chemosensors

Supplementary Material

Improved Recognition Accuracy of Myrrh Decoction Pieces by Electronic Nose Technology Using GC-MS Analysis and Sensor Selection

Gailian Zhou [1,2], Ting He [1], Xueting Xie [1], Jianfeng Qin [2,3,4], Wei Wei [2,3,4], Yujing Zhang [5] and Erwei Hao [2,3,4,*]

[1] Faculty of Pharmacy, Guangxi University of Chinese Medicine, Nanning 530200, China; zhougl@gxtcmu.edu.cn (G.Z.); 18897512615@163.com (T.H.); xxt13781186521@163.com (X.X.)
[2] Guangxi Key Laboratory of Efficacy Study on Chinese Materia Medica, Guangxi University of Chinese Medicine, Nanning 530200, China; qinjf@gxtcmu.edu.cn (J.Q.); weiw2017@gxtcmu.edu.cn (W.W.)
[3] Guangxi Collaborative Innovation Center of Research on Functional Ingredients of Agricultural Residues, Guangxi University of Chinese Medicine, Nanning 530200, China
[4] Guangxi Key Laboratory of TCM Formulas Theory and Transformation for Damp Diseases, Guangxi University of Chinese Medicine, Nanning 530200, China
[5] College of Electrical Engineering, Henan University of Technology, Zhengzhou 450001, China; 2021040@haut.edu.cn
* Correspondence: haoew@gxtcmu.edu.cn

Synthesis of WO_3 quantum dots: To prepare the WO_3 quantum dots, a straightforward solvothermal method was employed. Initially, a beaker containing 20 mL of OA, 2.5 mL of OLA, and 0.68 g of WCl_6 was subjected to ultrasonic dissolution and mixing using an ultrasonic-cleaning machine. The resulting solution was then transferred to a Teflon-lined stainless-steel autoclave and allowed to react at a temperature of 180 °C for a duration of 3 h. Once the reaction was complete, the sample was cooled down to room temperature (25 °C) and subsequently dissolved in ethanol and toluene. To ensure purity, the mixture underwent three rounds of centrifugation. Finally, the WO_3 quantum dots were obtained by dispersing the WO_3 mixture in toluene at a concentration of 20 mg/mL.

Synthesis of Fe_2O_3 hollow nanorods: In a glass beaker, 3 mmol of $FeSO_4$ was dissolved in 40 ml of ethylene glycol (EG) under vigorous stirring. Simultaneously, 3 mmol of $H_2C_2O_4$ was dissolved in 20 ml of deionized water with vigorous stirring. The $FeSO_4$ solution was then quickly added to the $H_2C_2O_4$ solution. After stirring vigorously at 25 °C, a red homogeneous mixture was formed. This solution was transferred to an 80 ml Teflon-lined autoclave and heated at 120 °C for 24 h in a furnace. Afterward, it was allowed to cool naturally. The resulting red precipitates of $FeC_2O_4{\cdot}2H_2O$ were collected by centrifugation, washed multiple times with distilled water and ethanol, and dried at 60 °C in an air atmosphere for 2 h. Then, the as-prepared $FeC_2O_4{\cdot}2H_2O$ powder (1 g) was dispersed in a NaOH solution (3 M) and stirred at 20 °C for 0.5 h. The powder sample was then collected by centrifugation, washed with ethanol several times, and dried at 60 °C in an air atmosphere for 12 h. The $Fe(OH)_3$ nanorods obtained previously were placed in a tube furnace, which was gradually heated to 400 °C with a ramping rate of 10 °C per minute. The temperature was maintained at 400 °C for 0.5 h in an air atmosphere. Finally, a brownish-red powder of hollowed-out hierarchical α-Fe_2O_3 nanorods was obtained.

