

Volatile Compounds in the Leaf of Plane Tree (*Platanus orientalis*) with Solid Phase Microextraction (SPME) Technique

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Abstract: Plane tree belongs to Platanaceae family. There is a widespread belief that *Platanus orientalis* leaves (POLs) have beneficial effects on joint disorders. Therefore, many people consume POLs as tea. To our knowledge, as there is no study on volatile compounds (VCs) of POLs, we objected to determine the VCs in POLs obtained from *Platanus orientalis* trees grown in Hatay province, Turkey. The VCs were extracted using solid phase micro-extraction (SPME) and analyzed by gas chromatography-mass spectrometry (GC-MS). A total of 140 VCs were found in POLs. Aldehydes, alcohols, ketones, terpenes and alkenes were determined in POLs as major VCs groups, which accounted for 32.40 %, 23.51 %, 18.08 %, 10.24 % and 4.82 % of total VCs identified, respectively. *Trans*, *trans*-2,4-heptadienal (6.62 %), nonanal (6.46 %), benzaldehyde (6.42 %), *cis*-3-hexen-1-ol (6.32 %), benzenemethanol (6.13 %) were the most abundant VCs identified in POLs. *Trans*-2-hexenal (3.46 %), 3-phenyl-2-butanone (2.87 %), *trans*-3,5-dimethyl-1,6-octadiene (2.80 %), 6-methyl-5-hepten-2-one (2.56 %), octan-1-ol (2.43 %), *trans*-geranyl acetone (2.17 %), *trans*-4,8-dimethyl-1,3,7-nonatriene (1.98 %), phenyl methyl ketone (1.69 %), 6-methyl-3,5-heptadiene-2-one (1.57 %) were the second most plentiful compounds found in POLs. 11H-dibenzo[b,e][1,4]diazepin-11-one,5,10-dihydro-5-[3-(methylamino)propyl] (1.38 %), benzeneethanol (1.36 %) and β -ionone (1.02 %) were found as the third most abundant VCs. The above-mentioned VCs were accounted for about 57 % of total VCs identified in POLs. The remaining VCs were below 1.00 % that is, found at trace levels. According to the VCs profiles of POL, its beneficial effects on health may be due to aldehydes, alcohols, ketones and terpenes.

Keywords: *Platanus orientalis* leaf, Volatile compounds, SPME

1. INTRODUCTION

Plane tree belonging to Platanaceae family is known for its grandeur and longevity. *Platanus orientalis* is one of the most common plane varieties in the world and it is the most widespread plane tree growing in Turkey. The common name of this variety is oriental plane. Among plane trees, it was the first variety to be discovered. The oriental plane is widely used as an ornamental, especially in urban areas and also is cultivated sometimes for timber. Plane tree roots have been used as a hemostatic agent and antivenom for snake bite [1]. The pollens of plane tree are an important source of airborne allergens such as asthma, allergic rhinitis and allergic conjunctivitis [2, 3] and also systemic reactions [4]. Nevertheless, plane leaves are used

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in traditional medicine, especially traditional Persian folk medicine, to treat several disorders such as dermatological, gastrointestinal, rheumatic and inflammatory [5-6]. Recently, the tea of plane tree leaf has widely been used for treating joint pains in the folk medicine in Turkey. It has indicated that the extract of leaves of plane tree resulted in a favorable effect on the removing the symptoms of food allergy in dogs [6]. According to Persian scientists and hakims, people suffer from joint pains such as rheumatism and arthritis or from teeth pain can cope with these pains with methods that are completely natural and herbal [1]. However, it is not known that what compounds are responsible for removing the symptoms of food allergy.

Previous chemical investigations of American sycamore (*Platanus occidentalis* L.) have shown the presence of triterpenoids or flavonoids which are probably responsible for its anti-inflammatory and antinociceptive activity [8]. It is known very-well that treating effect of plants is related to their chemical or biochemical composition. Some volatile compounds such as terpenes, aldehydes, alcohols, ketones occur in plants as a result of the mostly biochemical metabolic pathways. For example, volatile terpene compounds (citronellal, linalool, β -cubebene, β -pinene, myrcene, limonene, γ -terpinene, p -cymene, terpinolene, copaene, caryophyllene, citronellyl acetate, citronellol, geranyl acetate and δ -cadinene) isolated from lime leaf were found to be effective in inhibiting tumors in the digestive tract [9] and had good antioxidant properties [10]. On the other hand, mono- and sesquiterpenes have been used in studies of geographic variation within the species in wild populations [11]. In general, fragrant and volatile compounds from plants have been used in food industry as additives, medicines and aromatherapy [12].

