



# Progress in Essential Oils

by Brian M. Lawrence, R.J. Reynolds Tobacco Company

## petitgrain or Citrus Leaf Oils

In 1993, the composition of the range of petitgrain or the leaf oils of commercially important *Citrus* species were reviewed (Lawrence 1993). This current review will address the recent published literature and those studies that were not included last time. Each *Citrus* species will be treated separately.

### *Citrus aurantifolia* (Christm. et Panz.) Swingle

Key lime, or Mexican lime, is the common name for this species. A leaf oil of Galego lime (*C. aurantifolia*) was analyzed by Calvarano et al. (1982). It was found to possess the following composition:

|                             |                                    |
|-----------------------------|------------------------------------|
| $\alpha$ -thujene (0.01%)   | citronellal (2.50%)                |
| $\alpha$ -pinene (0.20%)    | linalool (1.24%)                   |
| camphene (t)                | decanal (0.81%)                    |
| $\beta$ -pinene (0.31%)     | terpinen-4-ol (0.15%)              |
| sabinene (0.38%)            | linalyl acetate (0.55%)            |
| myrcene (0.99%)             | neral (19.72%)                     |
| limonene (28.93%)           | $\alpha$ -terpineol (0.34%)        |
| octanal (0.10%)             | geranial (25.34%)                  |
| $\beta$ -ocimene* (1.58%)   | geraniol (0.25%)                   |
| p-cymene (0.68%)            | neryl acetate (0.62%)              |
| $\gamma$ -terpinene (2.20%) | $\alpha$ -terpinyl acetate (0.74%) |
| terpinolene (0.05%)         | nerol† (1.80%)                     |
| nonanal (t)                 | geranyl acetate (5.49%)            |

\*correct isomer not identified

† tentative identification

t = trace (<0.01%)

The leaves of the Mexican cultivar of *C. aurantifolia* grown in Cameroon were collected in the short dry season (July to August). Oils produced from the leaves was examined chromatographically using a combination of GC and GC/MS by Jazet Dongmo et al. (1998). The composition of this oil was found to be as follows:

|                                 |                             |
|---------------------------------|-----------------------------|
| (Z)-3-hexenol (0.09%)           | nerol (11.75%)              |
| $\alpha$ -pinene (0.25%)        | geraniol (4.76%)            |
| 6-methyl-5-hepten-2-one (4.39%) | geranial (14.49%)           |
| sabinene (0.51%)                | bornyl acetate (0.05%)      |
| $\beta$ -pinene (0.42%)         | citronellyl acetate (0.07%) |
|                                 | $\delta$ -elemene (0.23%)   |

|                                      |                                              |
|--------------------------------------|----------------------------------------------|
| myrcene (1.31%)                      | $\alpha$ -terpinyl acetate (0.60%)           |
| p-cymene (0.10%)                     | geranyl acetate (2.12%)                      |
| limonene (43.09%)                    | $\beta$ -elemene (0.25%)                     |
| (E)- $\beta$ -ocimene (1.98%)        | <i>trans</i> - $\alpha$ -bergamotene (0.08%) |
| $\gamma$ -terpinene (0.08%)          | $\alpha$ -humulene (0.14%)                   |
| <i>cis</i> -sabinene hydrate (0.10%) | germacrene D (0.16%)                         |
| terpinolene (0.06%)                  | $\alpha$ -selinene (0.05%)                   |
| linalool (1.34%)                     | bicyclogermacrene (0.09%)                    |
| limonene oxide* (0.11%)              | (E,E)- $\alpha$ -farnesene (0.23%)           |
| terpinen-1-ol (0.12%)                | $\beta$ -bisabolene (0.18%)                  |
| isopulegol (0.78%)                   | (Z,E)- $\alpha$ -farnesene (0.05%)           |
| menthone (0.37%)                     | germacrene B (0.46%)                         |
| borneol (0.56%)                      | spathulenol (0.16%)                          |
| terpinen-4-ol (0.14%)                | cubenol (0.05%)                              |
| $\alpha$ -terpineol (0.32%)          | $\beta$ -eudesmol (0.11%)                    |
| $\gamma$ -terpineol† (0.33%)         | $\beta$ -sinensal (0.05%)                    |
| neral (3.84%)                        |                                              |

\*correct isomer not identified

† the natural origin of  $\gamma$ -terpineol is in question

The leaf oil of a second cultivar (Lakeland) of *C. aurantifolia* also grown in Cameroon was found to possess the following composition:

|                                 |                                              |
|---------------------------------|----------------------------------------------|
| $\alpha$ -thujene (0.19%)       | $\beta$ -gurjunene (0.33%)                   |
| $\alpha$ -pinene (0.51%)        | <i>trans</i> - $\alpha$ -bergamotene (0.62%) |
| 6-methyl-5-hepten-2-one (0.04%) | (Z)- $\beta$ -farnesene (0.08%)              |
| sabinene (0.88%)                | allo-aromadendrene (0.04%)                   |
| $\beta$ -pinene (0.52%)         | dodecanol (0.17%)                            |
| myrcene (0.46%)                 | germacrene D (0.03%)                         |
| p-cymene (1.04%)                | $\alpha$ -selinene (0.06%)                   |
| limonene (5.12%)                | bicyclogermacrene (4.11%)                    |
| (Z)- $\beta$ -ocimene (1.54%)   | $\beta$ -bisabolene (1.90%)                  |
| (E)- $\beta$ -ocimene (8.42%)   | $\beta$ -cadinene (0.71%)                    |
| $\gamma$ -terpinene (3.24%)     | $\delta$ -cadinene (0.71%)                   |
| terpinolene (0.21%)             | (Z,E)- $\alpha$ -farnesene (0.24%)           |
| linalool (1.43%)                | cadina-1,4-diene (0.44%)                     |
| terpinen-4-ol (0.22%)           | elemol (8.29%)                               |
| $\alpha$ -terpineol (0.65%)     | nerolidol* (0.72%)                           |
|                                 | germacrene B (5.22%)                         |

