Fragrant Sesquiterpene Ketones as Trace Constituents from Frankincense Volatile Oil of *Boswellia sacra*

Supporting Information

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1 GC-MS Characterization of the Volatile Oils:

Table S1: Constituents in *Boswellia sacra* Flueck. volatile oil, from Somalia, obtained by hydrodistillation of gum resin material; Primavera Life GmbH, Oy-Mittelberg, Germany.

Nr.	*Compound*	*RI lit.*	*Reference*	*RI exp.*	*RPA*
1	Toluene	< 800			0.09%
2	Hashishene (5,5-Dimethyl-1-vinylbicyclo[2.1.1]hexane)	924			0.30%
3	Tricyclene	921	*1*	923	0.09%
4	α-Thujene	924	*1*	930	1.54%
5	α-Pinene	942	*2*	937	20.23%
6	Camphene	946	*1*	951	1.45%
7	Thuja-2,4(10)-diene	953	*1*	954	0.07%
8	Sabinene	969	*1*	974	4.27%
9	β-Pinene	974	*1*	979	1.67%
10	β-Myrcene	988	*1*	990	1.95%
11	δ-3-Carene	1008	*1*	1009	0.48%
12	p-Cymene	1020	*1*	1026	6.57%
13	Limonene	1024	*1*	1031	10.10%
14	Eucalyptole (1,8-Cineol)	1026	*1*	1034	0.35%
15	Oxygenated Monoterpene	1049	*2*	1050	0.03%
16	cis-Sabinene hydrate	1065	*1*	1071	0.10%
17	Oxygenated Monoterpene	-		1087	0.20%
18	Perillene	1102	*1*	1097	0.20%
19	α-Pinene oxide	1099	*1*	1100	1.17%
20	trans-Sabinene hydrate	1098	*1*	1101	0.07%
21	Isoamyl isovalerat (3-methylbutyl 3-methylbutanoat)	1100	*1*	1106	0.09%
22	Oxygenated Monoterpene	1108	*2*	1111	1.48%
23	trans-Thujone (β-Thujone)	1112	*1*	1119	0.12%
24	trans-p-Mentha-2,8-dienol	1119	*1*	1122	0.15%
25	α-Campholenal	1122	*1*	1128	0.86%
26	cis-Limomene epoxide	1132	*1*	1133	0.49%
27	trans-Limonene epoxide	1137	*1*	1137	0.48%
28	trans-Pinocarveol	1135	*1*	1142	1.16%
29	trans-Verbenol	1137	*1*	1147	2.03%
30	trans-Pinocamphone	1158	*1*	1161	0.21%
31	Pinocarvone (2(10)-Pinen-3-one)	1160	*1*	1163	0.27%
32	cis-Sabinol	1170	*2*	1170	0.07%
33	4-Terpineol	1182	*2*	1182	0.32%
34	p-Methylacetophenone	1186	*2*	1186	0.04%
35	p-Cymen-8-ol	1187	*2*	1188	0.64%
36	α-Terpineol	1193	*2*	1196	0.95%
37	Myrtenol	1198	*2*	1195	0.25%
38	Verbenone	1204	*1*	1208	1.80%
39	trans-Carveol	1215	*1*	1220	0.86%
40	cis-Carveol	1230	*2*	1234	0.10%
41	Carvone	1239	*1*	1245	0.81%
42	3,5-Dimethoxytoluene	1264	*2*	1265	0.35%
43	Bornyl acetate	1285	*1*	1285	0.96%
44	α-Cubebene	1348	*1*	1347	0.40%
45	α-Ylangene	1373	*1*	1370	0.18%
46	α-Copaene	1383	*2*	1376	1.53%
47	β-Bourbonene	1387	*1*	1385	0.40%
48	β-Elemene	1393	*2*	1390	2.36%
49	β-Caryophyllene	1426	*2*	1422	0.15%
50	(*Z*)-α-trans-Bergamotene	1432	*1*	1432	0.30%
51	α-Guiaene	1437	*1*	1438	0.07%
52	Aromadendrene	1439	*1*	1446	0.04%