Based on the common uses of *Platanus orientalis* leaves in traditional folk medicine, in the present study we were objected to determine the volatile compounds profile of *Platanus orientalis* leaf.

2. MATERIAL and METHODS

The leaves were collected from plane trees about twenty years in Harbiye region of Hatay province. The leaves dried under normal atmospheric condition in summer. VCs analyze of leaves was performed according to the procedures described by Güler [13] with minor modification. Dried samples were cut into in small pieces in cold mortar and taken into headspace vials (Agilent, Palo Alto, CA, USA). Three mL NaCl solution (3 % concentration) was added in samples. The adsorption of VCs was carried out using Solid Phase Micro-extraction Technique (SPME) by a divinylbenzene/carboxen/polydimethylsiloxan fiber (Supelco, Bellefonte, PA, USA). The extraction of VCs was done in water bath at 60 °C. The samples were hold in water bath for 45 min than fiber was inserted to headspace vial and kept at 30 min. For desorption of VCs, fiber hold in injection port at 250 °C for 5 min. The VCs were analyzed by gas chromatography-mass spectrometry (GC-MS) using HP-Innowax capillary column (60 m x 0.25 mm id x 0.25 μ m film thickness). The oven temperature program was initially held at 50 °C for 5 min and then programmed from 50 °C by a ramp of 5 °C min⁻¹ up to 230 °C, which was held for 5 min. Peak identification was carried out by comparing the mass spectra with the NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) library, version 0.2 L. Peak areas (arbitrary units) were calculated from the total ion current. The results from the VCs analyses were expressed as the percentage composition of each compound.

3. RESULTS and DISCUSSIONS

A total of 140 volatile compounds including aldehydes (25), ketones (25), alcohols (21), terpenes (21), phenyls and phenols (15), alkenes (9), alkanes (8), esters (6), furans (5), others (5; alkyne, acid, compound with sulfur, lactone and unknown) were identified in the leaf of

Platanus orientalis tree. As shown in Table 1. and Figure 1., aldehydes were the most abundant compounds accounting for 32.4 % of total volatile compounds identified in *Platanus orientalis* leaf, followed by alcohols (23.5 %), ketones (18 %), terpenes (10 %), alkenes (4.8 %), alkanes (2.8 %), esters (2.7 %), phenyls and phenols (2.0 %) and furans (1.8 %). A total of 17 volatile compounds (Figure 2) including *trans,trans*-2,4-heptadienal (6.6 %), nonanal (6.5 %), benzaldehyde (6.4 %), *cis*-3-hexen-1-ol (6.3 %) and benzenmethanol (6.2 %), *trans*-2-hexenal (3.5 %), 3-phenyl-2-butanone (2.9 %), *trans*-3,5-dimethyl-1,6-octadiene (2.8 %), 6-methyl-5-hepten-2-one (2.7 %), octan-1-ol (2.4 %), *trans*-geranyl acetone (2.17 %), *trans*-4,8-dimethyl-1,3,7-nonatriene (2.0 %), phenyl methyl ketone (1.7 %), 6-methyl-3,5-heptadiene-2-one (1.6 %), 11H-dibenzo[b,e][1,4]diazepin-11-one-5,10-dihydro-5-[3-(methylamino) propyl] (1.4 %) benzenethanol (phenylethyl alcohol) (1.4 %) and β -ionone (1.0 %) were constituted the majority of volatile compounds, which accounted for 57 % of total volatiles identified in head space of the leaf. These VCs are the mainly products derived from unsaturated fatty acids, carotenoids, phenylpropanoid/benzenoid and terpenes.