|                                    |                            |
|------------------------------------|----------------------------|
| $\gamma$ -terpineol† (0.05%)       | globulol (0.89%)           |
| neral (0.12%)                      | spathulenol (0.49%)        |
| nerol (0.29%)                      | $\alpha$ -cadinene (1.31%) |
| geraniol (0.19%)                   | viridiflorene (1.56%)      |
| geranial (0.36%)                   | humulene oxide* (0.88%)    |
| $\beta$ -elemene (1.52%)           | cubenol (1.76%)            |
| $\alpha$ -terpinyl acetate (0.22%) | $\gamma$ -eudesmol (3.48%) |
| neryl acetate (0.04%)              | T-cadinol (1.33%)          |
| geranyl acetate (0.27%)            | $\beta$ -eudesmol (5.16%)  |
| $\alpha$ -cubebene (0.08%)         | (Z,E)-farnesol (0.96%)     |
| $\alpha$ -copaene (0.05%)          | $\beta$ -sinensal (0.40%)  |
| bicycloelemene (0.06%)             | bergamotol* (0.16%)        |
| $\beta$ -elemene (1.77%)           | (Z,Z)-farnesol (0.06%)     |
| santalene* (0.11%)                 | (E,E)-farnesol (0.03%)     |
| $\beta$ -caryophyllene (3.40%)     | $\alpha$ -sinensal (0.06%) |

\*correct isomer not identified

† the natural origin of  $\gamma$ -terpineol is in question

A leaf oil of *C. aurantifolia* (Key lime) of Malaysian origin was the subject of analysis by Jantan et al. (1996). Using both GC and GC/MS, the authors determined that the lab-prepared oil had the following composition:

|                                |                                 |
|--------------------------------|---------------------------------|
| $\alpha$ -pinene (0.04%)       | $\delta$ -elemene (0.80%)       |
| sabinene (0.06%)               | neryl acetate (0.72%)           |
| $\beta$ -pinene (0.93%)        | geranyl acetate (6.61%)         |
| myrcene (0.79%)                | $\beta$ -elemene (1.59%)        |
| $\alpha$ -phellandrene (0.03%) | dodecanal (0.47%)               |
| $\delta$ -3-carene (0.03%)     | $\beta$ -caryophyllene (5.68%)  |
| limonene (16.41%)              | $\alpha$ -bergamotene* (t)      |
| (Z)- $\beta$ -ocimene (0.41%)  | $\alpha$ -humulene (0.77%)      |
| (E)- $\beta$ -ocimene (1.86%)  | (Z)- $\beta$ -farnesene (0.06%) |
| terpinolene (0.04%)            | $\alpha$ -guaiene (0.93%)       |
| linalool (1.07%)               | (E)- $\beta$ -farnesene (1.82%) |
| citronellal (0.97%)            | $\beta$ -bisabolene (0.14%)     |
| terpinen-4-ol (0.82%)          | (Z)-nerolidol (2.05%)           |
| $\alpha$ -terpineol (0.19%)    | elemol (0.54%)                  |
| decanal (0.61%)                | $\beta$ -eudesmol (0.34%)       |
| nerol (9.54%)                  | $\alpha$ -eudesmol (0.28%)      |
| neral (11.43%)                 | phytol (1.03%)                  |
| geraniol (7.53%)               |                                 |
| geranial (19.42%)              |                                 |

\*correct isomer not identified

t = trace (<0.01%)

Using a combination of GC and  $^{13}\text{C}$ -NMR, Rocca Serra et al. (1998) reported that a leaf oil of Mexican lime was found to contain the following constituents:

|                               |                        |
|-------------------------------|------------------------|
| myrcene (1.0%)                | neral (16.1%)          |
| limonene (34.1%)              | neryl acetate (1.6%)   |
| (Z)- $\beta$ -ocimene (0.7%)  | geranial (23.1%)       |
| (E)- $\beta$ -ocimene (2.4%)  | geranyl acetate (4.3%) |
| trans-sabinene hydrate (1.7%) | citronellol (0.8%)     |
| citronellal (1.8%)            | nerol (2.2%)           |
| linalool (1.2%)               | geraniol (2.4%)        |

A petitgrain oil of the leaves of Egyptian grown *C. aurantifolia* was found by Haggag et al. (1998) to contain the

following major components:

|                          |                              |
|--------------------------|------------------------------|
| $\alpha$ -pinene (4.11%) | $\alpha$ -terpineol (12.63%) |
| $\beta$ -pinene (0.14%)  | citronellol (21.39%)         |
| limonene (32.07%)        | geraniol (10.38%)            |
| p-cymene (0.28%)         | thymol (0.50%)               |
| citronellal (2.64%)      | carvacrol (0.38%)            |
| linalool (3.97%)         | eugenol (0.70%)              |
| nerol (1.48%)            |                              |

This analysis is obviously in error and therefore it should not be considered accurate. It is only included in this review for completeness.

A leaf oil produced from the Mexican lime cultivar (*C. aurantifolia*) grown in China was found by Huang et al. (2000) to possess the following composition:

|                                 |                                    |
|---------------------------------|------------------------------------|
| (E)-2-hexenal (0.02%)           | $\alpha$ -terpineol (0.14%)        |
| $\alpha$ -thujene (0.14%)       | decanal (0.06%)                    |
| $\alpha$ -pinene (0.55%)        | citronellol (0.39%)                |
| camphene (t)                    | nerol (1.73%)                      |
| 6-methyl-5-hepten-2-one (0.63%) | neral (15.86%)                     |
| sabinene (0.14%)                | geraniol (3.45%)                   |
| $\beta$ -pinene (0.11%)         | geranial (22.95%)                  |
| myrcene (0.85%)                 | thymol (0.09%)                     |
| $\delta$ -3-carene (0.04%)      | undecanal (0.06%)                  |
| p-cymene (2.94%)                | methyl geranate (0.13%)            |
| limonene (33.41%)               | citronellyl acetate (0.16%)        |
| 1,8-cineole (0.46%)             | neryl acetate (2.14%)              |
| (Z)- $\beta$ -ocimene (0.17%)   | geranyl acetate (4.75%)            |
| $\beta$ -phellandrene (0.20%)   | dodecanal (0.06%)                  |
| (E)- $\beta$ -ocimene (0.66%)   | $\beta$ -elemene (0.23%)           |
| $\gamma$ -terpinene (0.02%)     | $\beta$ -caryophyllene (1.09%)     |
| octanol (0.02%)                 | cis- $\alpha$ -bergamotene (0.12%) |
| cis-sabinene hydrate (0.02%)    | $\alpha$ -humulene (0.20%)         |
| cis-linalool oxide† (0.06%)     | (E,E)- $\alpha$ -farnesene (0.06%) |
| terpinolene (t)                 | germacrene B (0.08%)               |
| nonanal (0.08%)                 | $\beta$ -bisabolene (0.16%)        |
| linalool (1.26%)                | $\delta$ -cadinene (0.14%)         |
| isopulegol (0.33%)              | (E)-nerolidol (0.15%)              |
| citronellal (1.55%)             | spathulenol (0.20%)                |
| terpinen-4-ol (0.31%)           | caryophyllene oxide (0.14%)        |