Synthesis of $ZnFe_2O_4$ nanorods: To synthesize $ZnFe_2O_4$, the precursor $ZnFe_2(C_2O_4)_3$ was prepared. Initially, a vigorously stirred solution was prepared by combining 15 ml of deionized water with 0.288 g of $ZnSO_4{\cdot}7H_2O$ and 0.556 g of $FeSO_4{\cdot}7H_2O$. Subsequently, 45 ml of ethylene glycol (EG) containing 3 mmol of $H_2C_2O_4$ was added to the water solution. After vigorous stirring for 10 min, a yellow homogeneous mixture solution was formed. This mixture was then transferred into an 80 ml Teflon-lined autoclave and maintained at 120 °C for 24 h. Afterward, it was allowed to cool down to room temperature naturally. Yellow precipitates of $ZnFe_2(C_2O_4)_3$ were collected by centrifugation. The resulting product was washed several times with distilled water and ethanol, followed by drying at 60

Citation: Zhou, G.; He, T.; Xie, X.; Qin, J.; Wei, W.; Zhang, Y.; Hao, E. Improved Recognition Accuracy of Myrrh Decoction Pieces by Electronic Nose Technology Using GC-MS Analysis and Sensor Selection. *Chemosensors* **2023**, *11*, 396. https://doi.org/10.3390/chemosensors11070396

Academic Editor: Simonetta Capone

Received: 16 June 2023
Revised: 9 July 2023
Accepted: 10 July 2023
Published: 14 July 2023

°C under vacuum conditions for 2 h. The obtained $ZnFe_2(C_2O_4)_3$ precursor was further converted into $ZnFe_2O_4$ by heat treatment at 350 °C (with a ramping rate of 10 °C per minute) for 0.5 h in an air atmosphere to eliminate organic matter.

Synthesis of SnO_2 nanowires: Colloidal SnO_2 nanowires were synthesized using a previously reported one-step method. Initially, 0.6 g of $SnCl_4 \cdot 5H_2O$ was added to a beaker containing 20 mL of OA and 2.5 mL of OLA. The precursor solution was stirred with ultrasonication until it became clear and transparent. Next, 10 mL of anhydrous ethanol was added, and stirring continued until the solution became clear and transparent at room temperature. The precursor solution was then transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 6 h, respectively. Subsequently, it was cooled to room temperature in a cold-water bath. The resulting solution was dissolved in an appropriate amount of absolute ethanol and subjected to centrifugation at 8000 rpm for 8 min. The precipitate was washed twice with toluene and ethanol through repeated centrifugation. Finally, the product was well-dispersed in toluene at a concentration of 20 mg/mL.

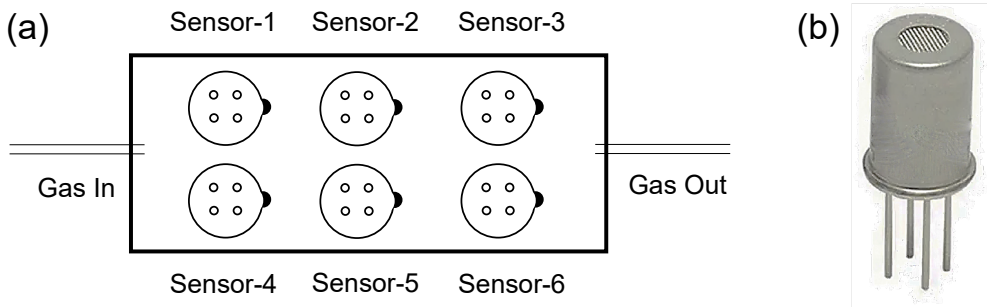

Figure S1. (**a**) The schematic of the sensor array consisting of six sensors. (**b**) Schematic diagram of gas sensor.

