1731	1735	1732	1733	1738	C=O stretching of alkyl ester
						1652	Amide I; C=C stretching (hydrocinamic acids of lignins); C=O
1633	1629	1636	1635		1635	1634	stretch (hemicellulose, bonded ketones, quinone…)
			1598	1601			Aromatic C=C skeletal stretching; COO- antisym. stretching (polygalacturonic, pectin ester)
			1558		1554	1558	Amide II
					1540		COO^- symmetric stretching
1516	1516	1517	1511	1516		1514	Aromatic skeletal. Typical of carotenoids
	1472	1472					C-H deformation (cellulose)
1464	1463	1463	1457		1464	1455	H_2O vapour; O-CH_3 stretch; C-H bend of CH_2 or CH_3
1417	1416	1432	1422	1418	1429	1417	CH_2 sym. bending (cellulose); arom C=C; COO- sym. stretch.
1361	1376		1378	1370	1380	1373	
			1313	1320		1320	C-H (cellulose)
1246	1242	1243	1230	1236	1241	1235	Amide III; C-C-O asym stretching acetylated glucomannan; C-O stretch of aryl ether; C-O and OH of COOH groups
1166	1168	1159	1146	1144	1150		C-O-C in bridge asym. (cellulose); C-C in plane (β-carotene)
1104	1106			1093			C-O-C stretching in the pyranose ring skeletal (cellulose)
		1074					C-O and C-H stretching (cellulose I as cellulose Iβ).
	1051			1047	1047		C-O stretching (cellulose, aromatic ether)
		1034			1031	1026	Si-O of silicates, PO_4 residues
1019	1013		1014	1009	1008		C-H bending (typical of carotenes);
							polygalacturonic acid (a variety of pectin in plant cuticles)
	917		888		888		ß-glycosidic linkages (glucose units of cellulose chains), O-C=O in-plane def. or a CH_2 rocking deform.
			812	804		797	Ring vibration (pectin)
	730		774	759	777	777	Stearic acid
719	719	719			718	693	In-plane deformation
			668			667	C-C out-of-plane bending

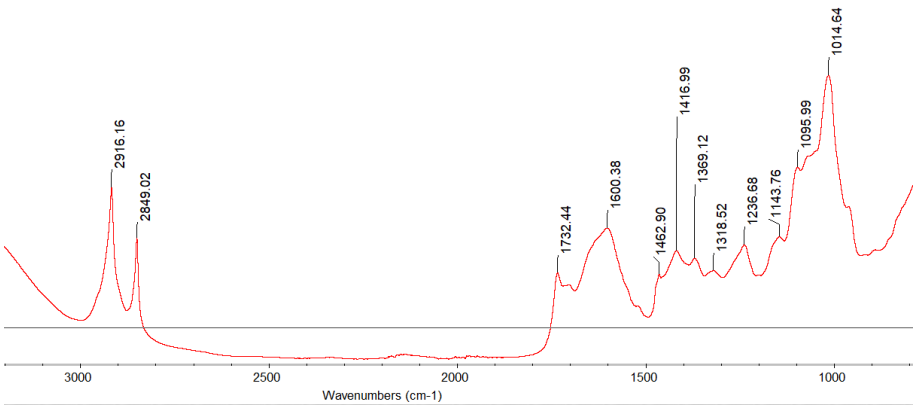

Figure S3. ATR-FTIR spectrum of *D. carota* subsp. *gummifer* hydromethanolic extract (concentrated gel).