† furanoid form

t = trace (<0.01%)

*Citrus aurantifolia* leaf oil produced in Malaysia was analyzed using GC/MS by Taufiq-Yap et al. (2001). The compounds identified in this oil were as follows:

|                              |                                       |
|------------------------------|---------------------------------------|
| $\alpha$ -terpineol (0.06%)  | neryl acetate (0.6%)                  |
| (E)- $\beta$ -ocimene (1.9%) | geranyl acetate (9.1%)                |
| limonene (26.8%)             | 4,8,8-trimethylspiro(2,6)-none (0.5%) |
| citronellal (1.5%)           | $\beta$ -caryophyllene (5.3%)         |
| neral (16.4%)                | $\gamma$ -elemene (1.1%)              |
| geranial (20.5%)             |                                       |
| 2-phenethanol (0.1%)         |                                       |

This analysis is both atypical and was found to contain unusual components and, as a result, the analysis should be ignored. It was only included in this review for completeness.

The fresh leaves of the Mexican lime tree (five years old) were pulverized in liquid nitrogen after the midrib was removed and the powder was extracted

using a mixture of pentane/diethyl ether (1:1). After removal of the spent powder, the extract was concentrated and then analyzed by GC and GC/MS by Gancel et al. (2002). The compounds characterized in the extract were as follows:

|                                   |                                  |
|-----------------------------------|----------------------------------|
| $\alpha$ -pinene (8) <sup>a</sup> | $\alpha$ -humulene (34)          |
| $\alpha$ -thujene (1)             | citronellyl acetate (4)          |
| $\beta$ -pinene (19)              | (E)- $\beta$ -farnesene (12)     |
| sabinene (17)                     | neral (667)                      |
| $\delta$ -3-carene (1)            | germacrene D (71)                |
| $\alpha$ -phellandrene (3)        | $\alpha$ -terpineol (5)          |
| myrcene (39)                      | dodecanal (6)                    |
| limonene (983)                    | $\alpha$ -selinene (13)          |
| $\beta$ -phellandrene (3)         | neryl acetate (49)               |
| (Z)- $\beta$ -ocimene (24)        | $\beta$ -bisabolene (80)         |
| $\gamma$ -terpinene (4)           | geranial (1126)                  |
| (E)- $\beta$ -ocimene (89)        | (Z,E)- $\alpha$ -farnesene (24)  |
| p-cymene (1)                      | (E,E)- $\alpha$ -farnesene (218) |
| terpineolene (1)                  | germacrene A (112)               |
| octanal (1)                       | geranyl acetate (200)            |
| nonanal (1)                       | germacrene C (65)                |
| $\delta$ -elemene (13)            | citronellol (7)                  |
| citronellal (46)                  | nerol (64)                       |
| decanal (7)                       | germacrene B (203)               |
| $\beta$ -bourbonene (14)          | geraniol (56)                    |
| linalool (20)                     | tetradecanal (4)                 |
| cis- $\alpha$ -bergamotene (2)    | (E)-nerolidol (t)                |
| trans- $\alpha$ -bergamotene (46) | hexadecanal (12)                 |
| $\beta$ -elemene (7)              | $\alpha$ -bisabolol (4)          |
| $\beta$ -caryophyllene (261)      | spathulenol (27)                 |
| undecanal (3)                     | geranic acid (8)                 |

<sup>a</sup> = mg/g (fresh weight)

Recently, Lota et al. (2002) compared the composition of the leaf oils of five cultivars of *C. aurantifolia*. A summary of the results of this study can be seen in T-1.

M. Calvarano, F. Salnitro and T. Sacco, *Essential oil from the leaves of the Tahiti lime (Citrus latifolia Tanaka) and Galego lime (Citrus aurantifolia Sw.) from Brazil*. Essenz. Deriv. Agrum., 52, 52-58 (1982).

B. M. Lawrence, *Progress in essential oils*. Perfum. Flavor., 18(5), 46-68 (1993).

P. M. Jazet Dongmo, P. H. Amvam Zollo, F. Fekam Boyom, C. Menut, G. Lamaty and J. M. Bessiere, *Chemical composition of essential oils from Citrus species grown in Cameroon*. Rivista Ital. EPPOS, (Numero Speciale), 156-162 (1998).

I. Jantan, A. S. Ahmad, A. R. Ahmad, N. A. Mohd Ali and N. Ayop, *Chemical composition of some Citrus oils from Malaysia*. J. Essent. Oil Res., 8, 627-632 (1996).

E. G. Haggag, S. M. A. Wahab, S. M. El-Zalabany, E. A. A. Moustafa, E. M. El-Kherasy and T. J. Mabry, *Volatile oils and pectins from Citrus aurantifolia (lime) and Citrus limonia (lemon)*. Asian J. Chem., 10, 828-833 (1998).

Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 110 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).

Y. H. Taufiq-Yap, T. H. Peh, G. C. L. Ee, A. M. Ali, M. Rahmani, M. A. Sukari and R. Muse, *Chemical variability and some biological activities of leaf essential oils from five species of Malaysian Citrus*. Orient. J. Chem., 17, 387-390 (2001).