The major volatiles, *trans, trans*-2,4-heptadienal has a fatty and green odor. It retards or prevents the development of 'off-flavors' in autoxidizing fats and oils [14]. Nonanal has a fatty and citrus-like flavor note. It is one of the main constituents in the oils of citrus fruits and also reported in over 200 food and beverages. *Cis*-3-hexen-1-ol and *trans*-2-hexenal with an intense grassy-green odor note are known as leaf alcohol and aldehyde, respectively. They act as an attractant to many predatory insects. It was observed that *cis*-3-hexen-1-ol had a less neurotoxicity effect in rat, compared with nonanal [12]. It is safer than nonanal.

Table 1. The percentage values of volatile compounds identified in *Platanus orientalis* leaf.

Volatile Compounds (140)	RT	RI	MEAN±SD
Aldehydes (25)			
Hexanal	10.55	842	0.12±0.02
2-Pentenal	12.37	1202	0.01±0.01
<i>trans</i> -Citral	13.71	1262	0.82±0.08
Heptenal	14.39	1291	0.12±0.03
<i>trans</i> -2-Hexenal	15.65	1353	3.46±0.40
Octanal	18.00	1484	0.75±0.11
<i>trans</i> -2-Heptenal	19.15	1561	0.67±0.32
Nonanal	21.19	1715	6.46±0.85
<i>trans,trans</i> -2,4-Hexadienal	21.64	1754	0.97±0.14
2-Octenal	22.30	1811	0.81±0.15
<i>trans,trans</i> -2,4-Heptadienal	23.33	1905	6.62±0.48
Benzaldehyde	25.09	2072	6.42±0.78
<i>trans,cis</i> -2,6-Nonadienal	26.51	>2100	0.43±0.02
<i>trans</i> -2-Decenal	27.88	>2100	0.59±0.15
Safranal	28.12	>2100	0.62±0.08
<i>cis</i> -Citral	28.84	>2100	0.14±0.03
2-Hydroxy-benzaldehyde	29.04	>2100	0.18±0.05
<i>trans,trans</i> -2,4-Nonadienal	29.35	>2100	0.97±0.14
4-Ethyl-benzaldehyde	29.67	>2100	0.19±0.07
2-Undecenal	30.42	>2100	0.59±0.14
<i>trans,cis</i> -2,4-Decadienal	30.76	>2100	0.34±0.03
Tridecanal	31.74	>2100	0.34±0.04
Myrtenal	32.71	>2100	0.14±0.03
Tetradecanal	36.17	>2100	0.54±0.15
4-Methoxy-benzaldehyde	36.62	>2100	0.06±0.01
	TOTAL		32.40±2.73
Ketones (25)			
3-Octanone	16.81	1413	0.29±0.07
2-Octanone	17.76	1470	0.13±0.03
6-Methyl-5-hepten-2-one	19.51	1586	2.56±0.10
Camphenilone	19.97	1619	0.30±0.09
Octamethyl-cyclotetrasiloxane	23.05	1879	0.12±0.04
11H-Dibenzo[b,e][1,4]diazepin-11-one, 5,10-Dihydro-5-[3-(methylamino)propyl]	23.42	1913	1.38±0.24
4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-, (R)-2-Butanone	23.49	1919	0.21±0.03
1,3-Dihydroxy-6-methoxy-1,2,3,4-tetrahydroquinolin-2-one	23.94	1960	0.19±0.02
3,5-Octadien-2-one	24.77	2042	0.24±0.07
4,8-Dimethyl-nona-3,8-dien-2-one	25.66	>2100	0.15±0.04
3,5-Octadiene-2-one	26.13	>2100	0.14±0.02
6-Methyl-3,5-heptadiene-2-one	26.70	>2100	1.57±0.25
Phenyl methyl ketone	28.31	>2100	1.69±0.50
Glycocyanidine	29.27	>2100	0.17±0.03
2-Hydroxy acetophenone	31.86	>2100	0.10±0.01
β-Damascenone	32.09	>2100	0.10±0.04
<i>trans</i> -Geranyl acetone	32.63	>2100	2.17±0.11
6-Methyl-5-hepten-2-one	32.80	>2100	0.34±0.17
3-Phenyl-2-butanone	33.01	>2100	2.87±0.07
6,10-Dimethyl-9-undecen-2-one	34.42	>2100	0.22±0.02
β-Ionone	34.62	>2100	1.02±0.29
2,3-Epoxy-β-ionone	35.78	>2100	0.67±0.09
6,10,14-Trimethyl-2-pentadecanone	38.00	>2100	0.70±0.10
3-Ethyl-4-methyl-1H-pyrrole-2,5-dione	41.01	>2100	0.24±0.04
5,6,7,7a-Tetrahydro-4,4,7a-trimethyl-2(4H)-benzofuranone	43.03	>2100	0.50±0.10
	TOTAL		18.08±0.20