4. GC-MS characterization of *Crithmum maritimum* and *Daucus carota* subsp. *gummifer* hydromethanolic extracts

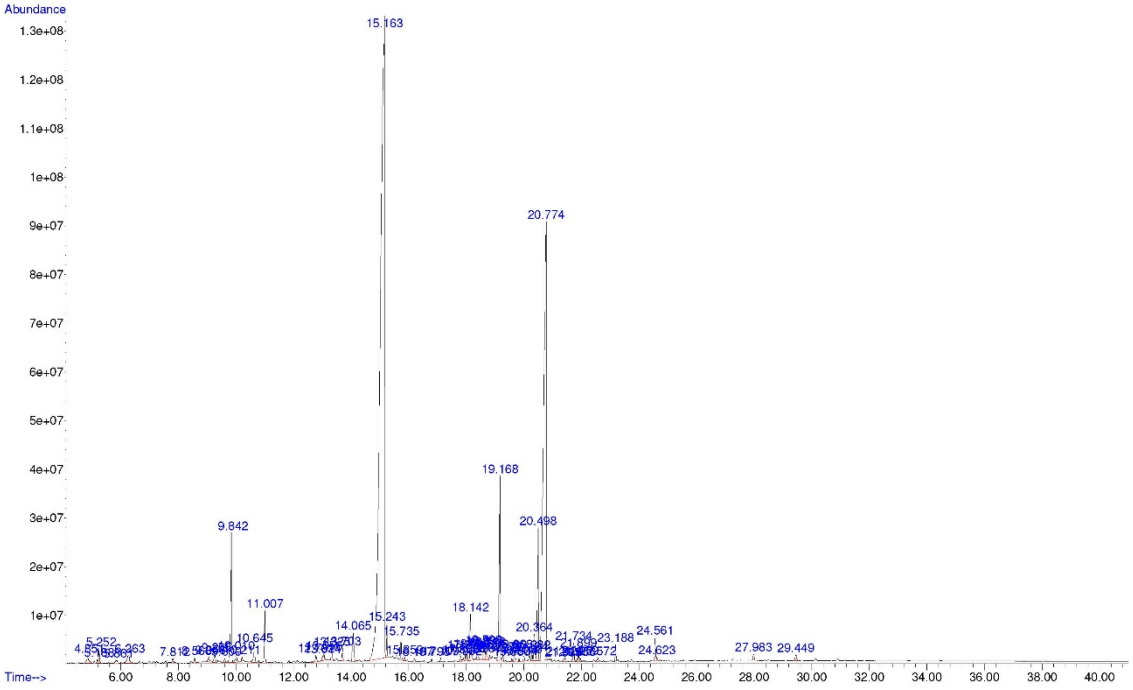

Figure S4. GC-MS spectrum of *C. maritimum* hydromethanolic extract

Table S4. GC/MS analysis of *C. maritimum* hydromethanolic extract

Peak	RT (min)	Area (%)	Library/ID
1	4.8513	0.3044	Oxime-, methoxy-phenyl-_
2	5.1872	0.0549	2H-Tetrazole, 2,5-dimethyl-
3	5.2505	0.2497	2-Cyclopenten-1-one, 2-hydroxy-
4	5.8591	0.1370	2,4-Hexadiyne
5	6.2632	0.4328	1,6-Anhydro-2,4-dideoxy-.beta.-D-ribo-hexopyranose
6	7.8114	0.0989	2-Formylhistamine
7	8.5661	0.1080	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-
8	9.0578	0.1438	Terpinen-4-ol
9	9.2672	0.2633	2-Pentenal, (E)-
10	9.6080	0.1124	N-Benzyl-2-phenethylamine
11	9.8417	2.7777	Benzene, 2-methoxy-4-methyl-1-(1-methylethyl)-
12	10.0072	0.2455	Cyclopentane, 1-ethyl-1-methyl-
13	10.2117	0.0689	Silane, butoxytrimethyl-
14	10.6450	0.4519	Thymol
15	11.0053	0.8798	2-Methoxy-4-vinylphenol
16	12.7823	0.2113	3,5-Dimethylanisole
17	13.0160	0.1051	Allyl(2-butoxy)dimethylsilane
18	13.0550	0.1587	7H-1-Benzopyran-7-one, 5-methoxy-6-methyl-2-phenyl-
19	13.3276	0.2410	1,2-Dimethoxy-4-(1-methoxyethenyl)benzene
20	13.7025	0.2206	1,3-Benzodioxole, 4-methoxy-6-(2-propenyl)-
21	14.0676	0.8009	Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-
22	15.1631	54.5754	Apiol
23	15.2459	0.4499	2,6-Dimethyl-1,3,5,7-octatetraene, E,E-
24	15.7376	0.3259	2-Propenoic acid, 3-(4-hydroxy-3-methoxyphenyl)-
25	15.8593	0.0635	1-[4-Acetyl-1-(4-amino-phenyl)-2,5-dimethyl-1H-pyrrol-3-yl]-ethanone
26	16.1952	0.0877	4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol
27	16.7990	0.0597	3-Methyl-2-butanone, 4-t-butyldimethylsilyloxy-
28	17.1105	0.0461	3,3-Dimethyl-5-phenyl-3H-pyrazole
29	17.8068	0.0896	1,2,3,1',2',3'-Hexamethyl-bicyclopentyl-2,2'-diene
30	17.9041	0.0438	Chromone, 3-methyl-7-nitro-