A-L. Gancel, D. Oll  , P. Ollitrault, F. Luro and J-M. Brillouet, *Leaf and peel volatile compounds of an interspecific Citrus somatic*

*hybrid [Citrus aurantifolia (Christm.) Swing. + Citrus paradise Macfayaden]*. Flav. Fragr. J., 17, 416-424 (2002).

M-L. Lota, D. de Rocca Serra, F. Tomi, C. Jacquemond and J. Casanova, *Volatile components of peel and leaf oils of lemon and lime species*. J. Agric. Food Chem., 50, 796-805 (2002).

## Citrus aurantium L.

Petitgrain bigarade, bitter orange leaf or just petitgrain oil is the common name given to the leaf oil produced from this species.

Calvarano (1968) reported that an Italian bitter orange petitgrain oil contained the following components:

|                             |                                      |
|-----------------------------|--------------------------------------|
| $\alpha$ -thujene (t)       | linalool (17.66%)                    |
| $\beta$ -pinene (0.11%)     | nonanal (0.03%)                      |
| camphene (t)                | citronellal (0.03%)                  |
| heptanal (0.02%)            | terpinen-4-ol (0.74%)                |
| sabinene (0.10%)            | $\alpha$ -terpineol (4.16%)          |
| $\beta$ -pinene (0.83%)     | decanal (0.12%)                      |
| myrcene (1.59%)             | citronellol (0.47%)                  |
| $\alpha$ -terpinene (0.02%) | neral (0.03%)                        |
| $\delta$ -3-carene (0.31%)  | nerol (1.22%)                        |
| p-cymene (0.76%)            | geranial (0.11%)                     |
| limonene (1.07%)            | geraniol (0.34%)                     |
| $\beta$ -ocimene* (0.21%)   | linalyl acetate (>60.00%)            |
| octanal (0.02%)             | methyl N-methyl anthranilate (2.51%) |
| $\gamma$ -terpinene (1.56%) |                                      |
| terpinolene (0.46%)         |                                      |

\*correct isomer not identified

t = trace (<0.01%)

An oil of bitter orange produced in Egypt was found by Karawya et al. (1970) to contain the following constituents:

|                             |                             |
|-----------------------------|-----------------------------|
| $\alpha$ -pinene (1.66%)    | linalool (4.95%)            |
| sabinene (0.95%)            | linalyl acetate (1.37%)     |
| $\beta$ -pinene (2.65%)     | neral (1.84%)               |
| camphene (1.15%)            | citronellol (1.84%)         |
| myrcene (0.92%)             | geranial (2.43%)            |
| limonene (26.79%)           | nerol + farnesol* (6.72%)   |
| $\beta$ -ocimene* (1.84%)   | geraniol (1.38%)            |
| p-cymene (1.50%)            | geranyl acetate (3.45%)     |
| $\gamma$ -terpinene (2.53%) | methyl anthranilate (2.42%) |
| $\alpha$ -terpineol (1.18%) |                             |
| citronellal (0.87%)         |                             |

\*correct isomer not identified

As these compounds were supposed to be listed in elution order from a non-polar column, some of the results appear to be erroneous.

Urbieta-Rehnfeld and Jennings (1974) determined that the main constituents of a redistilled Paraguayan petitgrain oil were as follows:

|                               |                             |
|-------------------------------|-----------------------------|
| myrcene (5.36%)               | $\alpha$ -terpineol (7.55%) |
| (Z)- $\beta$ -ocimene (1.68%) | $\alpha$ -terpinyl acetate  |
| (E)- $\beta$ -ocimene (3.32%) | (2.29%)                     |
| linalool (27.95%)             | geranyl acetate (2.61%)     |

Comparative composition (%) of the leaf oils of five cultivars of *Citrus aurantifolia*

T-1

| Compound                     | 1    | 2    | 3    | 4    | 5    |
|------------------------------|------|------|------|------|------|
| $\alpha$ -thujene            | t    | t    | -    | 0.2  | t    |
| $\alpha$ -pinene             | 0.2  | 0.2  | 0.2  | 1.1  | 0.1  |
| $\beta$ -pinene              | 0.3  | 0.3  | 0.3  | 0.2  | 0.5  |
| sabinene                     | 0.3  | 0.6  | 0.3  | 0.1  | 0.4  |
| $\delta$ -3-carene           | t    | t    | t    | t    | t    |
| myrcene                      | 1.0  | 0.9  | 0.9  | 0.6  | 0.8  |
| limonene                     | 34.1 | 32.9 | 31.7 | 22.9 | 22.1 |
| $\beta$ -phellandrene        | 0.2  | -    | 0.3  | 0.1  | 0.1  |
| 1,8-cineole                  | t    | 1.0  | t    | t    | t    |
| (Z)- $\beta$ -ocimene        | 0.7  | 0.4  | 0.5  | 0.4  | 0.8  |
| $\gamma$ -terpinene          | 0.1  | 0.1  | t    | t    | 0.1  |
| (E)- $\beta$ -ocimene        | 2.5  | 1.1  | 1.6  | 1.1  | 2.0  |
| p-cymene                     | t    | t    | t    | -    | t    |
| terpinolene                  | -    | -    | -    | t    | -    |
| octanal                      | -    | 0.1  | t    | -    | t    |
| 6-methyl-5-hepten-2-one      | 1.7  | 2.5  | 1.5  | 1.1  | 1.6  |
| allo-ocimene*                | t    | -    | t    | -    | -    |
| nonanal                      | -    | 0.1  | t    | -    | -    |
| cis-limonene oxide           | t    | 0.1  | 0.1  | 0.1  | -    |
| citronellal                  | 1.8  | 1.2  | 1.3  | 1.7  | 3.8  |
| decanal                      | 0.4  | 0.2  | 0.2  | 0.6  | 0.4  |
| linalool                     | 1.2  | 1.5  | 1.2  | 1.1  | 1.2  |
| trans- $\alpha$ -bergamotene | -    | t    | -    | 0.1  | -    |
| $\beta$ -elemene             | 0.1  | 0.2  | 0.1  | -    | 0.1  |
| $\beta$ -caryophyllene       | 0.3  | -    | 0.2  | 0.4  | 0.2  |
| terpinen-4-ol                | -    | 0.1  | -    | 0.1  | -    |
| undecanal                    | -    | -    | -    | -    | 0.1  |
| citronellyl acetate          | 0.1  | -    | 0.1  | 0.3  | 0.3  |
| $\alpha$ -humulene           | t    | -    | -    | 0.1  | t    |
| neral                        | 16.2 | 20.5 | 19.6 | 16.0 | 16.8 |
| $\alpha$ -terpinyl acetate   | -    | -    | -    | 0.1  | -    |
| $\alpha$ -terpineol          | 0.2  | 0.6  | 0.3  | 0.1  | 0.2  |
| germacrene D                 | 0.3  | -    | t    | -    | t    |
| neryl acetate                | 1.6  | 0.6  | 1.0  | 1.6  | 3.1  |
| geranial                     | 23.1 | 26.7 | 26.9 | 23.1 | 23.8 |
| geranyl acetate              | 4.3  | 2.2  | 3.5  | 4.6  | 8.3  |
| citronellol                  | 0.8  | 0.4  | 0.5  | 0.4  | 1.1  |
| nerol                        | 2.2  | 2.1  | 2.2  | 1.4  | 3.1  |
| geraniol                     | 2.4  | 1.9  | 2.3  | 1.6  | 3.8  |
| caryophyllene oxide          | 0.2  | 0.1  | 0.2  | 0.3  | 0.4  |
| (E)-nerolidol                | -    | -    | -    | 0.3  | -    |
| spathulenol                  | -    | -    | t    | -    | -    |
| santal-10-en-2-ol            | -    | -    | 0.1  | 8.5  | -    |
| $\beta$ -sinensal            | t    | -    | -    | -    | -    |
| manoyl oxide                 | 0.7  | -    | -    | -    | -    |