53	α-Humulene	1452	*1*	1458	0.10%
54	allo-Aromadendrene	1458	*1*	1462	0.33%
55	γ-Muurolene	1478	*1*	1475	0.66%
56	β-Eudesmene	1483	*2*	1491	1.06%
57	4-epi-Cubebol	1493	*1*	1494	1.09%
58	γ-Cadinene	1513	*1*	1514	0.93%
59	Cubebol	1514	*1*	1518	1.09%
60	trans-Calamenene	1521	*1*	1522	0.30%
61	Elemol	1548	*1*	1549	0.11%
62	Oxygenated sesquiterpene	-		1553	0.40%
63	Spatulenol	1577	*1*	1579	0.22%
64	Caryophyllene oxide	1582	*1*	1585	6.24%
65	Viridiflorol	1592	*1*	1596	0.58%
66	Humulene epoxide II	1608	*1*	1612	1.46%
67	1,10-diepi-Cubenol	1618	*1*	1616	0.32%
68	τ-Cadinol (epi-α-Cadinol)	1638	*1*	1644	0.84%
69	δ-Cadinol (α-Muurolol)	1644	*1*	1648	0.11%
70	Dimer of phellandrene	1795	*2*	1795	0.19%
71	Cembrene A	1965	*1*	1955	0.13%
72	Unidentified diterpene 5	2141	*2*	2138	0.04%
73	Incensole + Serratol (coelution)	2152	*2*	2151	0.43%
				Sum:	**87.53%**

Retention indices (RI) measured on a DB-5 column, exp.: experimental values, lit.: values from literature sources, Ref.: reference number, RPA: relative peak area

References for retention indices (table S1):

(1) Adams, R. P. *Identification of Essential Oil Components by Gas Chromatography / Mass Spectrometry, 4th Edition*; Allured Business Media: Carol Stream, IL, 2012.

(2) Hamm, S.; Bleton, J.; Connan, J.; Tchapla, A. *Phytochemistry* **2005**, 66, 12, 1499-1514.

Figure S1: GC-MS total ion chromatogram (DB-5 column) of *Boswellia sacra* volatile oil used in this study. Peak labels refer to table S1.

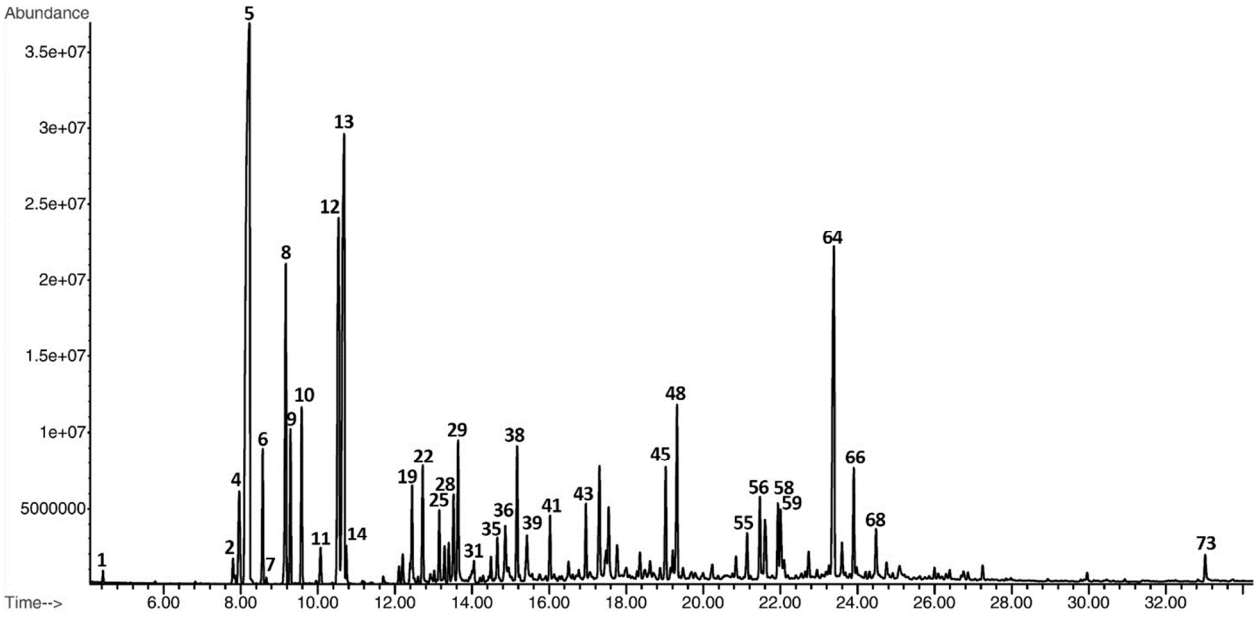


Table S2: Constituents in *Cyperus scariosus* R.Br. volatile oil, obtained by distillation of rhizomes, Northern India; Essence Pur Ltd., Utting am Ammersee, Germany.

