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Investigation of the alteration of the composition of various essential oils used in aroma lamp applications

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ABSTRACT: The alteration of the composition of 15 samples of various essential oils used in aroma lamps and their corresponding headspace samples were analysed by GC–FID, GC–FTIR–MS and GC-sniffing technique to obtain information on the changes of aroma compounds under cold and hot conditions. The samples investigated were genuine essential oil and corresponding cold headspace samples and headspace samples of heated tubs and half-full tubs after the heating experiments. No detectable quantities of volatile pyrolysis products with health-dangerous effects were found, but there were significant alterations in composition. Therefore, the aroma-relevant compounds of the essential oils investigated pass from the aroma lamp tub to the air without forming new components and the detected volatiles can thus be inhaled for aromatherapeutical use. Only a time-dependent change from highly volatile to less volatile essential oil constituents in the heating experiments was registered. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: essential oils; headspace; aroma compounds; aroma lamp; heating experiments; GC–FTIR–MS; GC sniffing technique

Introduction

The use of essential oils as aromatherapeutical applications in aroma lamps is of increasing interest for many people, because of the significant trend of the last years to natural healing methods and therapies.[1] In connection with our previous study[2] of essential oils in a complex candle matrix, the aim of this investigation was to analyse the composition of 15 commercially available essential oils in aroma lamps under cold and hot conditions. The changes in aroma compound composition of the genuine essential oil, the corresponding headspace sample and the headspace samples after heating the oil tub, as well as the headspace sample after evaporation of half of the essential oil volume from the tub, was investigated. The detection and identification of possible pyrolysis products, as well as changes in composition of aroma-relevant compounds under aromatherapeutical aspects, should be checked.

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Experimental

Materials

Seven commercial essential oil samples, orange, blood orange, lemon, mandarin, lemongrass, melissa and noble-fir (trade name 'O'Rioll', produced by Libro, Meisel Co., Wr. Neustadt, Austria) were acquired in Austria and were compared with eight samples acquired in Italy (San Giorgio Flavours Co., Torino, Italy; J. Vitalis Co., Brunico, Italy; Specchiasol Co., Bussolengo-Verona, Italy): orange, blood orange, lemon, mandarin, grapefruit, bergamot, cedarwood and peppermint.

Headspace Sample Preparation

The essential oils were put into the bowl-part ('tub') on the top of the aroma lamp. The commercial aroma lamp, with a tea-light candle as heating source (Bioladen Co., Austria), was placed in a desiccator (25 cm diameter), closed, and a pumping-trapping system (G24/02, Brey Co., Germany) and charcoal tubes (NIOSH, Dräger Co., Germany) installed at the

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exit of the desiccator system.[3] The pumping conditions were as follows: 3 h pumping (effective capacity of the pump: 1 l/min) for the production of headspace extracts under cold vs. room-temperature conditions (temperature, $24 \pm 1°C$); 2 h trapping time for headspace samples from a heated aroma lamp (4–6 h for reducing to half of the genuine essential oil amount) with a water temperature of $65 \pm 5°C$.

The trapped volatiles were each extracted from the charcoal tubes with 400 µl dichloromethane p.A. (Riedel-de-Haen Co., Germany).

Analysis

Gas Chromatography — Flame Ionization Detection (GC–FID)

The GC–FID apparatus GC-8000-Series (Fisons Co., Italy) with potentiometer recorder Servogor (Goerz Co., Austria), HP-5890A GC with HP-3396 integrator and HP-6890 autosampler (Hewlett-Packard, USA) or HRGC-5300 Mega Series (dual-column operation; Carlo Erba Instruments Co., Italy) with a 25 m × 0.32 mm i.d. (0.52 µm film thickness) HP-5 (Hewlett-Packard Co., USA) or 25 m × 0.25 mm i.d. (0.3 µm film thickness) OV-1 or 25 m × 0.25 mm i.d. (0.3 µm film thickness) Carbowax (both produced by the Dip. di Scienza e Technologia del Farmaco, Italy) columns were used. Parameters were as follows: carrier gas, hydrogen (100 kPa); make-up-gas, helium (80 kPa); injector temperature, 230–240°C; detector temperature, 250–260°C; split, 1:20; temperature programming, 40°C (5 min) to 220°C (5 min) with heating rate of 3°C/min or 40°C (4 min) to 220°C (5 min) with heating rate of 7°C/min; injected volume, 1 µl each.