\*correct isomer not identified; cultivars: 1. Mexican, 2. Ambilobe, 3. Antillaise, 4. New Caledonia and 5. Kirk

|                          |                  |
|--------------------------|------------------|
| linalyl acetate (44.29%) | nerol (1.01%)    |
| neryl acetate (0.55%)    | geraniol (2.33%) |

Using a combination of GC and IR de Vottero et al. (1978) determined that an oil produced from the leaves of the bitter orange tree grown in Argentina contained  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, limonene, octanal, p-cymene,  $\gamma$ -terpinene, linalool, linalyl acetate,  $\alpha$ -terpineol,  $\alpha$ -terpinyl acetate, citronellyl acetate, nerol, geraniol and geranyl acetate.

A leaf oil of bitter orange petitgrain produced in Algeria was found by Baaliouamer and Meklati (1986) to possess the following composition:

|                                       |                                |
|---------------------------------------|--------------------------------|
| $\alpha$ -pinene (0.19%)              | terpinen-4-ol (0.42%)          |
| $\beta$ -pinene (1.76%)               | $\alpha$ -terpineol (6.80%)    |
| sabinene (1.58%)                      | nerol (1.51%)                  |
| $\delta$ -3-carene (0.20%)            | neral (0.12%)                  |
| myrcene (1.82%)                       | geraniol (3.97%)               |
| limonene (1.25%)                      | linalyl acetate (28.94%)       |
| $\beta$ -phellandrene (0.01%)         | geranyl formate (2.00%)        |
| cyclofenchene† (0.57%)                | geranyl acetate (3.54%)        |
| $\gamma$ -terpinene (0.08%)           | $\beta$ -caryophyllene (0.21%) |
| $\beta$ -ocimene* (1.92%)             | bicycloelemene (0.20%)         |
| p-cymene (0.16%)                      | farnesyl acetate* (0.09%)      |
| terpinolene (0.30%)                   | phytol (0.23%)                 |
| <i>cis</i> -linalool oxide‡ (3.19%)   | 2,6,10-trimethyl-2,6,9,11-     |
| <i>trans</i> -linalool oxide‡ (0.07%) | dodecatetraenal† (0.11%)       |
| linalool (36.10%)                     |                                |

\*correct isomer not identified

† furanoid form

‡ unusual constituents require corroboration before their natural occurrence in this oil can be accepted

Bitter orange leaf oil produced in China was the subject of analysis by Lin et al. (1986). The composition of this oil was found to be:

|                                       |                                       |
|---------------------------------------|---------------------------------------|
| $\alpha$ -thujene (t)                 | neral (t)                             |
| $\alpha$ -pinene (0.25%)              | geraniol (0.98%)                      |
| camphene (t)                          | linalyl acetate (44.08%)              |
| $\beta$ -pinene (t)                   | geranial (t)                          |
| myrcene (1.02%)                       | <i>trans</i> -linalool oxide† (0.60%) |
| limonene (0.78%)                      | methyl anthranilate (3.49%)           |
| $\beta$ -ocimene* (0.30%)             | $\alpha$ -terpinyl acetate (1.11%)    |
| <i>trans</i> -linalool oxide‡ (0.30%) | <i>cis</i> -linalool oxide† (0.17%)   |
| <i>cis</i> -linalool oxide‡ (5.40%)   | neryl acetate (0.83%)                 |
| linalool (11.72%)                     | geranyl acetate (1.73%)               |
| p-mentha-1,4-dien-7-ol (0.07%)        | nonanal (0.45%)                       |
| <i>trans</i> -pinocarveol (t)         | $\beta$ -caryophyllene (0.11%)        |
| camphor (t)                           | $\alpha$ -humulene (1.35%)            |
| terpinen-4-ol (t)                     | $\gamma$ -muurolene (0.45%)           |
| $\alpha$ -terpineol (1.26%)           | (Z)-nerolidol (t)                     |
| nerol (t)                             | farnesol* (0.23%)                     |

\*correct isomer not identified

† furanoid form

‡ pyranoid form

t = trace (<0.01%)

Germana et al. (1990) analyzed a leaf oil of bitter orange and found that it contained the following components:

|                         |                       |
|-------------------------|-----------------------|
| $\beta$ -pinene (0.40%) | neryl acetate (0.82%) |
| sabinene (0.03%)        | neral (0.78%)         |

|                                |                             |
|--------------------------------|-----------------------------|
| myrcene (0.04%)                | geranyl acetate (0.49%)     |
| limonene (0.97%)               | geranial (0.93%)            |
| $\alpha$ -terpinene (0.02%)    | nerol (0.36%)               |
| $\beta$ -caryophyllene (0.10%) | geraniol (0.08%)            |
| linalool (94.10%)              | methyl anthranilate (0.11%) |
| benzaldehyde (0.07%)           | farnesol* (0.16%)           |
| $\alpha$ -terpineol (0.38%)    |                             |

\*correct isomer not identified

It was a surprise that linalyl acetate was not detected in this oil.

