Journal of Essential Oil Research
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tjeo20

Volatile Constituents of Mandarin (Citrus reticulata Blanco) Peel Oil from Burundi

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Version of record first published: 28 Nov 2011.

To cite this article: Simon Muhoho Njoroge, Hellen Njoki Mungai, Hiroshi Koaze, Nguyen Thi Lan Phi & Masayoshi Sawamura (2006): Volatile Constituents of Mandarin (Citrus reticulata Blanco) Peel Oil from Burundi, Journal of Essential Oil Research, 18:6, 659-662

To link to this article: http://dx.doi.org/10.1080/10412905.2006.9699197

J. Essent. Oil Res., **18**, 659-662 (November/December 2006)

Volatile Constituents of Mandarin (*Citrus reticulata* Blanco) Peel Oil from Burundi

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Abstract

The essential oil constituents of mandarin (*Citrus reticulata* Blanco) grown in Burundi were extracted by cold-pressing method and analyzed by GC and GC/MS. Fifty-eight constituents, amounting to 97.2% of the total volatiles were identified. Monoterpene hydrocarbons accounted for the most abundant chemical group (94.7%). Limonene was the most prominent constituent (84.8%), followed by γ-terpinene (5.4%), myrcene (2.2%) and α-pinene (1.1%). Sesquiterpene hydrocarbons accounted for a minor quantity (0.2%), where germacrene D and valencene were the main constituents. Oxygenated compounds of various chemical groups constituted 2.3%. Aliphatic aldehydes (0.7%) and terpene alcohols (0.7%) were the major chemical groups. The main constituents were linalool (0.7%), octanal (0.5%) and decanal (0.2%). Octyl acetate, α-sinensal, decanol and perillaldehyde occurred at 0.1% levels. Thymol, α-sinensal, methyl thymol, and the acetate esters, bornyl, α-terpinyl, geranyl, citronellyl and decyl acetates were detected, each at < 0.05%.

Key Word Index

Citrus reticulata, Rutaceae, mandarin oil, essential oil composition, limonene.

Introduction

Mandarins, *Citrus reticulata* Blanco (Rutaceae), are some of the most highly regarded *Citrus* fruits for fresh consumption. They are sometimes referred to as 'tangerines,' although 'mandarin' is the more common name. There are several varieties and hybrids of the mandarin species (1). The popular cultivated species include *C. unshiu* Marcovitch (Japanese Satsuma mandarins, also called Unshiu mikan), *C. nobilis* Loureiro (king mandarins), *C. deliciosa* Tenore (Mediterranean mandarins) and *C. reticulata* Blanco (common mandarins) (1,2). Mandarins are among the major *Citrus* fruits cultivated in several countries. Burundi is a small country (25,650 Km^2) located on the northeastern shoreline of lake Tanganyika, in east-central Africa. It is in the tropical zone, between 2°–4°S, and 29°– 31°E. It is surrounded by Congo, Rwanda and Tanzania. The altitude ranges between 772 m and 2,670 m above sea level. The temperature varies from 17°–23°C, and the average annual rainfall is about 150 cm. The two wet seasons are February to May and September to December, and the dry seasons are from June to August, and December to January. The main fruits in the country are bananas, papayas, mangoes, pineapples and *Citrus*. Mandarins are grown on a small scale for household consumption. They are of good eating quality, with pleasant taste, abundant juice and rich aroma. The surplus fruit is sold in the local markets and neighboring countries. Although many studies have been published on mandarin oils (2-6), the literature on Burundian *Citrus* fruits has been lacking. The volatile components of the *Citrus* genus have recently been reviewed (4). Limonene constitutes > 85% in most mandarin oils, while α-pinene, β-pinene, sabinene, α-phellandrene, β-phellandrene, (Z)-β-ocimene and terpinolene occur at < 2.0% (3,4). The sesquiterpene hydrocarbons, β-caryophyllene, β-cubebene, α-copaene, δ–elemene, β-elemene, α-humulene, germacrene D, α-farnesene, germacrene B and bicyclogermacrene, occur in some oils at < 0.1% (2-7). Oxygenated compounds, including octanal, decanal, linalool, α-terpineol, terpinen-4-ol, carvone, β-sinensal, α-sinensal, nootkatone, thymol, (E)-nerolidol, perillaldehyde and citronellol have been reported at minor quanti-

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Received: June 2005
Revised: August 2005
Accepted: October 2005

ties in some of the oils (2,4,6,7). Understanding of the aroma chemistry of mandarin oils of various origins is important, in view of the economic value and applications of these products. The volatile constituents of *Citrus* oils are influenced by origin, varieties, and cultural practices, among other factors (9). In this study, the qualitative and quantitative characteristics of the volatile constituents of mandarin peel oil from Burundi are reported.