31	17.9723	0.1286	1-(4-Hydroxyphenyl)-2-(3-hydroxyphenyl)ethane
32	18.0258	0.1160	Hexadecanoic acid, methyl ester
33	18.1427	0.9151	Benzeneacetic acid, 3-hydroxy-, ethyl ester
34	18.2011	0.1472	Phenol, 4-octyl-
35	18.3910	0.2008	n-Hexadecanoic acid
36	18.6003	0.1784	Benzene, (ethenyloxy)-
37	18.6393	0.1883	Scoparone
38	18.6831	0.1413	Chromone, 3-methyl-7-nitro-
39	18.7172	0.2059	2-(Ethyl(m-tolyl)amino)ethyl (E)-2-methylbut-2-enoate
40	18.8146	0.1142	Sorbitol
41	19.1700	3.7771	Falcarinol
42	19.2771	0.1505	1,2,4-Metheno-1H-cyclobuta[b]cyclopenta[d]furan,2,2a,3a,4,6a,6b-hexahydro-3a-methyl-
43	19.5789	0.0716	.alpha.-Methyl-2-naphthalenemethanol
44	19.6666	0.1797	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
45	19.8321	0.0505	Phytol
46	19.9976	0.1033	2,9-Heptadecadiene-4,6-diyn-8-ol, (Z,E)-
47	20.1924	0.1758	6-[(1Z)-1,3-Butadienyl]-1,4-cycloheptadiene
48	20.2800	0.1358	5,8,11-Eicosatriynoic acid, methyl ester
49	20.3628	0.6813	Benzene, 1-methyl-2-nitroso-
50	20.4991	2.7940	Benzene, 1-methyl-4-nitroso-
51	20.7766	23.8342	Dimethyl 1,2-diethenyltricyclo[3.1.0.0(2,4)]hexane-3,6-dicarboxylate
52	21.3657	0.0446	1-Phenyl-1-nonyne
53	21.4193	0.0961	2-Methyl-3-butene-2-thiol
54	21.7357	0.3972	3,4-Difluorobenzyl alcohol, 1-methylpropyl ether
55	21.8575	0.0506	1-[4-(tert-Butyl)phenyl]-2-(4-toluidino)-1-ethanone
56	21.9013	0.1760	Benzene, [(butylsulfonyl)ethynyl]-
57	21.9597	0.0702	2,5-Octadecadiynoic acid, methyl ester
58	22.5731	0.1031	3,7,11,Trimethyl-8,10- dodecedienylacetate
59	23.1866	0.2389	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester
60	24.5596	0.3765	9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester
61	24.6229	0.0717	Methyl 6,9,12-hexadecatrienoate
62	27.9822	0.1282	Vitamin E
63	29.4477	0.1489	Stigmasterol

