FLAVOUR AND FRAGRANCE JOURNAL
Flavour Fragr. J., **14**, 161–166 (1999)

Chemical composition of peel and leaf essential oils of *Citrus medica* L. and *C. limonimedica* Lush.

Marie-Laure Lota,[1] Dominique de Rocca Serra,[1] Félix Tomi ,[1] Jean-Marie Bessiere[2] and Joseph Casanova[1]*

[1]Université de Corse, Equipe Chimie et Biomasse, URA CNRS 2053, Route des Sanguinaires, 20 000 Ajaccio, France
[2]Université de Montpellier, Ecole Nationale Supérieure de Chimie, Laboratoire de Phytochimie, 34075, Montpellier cedex, France

Received 4 June 1998
Revised 23 September 1998
Accepted 29 September 1998

ABSTRACT: Five peel oils and six leaf oils of different varieties of citrons (*Citrus medica* and *C. limonimedica*) were obtained from fruits and leaves collected on trees submitted to the same pedoclimatic and cultural conditions. Their composition was investigated by capillary GC, GC–MS and Carbon-13 NMR. Three chemotypes: limonene, limonene/γ-terpinene and limonene/geranial/neral were observed for peel oils while leaf oils exhibited the limonene/geranial/neral composition. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: *Citrus medica*; *Citrus limonimedica*; Rutaceae; citron; peel and leaf composition; GC; GC–MS; ^{13}carbon NMR

Introduction

Citrus fruits (family Rutaceae) are among the most widely produced fruits all over the world. Some of these (oranges, mandarins, lemons, grapefruits) are common but others, like citrons, are less known although they were the first fruits of the genus *Citrus* to reach the Mediterranean region, about 300 BC. Commonly supposed to be indigenous to India, citrons have been known since remote antiquity in China and Mesopotamia.[1] Because of their sensitivity to cold and heat, citron trees are cultivated in the south of France (Corsica), southern Italy (Calabria), Greece, Israel, North Africa, Puerto Rico and for some varieties in China, Vietnam and Japan.

According to Tanaka, citrons are classified into two botanical species:[2] *Citrus medica* L., to which belong several varieties ('diamante', 'corsican', 'poncire commun', 'sarcodactylis', 'rhobs-el-arsa') and *C. limonimedica* Lush. whose 'ethrog' variety is the best known.

The citron crop goes mainly into the production of candied peel and a part is used for the flavouring of liquors[1] or for medical purposes.[3] The peel and rind of citron make up most of the fruit volume. Fruit of the 'corsican' variety is generally large and elliptical in shape, 7–10 cm in diameter, 8–14 cm in length, rind about 3–4 cm thick. This fruit, which is the only one with a sweet pulp, could be crystallized after softening the peel or used in the formulation of a regional liquor named 'cédratine'.[4,5] The fruit of the 'diamante' variety, widely cultivated in Calabria, is larger. The 'sarcodactylis' variety, cultivated in China, Japan and Vietnam, whose fruit splits into a number of finger-like sections, is especially used for its fragrance and for ornamental purposes.[6] 'Rhobs-el-arsa' means 'bread of the garden' in North Africa, because of the flat shape of the fruit. Fruit of the 'ethrog' variety is small and ellipsoid, a little larger than a lemon, and is used by the Jewish people in rites of the Feast of Tabernacles.[7,8] Trees of the 'poncire commun' variety have smaller leaves than those of other varieties.

The top note of the essential oil of citrons is used as fragrant agent in cosmetics, food products and liquors.[3–5] Several studies have been performed on the chemical composition of the peel oil of citrons, although the literature data are not easily comparable because the extraction conditions were quite different (cold-pressure, solvent extraction, steam distillation):

- Oils of variety 'diamante' from Calabria exhibited limonene (55–61%) and γ-terpinene (23–27%) as the main components, whatever the extraction mode.[9–11]
- The composition of the oils of varieties 'rugosa' and 'peretti' exhibited a content of limonene (60–62%) similar to variety 'diamante', but differed by a lower amount of γ-terpinene (11–12%) and by the presence of β-pinene (14–15%).[10]

* Correspondence to: J. Casanova, Université de Corse, Equipe Chimie et Biomasse, URA CNRS 2053, Route des Sanguinaires, 20 000 Ajaccio, France.

