

RESEARCH ARTICLE

Antique lavender essential oil from 1945, its chemical composition and enantiomeric distribution

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Abstract

Properly stored lavender from 1945 was collected in French market and Gas Chromatography and Mass Spectrometry (GCMS) analysis was carried out to see possible chemical transformation and chemical composition. Total of 102 peaks (100% components) were identified, out of them 10 were oxidized minor components (total 0.41%). The lavender essential oil was dominated by the linalool (40.8%), terpinen-4-ol (9.9%), α -terpineol (3.5%), linalyl acetate (16.4%), lavandulyl acetate (3.8%), and *trans*-caryophyllene (2.2%). Enantiomeric distribution of major monoterpenoids were also measured.

Keywords: Lavender oil-1945, linalool, linalyl acetate, terpinen-4-ol, oxidation, enantiomeric distribution, storage of essential oils.

Introduction

Lavandula angustifolia Mill. (also known as lavender) comprised of more than 39 known species is one of the most popular essential oils in aromatherapy from Lamiaceae family. The flowering plant of lavender (*Lavandula angustifolia* or *Lavandula officinalis*) is used to produce lavender essential oils. It is sweet aromatic and colourless essential oil. It is widely used in aromatherapy and fragrance industry because of its biological activities and aromatic potentials.

Proper storage of essential oils is always mandatory since lavender does not contain any antioxidant molecules in its essential oil (Hagvall et al., 2008). Presence of water molecules and aerial exposure causes severe oxidation of essential oils (Guenther, 1948).

The major components of lavender are linalool, linalyl acetate and caryophyllene (Sköld et al., 2007). Out of them *trans*-caryophyllene is most susceptible to oxidation to produce oxidized product (caryophyllene oxide) which is the least sensitizing molecule (Sköld et al., 2006). Highly oxidized lavender produces hydroxide, epoxides and hydroperoxides of linalool, linalyl acetate, and caryophyllene (Nilsson et al., 2008). Autooxidation happens in the allylic positions of double bonds in linalool and linalyl acetate (C6-C7) (Sköld et al 2007). They are found to possess sensitizing effect on skin (Nilsson et al., 2008), however there are few contact allergies have been reported (Letizia et al., 2003). So, proper handling and storage of fragrance compounds are always advised (Turek & Stintzing, 2013).

Numerous studies on lavender essential oils have been carried out, however this is the first report on chemical composition and enantiomeric distribution of 71 year old lavender so far from our understanding.

Materials and Methods

Plant Material

Essential oil sample was purchased in 1945 in Paris, France. The essential oil was stored on amber glass container in refrigerator until analysis was carried out.

Gas Chromatographic – Mass Spectral Analysis

The essential oil of lavender was analyzed by GC-MS using a Shimadzu GCMS-QP2010 Ultra operated in the EI mode ((electron energy = 70eV), scan range = 3.0 scans/sec), and GCMS Solution software. The GC column was Zebron ZB-5MS fused silica capillary column with a (5% phenyl)-polymethyl siloxane stationary phase a film thickness of 0.25 mm. The carrier gas was helium with a column head pressure 80 psi and flow rate of 1.37 ml/min. Injector temperature was 250 °C and the ion source temperature was 200 °C, increase in temperature rate 2 °C/min to 260 °C. The GC oven temperature program was programmed for 50 °C initial temperature, increase in rate 2 °C/min to 260 °C. A 5% w/v solution of the sample in CH₂Cl₂ was prepared and 0.1 µL was injected in splitting mode (30:1). Identification of the oil components was based on their retention indices determined by reference to a homologous series of n-alkanes, and by comparison of their mass spectral fragmentation patterns with those reported in the literature (Adams, 2007), and stored in the MS library.

Chiral Gas Chromatographic-Mass Spectral Analysis

Chiral analysis of the lavender essential oils was performed on a Shimadzu GCMS-QP2010S operated in the EI mode ((electron energy=70eV), scan range = 3.0 scans/sec). GC equipped with a Restek B-Dex 325 capillary column (30 m×0.25 mm ID×0.25 µm film). Oven temperature was started at 50 °C, and then gradually raised to 120 °C at 1.5 °C/min. The oven was then raised to 200 °C at 2 °C/min and held for 5 min. Helium was the carrier gas and was flow rate was maintained at 1.8ml/min. Samples were diluted 3% w/v with CH₂Cl₂ and then a 0.1 µL sample was injected in a split mode with a split ratio of 1:45.