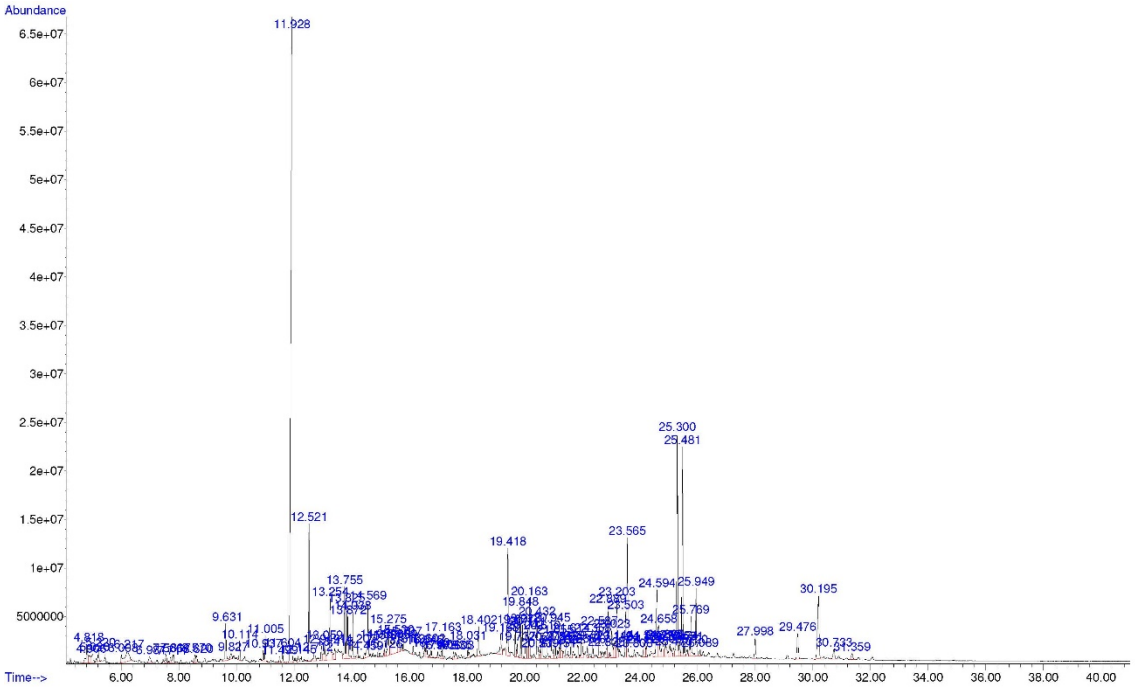

Figure S5. GC-MS spectrum of *D. carota* subsp. *gummifer* hydromethanolic extract

Table S5. GC/MS analysis of *D. carota* subsp. *gummifer* hydromethanolic extract