Gas Chromatography: Sniffing Technique

The instruments Fractovap Series 2101 with LT-programmer-210, electrometer Mod. 180 (Carlo Erba Instruments Co., Italy) and printer Servogor S (Brown Boveri Co., Austria) or HRGC-5300-HT Mega Series with an ODO-1 (olfactory detector outlet with make-up air supply and outlet splitter; Carlo Erba Instruments Co., Italy) and HP-3396 integrator (Hewlett-Packard, USA) as well as the columns: 25 m × 0.53 mm i.d. (0.3 µm film thickness) FSOT-RSL-150 (Biorad, The Netherlands) with glass splitter (Hewlett-Packard, USA) to a 0.2 m × 0.2 mm i.d. (0.33 µm film thickness, FID) and to a 0.2 m × 0.53 mm i.d. (0.5 µm film thickness, nose) HP-1 (Hewlett-Packard, USA) with the splitting ratio of 1:9 and a 25 m × 0.25 mm i.d. (0.3 µm film thickness, FID) in combination with a 25 m × 0.31 mm i.d. (0.3 µm film thickness, nose) OV-1 (Dip. di Scienza e Technologia del Farmaco, Italy) were used. Parameters were as follows: carrier gas, hydrogen (30 kPa or 1.5 ml/min); injector temperature, 230°C or 240°C; detector temperature, 250°C or 260°C; temperature progression, 25°C (6 min) to 220°C (5 min) with heating rate of 3°C/min or 50°C (1 min) to 220°C (5 min) with heating-rate of 3°C/min; injected volume, 1 or 3 µl each.

Gas Chromatography: Infrared Spectroscopy–Mass Spectrometry (GC–IR–MS)

The gas chromatograph HP-5890A with an HP-5965B IRD (MCT detector; data system, HP-9000/340) and HP-5970B MSD (data system, HP-9000/300; Hewlett-Packard, USA) with the columns: 30 m × 0.32 mm i.d. (0.25 µm film thickness) RSL-200 (Biorad, The Netherlands) or 60 m × 0.32 mm i.d. (0.25 µm film thickness) Stabilwax (Restek, USA) were used. Parameters as follows: carrier gas, helium (16.5 psi total flow); injector temperature, 240°C; transfer-line temperature, 270°C; light-pipe temperature, 250°C; IR wave range, 4000–750 cm^{-1}; MS scan range, 35–350 amu (70 eV, EI-mode, 0.43 s cyclus time); temperature progression, 40°C (1 min) to 230°C (5 min) with heating-rate of 8°C/min; injected volume, 1 µl.

MS- and IR-spectra correlations with spectral data from the libraries: NBS and Wiley (MS) as well as EPA__REVA and ROBERTET (IR) on-line.

Results and Discussion

Fifteen commercially available essential oil samples from Austria and Italy (Table 1) were used and their olfactory qualities evaluated by professional perfumers as follows: the odour of all the samples can be correlated to their essential oil names, but have poor quality with aroma characterizations such as 'old essential oils', 'dirty basic notes', 'cheap mass products' and 'odour not easy to correlate to pure essential oils', which is highly dependent on incorrect storage of these products and in some cases also on dilution and blending.

Using a dynamic method[2,4] the corresponding headspace samples of the essential oils at room temperature were first trapped (headspace 1). Then, using a commercial aroma lamp, the 15 essential oils were each placed into the tub on the top of the lamp and the headspace samples trapped after heating the tub to 65°C (headspace 2) and finally the same was done after evaporation of half of the starting amount of each oil (headspace 3). The odour of each headspace sample was evaluated again by professional perfumers (Table 1).

This olfactoric evaluation furnished the first information on a significant change of highly volatile aroma compounds to less volatile ones by loss of the characteristic top notes and registration of basic notes with partially fatty background notes.