Contract grant sponsor: Délégué Régional à la Recherche et à la Technologie pour la Corse, France, Contract grant number: 96-327.
Contract grant sponsor: Collectivité Territoriale de Corse.

 CCC 0882–5734/99/030161–06$17.50

- In one oil of the variety 'corsican' extracted with petroleum ether,[5] limonene (59%) and γ-terpinene (7%) were the major components. In one other sample obtained by direct sampling in the oil gland, limonene (51%) was associated with geranial and neral (13% and 7%).[4,5]
- The limonene/geranial/neral composition was also observed in the oil of the variety 'muliensis' from China.[12]
- In the oils of the variety 'sarcodactylis', four compositions may be distinguished: (a) limonene/γ-terpinene[3,6] (48–56%/23–32%); (b) limonene/Δ-3-carene[3] (70%/15%); (c) limonene/*p*-cymene[3] (48%/34%); and (d) neral/geranial/limonene[13] (22%/19%/11%).
- One oil of the variety 'common ethrog' exhibited a high proportion of limonene (81%),[7,8] while one oil of the variety 'yenemite ethrog' was characterized by the limonene/γ-terpinene composition (53%/14%).[8]

Only one study of leaf oil has been described and concerned the 'ethrog' variety.[7,8] Nevertheless, the sample was obtained from leaves preserved in alcohol before water distillation. Limonene (37.9%), geranial (8.2%), geraniol (6.2%), neral (5.1%), nerol (4.8%) and (*E*)-caryophyllene (4.8%) were the major components.

The aim of our work was to study the chemical variability of some varieties of the citron family. The citron trees are cultivated at the Station de Recherches Agronomiques (SRA) of the INRA-CIRAD in San Ghjulianu (Corsica, France) and therefore are submitted to the same pedoclimatic and cultural conditions. We will compare the chemical composition of peel oils on the one hand and of leaf oils on the other hand, in order to consider a potential utilization of these oils. All samples were investigated by GC and by ^{13}C-NMR spectroscopy, without purification of the components, following a methodology first reported by Formácek and Kubecska[14] and developed in our laboratory,[15] and well suited for chemical variability studies.[16,17] Some samples were also analysed by GC–MS.

Experimental

Plant Material

All trees were grown in the germplasm collection orchard of the SRA in San Ghjulianu (latitude 42°17′N, longitude 9°32′E, mediterranean climate, average rainfall 840 mm per year and temperature 15.2°C, soil derived from alluvial deposits and classified as fersiallitic, pH range 5.0–5.6). The trees were in good vigor, disease-free and without visible insect infestation. For each cultivar, about 500 g of leaves were collected in September 1996, while about 30 fruits were collected at the ripeness stage (November 1996). Leaves and fruits were collected revolving about the tree.

We analysed the leaf oil of six varieties: 'corsican' (synonym: 'de Corse'); 'diamante' (synonyms: 'calabrese', 'cedro liscio', 'liscia di diamante'); 'poncire commun'; 'rhobs-el-arsa'; 'sarcodactylis' (synonym: 'digité', 'fingered', 'Buddha's fingers'); and 'ethrog' (synonym: 'etrog') and conversely, only five peel oils because the citron trees of the variety 'poncire commun' do not produce fruits in the climatic conditions of San Ghjulianu.

All peel and leaf essential oils were investigated by GC and by ^{13}C-NMR spectroscopy. Several samples were also investigated by GC–MS (Tables 1 and 2).

Peel Extraction

The peel of fresh fruits was cold-pressed and then the essential oil was separated from the crude extract by centrifugation (10 min at 15,000 rpm).

Hydrodistillation

Fresh leaves (500 g) were subjected to hydrodistillation for 3 h using a Clevenger-type apparatus. Yields ranged between 0.09% and 0.27%.

Analytical GC

GC analysis was carried out using a Perkin-Elmer Autosystem and previously reported experimental parameters, (BP-1, polydimethylsiloxane and BP-20, polyethylene glycol columns).[18]

GC–MS

GC–MS analysis was performed: (a) on a Perkin-Elmer quadrupole MS system (model 910) coupled with the above gas chromatograph (BP-1 column);[18] (b) on a Hewlett-Packard Type 5890 (OPTIMA 1 column, polydimethylsiloxane).[19]

^{13}C-NMR

All ^{13}C-NMR spectra were recorded on a Bruker AC 200 FT spectrometer as reported previously[20] (10 mm probe, 200 mg of the oil in 2 ml $CDCl_3$, 3000 scans accumulated for each sample).