Nr.	Compound	RI lit.	Ref.	RI exp.	RPA
1	α-Pinene	942	1	932	0.31%
2	β-Pinene	974	1	978	0.48%
3	trans-Pinocarveol	1135	1	1143	0.25%
4	Myrtenal	1195	1	1197	0.30%
5	α-Cubebene	1348	1	1348	0.10%
6	Unidentified Compound			1367	1.90%
7	Cyclosativene	1371	1	1372	0.08%
8	α-Copaene	1374	1	1379	4.37%
9	cis-β-Elemene	1389	1	1392	0.23%
10	Cyperene	1398	1	1410	14.21%
11	β-Caryophyllene	1417	1	1423	0.11%
12	Norrotundene			1434	0.21%
13	Cypera-2,4(15)-diene	1443	2	1441	0.23%
14	Spirolepechinene	1449	1	1450	0.31%
15	Rotundene	1457	1	1467	6.14%
16	γ-Gurjunene + Unident. Comp.	1475	1	1476	2.13%
17	Aristolochene	1487	1	1487	0.16%
18	β-Selinene	1489	1	1493	2.50%
19	Valencene	1496	1	1495	0.75%
20	α-Selinene + α-Muurolene + Unidentified compound	1498/1500	1	1500	1.23%
21	Isorotundene (?)			1509	0.94%
22	δ-Amorphene	1511	1	1520	0.93%
23	trans-Calamenene	1521	1	1524	0.94%
24	Unidentified Compound			1541	1.97%
25	α-Calacorene	1544	1	1544	1.01%
26	Caryophyllene oxide	1582	1	1587	3.53%
27	β-Oplopenone	1607	1	1607	0.97%
28	Humulene epoxide II	1608	1	1615	1.56%
29	Unidentified Compound			1622	1.94%
30	Aristol-9-en-8-one			1628	3.88%
31	Unidentified Compound			1649	2.06%
32	Unidentified Compound			1658	1.15%
33	Unidentified Compound			1663	1.04%
34	Unidentified Compound			1666	1.93%
35	Mustakone	1676	1	1680	4.64%
36	Cyperotundone	1695	1	1705	7.64%
37	Unidentified Compound			1709	1.71%
38	Unidentified Compound			1714	1.03%
39	α-Cyperone	1752	3	1750	3.09%
40	Nootkatone	1806	1	1808	0.33%
41	Cyperadione	1845	2	1833	0.10%
42	Di-isooctyl-phthalate (plasticizer contaminant)	2540	4	2535	5.23%
				Sum:	**83.62%**

(?) denominates tentative identifications

Retention indices (RI) measured on a DB-5 column, exp.: experimental values, lit.: values from literature sources, Ref.: reference number, RPA: relative peak area

References for retention indices (table S2):