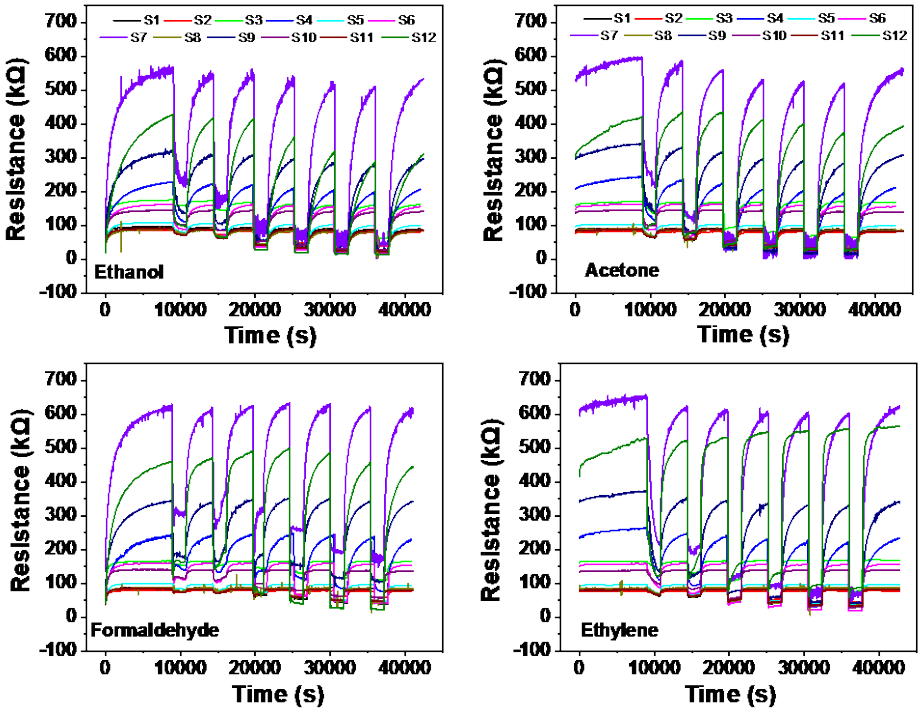

Figure S2. Dynamic response curves of 12 sensors to four target gases with concentrations of 0.5, 1, 5, 10, and 20 ppm respectively: (**a**) ethanol, (**b**) acetone (**c**) formaldehyde, and (**d**) ethylene.