Table 1. Chemical composition of peel essential oils of citrons

Constituents	RI (BP-20)	RI (BP-1)	E	S	C	D	R
α-Thujene*	1021	922	**0.8**	**0.7**	0.6	–	–
α-Pinene*	1021	930	**2.0**	**1.9**	**1.7**	0.1	**0.3**
β-Pinene	1109	971	**2.1**	**1.8**	**1.7**	0.2	0.1
Sabinene	1119	964	**0.4**	**0.3**	0.3	0.1	0.1
Myrcene	1157	978	**1.5**	**1.6**	**1.4**	**1.3**	**1.5**
α-Phellandrene	1162	997	0.1	0.1	0.1	tr	–
α-Terpinene	1179	1009	0.5	0.5	**0.5**	–	–
Limonene	1199	1021	**46.9**	**51.9**	**51.9**	**70.4**	**93.6**
(*Z*)-β-Ocimene	1228	1024	**0.6**	0.4	**0.9**	0.3	–
γ-Terpinene	1241	1048	**30.7**	**31.3**	**26.2**	tr	0.1
(*E*)-β-Ocimene	1245	1035	**0.8**	0.5	**1.2**	0.5	0.2
p-Cymene	1267	1012	0.3	0.5	0.2	–	–
Terpinolene	1278	1078	**1.3**	**1.3**	**1.1**	tr	tr
6-Methylhept-5-en-2-one	1332	942	–	–	–	–	0.2
allo-Ocimene	1367	1116	tr	tr	tr	–	–
cis-Limonene-1,2-epoxide	1443	1120	–	–	tr	–	tr
trans-Sabinene hydrate	1458	1053	0.1	tr	0.1	–	–
Citronellal	1473	1130	0.2	0.2	0.1	0.1	0.1
Linalol	1539	1082	0.3	0.2	0.3	0.3	0.2
trans-α-Bergamotene	1580	1432	0.4	0.2	0.4	**0.4**	0.3
(*E*)-Caryophyllene	1588	1420	0.2	0.1	0.2	0.2	0.1
Terpinen-4-ol	1595	1162	0.1	tr	tr	0.1	tr
(*E*)-β-Farnesene	1654	1448	–	–	–	–	tr
Citronellyl acetate	1657	1332	tr	0.1	tr	tr	0.1
Neral	1674	1213	**2.8**	**1.3**	**2.8**	**7.6**	0.4
α-Terpineol	1688	1172	0.3	0.2	0.3	0.1	tr
Germacrene-D	1704	1480	tr	0.4	0.1	tr	–
β-Bisabolene	1721	1500	**0.6**	0.1	**0.6**	**0.7**	**0.6**
Neryl acetate	1724	1340	0.3	–	**0.7**	**0.7**	–
Geranial*	1730	1242	**5.4**	**2.6**	**5.3**	**14.4**	**0.8**
α-Bisabolene*	1730	1496	0.1	tr	–	0.1	0.1
Geranyl acetate	1748	1358	**0.7**	0.2	**0.8**	**0.9**	0.2
Nerol	1790	1207	0.1	0.2	–	0.2	tr
Geraniol	1837	1232	0.1	0.2	–	0.2	tr
trans-Nerolidol	2031	1547	–	–	–	–	tr
α-Bisabolol	2217	1674	tr	tr	–	tr	tr
Monoterpene hydrocarbons			88.0	92.8	87.8	72.9	95.9
Oxygenated monoterpenes			10.4	5.2	10.4	24.6	1.8
Sesquiterpene hydrocarbons			1.3	0.8	1.3	1.4	1.1
Oxygenated sesquiterpenes			tr	tr	–	tr	tr
Others			–	–	–	–	0.2
Total identified			99.7	98.8	99.5	98.9	99.0

tr: ⩽0.05%.
Varieties: 'ethrog' (E), 'sarcodactylis' (S), 'corsican' (C), 'diamante' (D), 'rhobs-el-arsa' (R).
Order of elution and percentages of individual components are given on BP-20 column, except for compounds with an asterisk (percentages given on BP-1 column).
All compounds were identified by GC–RI on polar and apolar column. Components of C and R varieties were also identified by GC–MS. Bold letters indicate components identified by ^{13}C-NMR.