Table 1. Olfactory evaluations of the headspace samples of the essential oils investigated

Essential oil	Headspace[1]	Headspace[2]	Headspace[3]
Orange oil, Austria	Identical to genuine oil	More aldehyde-like	Terpene-like, fatty
Blood orange oil, Austria	Identical to genuine oil	More typical, better	Weak, fatty, stearine-like
Mandarin oil, Austria	Identical to genuine oil	Pure, better, stable odour	'Old terpene'-like, fatty
Lemon oil, Austria	Identical to genuine oil	Better odour, more typical	Not identical
Lemongrass oil, Austria	Identical to genuine oil	Pure, good distilled oil	Burned, stearine-like
Noble-fir oil, Austria	Identical to genuine oil	Typical, no fresh notes	Fatty, waxy, not identical
Melissa oil, Austria	Identical to genuine oil	Typical, not so pure	Fatty and musty
Orange oil, Italy	Identical to genuine oil	Typical orange-peel odour	Weak orange
Blood orange oil, Italy	Identical to genuine oil	Orange-like, not so fresh	Weak orange, fatty
Lemon oil, Italy	Identical to genuine oil	More terpene-like	Musty, 'dirty' geraniol
Mandarin oil, Italy	Identical to genuine oil	Typical mandarin-peel	Not identical
Grapefruit oil, Italy	Identical to genuine oil	Grapefruit-like, not fresh	Fatty, musty, bitter notes
Bergamot oil, Italy	Identical to genuine oil	Typical bergamot	Not identical
Cedarwood oil, Italy	Identical to genuine oil	Lemon-, mandarin-like	Not identical
Peppermint oil, Italy	Identical to genuine oil	Peppermint-like, not fresh	Weak menthol-like

[1]Headspace sample of genuine cold essential oil (full tub).
[2]Headspace sample of heated essential oil (full tub).
[3]Headspace sample of heated essential oil with evaporation of half the volume (half-full tub).

To identify the composition of the aroma-relevant volatiles of the 15 essential oils and the trapped headspace samples of the aroma lamp experiments, GC–FID, GC–FTIR–MS and GC-sniffing analyses were used. As a result, about 35 olfactory impact compounds could be identified in all the aroma systems investigated (Table 2).

Table 2. Alteration of aroma-relevant volatiles in aroma lamp applications (concentrations calculated as a percentage of the peak area of GC–FID analysis)

No.	Compound*	Oil	hs1	hs2	hs3	Oil	hs1	hs2	hs3	KI+
		Orange oil, Austria				*Orange oil, Italy*				
01	α-Pinene	0.55	0.33	0.09	tr	0.52	0.24	tr	tr	927
02	Sabinene	0.32	3.17	0.13	tr	0.32	1.89	tr	tr	963
03	β-Pinene	0.07	0.14	0.26	tr	tr	0.33	0.40	tr	965
04	Myrcene	1.98	2.12	1.81	tr	2.02	2.28	1.21	tr	982
05	δ-3-Carene	0.16	0.14	tr	tr	0.16	0.14	tr	tr	998
06	*p*-Cymene	0.09	0.21	0.18	tr	tr	0.21	tr	tr	1008
07	Limonene	95.40	96.07	94.37	11.21	96.01	96.11	91.56	15.96	1024
08	γ-Terpinene	0.26	0.13	0.16	tr	0.21	tr	0.17	tr	1047
09	Terpinolene	tr	tr	tr	tr	tr	tr	0.17	tr	1075
10	Linalol	0.33	0.51	1.21	10.92	0.34	0.63	2.36	5.89	1084
11	Citronellal	tr	tr	0.14	tr	tr	tr	0.15	tr	1130
12	Decanal	0.18	tr	1.57	7.12	tr	tr	1.35	2.77	1166
13	Neral	tr	tr	0.62	8.70	0.20	0.22	0.62	8.70	1184
14	Geranial	tr	tr	0.98	8.81	tr	tr	0.98	6.36	1208
15	Geraniol	tr	tr	0.22	tr	tr	tr	0.22	tr	1235
16	Linalyl acetate	tr	tr	0.22	2.67	tr	tr	0.21	2.69	1240
17	Geranyl acetate	tr	tr	tr	tr	tr	tr	tr	tr	1363
		Blood orange oil, Austria				*Blood orange oil, Italy*				
01	Butyl-3-methyl acetate	0.13	0.21	tr	tr	nd	nd	nd	nd	867
02	α-Pinene	0.51	0.19	tr	tr	0.53	0.20	tr	tr	927
03	Sabinene	0.32	0.54	tr	tr	0.31	0.25	tr	tr	963
04	β-Pinene	0.07	0.43	0.22	tr	tr	0.33	tr	tr	965
05	Myrcene	1.85	1.92	1.49	tr	1.20	2.30	1.87	0.36	982
06	δ-3-Carene	0.14	0.23	tr	tr	tr	0.15	tr	tr	998
07	*p*-Cymene	nd	nd	nd	nd	0.20	0.24	tr	tr	1008
08	Limonene	96.10	96.36	91.84	32.16	95.98	96.11	95.38	14.18	1024
09	γ-Terpinene	tr	tr	tr	tr	0.21	0.41	0.17	9.22	1047
10	Terpinolene	tr	tr	tr	tr	tr	tr	0.22	1.29	1075
11	Linalol	0.24	0.50	2.32	12.42	0.25	0.49	1.25	5.89	1084
12	Citronellal	0.05	tr	0.43	6.58	tr	tr	0.14	0.47	1130
13	Decanal	0.05	tr	0.28	6.70	tr	tr	0.62	2.77	1166
14	Neral	tr	tr	0.24	1.32	0.11	0.22	0.62	8.70	1184
15	Geranial	tr	tr	tr	11.90	tr	tr	0.98	6.36	1208
16	Geraniol	nd	nd	nd	nd	tr	tr	0.22	0.51	1235
17	Linalyl acetate	tr	tr	0.82	1.72	tr	tr	0.22	2.67	1240
18	Geranyl acetate	nd	nd	nd	nd	tr	tr	tr	0.22	1363

