http://dx.doi.org/10.4314/jpb.v8i2.6

Vol. 8 no. 2, pp. 98-102 (September 2011)

http://ajol.info/index.php/jpb

Journal of
PHARMACY AND BIORESOURCES

A comparison of the constituents of essential oils of *Citrus limon* peel and *C. aurantifolia* fruit

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Received 8th June 2011; Accepted 12th July 2011

Abstract
Essential oils of lime (*Citrus aurantifolia*) whole fruits and lemon (*Citrus limon*) peel from Nigeria have been analysed by combined GC and GC-MS. Both oils were of similar composition, but with differences in yields of components. The oils are composed largely of monoterpene hydrocarbons (*C. aurantifolia* 71.6 %; *C. limon* 81.2 %) and oxygenated monoterpenes (*C. aurantifolia* 23.4 %; *C. limon* 16.7 %). Limonene was the major component in lemon peel oil (65.4 %), while limonene (43.1 %) and ß-pinene (14.2 %) were characteristic of lime oil. Other monoterpenes such as *γ*-terpinene, *α*-terpineol, neral and geranial also occurred in moderate amounts in both oils. The sesquiterpenes amounted to 3.5 % in *C. aurantifolia* and 1.3 % in *C. limon*.

Keywords: *Citrus limon; Citrus aurantifolia;* Fruit peel; Rutaceae; Essential oil; Limonene; ß-Pinene

INTRODUCTION

Citrus aurantifolia Swingle, and *Citrus limon* (L.). N. L. Burm. family Rutaceae, have been cultivated for centuries throughout Asia and the Middle East (Burkill, 1995). In Southeast Asia, the peel of several local *Citrus* species including *C. aurantifolia* is used for cooking. Lime juice resembles lemon juice in its acidity, but is much more aromatic and is used in local medicine for treating wounds and eye troubles. On the other hand, lemon juice has found application in digestive troubles and jaundice in Nigeria (Burkill, 1995). Several *Citrus* species (Choi and Sawamura, 2001; Lota *et al.*, 2002; Selvaraj *et al*., 2004; Omobuwajo *et al.*, 2005; Smadja *et al*., 2005; Craske *et al*., 2005) have been investigated for their essential oils. The leaf essential oils of the Nigerian varieties of lime (Ekundayo *et al*., 1991) and lemon (Ekundayo *et al.*, 1990) were reported to yield limonene, neral and geranial as major constituents. Recently, essential oils composition from the peels of a related species, *C. sinensis* (Omobuwajo *et al.*, 2005), *C. reticulata* and *C. paradisi* (Karioti *et al.*, 2007) from Nigeria were reported.

Apart from the reports on the leaf oil constituents of these two plants, no other study on the Nigerian lime peel and lemon fruits is reported. We therefore investigated

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ISSN 0189-8442

oils from *C. limon* peel and *C. aurantifolia* fruit for their constituents.

EXPERIMENTAL

Plant material and extraction of oil. Fresh fruits of *C. aurantifolia* and *C. limon* were harvested from trees growing on the Obafemi Awolowo University (OAU) campus, and authenticated at the Botany Department (OAU) herbarium (*C. aurantifolia* UHI 4575; and *C. limon* UHI 4575A). Owing to the difficulty in removing the peels of *C. aurantifolia*, the whole fruits were cut into pieces and hydrodistilled for essential oil (light yellow, 0.56 % fresh weight) in a Clevenger-type apparatus according to the British Pharmacopoeia (1980). Peels of lemon fruits were similarly hydrodistilled (yellow, 0.25 %). The oils were stored separately in screw-capped vials and refrigerated until needed.

Gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS). The hydrodistillates from all samples were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). GC analyses were performed using a Perkin Elmer Autosystem Gas Chromatograph equipped with a fused silica DB-5 column (30 m × 0.25 mm, 0.25 µm film thickness composed of 5%-phenyl methylpolysiloxane [J & W Scientific]. Oven temperature was programmed from 60 -180 °C at 3 °C/min, injector and flame ionization detector (FID) temperature, at 300 and 320 °C, respectively. Helium was used as carrier gas at a flow rate of 1.49 mL/min under a column head pressure of 12.5 psi. Injections (0.5 µL) were performed in a split/splitless injector, in the split mode (1:13). For each essential oil, the peak area percentages were calculated as mean values of three injections. GC/MS analyses were performed with a Perkin-Elmer 8500 Gas Chromatograph equipped with a fused silica DB-5 as that of GC, connected with a Finnigan MAT Ion Trap Detector (ITD; software version 4.1) operating in EI mode at 70 eV. Injector, interface and ion-source temperatures were 300 °C, 260 °C and 220 °C, respectively. The oven temperature program and injection conditions were as described above for GC, final column temperature, 285 °C maintained for 15 min.

Helium was used as carrier gas at a flow rate of 1.49 mL/min with a column head pressure of 12.5 psi. The identification of the components was based on comparison of their mass spectra with those of Wiley and NBS Libraries using a computer search, and those described by Adams (2001), as well as by comparison of their retention indices with standard mixture of *n*-alkanes (*n*-octane to *n*-tetratriacontane) under the same condition.

RESULTS

Gas chromatographic-mass spectroscopic analysis of oils of *C. aurantifolia* fruits and *C. limon* fruit peel indicated both oils to comprise mainly monoterpenes (95 % in lime and 97.9 % in lemon) (Table 1). Sixty compounds were identified in lime fruit oil and 46 in lemon peel. The monoterpene group is represented mainly by hydrocarbons (71.6 % in lime and 81.2 % in lemon) which consisted chiefly of limonene (65.4 % in lemon), and limonene (43.1 %) and ß-pinene (14.2 %) in lime (Table 1).

The sesquiterpenes were present in relatively smaller proportions in *C. aurantifolia* fruit (3.5 %) and *C. limon* peel (1.3 %) oils investigated (Table 1). Notable representatives included (*cis*)-caryophyllene and *trans*-*α*-bergamotene in both oils, while (*cis*, *cis*)-*α*-farnesene and *β*-bisabolene occurred as additional sesquiterpene hydrocarbons in lime fruit and lemon peel oils respectively (Table 1). Other sesquiterpenes were detected in trace quantities (≤ 0.1 %).

Table 1: Composition of essential oils of *Citrus limon* peel and *C. aurantifolia* fruit

Compound	RT (min.)	*Citrus aurantifolia* (%)	*Citrus limon* (%)
α-thujene	4.09	0.2	0.2
α-pinene	4.25	1.6	0.9
camphene	4.56	0.3	tr
sabinene	4.83	Tr	0.6
β-pinene	5.32	**14.2**	4.0
myrcene	5.58	1.1	1.3
n-octanal	5.84	0.1	0.1
α-phellandrene	5.94	0.3	0.1
α-terpinene	6.30	0.9	0.3
o-cymene	6.52	0.2	-
limonene	6.93	**43.1**	**65.4**
1,8-cineole	7.00	0.1	-
benzene acetaldehyde	7.07	Tr	-
(*E*)- β-ocimene	7.29	0.4	0.2
γ-terpinene	7.73	7.4	7.7
trans-linalool oxide (furanoid)	8.06	0.3	tr
terpinolene	8.65	1.9	0.5
linalool	9.03	-	0.7
trans-sabinene hydrate	9.05	1.1	-
n-nonanal	9.15	0.1	0.1
endo-fenchol	9.47	0.4	-
1-terpineol	10.26	0.1	-
cis-limonene oxide	10.35	-	tr
trans-pinocarveol	10.40	0.1	-
cis- β-terpineol	10.63	0.2	-
camphor	10.70	-	0.1
citronellal	11.07	-	0.1
cis-linalyl oxide (pyranoid)	11.53	1.6	0.1
cis-3-pinanone	11.73	0.1	-
terpinen-4-ol	12.03	3.2	1.1
iso-verbanol	12.18	0.2	0.1
α-terpineol	12.71	7.7	2.6
dihydro carveol	12.82	0.1	tr
cis-piperitol	12.97	-	tr
n-decanal	13.14	0.4	-
trans-piperitol	13.20	-	tr
trans-carveol	13.64	-	0.1
nerol	14.09	0.3	0.9
citronellol	14.17	0.4	-
neral	14.67	2.6	4.3
piperitone	15.04	-	tr
geraniol	15.24	0.6	0.4
geranial	15.98	4.0	6.0
bornyl acetate	16.44	Tr	-
thymol	16.57	-	tr
trans-sabinyl acetate	17.02	Tr	-
n-undecanal	17.14	Tr	-
δ-elemene	18.62	0.1	-
citronellyl acetate	19.35	Tr	tr
neryl acetate	19.81	0.1	0.1
geranyl acetate	20.64	0.2	0.1
β-elemene	20.91	0.1	-