Results and Discussion

Essential Oil Composition

The lavender oil was purchased commercially in 1945 and stored in dark bottle for 71 years. A total of 102 peaks (100% components) were identified, out of them 10 oxidized minor components (total 0.41%) were detected (see Table 1). The studied lavender is the least oxidized as compared to studies carried out in stability studies of tea tree oil (Trachida et al., 2010). The lavender essential oil was dominated by the linalool (40.8%), terpinen-4-ol (9.9%), α-terpineol (3.5%), linalyl acetate (16.4%), lavandulyl acetate (3.8%), and *trans*-caryophyllene (2.2%). These results are quantitatively different than any result previously published in a significant review paper (Lawrence, 2012) and from ISO standard of French lavender (ISO lavender, 2016). Out of the published research high terpinen-4-ol, high linalool, and low linalyl acetate has not previously been reported (Lawrence, 2012), the maximum amount of terpinen-4-ol was reported as 5.0-6.2% (Chemat et al., 2006; Pavela, 2006).

Increase in oxidation products like linalool oxide, caryophyllene oxide indicates autoxidation of linalool and caryophyllene (Misharina et al., 2003; Sköld et al., 2008).

Linalool readily undergoes autooxidation to form cyclized molecule: furanoids and pyranoids (Sköld et al., 2008), so the concentration of furanoids and pyranoids in this report is relatively high as compared to freshly distilled lavender (Lawrence, 2012). Whereas due to large bulky acetate group, linalyl acetate is unable to form cyclized furanoid, and pyranoids. Sesquiterpene oxide is formed from oxidation of sesquiterpene (Hădărugă et al., 2014). Ascaridole glycol *cis* and *trans* along with epoxide are observed as oxidized product of terpinen-4-ol (Trachida et al 2010).

Enantiomeric distribution of lavender essential oil was also studied (Table-2), which is similar to previously studied lavender essential oil (Baser et al., 2005). Total 70.64% of monoterpene was enantiomerically analyzed to see the distribution. L-linalool, L-linalyl acetate, D-Terpinen-4-ol, and L- α -Terpineol were the major enantiomer in the studied lavender.

In addition to genetic variation, other factors such as age, vegetative cycle stage, climate, season, soil composition, etc. are among several things responsible for the considerable variation in essential oil compositions (Satyal & Pappas, 2016). Based on the observed chemical composition, this variety of French lavender may be treated as a distinct chemical composition. The large variation of chemical composition might be related to different distillation technique or could have plant material was genetically modified on time.

Table 1. Chemical composition of lavender EO purchased in 1945 in France

RI	Compound	%
795	<i>n</i> -Octane	0.02
863	<i>n</i> -Hexanol	0.03
922	Tricyclene	0.05
924	α -Thujene	0.1
932	α -Pinene	0.3
949	Camphene	0.3
971	Sabinene	0.02
977	Octen-3-ol	0.6
983	3-Octanone	0.9
988	Myrcene	0.4
989	<i>trans</i> -dehydroxy-Linalool oxide	0.04
995	Butyl butanoate	0.05
996	3-Octanol	0.2
1005	<i>cis</i> -dehydroxy-Linalool oxide	0.03
1008	δ -3-Carene	0.2
1011	Hexyl acetate	0.2
1019	<i>o</i> -Cymene	0.08
1024	<i>p</i> -Cymene	0.5
1028	Limonene	0.3
1030	β -Phellandrene	0.05
1031	1,8-Cineole	1.6
1034	<i>cis</i> - β -Ocimene	0.8
1045	<i>trans</i> - β -Ocimene	0.7
1057	γ -Terpinene	0.04
1069	<i>cis</i> -furanoid-Linalool oxide	0.4
1084	Terpinolene	0.04
1086	<i>trans</i> -furanoid-Linalool oxide	0.2
1091	Rosefuran	0.02
1100	Linalool	40.8
1103	Hotrienol	0.2
1104	Hexyl-propionate	0.03
1106	Octen-3-yl acetate	2.3
1118	3-Octanol acetate	0.2