Table 1. (Continued).

Alcohols (21)			
Hexen-1-ol	19.79	1605	0.62±0.12
<i>cis</i> -3-Hexen-1-ol	20.81	1684	6.32±0.77
1-Octen-3-ol	22.60	1838	0.95±0.07
2,6-Dimethyl-7-octen-2-ol	23.09	1883	0.13±0.03
<i>cis</i> -1,5-Octadien-3-ol	23.62	1931	0.56±0.09
Octan-1-ol	25.46	>2100	2.43±0.17
<i>trans</i> -2-Octen-1-ol	26.97	>2100	0.68±0.08
Nonan-1-ol	27.99	>2100	0.56±0.19
<i>cis</i> -Geraniol	31.34	>2100	0.59±0.28
α -Methyl-benzene-methanol	31.81	>2100	0.15±0.02
Cuminol	32.54	>2100	0.22±0.02
<i>cis</i> -Carveol	32.88	>2100	0.34±0.17
Benzene-methanol	33.25	>2100	6.13±1.46
Benzene-ethanol	34.02	>2100	1.36±0.31
<i>cis</i> -Farnesol	34.22	>2100	0.47±0.07
4-Phenyl-2-butanol	35.61	>2100	0.12±0.03
Nerolidol	36.28	>2100	0.98±0.04
2-Methoxy-benzene-ethanol	36.45	>2100	0.14±0.03
Octadecan-1-ol	38.79	>2100	0.16±0.07
(1 <i>S</i> *,6 <i>S</i> *,7 <i>S</i> *)-Tricyclo[5.3.2.0(1,6)]dodecan-7-ol	38.96	>2100	0.55±0.07
D11-Dodecene-1-ol	39.31	>2100	0.07±0.01
	TOTAL		23.51±1.19
Terpenes (21)			
Monoterpenes (10)			
dL-Limonene	14.77	1309	0.76±0.07
γ -Terpinene	16.55	1398	0.81±0.10
Styrene	16.98	1423	0.65±0.10
<i>trans</i> -4,8-Dimethyl-1,3,7-nonatriene	18.42	1510	1.98±0.05
Theaspirane A	24.32	1995	0.30±0.04
9-Hydroxy theaspiran A	25.32	2094	0.13±0.04
<i>cis</i> - α -Bisabolene	28.91	>2100	0.11±0.01
Camphene	29.09	>2100	0.34±0.10
p-Cymene	33.39	>2100	0.48±0.15
Allo ocimene	33.68	>2100	0.14±0.02
	TOTAL		5.70±0.24
Sesquiterpenes (11)			
α -Ylangene	22.98	1873	0.28±0.10
<i>trans</i> -Caryophyllene	26.88	>2100	0.40±0.11
β -Cyclocitral	27.50	>2100	0.85±0.05
α -Humulene	28.65	>2100	0.94±0.10
Zingiberene	29.57	>2100	0.21±0.08
β -Bisabolene	29.75	>2100	0.39±0.18
<i>trans,trans</i> - α -Farnesene	30.13	>2100	0.24±0.03
Δ -Cadinene	30.54	>2100	0.79±0.16
<i>trans</i> - β -Farnesene	31.01	>2100	0.08±0.04
1 <i>S</i> - <i>cis</i> -Calamenene	32.32	>2100	0.26±0.10
<i>cis</i> - α -Bisabolene epoxide	37.50	>2100	0.08±0.02
	TOTAL		4.53±0.52
Phenyls and Phenols (15)			
1,2,3,4-Tetramethyl-benzene	17.34	1445	0.25±0.10
2-Methyl-1,4-benzene-diol	25.98	>2100	0.13±0.04
<i>trans</i> -Anethole	32.23	>2100	0.26±0.12
2-Methyl-naphthalene	33.83	>2100	0.18±0.03
Phenol	35.90	>2100	0.15±0.05
5-Ethyl-m-xylene	36.08	>2100	0.05±0.00
2-Propenyl-benzene	36.71	>2100	0.17±0.02
2,5-Dimethyl-phenol	37.10	>2100	0.04±0.01