In 1995, Bussaada compared compositions of two leaf oils of bitter orange produced from leaves harvested in Greece (Crete) and Tunisia. The results of this study can be seen in T-2.

The leaf oil of *C. aurantium* was analyzed by GC and GC/MS in 1995 (Gurib-Fakim and Demarne). They found that the oil, which was produced from leaves harvested in Mauritius, contained:

|                                |                             |
|--------------------------------|-----------------------------|
| (Z)-3-hexenol (t)              | terpinen-4-ol (20.86%)      |
| myrcene (t)                    | citronellol (2.33%)         |
| $\alpha$ -phellandrene (0.12%) | geraniol (6.60%)            |
| (Z)- $\beta$ -ocimene (t)      | <i>cis</i> -carveol (0.98%) |
| (E)- $\beta$ -ocimene (t)      | geranyl formate (0.20%)     |
| octanol (0.34%)                | neryl acetate (0.53%)       |
| terpinolene (0.18%)            | geraniol (0.99%)            |
| linalool (66.10%)              | $\beta$ -copaene (0.23%)    |
| $\alpha$ -terpineol (0.30%)    |                             |

t = trace (<0.01%)

It should be noted that this leaf oil contains an unusual level of terpinen-4-ol and was found to be devoid of linalyl acetate.

In 1996, Mondello et al. and Dugo et al. (1996) analyzed five samples of Italian produced bitter orange leaf oil using HPLC-GC/MS. The oils were found to possess the following composition:

|                                      |
|--------------------------------------|
| hexanal (t)                          |
| tricyclene (t)                       |
| $\alpha$ -thujene (t-0.01%)          |
| $\alpha$ -pinene (0.03-0.30%)        |
| $\alpha$ -fenchene (t)               |
| camphene (t-0.01%)                   |
| sabinene (0.13-0.23%)                |
| $\beta$ -pinene (0.65-1.15%)         |
| 6-methyl-5-hepten-2-one (0.01-0.10%) |
| myrcene (0.56-1.24%)                 |
| $\alpha$ -phellandrene (t-0.03%)     |
| $\delta$ -3-carene (0.21-0.67%)      |
| $\alpha$ -terpinene (t-0.02%)        |
| o-cymene (0-0.01%)                   |
| p-cymene (0.03-0.08%)                |
| limonene (0.44-2.17%)                |
| $\beta$ -phellandrene (0.03-0.04%)   |
| 1,8-cineole (0.02-0.05%)             |
| (Z)- $\beta$ -ocimene (0.20-0.44%)   |



(E)- $\beta$ -ocimene (0.57-1.76%)  
 $\gamma$ -terpinene (0.01-0.09%)  
*cis*-sabinene hydrate (t-0.01%)  
*cis*-linalool oxide† (0.03-0.09%)  
*p*-mentha-2,4(8)-diene (0.02-0.06%)  
 terpinolene (0.08-0.22%)  
*p*-cymene (0.01-0.08%)  
*trans*-linalool oxide† (0.01-0.03%)  
 linalool (21.70-32.55%)  
 nonanal (0.02-0.05%)  
*cis*-*p*-menth-2-en-1-ol (t-0.01%)  
*trans*-*p*-menth-2-en-1-ol (t-0.02%)  
 citronellal (0.01-0.04%)  
 terpinen-4-ol (0.05-0.08%)  
 $\alpha$ -terpineol (3.09-5.63%)  
 nerol (0.75-0.99%)  
 neral (0.21-0.43%)  
 geraniol (0.71-0.95%)  
 linalyl acetate (50.68-62.57%)  
 geranial (0.38-0.64%)  
 methyl geranate (t-0.03%)  
 linalyl propionate (0.02-0.04%)  
 $\delta$ -elemene (0.01%)  
 $\alpha$ -cubebene (t-0.01%)  
 $\alpha$ -terpinyl acetate (0.08-0.16%)  
 citronellyl acetate (t)  
 $\alpha$ -copaene (t-0.01%)  
 neryl acetate (1.04-1.73%)  
 geranyl acetate (1.90-3.16%)  
 $\beta$ -elemene (t-0.02%)  
 methyl N-methyl anthranilate (t-0.14%)  
 $\beta$ -caryophyllene (0.48-0.61%)  
*trans*- $\alpha$ -bergamotene (t-0.01%)  
 (Z)- $\beta$ -farnesene (0.04-0.07%)  
 $\alpha$ -humulene (0.04-0.06%)  
 bicyclogermacrene (0.04-0.30%)  
 (E,E)- $\alpha$ -farnesene (0.01-0.06%)  
 $\beta$ -bisabolene (0-0.01%)  
 $\delta$ -cadinene (0.02-0.03%)  
 (E)-nerolidol (0.05-0.08%)  
 spathulenol (0.03-0.13%)  
 caryophyllene oxide (0.02-0.07%)

t = trace (<0.01%)