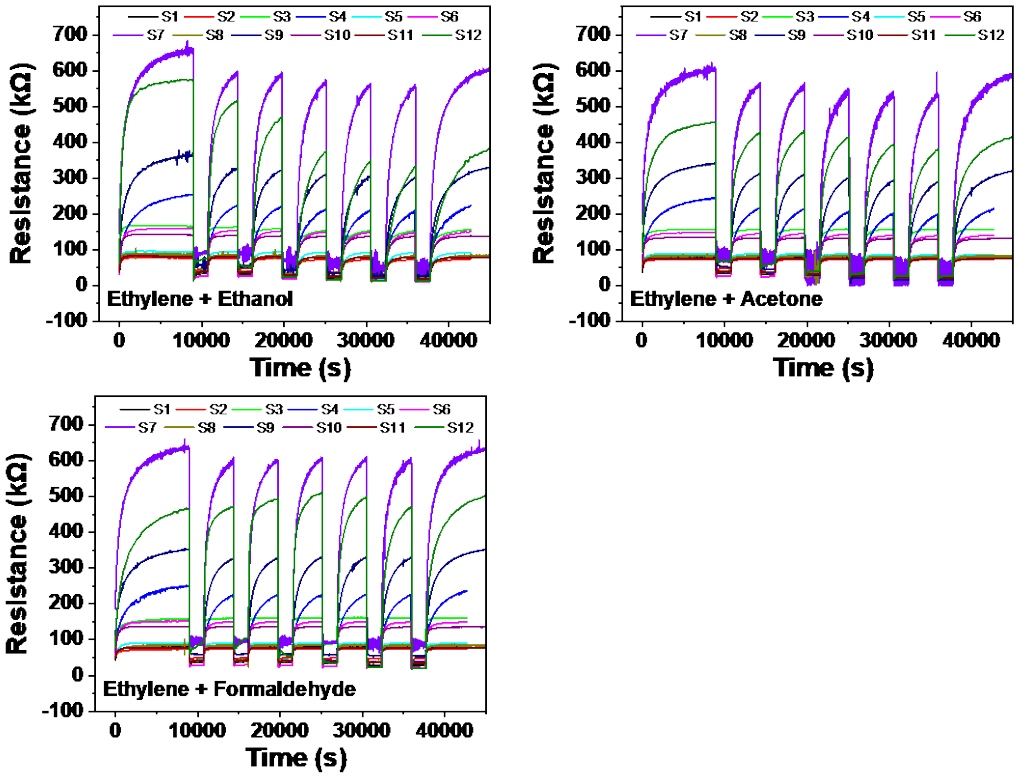

Figure S3. Dynamic response curves of 12 sensors to three types of mixed gases for six cycles: (**a**) 10 ppm ethylene and 10 ppm ethanol, (**b**) 10 ppm ethylene and 10 ppm acetone, and (**c**) 10 ppm ethylene and 10 ppm formaldehyde.

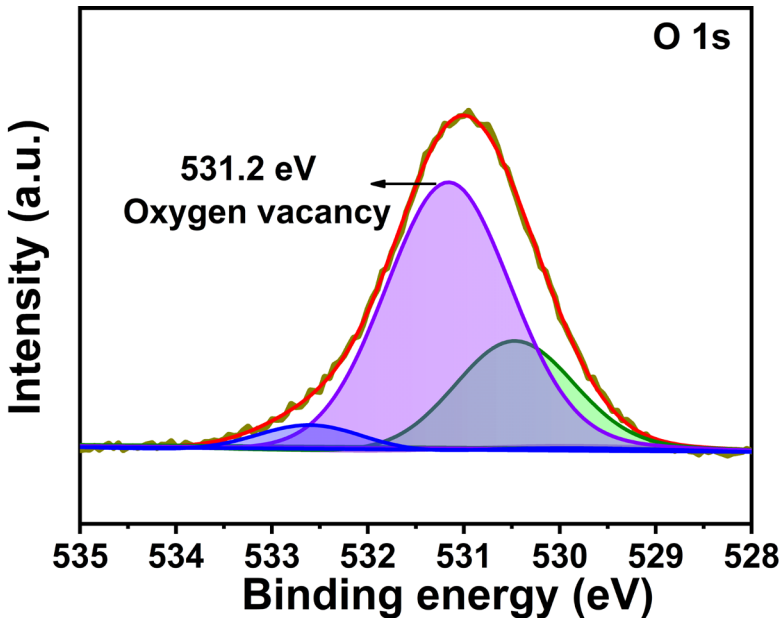

Figure S4. XPS spectra of O 1s and fitted data of SnO_2 nanowires.

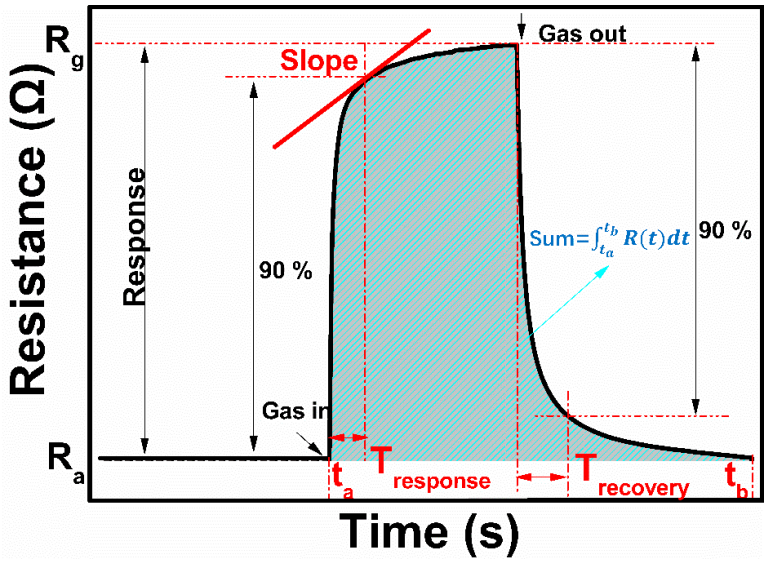

Figure S5. Schematic diagram of sensor parameters, including response, response and recovery time, integral area, and slope.

