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Comparative compositions of essential oils of *Citrus aurantium* growing in different soils

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Abstract

Leaves and peel hydrodistilled essential oils of *Citrus aurantium* from Constantine (Algeria) were analyzed by GC and GC/MS. The major compounds of the leaves essential oil were linalool (18.6%), γ-terpinene (6.9 %) and α-terpineol (15.1%) while the main components of the peel essential oil were linalool (12%), *cis*-linalool oxide (8.1%), *trans*-carveol (11.9%), *endo*-fenchyl acetate (5.5%) and carvone (5.8%).

Keywords:Citrus aurantium; essential oil; linalool; α-terpineol; *cis*-linalool oxide; *trans*-carveol, *endo*-fenchylacetate, carvone.

1. Introduction

Citrus plants (Rutaceae) [1] are the most popular and important food in the world [2]. Besides their pleasant flavor, they provide functional components such as vitamin C, folic acid, fibers and essential oils [3]. *Citrus aurantium* L. var *amara* commonly named bitter or sour orange "Narenja Agria" [4], is widespread in Central and South America but mainly in the Mediterranean countries [5], where it is used in a large area from the industry as a flavoring agent or a fragrance to medicine as a nasal decongestant and a dieting agent [6]. The chemical compositions of leaves essential oils (LEO) and peel essential oils (PEO) from bitter orange have been reported in the literature, where the main compounds in the LEO were linalool and linalyl acetate [7] whereas the PEO were dominated by limonene [8].

In continuation of our works on Rutaceae [9-13], we report here, the composition of the LEO and PEO of *Citrus aurantium* collected from Constantine (Eastern Algerian). A comparative study of the compositions of essential oils of *Citrus* growing in different countries is also carried on.

2. Experimental

Plant material

Citrus aurantium was collected in March 2013 from Constantine. A voucher specimen was deposited at the herbarium of the Laboratory of Therapeutic Substances, University of Constantine 1 (LOST ZK Ca/03/10).

Extraction

The hydrodistillation of *Citrus aurantium* leaves and peel, for 3 h in a Clevenger-type apparatus, yielded in the order 0.3 % and 0.7% (w/w) of a yellow oil which was stored at +4 °C, until analyzed by GC and GC-MS.

GC and GC/MS

GC analysis was performed on a Shimadzu GC17A gas chromatograph equipped with a cross-linked DB5-MS column (40 m × 0.18 mm, film thickness 0.18 μm). The oven temperature was programmed as isothermal at 60°C for 5 min, then raised to 275°C at 5°C/min and held at this temperature for 5 min. Helium was used as the carrier gas at a rate of 1 ml/min. GC/MS was performed using a Shimadzu QP5050 mass selective detector. Operating conditions were the same as for the analytical GC. The MS operating parameters were as follows: ionization potential, 70 ev; ionization current, 2A ion source temperature, 200ºC; resolution, 1000. scan time, 5 s; scan mass range, 40–400 u; split ratio, 1:10.

Identification of components

Essential oils components were identified based on their retention indices (determined with reference to a homologous series of normal alkanes), and by comparison of their mass spectral fragmentation patterns with those reported in the literature [14;15] and for the major components.

3. Results and discussion:

38 compounds were characterized in the LEO representing 95% of total oil content, with linalool (18.6%), γ-terpinene (6.9%) and α-terpineol (15.1%) as main components, whereas 32 compounds representing 96% of total oil content were identified in the PEO with the prevalence of linalool (12.0 %), *cis*-linalool oxide (8.1 %), *trans*-carveol (11.9%), *endo*-fenchyl acetate (5.5 %) and carvone (5.8%) as reported in table 1.

Table 1. Chemical composition of LEO and PEO of *Citrus aurantium* collected from Constantine.

