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SUPPLEMENTARY MATERIAL TO

Co-detection of eugenol and butylated hydroxyltoluene by green and selective hydrodistillation of *Heliotropium europaeum* L. using ionic liquids as additives

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1-Butyl-3-methylimidazolium chloride [C_4mim][Cl]. ^{1}H-NMR (300 MHz, DMSO) δ ppm: 0.75 (t, J = 7.2 Hz, 3H), 1.09-1.16 (m, 2H), 2.02-1.45 (m, 2H), 3.91 (s, 3H), 4.23 (t, J = 6.7 Hz, 2H), 7.98 (s, 1H), 8.09 (s, 1H), 9.84 (s, 1H). ^{13}C NMR (75 MHz, DMSO) δ ppm: 13.6 (CH_3-CH_2), 19.1 (CH_2-CH_3), 31.9 (CH_2-CH_2-CH_3), 36.1 (CH_3-N), 48.7 (CH_2-N), 122.7 ($CHNCH_3$), 123.9 (CH-N-CH_2), 137.2 (NCHN).

1-Butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6]. ^{1}H-NMR (300 MHz, DMSO) δ ppm: 0.90 (t, J = 7.4 Hz, 3H), 1.22-1.34 (m, 2H), 1. 68 -1.87 (m, 2H), 3.85 (s, 3H), 4.16 (t, J = 7.2 Hz, 2H), 7.61 (t, J = 1.7 Hz, 1H), 7.67 (t, J = 1.7 Hz, 1H), 9.00 (s, 1H).^{13}C NMR (75 MHz, DMSO) δ ppm: 13.4 (CH_3-CH_2), 19.2 (CH_2-CH_3), 31.7 (CH_2-CH_2-CH_3), 35.9 (CH_3-N), 49.0 (CH_2-N), 122.5 ($CHNCH_3$), 123.9 (CH-N-CH_2), 136.8 (NCHN).

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Table S-I. Chemical composition of the essential oil of aerial parts of *H. europaeum* by HD and ILs-HD methods

N°	Component[a]	RI[b]	Relative area percentages (%)				
			HD	IL-HD [C_4mim] [Cl]			IL-HD [C_4mim] [PF_6]
				A	B	C	
1	2-Hydroxy-3-hexanone	843	-	-	3.32	0.64	1.71
2	Hex-3(Z)-enol	848	-	-	-	-	0.07
3	3-Hexanol, 2-methyl-	853	-	0.45	6.37	1.60	2.75
4	Guanidine carbonate	868	-	1.31	1.52	3.34	2.82
5	2,5-Dimethyl pyrazine	908	-	-	-	-	0.08
6	Cyclohexanemethanamine, n-propyl-	930	-	-	0.91	-	-
7	3-Pentanol, 2,4-dimethyl-	930	-	-	-	-	0.02
8	butanamine, N-cyclohexylmethyl-1-propyl-	932	-	-	1.23	-	-
9	RS-2,3-hexanediol	942	-	-	-	-	0.07
10	1,3-Cyclohexanediol	942	-	-	1.72	-	-
11	Benzaldehyde	955	-	-	-	-	0.03
12	Borane, diethyl-propylamino	956	-	-	0.96	-	-
13	5-Methyl furfural	958	-	-	-	-	0.04
14	Phenol	977	-	-	-	-	0.08
15	Pyrazine, 2-ethyl-6-methyl-	996	-	-	-	-	0.03
16	Pyrazine, 2-ethyl-5-methyl-	999	-	-	-	-	0.04
17	Pyrazine, trimethyl-	1001	-	-	-	-	0.04
18	1-Hexanol, 2-ethyl-	1026	-	-	-	-	0.03
19	Benzyl alcohol	1030	0.60	1.08	3.08	6.53	0.71
20	Cyclopentyl isothiocyanate	1047	-	-	-	-	0.13
21	2-Buten-1-ol, 3-methyl-, benzoate	1062	-	-	-	-	0.22
22	Phenylethyl Alcohol	1110	0.68	0.61	0.98	-	0.28
23	2-Hexanol, 2,3-dimethyl-	1158	-	-	-	-	0.52
24	L-Valine, N-cyclopropylcarbonyl-, methyl ester	1183	3.15	2.72	1.10	-	-
25	Pyrrolo[1,2-a]pyrazine, octahydro-2-methyl-	1184	-	-	-	-	0.66
26	Benzofuran, 2,3-dihydro (coumaran)	1218	2.13	2.85	-	1.61	0.22
27	4-tert-Butyl-2-methylthiazole	1220	3.31	1.87	1.04	-	0.67
28	Indole	1289	1.35	2.79	1.40	4.01	0.15
29	Thymol	1292	0.78	-	-	-	-
30	Carvacrol	1301	0.56	-	-	-	0.03
31	2-methoxy-4-vinyl-phenol	1310	**9.08**	4.94	1.65	9.46	1.30
32	Lupinine	1318	0.27	-	-	-	-
33	Eugenol	1354	**2.82**	**1.76**	**1.70**	**3.98**	**72.35**
34	2-Heptyl-5-(5-hexenyl)pyrrolidine	1360	0.37	-	-	-	-
35	Isobutyl (1-propoxypropan-2-yl) carbonate	1362	-	0.64	-	2.49	-
36	Caryophyllene	1416	-	-	-	-	1.75