Table S1. Six myrrh components tested by GC–MS.

No.	Composition	S1	S2	S3	S4	S5	S6
1	1-Propanamine, 3-chloro-	-	0.61	-	-	-	-
2	Benzeneethanamine	-	0.48	-	-	-	-
3	2-(2-Methoxyphenyl)ethylamine	-	1.07	-	-	-	-
4	1,11-Undecanediamine	-	0.63	-	-	-	-
5	3,5-Dimethoxyphenethylamine	-	1.06	-	-	-	-
6	Phenylethanolamine	-	0.31	-	-	-	-
7	4-Acetyl-1-methylcyclohexene	0.21	-	-	-	-	-
8	(4aS,8aR)-3,8a-Dimethyl-5-methylene-4,4a,5,6,7,8,8a,9-octahydronaphtho[2,3-b]furan	1.5	-	-	-	-	-
9	3,7-Cyclodecadien-1-one, 3,7-dimethyl-10-(1-methylethylidene)-, (E,E)-	0.22	-	0.39	-	-	-
10	Cyclohexanemethanol, 4-ethenyl-.alpha.,.alpha.,4-trimethyl-3-(1-methylethenyl)-, [1R-(1.alpha.,3.alpha.,4.beta.)]-	0.38	-	-	-	-	-
11	Cyclohexanol, 3-(aminomethyl)-3,5,5-trimethyl-	-	0.47	-	-	-	-
12	3-Buten-2-ol, 2-methyl-	-	-	-	0.27	-	-
13	Junenol	-	-	0.86	-	-	-
14	3-Methylbenzyl alcohol	-	-	-	-	0.08	-
15	Cyclopropanemethanol, .alpha.-butyl-	-	-	-	-	-	0.04
16	Toluene	0.08	-	-	-	-	-
17	p-Cymene	0.42	-	-	-	-	-
18	4,7-Methanobenzofuran, 2,2'-oxybis[octahydro-7,8,8-trimethyl-, [2.alpha.(2'R*,3'aS*,4'R*,7'R*,7'aS*),3a.alpha.,4.alpha.,7.alpha.,7a.alpha.]-	0.17	-	-	-	-	-
19	(1R,4aS,8aR)-1-Isopropyl-4,7-dimethyl-1,2,4a,5,6,8a-hexahydronaphthalene	0.14	-	-	-	-	-
20	Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,(1S-cis)-	1.79	3.95	3.96	-	-	0.49
21	Benzene, 1-ethyl-2,3-dimethyl-	-	0.5	-	-	-	-
22	Naphthalene, 1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethyl-2-(1-methylethenyl)-, [2R-(2.alpha.,4a.alpha.,8a.beta.)]-	-	13.23	3.9	-	2.59	-
23	o-Cymene	-	-	0.21	0.27	0.51	0.37
24	(4R,4aS,6S)-4,4a-Dimethyl-6-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene	-	-	1.46	-	-	-
25	1H-Cyclopropa[a]naphthalene, 1a,2,3,3a,4,5,6,7b-octahydro-	-	-	-	1.22	2.42	-