Identification of Components

Identification of the individual components of samples was based: (a) on comparison of their GC retention indices (RI) on apolar and polar columns, determined relative to the retention time of a series of *n*-alkanes with linear interpolation, with those of authentic compounds; (b) on computer matching with mass spectral libraries (NIST or WILEY) and comparison with spectra of authentic samples or literature data;[21–23] and (c) on comparison of the resonances in the ^{13}C-NMR spectrum of the mixture with those of the reference spectra compiled in our spectral library with the help of laboratory produced software.[15]

Results and Discussion

All trees were submitted to the same pedo-climatic and cultural conditions and extraction conditions were identical for all samples. Therefore, the influence of environmental and technical parameters on the chemical composition of essential oils was avoided.

Peel Oils

The chemical composition of the five samples are presented in Table 1. The 36 components identified

Table 2. Chemical composition of leaf essential oils of citrons

Constituents	RI (BP-20)	RI (BP-1)	E	S	C	D	R	P
α-Thujene*	1021	922	tr	tr	–	tr	tr	tr
α-Pinene*	1021	930	0.2	0.3	0.2	0.2	0.2	0.2
β-Pinene	1109	971	0.1	0.1	–	tr	0.2	0.1
Sabinene	1119	964	**0.6**	**1.2**	0.4	0.3	**0.5**	**0.6**
Δ-3-Carene	1145	1005	tr	tr	–	–	**0.6**	tr
Myrcene	1157	978	**1.0**	**1.3**	**1.1**	**1.2**	**0.9**	**1.1**
Limonene	1199	1021	**27.8**	**38.7**	**37.3**	**43.2**	**37.4**	**33.1**
1,8-Cineole	1208	1021	**1.0**	**1.7**	**0.9**	**0.7**	**0.4**	**0.4**
(*Z*)-β-Ocimene	1228	1024	0.4	**0.7**	**0.4**	0.3	0.5	0.4
γ-Terpinene	1241	1048	**0.5**	**0.4**	0.1	0.1	–	0.1
(*E*)-β-Ocimene	1245	1035	**0.6**	**1.1**	**0.7**	**0.5**	**6.5**	0.6
p-Cymene	1267	1012	0.1	0.1	tr	–	–	tr
Terpinolene	1278	1078	tr	0.1	tr	tr	0.1	tr
Octanal	1285	978	tr	–	–	0.2	–	0.1
6-Methylhept-5-en-2-one	1332	942	**6.7**	**3.8**	**5.0**	**4.9**	**1.9**	**2.8**
Nonanal	1388	1082	0.2	**0.4**	0.1	**0.4**	tr	**0.7**
cis-Limonene-1,2-epoxide	1443	1120	–	tr	tr	–	–	–
trans-Limonene-1,2-epoxide	1453	1122	tr	–	tr	–	–	tr
Citronellal	1473	1130	**1.5**	**2.1**	**0.6**	**0.8**	**0.8**	**1.1**
Decanal	1492	1183	tr	0.1	tr	0.3	–	0.2
Linalool	1539	1082	**1.6**	**1.1**	**1.5**	**1.3**	**1.2**	**1.6**
Octanol	1551	1051	tr	tr	–	0.1	–	0.1
(*E*)-Caryophyllene	1588	1420	0.1	0.2	0.1	0.1	0.1	0.2
Terpinen-4-ol	1595	1162	0.2	0.3	0.1	0.1	0.1	0.2
Undecanal	1598	1288	tr	0.1	tr	0.1	–	0.3
(*E*)-β-Farnesene	1654	1448	tr	–	tr	–	–	–
Citronellyl acetate	1657	1332	tr	tr	tr	tr	0.1	0.1
Neral	1674	1213	**14.8**	**14.0**	**13.6**	**11.9**	**14.3**	**16.3**
α-Terpineol	1688	1172	**0.7**	**1.0**	**0.5**	0.4	0.2	0.4
Dodecanal	1708	1389	tr	–	–	–	–	tr
β-Bisabolene	1721	1500	tr	–	tr	0.1	0.1	tr
Neryl acetate	1724	1340	**0.6**	0.2	**0.9**	**0.5**	**1.1**	**1.0**
Geranial*	1730	1242	**21.3**	**20.1**	**19.4**	**17.0**	**20.0**	**23.4**
Piperitone*	1730	1232	0.1	–	tr	tr	0.1	0.1
Geranyl acetate	1748	1358	**2.4**	0.3	**1.7**	**1.1**	**3.0**	**1.4**
Citronellol	1756	1207	**1.4**	**1.1**	**0.7**	**0.7**	**1.2**	**1.2**
Nerol	1790	1207	**7.3**	**4.2**	**6.0**	**5.7**	**2.1**	**5.5**
Geraniol	1837	1232	**6.8**	**3.8**	**6.6**	**6.0**	**2.5**	**5.0**
Caryophyllene oxide	1974	1574	tr	–	0.1	tr	0.1	tr
(*E*)-Nerolidol	2031	1547	tr	–	–	tr	0.2	0.2
α-Bisabolol	2217	1674	–	–	–	tr	0.1	tr
Geranic acid	2340	1358	tr	–	tr	–	–	tr
Monoterpene hydrocarbons			31.3	44.0	40.2	45.8	46.9	36.2
Oxygenated monoterpenes			59.7	49.9	52.5	46.2	47.1	57.7
Sesquiterpene hydrocarbons			0.1	0.2	0.1	0.2	0.2	0.2
Oxygenated sesquiterpenes			–	–	0.1	–	0.4	0.2
Others			6.9	4.4	5.1	5.8	1.9	4.1
Total identified			98.0	98.5	98.0	98.0	96.5	98.4