Table 2 Continued over page

Table 2. Continued

No.	Compound*	Oil	hs1	hs2	hs3	Oil	hs1	hs2	hs3	KI+
		Mandarin oil, Austria				*Mandarin oil, Italy*				
01	α-Thujene	0.23	tr	tr	tr	0.57	0.37	0.12	tr	922
02	α-Pinene	1.03	0.55	0.26	tr	1.68	1.18	0.32	tr	927
03	Camphene	tr	tr	tr	tr	nd	nd	nd	nd	941
04	Sabinene	0.32	0.49	0.18	tr	tr	tr	0.35	tr	963
05	β-Pinene	0.49	tr	tr	tr	1.41	1.14	0.16	tr	965
06	Myrcene	1.85	2.17	1.67	0.88	1.72	2.29	1.49	tr	982
07	δ-3-Carene	0.14	tr	tr	0.65	tr	tr	0.13	tr	998
08	α-Terpinene	0.12	tr	tr	tr	0.27	0.22	2.28	tr	1005
09	*p*-Cymene	0.65	tr	1.67	1.34	1.00	2.17	tr	tr	1008
10	Limonene	88.89	91.25	89.55	50.27	77.44	79.74	74.47	4.09	1024
11	*trans*-β-Ocimene	tr	tr	tr	tr	nd	nd	nd	nd	1044
12	γ-Terpinene	4.83	3.64	5.10	2.96	14.65	12.09	17.85	tr	1047
13	Terpinolene	0.36	tr	0.33	0.90	0.72	0.59	1.16	tr	1075
14	Linalol	0.33	0.46	5.10	2.96	0.02	0.16	0.39	5.10	1084
15	Citronellal	nd	nd	nd	nd	0.02	tr	0.08	tr	1130
16	Decanal	0.13	tr	0.33	6.35	0.21	tr	0.22	14.96	1166
17	Neral	0.16	tr	0.72	0.55	0.09	tr	0.38	tr	1184
18	Geranial	tr	tr	0.21	1.17	nd	nd	nd	nd	1208
19	Geraniol	tr	tr	tr	0.83	nd	nd	nd	nd	1235
20	Linalyl acetate	tr	tr	0.27	0.77	nd	nd	nd	nd	1240
21	Geranyl acetate	0.15	tr	tr	1.54	0.31	tr	0.20	11.23	1363
22	β-Caryophyllene	tr	tr	tr	0.78	0.06	tr	0.18	5.73	1397
23	β-Bisabolene	nd	nd	nd	nd	0.11	tr	0.12	8.07	1492
		Lemon oil, Austria				*Lemon oil, Italy*				
01	α-Thujene	tr	0.24	0.13	tr	tr	0.32	0.17	tr	922
02	α-Pinene	0.62	1.07	0.53	tr	1.11	1.42	0.63	0.07	927
03	Camphene	tr	tr	tr	tr	tr	tr	tr	tr	941
04	Sabinene	0.41	0.21	tr	tr	0.27	0.11	0.02	tr	963
05	β-Pinene	15.16	10.85	5.42	1.03	12.66	6.86	3.33	0.46	965
06	Myrcene	1.61	1.76	1.14	1.09	2.43	1.84	1.62	1.10	982
07	δ-3-Carene	0.11	0.14	tr	tr	tr	tr	tr	tr	998
08	α-Terpinene	0.24	tr	tr	tr	tr	tr	tr	tr	1005