Table S-I. Continued

N°	Component[a]	RI[b]	Relative area percentages (%)				
			HD	IL-HD [C_4mim] [Cl]			IL-HD [C_4mim] [PF_6]
				A	B	C	
37	α-Humulene	1450	-	-	-	-	0.20
38	2,5-Ccyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-methylene-	1471	-	-	-	-	0.04
39	2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	1470	0.57	-	0.93	-	-
40	1-Dodecanol	1471	-	-	-	-	0.07
41	β-Ionone	1483	1.28	-	-	-	0.15
42	1-Dodecanamine, N, N-dimethyl	1504	-	-	-	-	1.34
43	Butylated hydroxytoluene	1512	**57.08**	**39.96**	**65.39**	**59.07**	**8.95**
44	Methanone, dicyclohexyl-	1515	1.03	1.09	-	-	0.09
45	2(4H)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-, (R)-	1521	4.15	5.74	2.49	5.66	0.35
46	Phenol, 2-methoxy-4-(2-propenyl)-, acetate	1526	-	-	-	-	0.04
47	Megastigmatrienone	1574	2.06	-	-	-	0.18
48	Caryophyllene oxide	1578	-	-	-	-	0.07
49	Phthalic acid, ethyl pentadecyl ester	1592	0.33	-	-	-	-
50	Diethyl Phthalat	1592	-	-	-	-	0.04
51	Spiro[3.6]deca-5,7-dien-1-one,5,9,9-trimethyl	1620	-	-	-	-	0.24
52	Methyl dihydrojasmonate	1652	0.64	-	-	-	0.06
53	1-Tetradecanamine, N,N-dimethyl-	1704	-	-	-	-	0.06
54	Octanoic acid, octyl ester	1778	0.53	-	-	-	-
55	2-Pentadecanone, 6,10,14-trimethyl-	1844	0.46	3.28	-	-	-
56	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	1865	2.29	0.88	2.00	1.62	0.27
57	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	1914	1.25	-	-	-	-
58	Dibutyl phthalate	1958	3.22	0.95	2.22	-	0.19
59	n-Hexadecanoic acid	1963	-	-	-	-	0.13
60	Phytol	2105	-	**18.20**	-	-	0.06
61	Oleic Acid	2129	-	-	-	-	0.06
62	Pentatriacontane	2274	-	1.05	-	-	-
63	Diisooctyl adipate	2357	-	6.18	-	-	0.39
64	Hexacosane	2440	-	0.91	-	-	-
65	Octacosane	2737	-	0.74	-	-	0.04
66	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester	3177	-	-	-	-	0.19

[a] Components are listed according to their elution from a HP-5MS column; RI[b]: retention index relative to standard mixture of n-alkanes ; HD: Hydrodistillation; .A: ILs-HD [C4mim] [Cl] 2.5%; B: ILs-HD [C4mim] [Cl] 5%, C: ILs-HD [C4mim] [Cl] 10%.