tr: ⩽0.05%.
Varieties: 'ethrog' (E), 'sarcodactylis' (S), 'corsican' (C), 'diamante' (D), 'rhobs-el-arsa' (R), 'poncire commun' (P).
Order of elution and percentages of individual components are given on BP-20 column, except for compounds with an asterisk (percentages given on BP-1 column).
All compounds were identified by GC–RI on polar and apolar column. Components of S, C, D, R and P varieties were also identified by GC–MS. Bold letters indicate components identified by ^{13}C-NMR.

accounted for 98.8–99.7% of the total oil. Oil compositions differed only quantitatively. The major component was always limonene (46.9–93.6%), associated with γ-terpinene (tr–31.3%), geranial (0.8–14.4%) and neral (0.4–7.6%).

The five samples could be subdivided into three groups:

- The composition of the 'rhobs-el-arsa' oil exhibited a high amount of limonene (93.6%) and the contents of all other components were very low (⩽1.5%), geranial and neral particularly, which accounted for 0.8% and 0.4% respectively.
- The 'diamante' oil also exhibited a high content of limonene (70.4%) and was also characterized by the presence of geranial and neral in appreciable proportions (14.4 and 7.6%, respectively). The composition of our 'diamante' oil differed from that of Calabria, which exhibited very low contents of geranial and neral.[9–11]

- The oils of the 'corsican', 'sarcodactylis' and 'ethrog' varieties belonged to the limonene/γ-terpinene chemotype (46.9–51.9% and 26.2–31.3%), while contents of geranial and neral ranged from 1.3 to 5.4%. Our 'corsican' citron oil has a similar composition with that reported by Huet.[4,5] Nevertheless, a more detailed composition is presented in this study. Conversely, the composition of our oil from 'ethrog' citron exhibited a higher content of γ-terpinene than those from Israel[7,8] and Italy.[10] The oil of our 'sarcodactylis' cultivar was similar with those from Japan[6] and one sample from Vietnam[3] but differed from those of China[3,13] and one other sample from Vietnam.[3]

Leaf Oils

The composition of oils of the six varieties are reported in the Table 2. The total of 42 components identified accounted for 96.5–98.5% of the oil. Although limonene was the major component (27.8–43.2%), the oxygenated fraction was preponderant in all samples and ranged from 49.4% to 66.6% of the oil. It was essentially constituted by oxygenated acyclic monoterpenes, geranial (17.0–23.4%), neral (11.9–16.3%), geraniol (2.5–6.8%), nerol (2.1–7.3%) and their acetates (0.3–3.0% and 0.2–1.1%, respectively), citronellal (0.6–2.1%), citronellol (0.7–1.4%) and linalool (1.1–1.6%). The nor-monoterpenic 6-methylhept-5-en-2-one was present in an appreciable amount (1.9–6.7%). The proportions of 1,8-cineole, myrcene, sabinene, (*Z*)-β-ocimene, α-terpineol and nonanal were very low ($\leqslant$1.7% for each).