26	1,1,3a,7-tetramethyl-, [1aR-(1a.alpha.,3a.alpha.,7b.alpha.)]-Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, [1S-(1.alpha.,4a.beta.,8a.alpha.)]-	-	-	-	1.53	-	-
27	(4aS,8aS)-3,8a-Dimethyl-5-methylene-4,4a,5,6,8a,9-hexahydronaphtho[2,3-b]furan	-	-	-	1.18	-	-
28	Benzofuran, 6-ethenyl-4,5,6,7-tetrahydro-3,6-dimethyl-5-isopropenyl-, trans-	27.94	-	-	-	-	-
29	Benzene, 1-methoxy-2-methyl-	0.12	-	-	-	-	-
30	Propanal, 2-methyl-	-	-	-	0.38	-	0.02
31	Methacrolein	-	-	-	0.46	-	-
32	Butanal, 3-methyl-	-	-	-	0.23	-	0.02
33	Acetaldehyde	-	-	-	-	-	2.34
34	2-Dodecen-4-yne, (E)-	-	-	-	-	-	0.03
35	Epicurzerenone	-	3.24	1.41	0.74	0.39	
36	Bicyclo[3.1.0]hex-2-ene, 2-methyl-5-(1-methylethyl)-	-	-	1.42	0.27	15.52	24.41
37	2-Methyl-1,5-(4H)-dihydropyrido-(2,3-b)1,4-diazepine-4-one	-	0.83	-	-	-	-
38	trans-.alpha.-Bergamotene	5.47	2.32	-	-	-	-
39	3,7-Cyclodecadien-1-one, 10-(1-methylethenyl)-, (E,E)-	-	-	-	-	0.1	-
40	Acetone	-	-	-	4.93	-	0.78
41	2-Pentanone	-	-	-	0.17	-	0.03
42	1,5,5-Trimethyl-6-methylene-cyclohexene	-	-	1.41	-	-	0.76
43	(5R,6R)-3,6-Dimethyl-5-(prop-1-en-2-yl)-6-vinyl-6,7-dihydrobenzofuran-4(5H)-one	-	-	-	-	-	0.14
44	2-(6-Fluoro-4-oxo-1,4-dihydroquinolin-1-yl)acetonitrile	-	1.36	-	-	-	-
45	Tricyclo[4.1.0.0(2,4)]heptane, 3,3,7,7-tetramethyl-5-(2-methyl-1-propenyl)-	-	-	-	-	0.2	-
46	Longipinane, (E)-	-	-	-	-	0.16	-
47	3,5,8a-trimethyl-4,4a,8a,9-tetrahydronaphtho[2,3-b]furan	-	-	-	5.27	0.3	0.07
48	Ethylene oxide	-	-	-	15.38	-	-
49	Tricyclo[2.2.1.0(2,6)]heptane, 1,7-dimethyl-7-(4-methyl-3-pentenyl)-, (-)-	-	-	-	0.42	-	-
50	Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-	-	-	-	0.86	-	-
51	5,5-Dimethyl-1-vinylbicyclo[2.1.1]hexane	-	-	-	-	-	0.10