Compounds [a]	**RI**[b]	**LEO (%)**	**PEO (%)**
n-Octane	798	-	1.5
n-Nonane	897	-	0.2
α-Thujone	928	-	0.5
α-Thujene	930	0.3	-
α-Pinene	937	1.7	2.3
β-Pinene	977	1.6	2.3
Sabinene	974	1.8	-
n-Decane	998	0.2	1.5
δ-3-Carene	1009	0.9	-
γ-Terpinene	1015	7.0	-
p-Cymene	1024	2.0	0.3
Limonene	1028	0.5	2.5
1,8-Cineole	1032	3.0	3.6
Linalool	1095	18.6	12.0
1,8-Cineole	1097	2.6	3.5
p-Mentha-1,3,8- triene	1110	-	1.5
cis-Linalool oxide	1133	0.5	8.1
cis-Limonene oxide	1135	-	0.8
Camphor	1142	2.0	1.8
β-Citronellol	1153	1.8	
Menthone	1154	-	0.5
Isomenthone	1165	0.1	-
p-Cymen-8-ol	1187	-	2.9
α-Terpineol	1190	15.1	-
Methyl chavicol	1198	0.7	-
trans-Carveol	1218	-	11.9
endo-Fenchyl alcohol	1222	3.2	-
endo-Fenchyl acetate	1222	-	5.5
β-Citronellol	1230	2.7	-
cis-Carveol	1232	-	3.8
Carvacrol	1233	2.3	-
exo-Fenchyl acetate	1237	-	0.3
Pulegone	1240	1.3	2.0
Neral	1242	1.7	-
Carvone	1244	0.8	5.8
Piperitone	1256	-	3.2
cis-Geraniol	1258	1.8	-
Geranial	1272	1.9	-
trans-Anethole	1288	-	2.3
Safrole	1290	-	0.8
Thymol	1295	1.4	1.8
Carvacrol	1301	-	3.4
Citronellyl acetate	1360	1.7	-
Geranyl acetate	1392	-	2.4

β-Elemene	1397	3.0	-
Dodecanal	1415	-	1.5
β-Caryophyllene	1428	1.7	-
Aromadendrene	1444	0.2	-
β-Selinene	1493	0.5	-
α-Selinene	1501	0.6	-
cis-Nerolidol A	1539	0.2	-
Elemol	1559	0.8	-
Spathulenol	1588	3.3	-
Caryophyllene oxide	1592	3.2	2.4
β-Oplopenone	1621	3.4	-
cis-Nerodiol	1687	-	2.1
α-Sinensal	1769	2.1	-
Benzyl benzoate	1781	0.1	-
total	-	**95%**	**96%**

[a] RI (retention index) measured relative to n-alkanes (C_6-$C2_4$) using a DB5 MS column
[b] Compounds listed in order of their RI.

Oxygenated and aliphatic monoterpenes are predominent in the LEO and PEO of *Citrus aurantium* collected from Constantine, where linalool (18.6% and 12%) is the main component of both essential oils. Except with the latter component, the composition of the LEO and PEO are very different. A lot of works have been reported on the essential oil of *Citrus* species, table 2 reports the plant material data.

Table 2: Material plant data of reported essential oil of *Citrus.*

Code	**Species**	**Origin**	**reference**
Ca1	*Citrus aurantium* L.	Zaghouan, Tunisia.	[16; 17]
Ca2	*Citrus aurantium* L.	Nabel, Tunisia	[18]
Ca3	*Citrus aurantium* L.	Tunisia	[19]
Ca4	*Citrus aurantium* L.	Northern Greece	[20]
Ca5	*Citrus aurantium* L.	Corsica	[21]
Ca6 Ca7	*Citrus aurantium* L.	Antalya, Marmaris, Turkey	[22]
Ca8	*Citrus aurantium* L.	Italy	[23]
Ca9 Ca10 Ca11	*Citrus aurantium* L.	Egypt	[23]
Ca12	*Citrus aurantium* L. "chinotto"	Italy	[24]
Ca13	*Citrus aurantium* L.	Brazil	[21]
Ca14	*Citrus aurantium* L.	Banes, eastern of Cuba	[25]
Ca15	*Citrus aurantium* L.	Iran	[26]
Ca16	*Citrus aurantium* L.	Mauritius	[27]
Cgo	*Citrus grandis* obseck	Zaghouan, Tunisia	[16; 17]
Crb1	*Citrus reticulate* blanco	Zaghouan, Tunisia	[16; 17]
Crb2	*Citrus reticulate* blanco	India	[28]
Cs	*Citrus sinensis*	Mitidja, Algeria	[29]
CsMal	*Citrus sinensis* Maltaise blanc	Zaghouan, Tunisia	[16; 17]
CsV	*Citrus sinensis* Valancia late	Zaghouan Tunisia	[16; 17]
CsMes	*Citrus sinensis* Meski	Zaghouan, Tunisia	[16; 17]
CsT	*Citrus sinensis* Thomson Novel	Zaghouan, Tunisia	[16; 17]
CsH	*Citrus sinensis* Hongjiang	China	[30]
CsW	*Citrus sinensis* Washington Navel	China	[30]

From table 3, representing the major components of LEO and PEO of *Citrus aurantium,* growing in the Mediterranean area, it appears that PEO is characterized by limonene as a chemotype, it is found at its highest percent in Ca1 (96.6%) growing in Tunisia [16; 17]. The LEO is represented by linalool, more abundant in Ca1