09	*p*-Cymene	0.46	1.30	4.77	6.27	0.22	0.99	3.18	5.73	1008
10	Limonene	65.95	72.95	63.36	56.00	69.07	73.13	67.09	58.24	1024
11	*cis*-β-Ocimene	tr	0.08	tr	tr	nd	nd	nd	nd	1029
12	*trans*-β-Ocimene	tr	0.15	tr	tr	tr	tr	tr	tr	1039
13	γ-Terpinene	1.51	9.43	8.12	4.66	1.96	9.05	9.55	5.03	1047
14	Terpinolene	0.09	0.41	0.35	tr	0.24	0.58	0.42	0.11	1075
15	Linalol	tr	0.16	0.32	1.11	0.53	0.66	0.73	0.89	1084
16	Citronellal	tr	0.13	0.29	tr	0.15	0.27	0.41	0.04	1130
17	Decanal	0.16	0.16	0.32	1.61	0.62	0.57	1.12	2.09	1166
18	Neral	0.42	tr	0.16	tr	0.57	0.08	0.33	0.02	1184
19	Geranial	0.66	0.55	2.02	3.00	1.12	1.00	2.76	3.98	1208
20	Geraniol	tr	tr	tr	tr	nd	nd	nd	nd	1235
21	Linalyl acetate	1.07	0.63	3.07	5.38	0.65	0.39	1.88	3.85	1240
22	Neryl acetate	0.34	0.14	2.02	2.76	1.85	1.23	3.05	3.99	1344
23	Geranyl acetate	0.46	0.14	2.09	3.56	tr	0.22	0.92	1.34	1363
24	β-Caryophyllene	0.23	tr	1.06	1.19	0.16	tr	0.64	0.82	1397
25	*trans*-β-Bergamotene	0.35	0.10	1.79	3.31	1.02	0.77	2.59	3.96	1424
26	β-Bisabolene	0.54	tr	2.10	4.51	0.61	0.08	2.22	4.44	1492
27	α-Bisabolol	tr	tr	tr	0.64	nd	nd	nd	nd	1655
		Lemongrass oil, Austria				*Grapefruit oil, Italy*				
01	α-Pinene	tr	1.33	tr	tr	0.54	0.29	tr	tr	927
02	Camphene	tr	tr	tr	tr	nd	nd	nd	nd	941
03	Sabinene	0.27	4.26	tr	tr	0.29	0.31	0.14	tr	963
04	6-Methyl-5-hepten-2-one	2.39	12.52	0.79	0.48	nd	nd	nd	nd	977
05	Myrcene	0.99	6.21	0.16	0.32	1.58	1.94	1.55	0.59	982
06	α-Terpinene	nd	nd	nd	nd	tr	tr	tr	tr	1005
07	*p*-Cymene	nd	nd	nd	nd	1.42	0.36	0.16	tr	1008
08	1,8-Cineole	0.44	2.50	0.44	0.29	nd	nd	nd	nd	1015
09	Limonene	2.05	24.25	0.60	0.48	93.52	95.34	95.47	18.73	1024
20	cis-β-Ocimene	tr	0.74	tr	0.18	nd	nd	nd	nd	1029
11	*trans*-β-Ocimene	tr	0.51	tr	0.12	nd	nd	nd	nd	1039
12	γ-Terpinene	nd	nd	nd	nd	tr	0.60	0.15	0.61	1047