n-dodecanal	21.65	0.1	-
cis-*α*-bergamotene	21.89	Tr	tr
(*E*)-caryophyllene	21.99	0.4	0.3
γ-elemene	22.62	0.1	-
trans-*α*-bergamotene	22.77	0.6	0.3
α-humulene	23.03	Tr	tr
(*E*)- *β*-farnesene	23.37	0.1	tr
β-santalene	23.68	0.1	0.1
β-chamigrene	24.32	Tr	-
germacrene D	24.51	0.1	-
β-selinene	24.97	0.1	-
α-zingiberene	25.21	0.1	tr
(*E*,*E*)-*α*-farnesene	25.81	1.5	-
β-bisabolene	25.90	-	0.5
β-sesquiphellandrene	26.84	Tr	-
(*E*)-*γ*-bisabolene	27.53	0.1	-
β-bisabolol	31.91	Tr	tr
α-bisabolol	32.57	0.1	0.1
Total (*identified compounds*)		**99.2**	**99.5**

DISCUSSION

The occurrence of limonene as a major component in these oils is in accordance with previous reports on *Citrus* species (Omobuwajo *et al*., 2007; Smadja *et al.*, 2005; Karioti *et al.*, 2007). Other monoterpenes such as *γ*-terpinene, *α*-terpineol, neral and geranial occurred in both oils in moderate proportions (2.6-7.7 %). Gamma-terpinene and *α*-terpineol also occurred in comparable yields in *C. reticulata* peel oil from Nigeria investigated by Karioti *et al* (2007). The yield of *α*-terpineol (7.7 %) was higher in lime fruit oil, while lemon peel oil gave higher amounts of neral (4.3 %) and geranial (6 %). In addition, terpinen-4-ol (3.2 %) and ß-pinene (4 %) were detected in lime and lemon oils respectively. The composition of oils of both *Citrus* species in our study is different from that of their respective leaf oils, and also from *C. reticulata* leaf oil (Karioti *et al*., 2007). The minor components, geranial and neral in the peel and fruit oils in the *Citrus* species we examined were found to be among the principal components of the Nigerian varieties of lemon leaf oil (Ekundayo *et al*., 1990) and lime leaf (Ekundayo *et al*., 1991) oils, in addition to limonene which was also a major component in both leaf oils.

Lime peel oils from France (Lota *et al*., 2002) and India (Selvaraj *et al*., 2004) differed slightly from our study, in that *γ*-terpinene predominated in these varieties in addition to ß-pinene and limonene. Furthermore, the Mexican lime oil (Craske *et al*., 2005) was found to possess identical major and moderate components with the Nigerian fruit oil. Lemon peel oils from Crete (Vekiari *et al*., 2002), France (Lota *et al*., 2002) and India (Mahalwal and Ali, 2003) showed significantly different composition in comparison with our investigation.

Conclusion

According to our investigation, both lemon peel and lime fruit oils exhibited qualitative similarities in composition, but marked differences existed in the yields of the major components (limonene in lemon peel oil, and limonene and ß-pinene in lime fruit oil), and this clearly distinguished lime fruit oil from lemon peel oil. Lemon oil in our study is of a distinct chemical composition compared with similar oils obtained elsewhere.

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