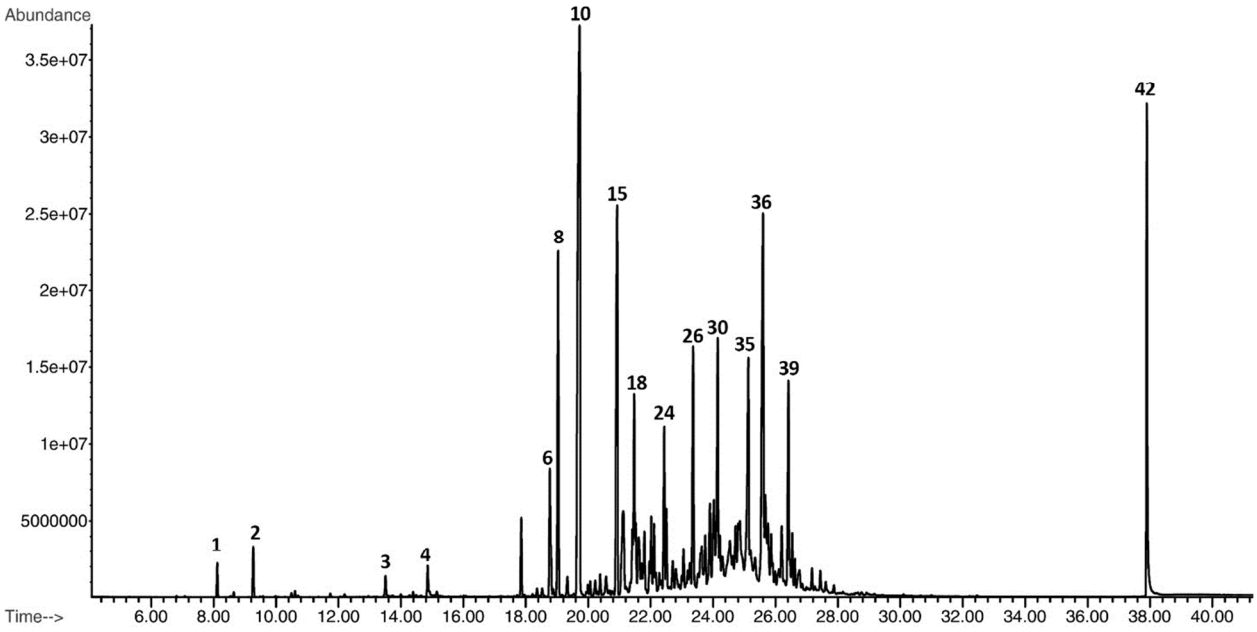
(1) Adams, R. P. *Identification of Essential Oil Components by Gas Chromatography / Mass Spectrometry, 4th Edition*; Allured Business Media: Carol Stream, IL, 2012.

(2) Andriamaharavo, N. R. *Retention Data.* NIST Mass Spectrometry Data Center, 2014.

(3) Morteza-Semnani, K.; Saeedi, M. *Flavour Fragr. J.* **2005**, 20, 3, 332-334.

(4) Kotowska, U.; Zalikowski, M.; Isidorov, V.A. *Environ. Monit. Asses.* **2012**, 184, 5, 2893-2907.

Figure S2: GC-MS total ion chromatogram of *Cyperus scariosus* volatile oil used in this study. Numbers refer to compounds from table S2.



2 Analytical Data for the Isolated Reference Substance Mustakone (**2**):

Mustakone (**2**): colorless oil, strong woody-spicy odor

^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.75 (q, J=1.5, 1 H, H-3), 2.70 (dd, J=6.6, 1.7 Hz, 1 H, H-1), 2.68 (s, 1 H, H-6), 2.02 (d, J=1.5 Hz, 3 H, H-14), 1.99 (dd, J=6.8, 1.5 Hz, 1 H, H-5), 1.87 - 1.92 (m, 1 H, H-9), 1.70 - 1.80 (m, 3 H, H-7, H-8, H-9), 1.49 - 1.57 (m, 2 H, H-8, H-11), 0.99 (s, 3 H, H-15), 0.87 (d, J=6.8 Hz, 3 H, H-12), 0.86 (d, J=6.8 Hz, 3 H, H-13);

^{13}C NMR ($CDCl_3$, 90 MHz): δ 204.0 (C=O, C-2), 169.9 (C, C-4), 121.4 (CH, C-3), 57.3 (C, C-10), 56.6 (CH, C-1), 56.0 (CH, C-5), 54.5 (CH, C-6), 45.4 (CH, C-4), 36.7 (CH_2, C-9), 31.8 (CH, C-11), 23.6 (CH_3, C-15), 22.0 (CH_2, C-8), 20.3 (CH_3, C-14), 19.9 (CH_3, C-13), 19.5 (CH_3, C-12);

NMR data in agreement with previous reports by Nyasse et al. [1]

EI-MS: *m/z* 218 $[M]^+$ (13), 175 (86), 161 (37), 148 (52), 147 (100), 135 (38), 133 (57), 122 (67), 119 (38), 105 (66), 91 (53)

HR-MS (ESI-qToF): *m/z* $[M+H]^+$ 219.1757 (calculated for $C_{15}H_{23}O^+$ 219.1743)

Retention indices (n-alkanes C_6-C_{26}): 1658 (DB-1), 1685 (DB-5), 2260 (DB-WAX), 2255 (DB-FFAP)

R_f (silica gel, petroleum ether/diethyl ether 80:20): 0.26

Reference:

(1) Nyasse, B.; Ghogomu, R.; Sondengam, T. B. L.; Martin, M. T.; Bodo, B. *Phytochemistry* **1988**, 27, 10, 3319-3321.