Table 2 Continued over page

Table 2. Continued

No.	Compound*	Oil	hs1	hs2	hs3	Oil	hs1	hs2	hs3	KI+
13	Terpinolene	nd	nd	nd	nd	tr	tr	0.11	0.27	1075
14	Linalol	3.47	4.37	3.52	0.84	0.12	0.14	0.53	1.55	1084
15	Isopulegol	1.68	2.47	0.33	0.62	nd	nd	nd	nd	1122
16	Citronellal	2.82	0.68	1.69	2.23	tr	0.12	0.29	1.49	1130
17	δ-Terpineol	0.79	0.50	1.64	2.02	nd	nd	nd	nd	1143
18	Isopulegone	1.68	2.47	0.33	0.62	nd	nd	nd	nd	1152
19	Terpinen-4-ol	1.44	1.25	0.49	0.15	nd	nd	nd	nd	1158
20	Neral	34.78	18.68	39.46	30.94	0.15	0.41	tr	6.21	1184
21	Pulegone	nd	nd	nd	nd	0.17	0.18	0.11	0.58	1204
22	Nerol	nd	nd	nd	nd	tr	0.16	0.31	2.00	1206
23	Geranial	46.89	16.37	48.77	56.78	0.11	tr	0.18	1.23	1208
24	Terpinen-4-yl acetate	0.49	tr	0.24	0.15	nd	nd	nd	nd	1270
25	Geranyl acetate	0.29	tr	0.31	0.62	nd	nd	nd	nd	1363
26	α-Cubebene	nd	nd	nd	nd	tr	tr	tr	0.67	1369
27	β-Cubebene	0.30	tr	0.32	0.89	nd	nd	nd	nd	1372
28	β-Caryophyllene	0.24	tr	0.19	0.66	0.17	tr	0.23	0.49	1397
29	α-Humulene	nd	nd	nd	nd	tr	tr	0.13	0.21	1434
30	δ-Cadinene	nd	nd	nd	nd	tr	tr	0.28	0.53	1501
			Noble-fir oil, Austria				*Cedarwood oil, Italy*			
01	α-Thujene	0.20	tr	tr	tr	0.29	tr	0.18	tr	922
02	α-Pinene	0.56	0.41	tr	tr	1.46	0.92	0.95	tr	927
03	Camphene	7.66	4.59	tr	tr	tr	tr	tr	tr	941
04	Sabinene	nd	nd	nd	nd	1.71	tr	tr	0.52	963
05	β-Pinene	3.78	2.35	1.61	0.52	10.86	6.92	9.47	0.65	965
06	Myrcene	11.08	6.44	2.97	2.53	1.37	1.73	1.23	0.55	982
07	δ-3-Carene	0.60	0.94	0.88	0.64	nd	nd	nd	nd	998
08	α-Terpinene	1.78	2.00	0.57	2.86	nd	nd	nd	nd	1005
09	*p*-Cymene	2.06	2.38	0.90	1.78	1.26	1.46	2.83	tr	1008
10	Limonene	65.09	75.07	57.67	16.61	70.41	77.53	67.57	3.12	1024
11	*trans*-β-Ocimene	nd	nd	nd	nd	0.16	tr	tr	tr	1039
12	γ-Terpinene	0.29	0.14	0.35	1.33	7.42	6.62	7.28	1.11	1047
13	Terpinolene	0.24	0.16	0.32	1.32	0.42	0.36	0.41	1.52	1075
14	Linalol	0.35	0.21	0.51	1.78	0.54	1.23	0.85	11.29	1084