(64.1%) [16; 17] and Ca2 (62.4%) [18] from Tunisia, Ca4 (58.2%) from Greece [20] and Ca9 (54.6%) from Egypt [23], it is followed by linalyl acetate, widespread in a high to a moderate amount in Ca9 (54.6%) [21], Ca5 (35%) from Corsica [21], Ca2(16.1%) [18] both from Tunisia and Ca4 (12.4%) [22]. α-Terpineol is mainly found in Ca3 (11.7%) [19], Ca4 (7.1%) [20], Ca5 (8.7%) [21], followed by geranyl acetate in Ca3 (6 %) [19], Ca5 (5.6%) [21] and geraniol in Ca3 (7.1%) [19] and Ca5 (5.9%) [21].

Table 3: Percentages of major components (≥5%) of LEO and PEO of *C. aurantium* growing in the Mediterranean area

Compounds*	Percentage (%)															
	Ca1 [16; 17]		Ca2 [18]	Ca3 [19]		Ca4 [20]		Ca5 [21]		Ca6 [22]	Ca7 [22]	Ca8 [23]	Ca9 [23]	Ca10 [23]	Ca11 [23]	Ca12 [24]
	L	P	L	L	P	L	P	L	P	P	P	P	L	P	P	P
Limonene	-	96.9	-	-	90.6	-	94.7	-	91.8	94.4	93.7	93.4	-	96.5	94.5	80.1
Linalool	64.1	-	62.4	36.8	-	58.2	-	26.3	-	-	-	-	27.8	-	-	5.5
Linalyl acetate	-	-	-	22.1	-	12.4	-	35	-	-	-	-	54.6	-	-	-
α-Terpineol	-	-	-	11.7	-	7.1	-	8.7	-	-	-	-	-	-	-	-
Cavacryl methyl oxide	8.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Geranyl acetate	-	-	-	6.0	-	-	-	5.6	-	-	-	-	-	-	-	-
Geraniol	-	-	-	7.1	-	-	-	5.9	-	-	-	-	-	-	-	-

L: leaves, P: peel
* The compounds appear according to their RI

In table 4, representing the major components of *C. aurantium* growing in other countries, as reported previously, limonene is as a chemotype of the PEO, its highest yield was in Ca13 (93%) growing in Brazil [21]. Except LEO of Ca15 from Iran [26], which is distinguished by its high content in limonene (62%) and low content in linalool (7.5%), LEO are linalool chemotype with the highest percentage in Ca16 from Mauritius (66.1%) [27]. Beside the common main presence of linalool (24.1%), Ca13 LEO from Brazil is characterized by the exclusive main presence of linalyl acetate (36.7%), geranyl acetate (5.8%) and geraniol (6%) [21] while cavacryl methyl oxide was exclusive to Ca1 (8.1%) [16; 17].
Thus, PEO of *C. aurantium* growing in the Mediterranean area and other countries are limonene chemotype (62.0%-96.6%). Exceptionally, linalool (5.5%) is mainly found in the PEO of Ca12 from Italy [24]. In another part, LEO of *C. aurantium* are linalool chemotype except for Ca15 from Iran which is limonene chemotype [26].

Table 4: Percentages of major components (≥5%) of LEO and PEO of *C. aurantium* growing in other countries

Compounds*	Percentage (%)				
	Ca13 [21]		Ca14 [25]	Ca15 [26]	Ca16 [27]
	L	P	P	L	L
Limonene	-	93	86.2	62	-
Linalool	24.1	-	-	7.5	66.1
Linalyl acetate	36.7	-	-	-	-
α-Terpineol	8.8	-	-	-	-
Geranyl acetate	5.8	-	-	-	-
Geraniol	6.1	-	-	-	-

* The compounds appear according to their RI

From table 5, as for PEO of *C. aurantium* presented in tables 3 and 4, almost PEO of *C. sinensis* are limonene chemotype [27;14;15]; the highest content (97.3%) is found in CsMes from Zaghouan-Tunisia [17] whereas the lowest content (78.5%) is found in Cs from Mitidja-Algeria [27] which is also distinguished by the main presence of β-myrcene (5.3%). However, the compositions of LEO of *C. sinensis* are different from those of *C. aurantium* LEO which were linalool chemotype. Isoborneol is a chemotype of LEO of CsMal (55.8%), CsV (54.6%) and

CsT (30.7%) from Tunisia [14 ; 15], followed by linalool, more abundant in CsMes (45.8%), CsT (23.1%) and CsV (22.3%) [14 ; 15]. Cavacryl methyl oxide characterized the LEO of CsMes (27.3%) and CsT (15.9%). The main presence of terpinolene (5.1%), γ-terpinene (5%), citronellol (12.2%) is exclusive to CsMal, Csv, CsMes and CsT [14;15], respectively.