Peak	RT (min)	Area (%)	Library/ID
1	4.8170	0.8156	Oxime-, methoxy-phenyl-
2	4.9047	0.3327	1-Butanol
3	5.0215	0.4478	Tiglic acid
4	5.2211	0.3062	2-Cyclopenten-1-one, 2-hydroxy-
5	6.0098	0.1819	Phenol
6	6.2192	1.1207	1,6-Anhydro-2,4-dideoxy-.beta.-D-ribo-hexopyranose
7	6.9836	0.2942	Benzeneacetaldehyde
8	7.5678	0.3091	Benzene, 2-methoxy-4-methyl-1-(1-methylethyl)-
9	7.7090	0.1360	Phenol, 2-methoxy-
10	7.8161	0.3355	Thiophene-3-ol, tetrahydro-, 1,1-dioxide
11	8.5707	0.2629	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-
12	8.6194	0.1738	4-Ethylbenzamide
13	9.6321	0.9928	Benzofuran, 2,3-dihydro-
14	9.8268	0.2266	5-Hydroxymethylfurfural
15	10.1141	0.4072	Geraniol
16	10.9369	0.2497	2,3-Dehydro-1,8-cineole
17	11.0051	0.5331	2-Methoxy-4-vinylphenol
18	11.4968	0.1022	Phenol, 2,6-dimethoxy-
19	11.6039	0.2777	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate, (Z)-
20	11.9252	22.7288	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate, (Z)-
21	12.1443	0.2090	Benzoic acid, 3,4-dihydroxy-, methyl ester
22	12.5192	2.7038	Caryophyllene
23	12.7139	0.3300	2,4-Dimethylanisole
24	12.9476	0.3458	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-
25	13.0596	0.4974	7H-1-Benzopyran-7-one, 5-methoxy-6-methyl-2-phenyl-
26	13.2544	1.8704	2,6-Dimethyl-3,5,7-octatriene-2-ol, ,E,E-
27	13.4150	0.4433	2,4-Difluorobenzoic acid, 4-chlorophenyl ester
28	13.7558	1.4863	6-epi-shyobunol
29	13.8240	1.0196	6-epi-shyobunol
30	13.8727	0.8066	2-Pentene, 2-methyl-
31	14.0382	0.8926	7-Oxabicyclo[4.1.0]heptane, 1-methyl-4-(1-methylethenyl)-
32	14.2086	0.3386	2,3,5,6-Tetrafluoroanisole
33	14.4569	0.1671	1H-3a,7-Methanoazulene, octahydro-1,4,9,9-tetramethyl-
34	14.5689	1.3036	Caryophyllene oxide
35	14.9292	0.2714	Apiol
36	15.1239	0.1109	Benzenemethanol, 2,4-dimethyl-
37	15.1629	0.2980	3-Methylene-bicyclo[3.2.1]oct-6-en-8-ol
38	15.2748	0.8895	2,4-Dimethyl-3-nitrobicyclo[3.2.1]octan-8-one
39	15.3722	0.5938	Pentanamide, N-tetrahydrofurfuryl-
40	15.5280	1.3467	1,2,3,5-Cyclohexanetetrol, (1.alpha.,2.beta.,3.alpha.,5.beta.)-
41	15.6400	0.4850	Cyclohexane, 1R-acetamido-2,3-cis-epoxy-4-trans-acetoxy-
42	15.7958	0.2512	cis-9-Hexadecenal
43	16.1317	0.1797	1,3,5-Triethyl-1-oxycyclotrisiloxane
44	16.5455	0.3570	Benzoic acid, 4-hydroxy-3,5-dimethoxy-, hydrazide
45	16.6040	0.2947	Caryophyllene oxide
46	16.7647	0.2264	4-Isopropyl-trans-bicyclo[4.3.0]-2-nonen-8-one, (4R,S)-
47	16.9837	0.1029	2,6,10-Dodecatrien-1-ol, 3,7,11-trimethyl-9-(phenylsulfonyl)-, (E,E)-
48	17.1055	0.1626	trans-Z-.alpha.-Bisabolene epoxide
49	17.1639	0.4616	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1.alpha.,2.beta.,5.alpha.)]-
50	17.5339	0.1564	1-Cyclohexene-1-carboxaldehyde, 4-(1-methylethyl)-
51	17.6020	0.2695	6-Octen-1-ol, 3,7-dimethyl-, propanoate
52	18.0305	0.2683	Hexadecanoic acid, methyl ester
53	18.4005	0.9902	n-Hexadecanoic acid
54	19.1698	0.7739	Pyrido[3,4-d]pyridazine-4,5(3H,6H)-dione, 1-(2-furfuryl)-7-methyl-
55	19.4181	2.6122	4-Hydroxy-4-(4,6-dimethylcyclohex-3-enyl)butan-2-one
56	19.6761	0.6248	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
57	19.7345	0.2918	7,10,13-Hexadecatrienoic acid, methyl ester
58	19.8465	0.8915	Phytol
59	19.9195	0.6545	Bicyclo[4.1.0]heptan-3-ol, 3,7,7-trimethyl-, [1S-(1.alpha.,3.alpha.,6.alpha.)]-
60	20.0412	0.7440	9,12-Octadecadienoic acid (Z,Z)-
61	20.1094	0.7385	9,12,15-Octadecatrienoic acid, (Z,Z,Z)-