15	Camphor	tr	0.17	0.58	1.86	nd	nd	nd	nd	1111
16	Borneol	5.08	3.95	26.69	19.54	nd	nd	nd	nd	1142
17	Decanal	nd	nd	nd	nd	0.14	tr	0.17	9.50	1166
18	Geranial	0.44	tr	0.46	0.60	0.63	0.61	0.99	15.73	1208
19	Geraniol	nd	nd	nd	nd	1.06	0.77	1.74	2.22	1235
20	Linalyl acetate	0.22	tr	0.40	0.45	1.23	1.84	2.46	24.02	1240
21	Terpinen-4-yl acetate	0.31	tr	2.68	0.68	nd	nd	nd	nd	1270
22	Neryl acetate	nd	nd	nd	nd	0.31	tr	0.75	1.59	1344
23	Geranyl acetate	0.18	0.43	0.61	0.61	0.40	tr	0.96	2.30	1363
24	β-Caryophyllene	tr	tr	0.31	3.10	0.13	tr	0.26	tr	1397
25	α-Santalene	tr	tr	0.45	1.40	nd	nd	nd	nd	1407
26	*trans*-β-Bergamotene	tr	tr	tr	0.48	0.30	tr	0.73	1.15	1424
27	α-Humulene	tr	tr	tr	1.34	nd	nd	nd	nd	1434
28	β-Bisabolene	tr	tr	tr	0.61	0.43	tr	1.13	3.35	1492
			Melissa oil, Austria				*Peppermint oil, Italy*			
01	α-Pinene	0.89	6.75	tr	tr	0.72	5.28	0.32	tr	927
02	Sabinene	0.81	6.43	tr	tr	0.53	1.52	0.62	tr	963
03	β-Pinene	0.53	0.97	tr	tr	1.31	7.11	0.21	tr	965
04	Myrcene	0.50	0.63	tr	tr	0.36	0.72	0.27	tr	982
05	δ-3-Carene	3.76	2.74	0.64	0.99	nd	nd	nd	nd	998
06	α-Terpinene	nd	nd	nd	nd	0.12	tr	0.21	tr	1005
07	*p*-Cymene	3.63	3.03	1.38	0.34	0.39	1.30	2.93	0.64	1008
08	1,8-Cineole	nd	nd	nd	nd	5.78	19.51	2.93	1.15	1015
09	Limonene	39.40	34.81	5.18	17.12	2.27	11.47	0.93	0.64	1024
10	*cis*-β-Ocimene	nd	nd	nd	nd	0.14	tr	tr	tr	1029
11	*trans*-β-Ocimene	0.29	0.81	tr	0.33	nd	nd	nd	nd	1039
12	γ-Terpinene	0.73	0.33	tr	0.65	0.34	tr	tr	0.21	1047
13	*trans*-Sabinene hydrate	nd	nd	nd	nd	0.87	0.77	0.93	0.22	1062
14	Terpinolene	nd	nd	nd	nd	0.65	0.86	0.81	0.23	1075
15	Linalol	nd	nd	nd	nd	0.27	0.34	0.40	2.46	1084
16	Isopulegol	0.59	0.37	0.80	0.56	nd	nd	nd	nd	1122
17	Citronellal	10.13	2.53	1.56	1.28	nd	nd	nd	nd	1130
18	Menthone	nd	nd	nd	nd	20.75	21.15	15.67	2.46	1142
19	Menthofurane	nd	nd	nd	nd	4.45	5.39	3.34	0.54	1147