Table 5: Major component (≥5%) of LEO and PEO of *C. sinensis.*

Compounds*	Percentage (%)								
	CsMal [16 ; 17]		CsV [16; 17]		CsMes [16; 17]		CsT [16; 17]		Cs [29]
	L	P	L	P	L	P	L	P	P
β-Myrcene	-	-	-	-	-	-	-	-	5.3
γ-Terpinene	-	-	5.0	-	-	-	-	-	-
Terpinolene	5.1	-	-	-	-	-	-	-	-
Limonene	-	96.0	-	96.3	-	97.3	-	96.6	78.5
Linalool	-	-	22.3	-	45.8	-	23.1	-	-
Isoborneol	55.8	-	54.6	-	-	-	30.7	-	-
α-Terpineol	-	-	-	-	15.5	-	-	-	-
Citronellol	-	-	-	-	-	-	12.2	-	-
Cavacryl methyl oxide	-	-	-	-	27.3	-	15.9	-	-
8-Hydroxymenthol	-	-	-	-	7.9	-	-	-	-

*The compounds appear according to their RI

Table 6 shows that PEO of *C. reticulate* and *C. grandis* are also limonene chemotype. PEO of *C. grandis* (Cgo) from Zaghouan (Tunisia) is the highest limonene-content (95.4%) [17]. PEO of C. reticulates from India (Crb2), which is the lowest limonene-content (46.7%), is also characterized by the main presence of geranial (19.0%) and neral (14.5%). However, LEO of Cgo is not linalool chemotype, it's mainly characterized by isoborneol (45.2%), linalool (25.9%) and linalyl acetate (22.8%) [16;17].

Table 6: Major components (≥5%) of PEO and LEO of *C. grandis* and PEO of *C. reticulate*

Compounds*	Percentage (%)			
	Crb1 [16; 17]	Crb2 [28]	Cgo [16; 17]	
	L	P	L	P
Limonene	-	92.6	-	95.4
Linalool	73	-	25.9	-
Isoborneol	-	-	45.2	-
Linalyl acetate	10.9	-	22.8	-
Geranial	-	-	-	-
Neral	-	-	-	-

*Compounds listed in order of their RI

Thus, the composition of the PEO of *C. aurantium*, collected from Constantine, is different from the reported PEO of *Citrus* genus which are limonene chemotype. It's mainly characterized by linalool (12.0%), *cis*-linalool oxide (8.1%), *trans*-carveol (11.9%), *endo*-fenchyl acetate (5.5%) and carvone (5.8%). However, linalool (18.6%), γ-terpinene (6.9%) and α-terpineol (15.1%) are the main components of the LEO. γ-Terpinene (5.0%) is also mainly found in the LEO of *C. sinensis* Valancia from Zaghouan (Tunisia) (CsV) [16] while α-terpineol (11.7%, 7.1%, 8.7%, 8.8%, 15.5%) is mainly characterizing LEO of *C. aurantium* (Ca3) from Tunisia [19], Ca4 from Northern Greece [20], Ca5 from Corsica [21], Ca13 from Brazil (8.8%) and of *C. Sinensis* from Mitidja (Algeria), respectively. Only linalool is shared with both LEO and PEO of *C. aurantium* from Constantine. This component has been mainly found in the reported anticorrosive essential oil of *Warionia saharea* [31]. Thus, it'll be interesting to test the LEO and PEO of *C. aurantium* from Constantine, as anticorrosive inhibitors [32].

Conclusion

Through this investigation, it appears that limonene is the chemotype of PEO of *Citrus* genus whereas the LEO are linalool, linalyl acetate or isoborneol chemotypes, differently from PEO and LEO of *C. aurantium* collected from Constantine and LEO of *C. aurantium* from Iran which is characterized by its high content in linalool and low limonene-content. The PEO of *C. aurantium* from Italy is distinguished by the main presence of linalool together with the chemotype limonene. LEO of *C. aurantium* of Constantine is characterized by the main presence of linalool, γ-terpinene and α-terpineol while the major components of the PEO were linalool, *cis*-linalool oxide, *trans*-carveol, *endo*-fenchyl acetate and carvone.

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