Figure S3: ^{1}H NMR spectrum for mustakone (**2**). Impurities are marked, namely peaks for cyperotundone, acetonitrile (HPLC separation) and dichloromethane.

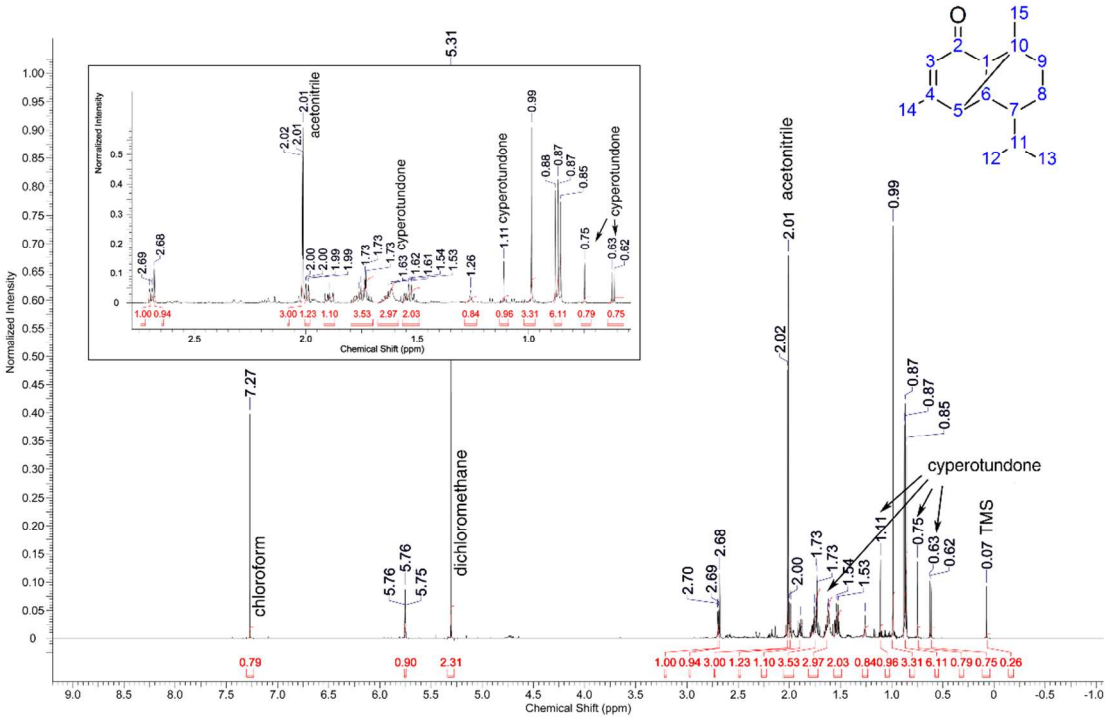


Figure S4: ^{13}C NMR spectrum for mustakone (**2**). Smaller peaks can mostly be attributed to the main impurity cyperotundone.