Experimental

The mandarin fruit at its best harvest maturity in early May, 2004 was obtained from Bujumbura, the capital of Burundi having been cultivated in the surrounding areas. The fruit peel had a smooth texture and orange yellow color. The sample was kept under refrigeration until preparation of the oil, which was completed within a few days of sample acquisition. The peel oils were prepared in the Department of Food Science and Technology, Kigali Institute of Science, Technology and Management, Kigali, Rwanda. Standard chemical compounds for identification of the oil constituents were purchased from Wako Pure Chemical Industries, Osaka, Japan, Fluka Fine Chemicals, Switzerland, and Aldrich Chemical Co., USA. The peel essential oils were isolated by cold-pressing method as described previously (5,10,11). The peel flavedo was pressed by hand to express the oil, which was collected in a brine solution on ice. The extract was centrifuged at 2000 g for 15 min at 4°C. The supernatant was dehydrated with anhydrous sodium sulfate at 5°C for 24 h, and then filtered. The cold-pressed oil was kept at -21°C until analyzed.

Gas chromatography was conducted using a Shimadzu GC-17A gas chromatograph, fitted with DB-Wax fused silica capillary column (60 m x 0.25 mm, 0.25 µm film thickness, J & W Scientific, Folsom, CA, USA), and a flame ionization detector (FID). The column temperature was programmed from 70°C (2 min) to 230°C (20 min) at an increasing rate of 2°C/min. The injector and detector temperatures were 250°C. The oil sample of 0.5 µL was injected. The split ratio of the detector was 1:50. Nitrogen was the carrier gas at a flow rate of 2 mL/min. The separated peaks were integrated using a Shimadzu C-R8A Chromatopack integrator (Shimadzu, Kyoto).

Gas chromatography/mass spectrometry (GC/MS) was conducted using a Shimadzu GC-17A coupled with a Shimadzu QP-5050A MS (Shimadzu, Kyoto). The GC operating conditions were the same as those described above. The MS conditions were: ionization voltage, of 70 eV; ion source temperature, of 250°C; scanning range of 25–400 m/z. The oil sample of 0.2 µLwas injected, and the split ratio was 1:50. Identification of the constituents was achieved by comparing their mass spectra with those of compounds registered in the NIST 107 and Wiley 229 commercial spectral libraries of the GC/MS. In addition, the retention indices (RI) of the constituents were compared to those of standard compounds determined under similar conditions, in relation to a homologous series of n-alkanes (C_9–C_{27}) for confirmation of identity. Where standard compounds were not available, only MS data was used, and the identification was tentative. The constituents were quantified (% weight per weight) using internal standards (hexanol and nonadecane).