Table 1. (Continued).

1-Methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-imino-naphthalene	37.20	>2100	0.07±0.01
2,6-Dimethyl-phenol	37.31	>2100	0.23±0.03
m-Cresol	37.55	>2100	0.12±0.04
<i>trans</i> -Stilbene	38.64	>2100	0.14±0.01
Tymol	39.80	>2100	0.06±0.01
Biphenylene	40.06	>2100	0.10±0.01
3-Ethyl-1-naphthol	40.46	>2100	0.09±0.04
TOTAL			2.04±0.20
Alkenes (9)			
4-Methyl-2,7-octadiene	19.39	1577	0.31±0.07
7-Methyl-3,4-octadiene	20.17	1635	0.31±0.13
<i>trans</i> -3,5-Dimethyl-1,6-octadiene	21.46	1738	2.80±0.41
<i>cis</i> -3-Ethyl-2-methyl-1,3-hexadiene	21.93	1779	0.12±0.02
2,5-Dimethyl-2,4-hexadiene	24.54	2020	0.08±0.00
4,8-Dimethyl-1,7-nonadiene	25.88	>2100	0.13±0.02
4-Methyl-2,6-octadien	27.06	>2100	0.70±0.26
1,2,4,4-Tetramethyl-cyclopentene	27.62	>2100	0.26±0.06
<i>trans</i> - 6-(2-Butenyl)-1,5,5-trimethyl-cyclohexene	33.54	>2100	0.10±0.02
TOTAL			4.82±0.51
Alkanes (8)			
Tetradecane	21.06	1704	0.41±0.05
9-Methyl-nonadecane	22.16	1798	0.57±0.16
Octadecane	22.75	1852	0.25±0.07
Pentadecane	23.82	1949	0.17±0.07
Hexadecane	26.38	>2100	0.21±0.01
Heptadecane	28.79	>2100	0.71±0.04
<i>cis</i> -1,2-Divinylcyclohexane	30.23	>2100	0.32±0.09
Cyclododecane	34.76	>2100	0.15±0.04
TOTAL			2.78±0.37
Esters (6)			
Benzoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	13.44	1250	0.42±0.07
Tiglic acid, <i>cis</i> -3-hexenyl ester	28.38	>2100	0.28±0.04
Acetic acid, phenyl methyl ester	30.00	>2100	0.75±0.16
Benzoic acid, 2-hydroxy-, methyl ester	31.27	>2100	0.74±0.41
Benzoic acid, <i>cis</i> -3-hexen-1-ol ester	38.35	>2100	0.42±0.08
Phthalic acid, ethyl ester	42.95	>2100	0.12±0.03
TOTAL			2.72±0.54
Furans (5)			
2-Ethyl-furan	5.95	914	0.01±0.00
2-Pentyl-furan	15.94	1367	1.00±0.05
2-(2-Propenyl)-furan	22.37	1817	0.07±0.02
Dihydro-β-agarofuran	29.20	>2100	0.28±0.04
2-Methyl-5-(1,1,5-trimethyl-5-hexenyl)-furan	34.88	>2100	0.43±0.11
TOTAL			1.80±0.11
Others (5)			
Unknown	18.92	1545	0.86±0.14
4-Nonyne	22.04	1788	0.25±0.09
Ethyl-dimethyl-thiophene	31.07	>2100	0.22±0.06
Mint furanone	34.15	>2100	0.07±0.01
<i>trans,trans</i> -2,4-Hexadienoic acid	38.53	>2100	0.21±0.02
TOTAL			1.61±0.02

RI: retention index based on the identified VCs retention time (RT) and calculated from a linear equation between each pair of straight alkanes (C5-C25).