† furanoid form

Mondello et al. (1996) also reported the results of another analysis of bitter orange petitgrain oil of Italian origin. This oil was found to contain the following components:

|                                 |                                    |
|---------------------------------|------------------------------------|
| tricyclene (t)                  | nerol (1.28%)                      |
| $\alpha$ -thujene (0.02%)       | neral (0.40%)                      |
| $\alpha$ -pinene (0.17%)        | linalyl acetate (39.75%)           |
| camphene (t)                    | geranial (0.67%)                   |
| sabinene (0.45%)                | $\delta$ -elemene (0.02%)          |
| $\beta$ -pinene (2.20%)         | $\alpha$ -cubebene (0.02%)         |
| 6-methyl-5-hepten-2-one (0.08%) | $\alpha$ -terpinyl acetate (0.06%) |
| myrcene (2.31%)                 | citronellyl acetate (0.11%)        |
| $\alpha$ -phellandrene (0.05%)  | $\alpha$ -copaene (0.01%)          |
| $\delta$ -3-carene (1.15%)      | neryl acetate (2.27%)              |
| $\alpha$ -terpinene (0.03%)     | geranyl acetate (4.22%)            |
| <i>p</i> -cymene (0.12%)        | $\beta$ -elemene (0.04%)           |

## Comparative percentage composition of bitter orange leaf oil from two different origins

T-2

| Compound                      | Greece (April)<br>leaf oil | Tunisia (April)<br>leaf oil |
|-------------------------------|----------------------------|-----------------------------|
| $\alpha$ -pinene              | 0.14                       | 0.20                        |
| camphene                      | t                          | t                           |
| $\beta$ -pinene               | 2.15                       | 1.26                        |
| sabinene                      | 0.33                       | 0.21                        |
| myrcene                       | 2.29                       | 2.30                        |
| $\alpha$ -terpinene           | 0.03                       | 0.03                        |
| limonene                      | 0.60                       | 0.68                        |
| $\beta$ -phellandrene         | 0.04                       | 0.03                        |
| (Z)- $\beta$ -ocimene         | 3.00                       | 0.91                        |
| $\gamma$ -terpinene           | 0.03                       | 0.04                        |
| (E)- $\beta$ -ocimene         | 1.11                       | 2.33                        |
| terpinolene                   | 0.58                       | 0.49                        |
| <i>trans</i> -linalool oxide* | 0.02                       | 0.04                        |
| <i>cis</i> -linalool oxide*   | 0.04                       | 0.02                        |
| linalool                      | 24.70                      | 36.81                       |
| linalyl acetate               | 35.50                      | 22.06                       |
| $\beta$ -caryophyllene        | 0.42                       | 0.31                        |
| terpinen-4-ol                 | 0.15                       | 0.15                        |
| $\alpha$ -terpineol           | 8.30                       | 11.67                       |
| neryl acetate                 | 3.20                       | 3.20                        |
| farnesene*                    | 0.02                       | 0.11                        |
| geranyl acetate               | 6.15                       | 6.02                        |
| nerol                         | 2.20                       | 2.44                        |
| geraniol                      | 6.10                       | 7.07                        |
| nerolidol*                    | 0.25                       | 0.02                        |

\* correct isomer not identified  
 t = trace (<0.01%)

|                                       |                                              |
|---------------------------------------|----------------------------------------------|
| limonene (2.02%)                      | methyl N-methyl anthranilate (0.17%)         |
| 1,8-cineole (0.06%)                   | $\beta$ -caryophyllene (0.71%)               |
| (Z)- $\beta$ -ocimene (0.89%)         | <i>trans</i> - $\alpha$ -bergamotene (0.01%) |
| (E)- $\beta$ -ocimene (3.64%)         | $\alpha$ -humulene (0.07%)                   |
| $\gamma$ -terpinene (0.18%)           | (Z)- $\beta$ -farnesene (0.07%)              |
| <i>cis</i> -linalool oxide† (0.05%)   | bicyclogermacrene (0.28%)                    |
| terpinolene (0.59%)                   | (E,E)- $\alpha$ -farnesene (0.05%)           |
| <i>trans</i> -linalool oxide† (0.03%) | $\delta$ -cadinene (0.04%)                   |
| linalool (29.80%)                     | (E)-nerolidol (0.06%)                        |
| citronellal (0.05%)                   | spathulenol (0.03%)                          |
| terpinen-4-ol (0.12%)                 | caryophyllene oxide (0.02%)                  |
| $\alpha$ -terpineol (5.39%)           |                                              |

† furanoid form  
 t = trace (<0.01%)

In addition, the authors pointed out that it was possible to determine when the leaf oils of other commercially important *Citrus* species were added, either mistakenly or purposely to the bitter orange petitgrain oil. A summary of the compounds that, according to the authors, are unique to lemon, sweet orange and mandarin petitgrain oils and not found in bitter orange petitgrain can be seen in T-3.

| Lemon Petitgrain                                   | Orange Petitgrain               | Mandarin Petitgrain             |
|----------------------------------------------------|---------------------------------|---------------------------------|
| $\alpha$ -fenchene                                 | $\alpha$ -fenchene              | $\alpha$ -fenchene              |
| o-cymene                                           | o-cymene                        | octanol                         |
| <i>cis</i> -sabinene hydrate                       | <i>cis</i> -p-menth-2-en-1-ol   | -                               |
| nonanal                                            | $\beta$ -cubebene               | nonanal                         |
| <i>cis</i> -limonene oxide                         | <i>trans</i> -p-menth-2-en-1-ol | <i>trans</i> -p-menth-2-en-1-ol |
| isopulegol                                         | thymol                          | thymol                          |
| undecanal                                          | $\alpha$ -selinene              | $\alpha$ -selinene              |
| 2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol | valencene                       | methyl anthranilate             |
| camphenol                                          | $\beta$ -sinsensal              | methyl N-dimethyl anthranilate  |
| $\alpha$ -bisabolol                                | $\alpha$ -sinensal              | -                               |

Two samples of bitter orange petitgrain oil were the subject of analysis by Rocca Serra et al. (1998) using GC and  $^{13}\text{C}$ -NMR. The range of components found in these oils were as follows:

|                                  |                                  |
|----------------------------------|----------------------------------|
| $\beta$ -pinene (4.2-4.7%)       | linalool (33.2-36.9%)            |
| sabinene (0.5-0.6%)              | linalyl acetate (21.7-22.5%)     |
| myrcene (2.6-2.8%)               | $\alpha$ -terpineol (10.8-11.9%) |
| limonene (0.7-0.8%)              | neryl acetate (2.7-2.9%)         |
| (Z)- $\beta$ -ocimene (1.0-1.1%) | geranyl acetate (5.1-5.5%)       |
| (E)- $\beta$ -ocimene (2.9-3.2%) | nerol (2.1-2.3%)                 |
| terpinolene (0.6%)               | geraniol (5.9-6.7%)              |