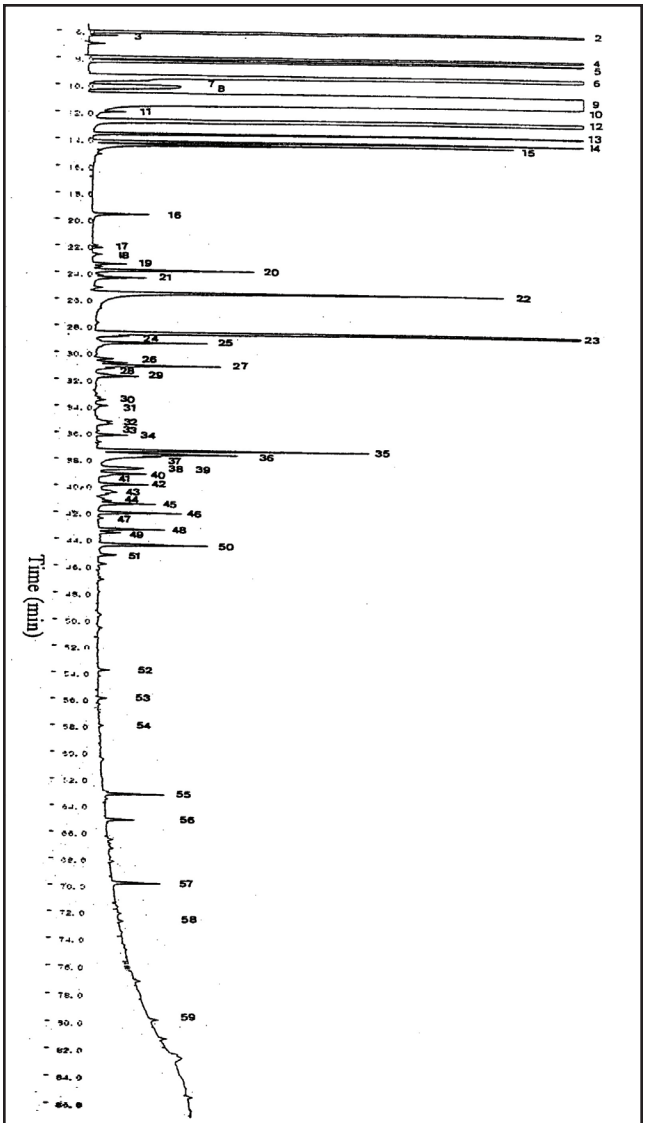

Figure 1. GC chromatogram of mandarin peel oil from Burundi

Results and Discussion

The average weight of the mandarin whole fruit was 91 g, out of which the flavedo constituted 22% (w/w). The yield of essential oil (weight of oil/weight of fruit) was 0.08%. The oil had a strong aroma characteristic of the fruit. The GC elution profile of the constituents is shown in Figure 1, and the identity of the constituents and their concentrations (%) are given in Table I. A total of 59 compounds amounting to 97.2% were separated, out of which 58 (97.1%) were identified. The components were categorized into chemical groups as summarized in the Table I.

Hydrocarbons: The oil contained 12 monoterpene hydrocarbons, amounting to 94.7%. The main constituents were limonene (84.8%), γ-terpinene (5.4%), myrcene (2.2%) and α-pinene (1.1%). The quantities of the major monoterpene

Table I. Volatile constituents of mandarin peel oil from Burundi

Compound	RI (compound)	RI (standard compound)	Concentration % (w/w)	Identification
ethyl acetate	947	949	0.1	RI, MS
α-pinene	1031	1033	1.1	RI, MS
α-fenchene[t]	1046		t	MS
β-pinene	1118	1121	0.4	RI, MS
sabinene	1129	1132	0.3	RI, MS
myrcene	1163	1167	2.2	RI, MS
α-phellandrene	1173	1175	*	RI, MS
α-terpinene	1188	1190	0.1	RI, MS
limonene	1213	1209	84.8	RI, MS
1,8-cineole	1221	1223	0.4	RI, MS
β-phellandrene	1223	1224	*	RI, MS
γ-terpinene	1255	1255	5.4	RI, MS
p-cymene	1276	1279	0.1	RI, MS
terpinolene	1288	1292	0.3	RI, MS
octanal	1291	1293	0.5	RI, MS
nonanal	1392	1396	*	RI, MS
trans-limonene oxide	1463	1466	t	RI, MS
trans-sabinene hydrate	1467	1471	t	RI, MS
δ-elemene	1472	1478	*	RI, MS
octyl acetate	1474	1480	0.1	RI, MS
citronellal	1478	1481	*	RI, MS
decanal	1497	1500	0.2	RI, MS
linalool	1546	1549	0.7	RI, MS
β-cubebene[t]	1551		*	MS
octanol	1558	1562	*	RI, MS
bornyl acetate	1585	1586	*	RI, MS
methyl thymol[t]	1591		0.1	MS
α-terpinyl acetate	1599	1599	*	RI, MS
terpinen-4-ol	1601	1603	*	RI, MS
β-caryophyllene	1602	1605	t	RI, MS
(Z)-β-farnesene	1633	1636	t	RI, MS
l-menthol	1647	1646	t	RI, MS
β-elemene[t]	1648		*	MS
citronellyl acetate	1662	1663	*	RI, MS
isoborneol	1675	1674	*	RI, MS
dodecanal	1706	1711	t	RI, MS
germacrene D[t]	1709		0.1	MS
neryl acetate	1723	1725	*	RI, MS
valencene	1725	1728	0.1	RI, MS
β-bisabolene[t]	1729		*	MS
geranial	1735	1734	*	RI, MS
bicyclogermacrene[t]	1744		*	MS
(E)-2-undecenal[t]	1753		*	MS
geranyl acetate	1756	1758	*	RI, MS
α-citronellol[t]	1760	1760	*	MS
decanol	1764	1766	0.1	RI, MS
β-citronellol[t]	1768		*	MS
perillaldehyde	1784	1788	0.1	RI, MS
nerol	1798	1802	*	RI, MS
tridecanal	1806	1812	*	RI, MS
germacrene B[t]	1832		*	MS
(Z)-nerolidol	1995	1999	t	RI, MS
isosafrole[t#]	2037		t	MS
thymol	2180	2180	*	RI, MS
β-sinensal	2227	2233	*	RI, MS
decanoic acid	2293	2292	t	RI, MS
α-sinensal	2329	2336	0.1	RI, MS
undecanoic acid	2394	2394	t	RI, MS
1,4,7,10-tetraoxacyclodecane[t]	2492		t	MS