Table 2 Continued over page

Table 2. Continued

No.	Compound*	Oil	hs1	hs2	hs3	Oil	hs1	hs2	hs3	KI+
20	Isomenthone	nd	nd	nd	nd	3.39	3.93	3.12	1.16	1151
21	Neomenthol	nd	nd	nd	nd	3.22	1.32	3.95	1.54	1159
22	Menthol	nd	nd	nd	nd	42.16	15.20	52.05	71.22	1169
23	Neral	2.67	0.77	8.23	0.92	nd	nd	nd	nd	1184
24	Citronellol	21.78	34.10	56.47	4.36	nd	nd	nd	nd	1202
25	Pulegone	nd	nd	nd	nd	2.22	0.27	3.10	3.10	1204
26	Piperitone	nd	nd	nd	nd	0.15	0.46	0.56	2.01	1205
27	Nerol	0.21	0.36	0.41	0.32	nd	nd	nd	nd	1206
28	Geranial	4.25	1.17	11.28	20.17	nd	nd	nd	nd	1208
29	Menthyl acetate	nd	nd	nd	nd	3.60	2.21	6.19	1.77	1279
30	Eugenol	1.88	0.44	1.03	0.46	nd	nd	nd	nd	1320
31	Citronellyl acetate	0.97	0.54	3.02	0.32	nd	nd	nd	nd	1335
32	Neryl acetate	0.55	0.57	3.74	0.27	nd	nd	nd	nd	1344
33	α-Cubebene	1.08	0.56	2.45	1.43	nd	nd	nd	nd	1369
34	β-Bourbonene	nd	nd	nd	nd	0.29	tr	0.52	0.26	1372
35	β-Elemene	0.34	0.45	1.37	1.57	nd	nd	nd	nd	1374
36	β-Caryophyllene	1.33	0.22	0.68	1.95	1.28	0.79	2.34	0.80	1401
37	*trans*-β-Bergamotene	nd	nd	nd	nd	tr	tr	tr	tr	1424
38	*trans*-β-Farnesene	nd	nd	nd	nd	1.28	tr	0.26	0.27	1444
39	Germacrene-D	nd	nd	nd	nd	0.64	tr	0.45	0.23	1462
40	Bicyclogermacrene	nd	nd	nd	nd	0.14	tr	tr	1.28	1485
41	β-Bisabolene	nd	nd	nd	nd	tr	tr	tr	1.52	1492
			Bergamot oil, Italy							
01	α-Thujene	tr	tr	tr	tr					922
02	α-Pinene	0.46	0.72	tr	tr					927
03	Sabinene	tr	tr	tr	tr					963
04	β-Pinene	2.97	4.28	tr	tr					965
05	Myrcene	1.78	1.87	2.26	3.05					982
06	*p*-Cymene	0.67	1.24	tr	tr					1008
07	Limonene	24.50	33.34	1.89	0.65					1024
08	*cis*-β-Ocimene	0.46	0.35	0.78	tr					1029
09	*trans*-β-Ocimene	0.82	0.62	1.35	3.50					1039
10	γ-Terpinene	2.54	2.54	tr	tr					1047
11	Terpinolene	tr	tr	tr	tr					1075
12	Linalol	22.49	18.69	24.37	78.84					1084
13	Decanal	tr	tr	0.31	0.91					1166
14	Geranial	0.26	0.24	0.59	0.70					1208
15	Linalyl acetate	40.61	33.56	63.08	4.07					1240
16	Neryl acetate	0.21	tr	0.49	1.82					1344
17	Geranyl acetate	0.38	0.23	0.79	0.87					1363
18	β-Caryophyllene	0.11	tr	0.25	tr					1401
19	*trans*-β-Bergamotene	0.91	tr	0.28	tr					1424
20	β-Bisabolene	0.13	tr	0.48	tr					1492

*In order of detection.
hs1 = Headspace sample of genuine essential oil under cold conditions.
hs2 = Headspace sample of genuine essential oil under heating conditions.
hs3 = Headspace sample of heated essential oil with evaporation of half of the volume.
KI+, Kováts indices of the compounds on an unpolar 25 m × 0.25 mm OV-1 column.
tr, trace compounds with a concentration of less than 0.01% peak area of GC–FID analysis.
nd, not detected.

In general, an alteration was found in the composition of the headspace samples of the essential oils trapped in aroma lamp experiments, and significant changes from highly volatile, mainly monoterpene hydrocarbons, to less volatile monoterpene alcohols as well as sesquiterpenes or partially non-terpenic, oxygenated compounds (e.g. decanal) could be detected. This result is better than the olfactory data from the single headspace samples shown in Table 1.

No volatile, commonly known, health-endangering pyrolytic products were identified in detectable quantities, therefore a statement can be made that, at least from this point of view, the use of essential oils in aroma lamps for aromatherapy is a serious application in alternative medicine. The aroma-relevant volatiles only differ in their composition after aroma lamp heating of commercially available essential oils without forming detectable volatile pyrolytic products with known deleterious effects. Furthermore, it was shown that even cheap 'old', 'diluted' or 'blended' commercially available essential oils can be also used in aroma lamps: the customer has been deceived only with respect to the olfactory quality of such essential oils. These results, obtained with various essential oils, are

in agreement with the findings of our previous study performed with aroma candles.[2] However, by contrast to the latter, the olfactory quality of the essential oil residues in the tub suffered to a great extent.

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