62	20.1629	1.2323	3-Carene
63	20.4307	1.1580	Ar-tumerone
64	20.5378	0.2069	Bicyclo[3.1.1]hept-2-en-4-ol, 2,6,6-trimethyl-, acetate
65	20.6109	0.8580	Hexan-3-yl (E)-2-methylbut-2-enoate
66	20.7764	0.3497	Cyclopropanol, 1-(3,7-dimethyl-1-octenyl)-
67	20.9468	1.0063	3-Methyl-2-butenoic acid, 2,7-dimethyloct-7-en-5-yn-4-yl ester
68	21.0539	0.4908	2-Butenoic acid, 2-methyl-, 2-methylpropyl ester, (E)-
69	21.1513	0.1800	2-Buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-
70	21.2048	0.2704	2-Butenoic acid, 3-methyl-, phenylmethyl ester
71	21.2535	0.6101	Benzyl .beta.-d-glucoside
72	21.4385	0.3716	Ethylmalononitrile, 1-cyclohexyl-
73	21.6138	0.4928	2-Dodecylcyclohexanone
74	21.8378	0.4416	Butylphosphonic acid, butyl 3-phenylpropyl ester
75	21.9790	0.5768	Silane, trichlorocyclohexyl-
76	22.1786	0.2419	Cyclohexanecarboxylic acid, 3-phenylpropyl ester
77	22.3587	0.4709	Cyclohexanecarboxylic acid, 4-nitrophenyl ester
78	22.5875	0.7656	3-Methyl-2-butenoic acid, 2-methyloct-5-yn-4-yl ester
79	22.8358	0.2559	2-Dimethylamino-2'-methoxyacetophenone
80	22.8894	1.0544	3-Methyl-2-butenoic acid, 2-methyloct-5-yn-4-yl ester
81	23.0208	0.8466	Cyclopentane, 1-ethyl-1-methyl-
82	23.1085	0.3009	3-Methyl-2-butenoic acid, 2,7-dimethyloct-7-en-5-yn-4-yl ester
83	23.1426	0.3489	3-Methyl-2-butenoic acid, 2,7-dimethyloct-7-en-5-yn-4-yl ester
84	23.2010	1.3329	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester
85	23.5028	0.9459	1,5-Heptadien-4-one, 3,3,6-trimethyl-
86	23.5661	2.4215	Anhydro-4,6-dimethyl-3-[p-chlorophenyl]-7-hydroxy-1,2,4-triazolo[1,5a] pyrimidinium-5-one
87	23.8096	0.2017	Hexane, 1-bromo-6-chloro-
88	24.1406	0.3296	1,2-Benzenediol, o-(3-methylbut-2-enoyl)-
89	24.1698	0.3228	1,2-Benzenediol, o-(3-methylbut-2-enoyl)-
90	24.2185	0.2691	3-Methyl-2-butenoic acid, 2-methyloct-5-yn-4-yl ester
91	24.5934	2.3798	9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester
92	24.6567	0.9178	Cyclooctene, 3-ethenyl-
93	24.7736	0.6793	2-Pentene, 4,4-dimethyl-
94	24.8855	0.4922	Lomustine
95	25.0365	0.4575	5-Nitro-2-thienylmethylenecyclohexanecarboxylic hydrazide
96	25.1728	0.2426	1,1-Propanedicarbonitrile, 1,2-dicyclohexyl-
97	25.2994	5.4961	1,1-Propanedicarbonitrile, 1,2-dicyclohexyl-
98	25.3724	0.4097	2-Butyl-.delta.1-pyrroline
99	25.4795	4.9199	3-Methylbut-2-enoic acid, 2,3,4,6-tetrachlorophenyl ester
100	25.5525	0.3324	Squalene
101	25.7181	0.2254	Hexacosane
102	25.7716	0.9295	3-Methyl-2-butenoic acid, cyclobutyl ester
103	25.9469	1.7053	3-Methyl-but-2-enoic acid, 1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl ester
104	26.0881	0.1335	Ethyl 2-(methylamino)-1-phenyl-3-cyclohexene-1-carboxylate
105	27.9966	0.5581	Vitamin E
106	29.4766	0.8805	Stigmasterol
107	30.1924	2.5249	γ-Sitosterol
108	30.7328	0.4060	β-Amyrin
109	31.3608	0.2599	α-Amyrin