Table I. continued

Compound	Concentration % (w/w)
Totals	
Aliphatic hydrocarbons[b]	1(t)
Monoterpene hydrocarbons[b]	12 (94.7)
Sesquiterpene hydrocarbons[b]	9 (0.2)
Aliphatic aldehydes[b]	6 (0.7)
Terpene aldehydes[b]	5 (0.2)
Ketones[b]	-
Aliphatic alcohols[b]	2 (0.1)
Terpene alcohols[b]	10 (0.7)
Aliphatic esters[b]	2 (0.2)
Terpene esters[b]	5 (*)
Ethers[b]	3 (0.5)
Acids[b]	2 (t)
Oxides[b]	2 (t)
Oxygenated compounds[b]	37 (2.4)
Total separated compounds[b]	59 (97.2)

[a]concentration (%w/w), mean of triplicate determinations; RI = retention index on DB-Wax column; MS = identification was based on comparison of mass spectra; [t]tentatively identified; *concentration was more than 0.005 but less than 0.05%; - = not detected; t = detected at a concentration less than 0.005%; [b]the un-bracketed values refer to the number of components, and the numbers in brackets refer to their percentage concentration; [#]correct isomer not identified

hydrocarbons were closely similar to those reported for most mandarin oils (2,3,4). Limonene varied between 57 and 97% among different mandarin varieties (2,4,5). The present oil exhibited a more complex composition of monoterpene hydrocarbons than reported for most mandarin oils (3,4). Sesquiterpene hydrocarbons constituted a low amount (0.2%). Germacrene D and valencene were the main constituents, each at 0.1%. δ- and β-Elemene, (Z)-farnesene, β-cubebene, germacrene B, bicyclogermacrene and β-caryophyllene occurred at < 0.05%. The occurrence of these compounds concurred with other mandarin oils reported recently (2,4). One aliphatic hydrocarbon, 1,4,7,10-tetraoxacyclodecane (12-crown-4-ether) was detected. The compound has been reported in at a minor quantity in Kenyan Valencia and Washington navel peel oils (2). Methyl-N-methyl anthranilate, a compound reported to be a major contributor to tangerine aroma (12), was not detected in the oil. Thirty seven oxygenated compounds amounting to 2.4% were identified. Aliphatic aldehydes (0.7%), terpene alcohols (0.7%) and ethers (0.5%) formed the major chemical groups. Among the aliphatic aldehydes, octanal (0.5%) and decanal (0.2%) were the most prominent. Nonanal, dodecanal, (E)-2-undecenal and tridecanal occurred at < 0.05%. Perillaldehyde and α-sinensal were the main terpene aldehydes, each at 0.1%. Citronellal, geranial and β-sinensal occurred at < 0.05%. Aldehydes are known to be important contributors to mandarin flavor, and their constitution in the present oil agreed with previous reports (3,4). Ketones were virtually absent in the oil. Two aliphatic alcohols, octanol (< 0.05%) and decanol (0.1%), were found. Among the 10 terpene alcohols detected (0.7%), linalool was the main constituent (0.7%). Menthol, isoborneol, terpinen-4-ol, citronellol, nerol, (Z)-nerolidol and thymol each occurred at < 0.05%. Three ethers, 1,8-cineole (a monoterpene cyclic ether), methyl thymol, and isosafrole (a phenolic ether), were found. The compounds are important in flavor and fragrance industry (13,14). Esters amounted to 0.2%. The compounds were mostly of the acetate type, including acetyl, octyl, bornyl, α-terpinyl, geranyl, citronellyl and neryl acetates. Majority of the esters have been reported in other mandarin oils (2,3,4). Two acids, decanoic and undecanoic were detected at trace levels. *trans*-Limonene oxide occurred at a trace quantity. The study showed that the qualitative and quantitative characteristics of the Burundian mandarin peel oil were close to those of similar oils from other origins. The variations of some constituents could occur due to environmental influences.

Acknowledgments

We thank Peter Mugisha of Kigali Institute of Science, Technology and Management, Rwanda, for his assistance in obtaining the samples. We are grateful to the Japanese Society for the Promotion of Science (JSPS), for granting the Invitation Fellowship for research in Japan to Simon Muhoho Njoroge under the 'Fiscal 2004 that facilitated the conclusion of this work.

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