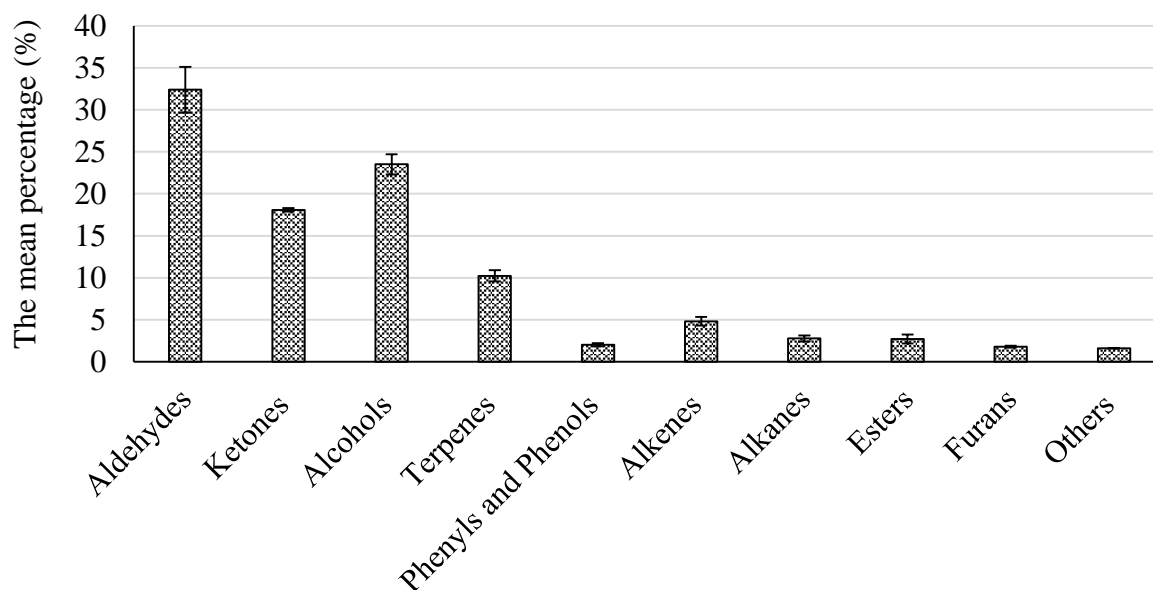


Figure 1. The percentage of volatile compounds identified in *Platanus orientalis* leaf according to the chemical groups.

Aldehydes, alcohols and also ketone containing six, seven, eight and nine carbons such as *cis*-3-hexen-1-ol, *trans*-2-hexenal, *trans*, *trans*-2,4-heptadienal, 2-octanone, 1-octanol and nonanal are formed either from linoleic acid or linolenic by oxidative degradation or from β -scission reactions via unsaturated fatty acids [15]. Glycolipids and phospholipids are rich in linolenic acid and linoleic acids [16]. Octanol or volatiles compounds containing octane give a typical fungal odor. β -Ionone, benzaldehyde, benzenethanol, *cis*-3-hexen-1-ol and nonanal were identified in various tea types (white, green e.g.) as main volatile compounds.

Another major VC benzenemethanol is used in perfumes and flavors, dyes for nylon, textiles, and plastics, hair products, plastic packaging and cosmetic industry. But, it is listed as a liver toxicant, neurotoxicant, and immunotoxicant [17]. Benzaldehyde, simplest aromatic aldehyde, is accepted in the European Union as a flavoring agent since it occurs naturally in many foods and is the primary component of bitter almond oil. Benzaldehyde having carcinostatic (anti-cancer) properties does not accumulate in any specific tissues and is metabolized, and then excreted in urine [18].