5. Mycelial growth inhibition tests

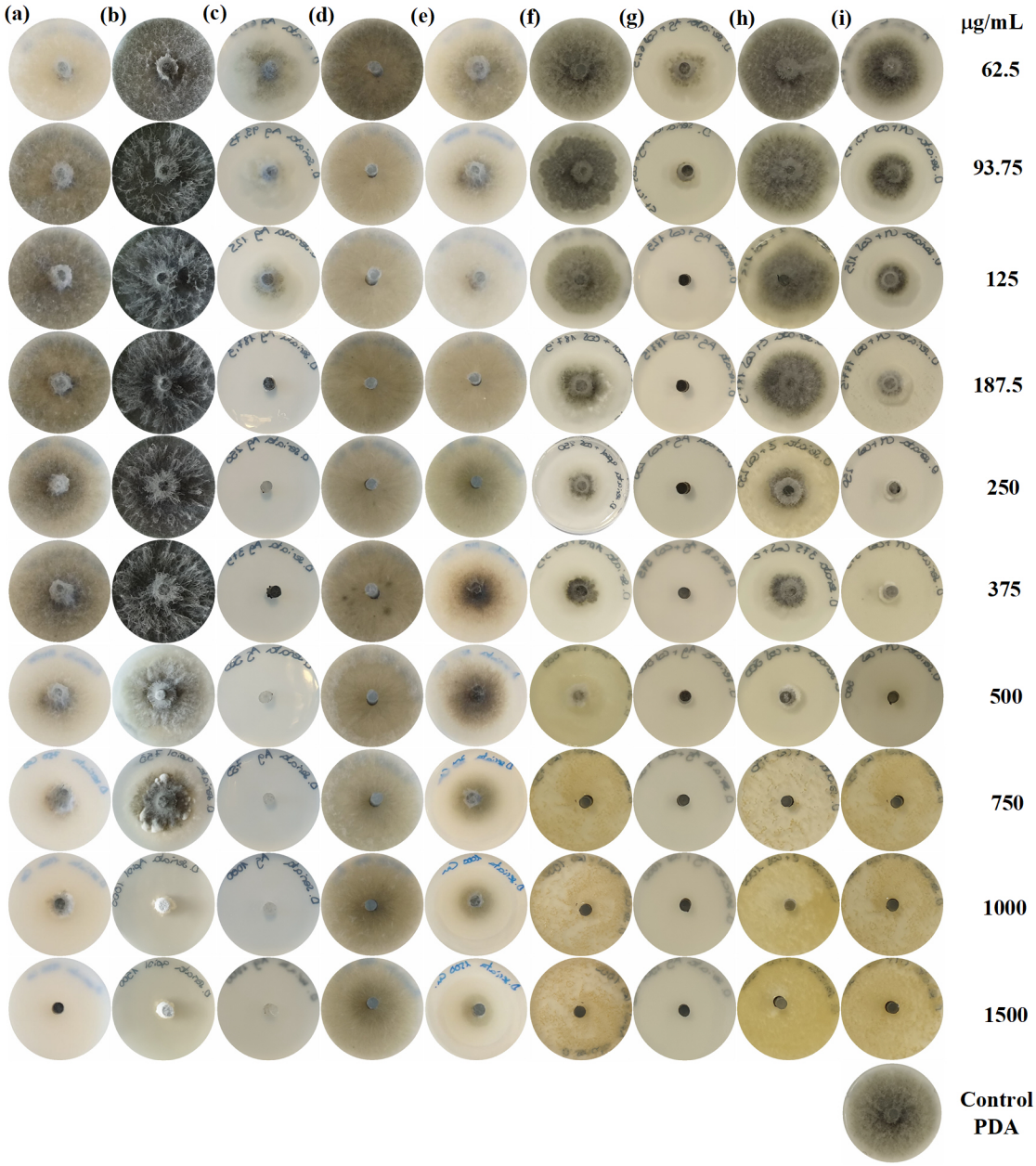

Figure S6. Sensitivity test for *D. seriata*. Radial growth of mycelium for: (**a**) COS, (**b**) apiole, (**c**) geranyl acetate, (**d**) *D. carota* extract, (**e**) *C. maritimum* extract, (**f**) COS–apiole, (**g**) COS-geranyl acetate, (**h**) COS-*D. carota* extract, (**i**) COS-*C. maritimum* extract. From top to bottom: 62.5, 93.75, 125, 187.5, 250, 375, 500, 750, 1000 and 1500 µg·mL^{-1}. Only one replicate is shown.