1124	<i>cis</i> -p-Menth-2-en-1-ol	0.04
1127	<i>allo</i> -Ocimene	0.06
1138	Nopinone	0.03
1140	<i>trans</i> -Pinocarveol	0.02
1147	Camphor	0.8
1150	Nerol oxide*	0.02
1162	Lavandulol	0.9
1169	<i>cis</i> -pyranoid-Linalool oxide	0.04
1172	Borneol	2.3
1174	<i>trans</i> -pyranoid-Linalool oxide	0.04
1180	Terpinen-4-ol	9.9
1183	<i>p</i> -methyl-Acetophenone	0.04
1186	Cryptone+ <i>p</i> -Cymenol [2:1]	0.4
1187	2,6-dimethyl-octa-3,7-diene-2,6-diol*	0.09
1191	Hexyl butanoate	0.2
1194	α-Terpineol	3.5
1200	3- <i>cis</i> -Octenyl acetate	0.04
1207	3- <i>trans</i> -Octenyl acetate	0.09
1209	Verbenone	0.03
1211	Linalool formate	0.3
1216	γ -Geraniol	0.07
1218	<i>trans</i> -Carveol	0.02
1223	Nerol	0.5
1228	Bornyl formate	0.1
1241	Cumin aldehyde	0.1
1243	Carvone	0.03
1249	Linalyl acetate	16.4
1253	Piperitone	0.01
1266	Geranial	0.04
1271	Linalool hydroperoxide*	0.03
1273	<i>trans</i> -Ascaridol glycol*	0.03
1275	Neryl formate	0.06
1277	Phellandral	0.05
1282	Lavandulyl acetate	3.8
1283	Bornyl acetate	0.4
1290	<i>p</i> -Cymen-7-ol	0.08
1296	Geranyl formate	0.2
1312	Epoxylinallyl acetate*	tr
1331	Hydroperoxy linalyl acetate*	0.08
1338	Hydroxylinallyl acetate*	0.06
1344	Benzyl butanoate	0.03
1345	α -Terpinyl acetate	0.04
1357	Neryl acetate	1.00
1359	<i>epoxy</i> -Ascaridole*	0.03
1377	Geranyl acetate	2.0
1379	3,4-dihydro-Coumarin	0.03
1383	α -Bourbonene	0.04

1384	Hexyl hexanoate	0.03
1386	7- <i>epi</i> -Sesquithujene	0.03
1412	α - <i>cis</i> -Bergamotene	0.05
1419	<i>tran</i> -Caryophyllene	2.2
1432	α - <i>trans</i> -Bergamotene + Coumarin (tr)	0.2
1434	Isoamyl octanoate + Elemene < γ >	0.03
1443	<i>cis</i> - β -Farnesene	0.04
1446	<i>epi</i> - β -Santalene	0.03
1451	<i>trans</i> - β -Farnesene	0.5
1455	α -Humulene	0.05
1456	Sesquisabinene	0.04
1480	Germacrene D	0.1
1483	Neryl isobutanoate	0.06
1485	<i>p</i> -Menthane-1,2,4-triol*	0.03
1506	β -Bisabolene	0.06
1512	δ -Amorphene	0.1
1517	Isobicyclgermacrene	0.2
1581	Caryophyllene oxide	0.4
1598	Oxidized sesquiterpene*	0.04
1640	<i>Epi</i> - α -Cadinol	0.09
1746	α -Bisabolol oxide A	0.05
1897	Thiogeraniol	0.04
Total compound identified (102)		100%
Compounds produced by oxidation (10)		0.41%

Where RI Retention Index determined to a series of n-Alkanes on ZB-5 column; compounds are listed in order of elution (Increasing RI), % refers to Percent of total oil, "tr" indicates trace components present less than 0.01% of total oil composition. Those components with asterisk "*" are oxidized products.

Table 2. Enantiomeric distribution of major monoterpenes in Lavender essential oil from 1945.

Compounds	Relative %	ee (%)	ed [d to l] (%)
Linalool	40.8	78	11 to 89
Linalyl acetate	16.4	52	2 to 98
Terpinen-4-ol	9.9	100	0 to 100
α - Terpineol	3.5	48	26 to 74
Total %	70.6		

Where "ee" stands for enantiomeric excess and "ed" stands for enantiomeric distribution

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