The six leaf oils belonged to the limonene/geranial/neral chemotype and exhibited only slight quantitative differences. The oil of 'rhobs-el-arsa' citron exhibited a higher content of (*E*)-β-ocimene (6.5% vs. 0.5–1.1%) and lower contents of nerol and geraniol. The oils of the five other varieties could only be differentiated by their relative ratios of limonene and geranial/neral, respectively lower and slightly higher for the varieties 'ethrog' and 'poncire commun'.

Only the variety 'ethrog' has been described in the literature.[7,8] Comparison with our sample is difficult because the oil was obtained by hydrodistillation after maceration of leaves in alcohol.[8] Indeed, we observed quantitative variations, especially for the oxygenated acyclic monoterpenes such as geranial and neral, whose contents are three-fold lower than those of our sample.

According to our results, the composition of peel oils, which are subdivided in three well differentiated groups, limonene, limonene/γ-terpinene and limonene/geranial/neral, can provide information on the infraspecific differentiation of citrons. However, the limonene and limonene/γ-terpinene chemotypes are found for most peel oils of *Citrus*: bitter orange (*C. aurantium* L.),[24,25] sweet orange (*C. sinensis* (L.) Obs.),[24,26] grapefruit (*C. paradisi* Macf.),[24,27] mandarin (*C. reticulata* Blanco),[24,28] lemon (*C. limon* (L.) Burm)[29] and lime (*C. aurantifolia* (Chrism.) Swing.).[30,31]

Conversely, all leaf oils of citrons analysed in this study exhibited a limonene/geranial/neral composition which differed from that of most other *Citrus* leaf oils: (a) linalool/linalyl acetate in bitter orange oil;[32] (b) sabinene and sabinene/linalool in sweet orange oil[32,33] and grapefruit oil,[27] (c) methyl *N*-methylanthranilate (alone or associated with γ-terpinene), linalool/thymol and linalool/sabinene in mandarin oil.[32,33] The compositions of lemon and lime oils were qualitatively similar to that of citrons (limonene/neral/geranial chemotype) but differed quantitatively.[34,35]

Acknowledgements — The authors are indebted to the Délégué Régional à la Recherche et à la Technologie pour la Corse for financial support (Convention No. 96-327), to the Collectivité Territoriale de Corse for a research grant (MLL) and to INRA-CIRAD of Corsica for welcome and availability of plant material.