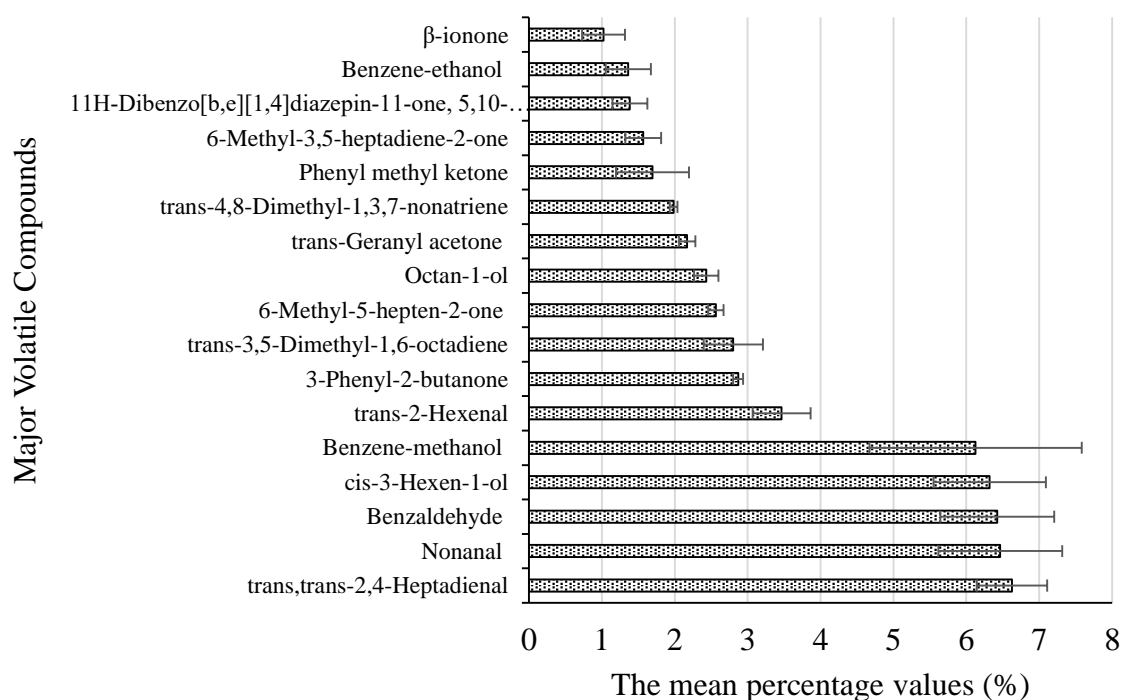


Figure 2. Major volatile compounds identified in *Platanus orientalis* leaf.

Actually, benzaldehyde, benzenmethanol, 3-phenyl-2-butanone and benzenethanol are phenyl propanoid/benzenoid derivatives [19]. These compounds and also VCs derived from unsaturated fatty acids were more abundant over the other VCs, in terms of their percentages.

Trans-4,8-dimethyl-1,3,7-nonatriene was the most abundant terpene identified in leaf. This compound was found to be in bergamot oil. It was reported that plants synthesize and emit to volatile compounds such as mainly *trans*-4,8-dimethyl-1,3,7-nonatriene and *cis*-3-hexen-1-ol in response to insect herbivory [20]. Geranyl acetate is a natural constituent of most essential oils and is used in cosmetic industry as a flavoring agent. β -Ionone is a product obtained from oxidative degradation of β -carotene [19]. Ketone 6-methyl-3,5-heptadiene-2-one is a product of lycopene degradation, which is one of main constituents of watermelon flavor [21]. Actually, both β -carotene and lycopene are terpene. It is well-known that terpenes have therapeutic properties such as antimicrobial and anticancerogenic.

4. CONCLUSION

A complex volatile compounds profile including the carotenoid, the unsaturated fatty acid, the terpene, the phenylpropanoid/benzenoid derivatives, the glycoside hydrolysis and the Maillard reaction products (furans) was identified in *Platanus orientalis* leaves. The diversity of VCs identified indicates that POLs may have a complex chemical and also biochemical composition with the probably majority of phenylpropanoid/benzenoid and unsaturated fatty acids. It is probably that the degradation products derived from phenylpropanoid/benzenoid and unsaturated fatty acids or themselves may be mainly related to the treating effects of Plane tree leaf in folk medicine.

Conflict of Interests

Authors declare that there is no conflict of interests.

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