52	(1R,2S,6S,7S,8S)-8-Isopropyl-1-methyl-3-methylenetricyclo[4.4.0.02,7]decane-rel-		1.54	-	-	9.28	7.27
53	Cyclohexene, 1-methyl-	0.09	-	-	-	-	-
54	(1S)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	1.56	-	-	-	12.52	-
55	.beta.-Pinene	0.34	-	-	-	0.82	1.01
56	.alpha.-Phellandrene	0.39	-	-	-	0.18	0.29
57	D-Limonene	0.28	-	0.44	2.02	1.03	2.05
58	Cyclohexene, 4-ethenyl-4-methyl-3-(1-methylethenyl)-1-(1-methylethyl)-, (3R-trans)-	1.38	9.81	10.01	2.94	3.88	2.02
59	.alpha.-Cubebene	2.43	-	1.28	-	0.33	-
60	Copaene	0.13	-	-	0.13	-	-
61	(-)-.beta.-Bourbonene	14.25	7.52	4	4.09	4.62	4.39
62	Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1.alpha.,2.beta.,4.beta.)]-	9.3	8.11	8.67	5.18	3.57	-
63	.beta.-copaene	1.85	-	1.7	1.83	-	-
64	trans-.alpha.-Bergamotene	7.67	-	-	-	-	-
65	(S,1Z,6Z)-8-Isopropyl-1-methyl-5-methylenecyclodeca-1,6-diene	1.74	-	-	1.09	0.71	0.81
66	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-	0.64	1.79	2.17	-	0.91	-
67	1,2,4-Metheno-1H-indene, octahydro-1,7a-dimethyl-5-(1-methylethyl)-,[1S-(1.alpha.,2.alpha.,3a.beta.,4.alpha.,5.alpha.,7a.beta.,8S*)]-	0.29	-	-	-	0.17	-
68	Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	2.11	1.71	1.21	-	-	-
69	Germacrene D	9.82	7.11	-	-	-	0.19
70	Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]	1.85	-	6.09	-	-	-
71	.beta.-Bisabolene	1.31	-	-	-	-	-
72	1-Isopropyl-4,7-dimethyl-1,2,3,5,6,8a-hexahydronaphthalene	0.32	-	-	-	1.23	-
73	1,4-Methano-1H-indene, octahydro-4-methyl-8-methylene-7-(1-methylethyl)-, [1S-(1.alpha.,3a.beta.,4.alpha.,7.alpha.,7a.beta.)]-	0.49	-	-	-	-	-
74	Selina-3,7(11)-diene	0.38	-	-	-	-	-
75	1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-, (E,E)-	1.2	-	3.64	-	1.26	-

76	(1R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	-	5.82	1.89	0.13		23.75
77	Bicyclo[3.1.1]heptane, 6,6-dimethyl-2-methylene-, (1S)-	-	0.73	-	-	-	-
78	.alfa.-Copaene	-	6.46	11.34	4.83	6.75	0.83
79	.beta.-ylangene	-	3.02	-	1.09	0.88	1.47
80	Bicyclo[3.1.1]hept-3-ene-spiro-2,4'-(1',3'-dioxane), 7,7-dimethyl-	-	2.42	-	-	-	-
81	.gamma.-Muurolene	-	4.89	3.07	-	-	-
82	7-epi-Silphiperfol-5-ene	-	2.11	-	-	-	-
83	Camphene	-	-	0.62	0.17	0.29	
84	3-Carene	-	-	1.61	1.55	1.63	
85	.alfa.-Copaene	-	-	11.42	3.83	8.75	0.83
86	1H-Cycloprop[e]azulene, 1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-tetramethyl-, [1aR-(1a.alpha.,4.alpha.,4a.beta.,7b.alpha.)]-	-	-	5.43	-	3.79	1.03
87	Caryophyllene	-	-	3.61	1.07	1.01	-
88	(1S,2E,6E,10R)-3,7,11,11-Tetramethylbicyclo[8.1.0]undeca-2,6-diene	-	-	0.53	-	-	-
89	isoledene	-	-	1.29	-	-	-
90	(1R,9R,E)-4,11,11-Trimethyl-8-methylenebicyclo[7.2.0]undec-4-ene	-	-	1.48	-	0.77	-
91	Naphthalene, 1,2,3,5,6,7,8,8a-octahydro-1,8a-dimethyl-7-(1-methylethenyl)-, [1R-(1.alpha.,7.beta.,8a.alpha.)]-	-	-	0.63	-	-	-
92	1H-Cycloprop[e]azulene, 1a,2,3,5,6,7,7a,7b-octahydro-1,1,4,7-tetramethyl-, [1aR-(1a.alpha.,7.alpha.,7a.beta.,7b.alpha.)]-	-	-	2.25	-	-	-
93	(-)-.alpha.-Panasinsen	-	-	0.27	-	-	0.04
94	Bicyclo[3.1.0]hexane, 4-methylene-1-(1-methylethyl)-	-	-	-	-	5.31	8.44
95	.beta.-Pinene	-	-	-	-	0.82	1.01
96	.beta.-Myrcene	-	-	-	-	0.99	2.72
97	1,3-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	-	-	-	-	0.09	5.19
98	trans-.beta.-Ocimene	-	-	-	-	0.27	0.49
99	.beta.-Ocimene	-	-	-	0.30	0.55	1.39
100	Cyclohexene, 4-methylene-1-(1-methylethyl)-	-	-	-	-	0.15	-
101	Tricyclo[5.4.0.0(2,8)]undec-9-ene,2,6,6,9-tetramethyl-, (1R,2S,7R,8R)-	-	-	-	-	0.36	-
102	Bicyclogermacrene	-	-	-	-	0.23	-
103	1H-Cyclopropa[a]naphthalene, 1a,2,3,5,6,7,7a,7b-octahydro-1,1,7,7a-tetramethyl-, [1aR-	-	-	-	2.84	2.75	0.29