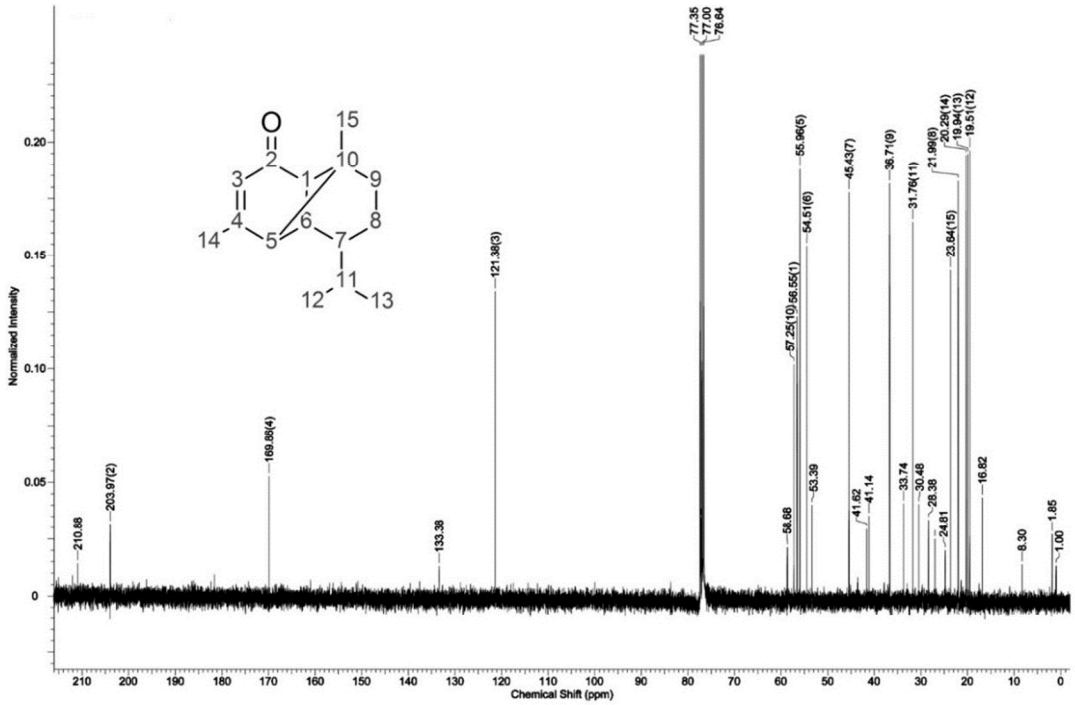


Figure S5: GC-MS total ion chromatogram of the reference substance mustakone (**2**). The second, closely eluting peak is the impurity of cyperotundone. The two substances could not be separated by preparative HPLC or column chromatography.

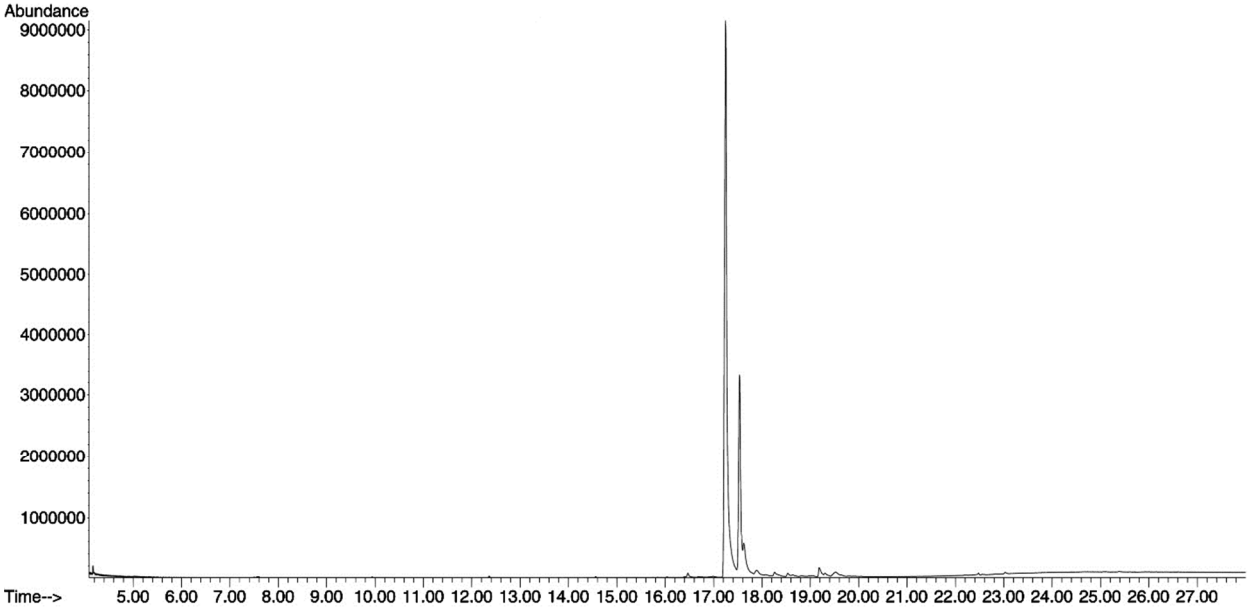


Figure S6: Setup for the preparative gas chromatography