References

1. J. C. Praloran, *Les Agrumes*, Maisonneuve G. P. & Larose, Paris (1971).
2. L. Blondel, *Fruits*, **33**, 695 (1978).
3. N. X. Dung, N. M. Pha, V. N. Lô, N. H. Thiên and P. A. Leclercq, *J. Essent. Oil Res.*, **8**, 15 (1996).
4. R. Huet, *Fruits*, **39**, 689 (1984).
5. R. Huet, *Fruits*, **41**, 113 (1986).
6. H. Shiota, *Flavour Fragr. J.*, **5**, 33 (1990).
7. Z. Fleisher and A. Fleisher, *J. Essent. Oil Res.*, **3**, 377 (1991).
8. Z. Fleisher and A. Fleisher, *Perfum. Flavor.*, **21**(6), 11 (1996).
9. C. Capello, M. Calvarano, A. Di Giacomo and D. Gioffrè, *Essenze Deriv. Agrum.*, **52**, 59 (1982).
10. A. Cotroneo, A. Verzera, M. Alfa and G. Dugo, *Essenze Deriv. Agrum.*, **56**, 105 (1986).
11. M. Poiana, V. Sicari and B. Mincione, *J. Essent. Oil Res.*, **10**, 145 (1998).
12. M. Wen, Y. Huang, S. Xiao, W. Ren, H. Zaho and S. Yiang, *Acta Bot. Sinica*, **28**, 511 (1986).
13. L. Zhu, Y. Li, B. Li, B. Lu and N. Xia, *Citrus medica* L. var. *sarcodactylis* (Noot.) Swingle (Rutaceae), in *Aromatic Plants and Essential Constituents*, p. 131, Hai Feng Publishing Co., Chai Wan, Hong Kong (1993).
14. V. Formácek and K.-H. Kubeczka, *Essential Oils Analysis by Capillary Gas Chromatography and ^{13}C-NMR Spectroscopy*, Wiley, Chichester (1982).
15. F. Tomi, P. Bradesi, A. Bighelli and J. Casanova, *J. Magn. Reson. Anal.*, **1**, 25 (1995).
16. D. Ristorcelli, F. Tomi and J. Casanova, *J. Essent. Oil Res.*, **8**, 363 (1996).
17. L. Salgueiro, R. Vila, F. Tomi, X. Tomas, S. Cañigueral, J. Casanova, A. Proença da Cunha and T. Adzet, *Phytochemistry*, **45**, 1177 (1997).
18. J. P. Mariotti, J. Costa, A. Bianchini, A. F. Bernardini and J. Casanova, *Flavour Fragr. J.*, **12**, 205 (1997).
19. S. Breheret, T. Talou, S. Rapior and J.-M. Bessiere, *J. Agric. Food Chem.*, **45**, 831 (1997).
20. M. Mundina, R. Vila, F. Tomi, M. P. Gupta, T. Adzet, J. Casanova and S. Cañigueral, *Phytochemistry*, **47**, 1277 (1998).
21. Library Search Systems: (i) Perkin Elmer; (ii) Hewlett-Packard. Using these softwares the following databases were searched:

(a) NIST/EPA/NIH/mass spectral data base, version 4.1, 1992; (b) F. W. McLafferty, Wiley/NBS Registry of Mass Spectral Data, 4th edn, Wiley, New York (1988).
22. R. P. Adams, *Identification of Essential Oils by Ion Trap Mass Spectroscopy*, Academic Press, New York (1989).
23. W. Jennings and T. Shibamoto, *Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography*, Academic Press, New York (1988).
24. L. Mondello, P. Dugo and K. D. Bartle, *Flavour Fragr. J.*, **10**, 33 (1995).
25. B. M. Lawrence, Bitter orange oil, in *Essential Oils*, (a) pp. 19, 25 (1976–1978); (b) pp. 55, 125 (1981–1987); (c) p. 170 (1988–1991); (d) pp. 107, 171 (1992–1994), Allured, Carol Stream, IL (1995).
26. B. M. Lawrence, Orange oil, in *Essential Oils*, (a) p. 22 (1979–1980); (b) pp. 43, 113, 126, 222 (1981–1987); (c) p. 116 (1988–1991); (d) pp. 47, 164 (1992–1994), Allured, Carol Stream, IL (1995).
27. B. M. Lawrence, Grapefruit oil, in *Essential Oils*, (a) p. 3 (1979–1980); (b) pp. 41, 90, 158 (1981–1987); (c) pp. 25, 167 (1988–1991); (d) pp. 118, 155 (1992–1994), Allured, Carol Stream, IL (1995).
28. B. M. Lawrence, 'Progress in essential oils: mandarin oil', *Perfum. Flavor*., **21**(2), 25 (1996).
29. B. M. Lawrence, 'Progress in essential oils: lemon oil', *Perfum. Flavor*., **21**(1), 41 (1996).
30. B. M. Lawrence, 'Progress in essential oils: lime oil', *Perfum. Flavor*., **21**(4), 62 (1996).
31. S. M. Njoroge, H. Ukeda, H. Kusunose and M. Sawamura, *Flavour Fragr. J*., **11**, 25 (1996).
32. G. Dugo, L. Mondello and A. Cotroneo, *Perfum. Flavor*., **21**(3), 17 (1996).
33. Z. Fleisher and A. Fleisher, *Perfum. Flavor*., **16**(1), 43 (1991).
34. B. M. Lawrence, Lemon petitgrain oil, in *Essential Oils*, p. 114 (1992–1994), Allured, Carol Stream, IL (1995).
35. B. M. Lawrence, Lime leaf oil, in *Essential Oils*, p. 117 (1992–1994), Allured, Carol Stream, IL (1995).