104	(1a.alpha.,7.alpha.,7a.alpha.,7b.alpha.)]-4,5-di-epi-aristolochene	-	-	-		0.23	
105	Cyclohexene, 6-ethenyl-6-methyl-1-(1-methylethyl)-3-(1-methylethylidene)-, (S)-	-	-	-	0.82	0.83	
106	Bicyclo[4.4.0]dec-1-ene, 2-isopropyl-5-methyl-9-methylene-	-	-	-	-	0.48	0.65
107	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	-	-	-	0.36	-	0.76
108	Caryophyllene	-	-	-	1.07	-	-
109	Spiro[5.5]undeca-1,8-diene, 1,5,5,9-tetramethyl-, (R)-	-	-	-	0.27	-	-
110	Humulene	-	-	-	1.26	-	-
111	1H-Cyclopenta[1,3]cyclopropa[1,2]benzene, octahydro-7-methyl-3-methylene-4-(1-methylethyl)-, [3aS-(3a.alpha.,3b.beta.,4.beta.,7.alpha.,7aS*)]-	-	-	-	18.76	-	-
112	Aromandendrene	-	-	-	3.69	-	-
113	Azulene, 1,2,3,5,6,7,8,8a-octahydro-1,4-dimethyl-7-(1-methylethenyl)-, [1S-(1.alpha.,7.alpha.,8a.beta.)]-	-	-	-	1.87	-	-
114	2,6,10,10-Tetramethylbicyclo[7.2.0]undeca-2,6-diene	-	-	-	3.57	-	-
115	(+)-3-Carene	-	-	-	-	-	1.55
116	(+)-4-Carene	-	-	-	-	-	0.11
117	.gamma.-Terpinene	-	-	-	-	-	0.23
118	Di-epi-.alpha.-cedrene	-	-	-	-	-	0.03
119	.alpha.-Bourbonene	-	-	-	-	-	0.68
120	Cyclohexene, 1,5,5-trimethyl-3-methylene-	-	-	-	-	-	0.19
121	Naphthalene, 1,2,3,4,4a,5,6,8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-, (1.alpha.,4a.beta.,8a.alpha.)-	0.98	-	-	-	-	-
122	(1R,9R,E)-4,11,11-Trimethyl-8-methylenec'c'c'cbicyclo[7.2.0]undec-4-ene	-	-	-	-	-	0.51
123	3,6,8-Nonatrienoic acid, 5-methyl-, ethyl ester	0.71	-	-	-	-	-
124	Diethyl chloromalonate	-	2.13	-	-	-	-
125	Propanedioic acid, (hydroxyimino)-, diethyl ester	-	3.48	-	-	-	-
126	Propanoic acid, 2,3-dibromo-, ethyl ester	-	1.27	-	-	-	-
127	Benzylcarbamate	-	-	0.28	-	-	-
128	Succinic acid, di(2,4-dichlorobenzyl) ester	-	-	-	-	0.23	-

129	Acetic acid, methyl ester	-	-	-	1.47	-	0.15
130	Androsta-1,4-dien-3-one, 17-hydroxy-17-methyl-, (17.alpha.)-	-	-	-	0.15	-	-