The leaf oil of a third cultivar of bitter orange was found to possess a different composition. The components found in this oil were:

|                              |                            |
|------------------------------|----------------------------|
| $\alpha$ -thujene (0.4%)     | p-cymene (0.3%)            |
| $\alpha$ -pinene (2.2%)      | terpinolene (0.7%)         |
| $\beta$ -pinene (36.7%)      | citronellal (1.0%)         |
| sabinene (5.7%)              | linalool (22.6%)           |
| $\delta$ -3-carene (1.8%)    | terpinen-4-ol (0.8%)       |
| myrcene (0.7%)               | neral (0.7%)               |
| limonene (4.0%)              | $\alpha$ -terpineol (1.3%) |
| 1,8-cineole (2.4%)           | geraniol (1.0%)            |
| $\gamma$ -terpinene (7.7%)   | geranyl acetate (0.5%)     |
| (E)- $\beta$ -ocimene (6.2%) |                            |

Finally, the leaf oil of another cultivar of bitter orange of Australian origin had yet another chemical composition. This oil was found to contain the following constituents:

|                            |                                       |
|----------------------------|---------------------------------------|
| $\alpha$ -thujene (0.5%)   | (Z)- $\beta$ -ocimene (0.5%)          |
| $\alpha$ -pinene (1.9%)    | $\gamma$ -terpinene (3.2%)            |
| $\beta$ -pinene (4.4%)     | (E)- $\beta$ -ocimene (15.1%)         |
| sabinene (52.6%)           | terpinolene (0.8%)                    |
| myrcene (3.5%)             | <i>trans</i> -sabinene hydrate (0.6%) |
| $\alpha$ -terpinene (2.0%) | linalool (1.0%)                       |
| limonene (2.3%)            | terpinen-4-ol (7.0%)                  |
| 1,8-cineole (0.8%)         |                                       |

The main compounds found in the leaf oils of five *C. aurantium* cultivars (Chania, Brazilian, Keen and bittersweet) were the subject of analysis by Protopapadakis and Papanikolaou (1998). The range of components characterized was as follows:

|                                    |
|------------------------------------|
| $\beta$ -pinene (1.71-2.25%)       |
| myrcene (2.03-2.29%)               |
| limonene (6.82-11.13%)             |
| (Z)- $\beta$ -ocimene (2.07-2.61%) |
| linalyl acetate (37.39-39.85%)     |
| geranyl acetate (5.19-5.50%)       |
| neryl acetate (1.70-2.78%)         |
| linalool (24.24-26.32%)            |
| geraniol (4.85-8.43%)              |
| nerol (1.70-1.93%)                 |
| $\alpha$ -terpineol (7.11-7.90%)   |

Adami et al. (2000) compared the major constituents of an oil, supercritical  $\text{CO}_2$  extract and a diethyl ether extract of bitter orange leaves obtained from trees grown in Reggio Calabria (Italy). The results of this study are shown in T-4. It is of interest to note that the level of linalyl acetate in the oil is 50% reduced over the extracts of the same batch of leaves. This is presumably due to hydrolysis of the ester during the distillation process.

The leaf oils of two cultivars of *C. aurantium* (Australian and Guangpi) grown in China were analyzed by Huang et al. (2000). The constituents identified in these oils were found to be:

|                                      |
|--------------------------------------|
| $\alpha$ -thujene (0.45-0.48%)       |
| $\alpha$ -pinene (2.08-2.15%)        |
| camphene (0.07%)                     |
| sabinene (54.39-55.10%)              |
| $\beta$ -pinene (4.37-4.91%)         |
| myrcene (3.04-3.06%)                 |
| $\alpha$ -phellandrene (0.11-0.12%)  |
| $\delta$ -3-carene (0.21-0.65%)      |
| $\alpha$ -terpinene (0.62-0.73%)     |
| p-cymene (0.10-0.13%)                |
| limonene (1.85-1.92%)                |
| (Z)- $\beta$ -ocimene (0.53-0.59%)   |
| $\beta$ -phellandrene (0.72-0.75%)   |
| (E)- $\beta$ -ocimene (18.55-18.57%) |
| $\gamma$ -terpinene (1.15-1.31%)     |
| octanol (0.03%)                      |

*cis*-sabinene hydrate (0.34-0.43%)  
*cis*-linalool oxide† (0.03%)  
 terpinolene (0.33-0.34%)  
 nonanal (0.18-0.23%)  
 linalool (0.42%)  
 isopulegol (0.06-0.07%)  
 citronellal (0.06-0.09%)  
 terpinen-4-ol (1.94-2.33%)  
 α-terpineol (0.10-0.15%)  
 decanal (0.06%)  
 citronellol (0.03-0.04%)  
 nerol (0.06-0.07%)  
 neral (0.02%)  
 geraniol (0.05-0.06%)  
 geranial (0.04%)  
 thymol (t)  
 citronellyl acetate (0.04-0.07%)  
 neryl acetate (0.54-0.61%)  
 geranyl acetate (0.06-0.07%)  
 β-elemene (0.03%)  
 β-caryophyllene (0.76-0.84%)  
 α-humulene (0.10-0.11%)  
 (E,E)-α-farnesene (0.04-0.11%)  
 germacrene B (0.29-0.34%)  
 valencene (0.49-0.52%)  
 δ-cadinene (0.07-0.09%)  
 (E)-nerolidol (0.02-0.03%)  
 spathulenol (0.26-0.33%)  
 caryophyllene oxide (0.38-0.43%)

† furanoid form

t = trace (<0.01%)

Huang et al. found that the leaf oil of the Chinese Zhulan cultivar possessed the following composition:

|                                  |                             |
|----------------------------------|-----------------------------|
| α-thujene (1.82%)                | α-terpineol (0.08%)         |
| α-pinene (4.04%)                 | decanal (t)                 |
| camphene (0.05%)                 | citronellol (0.20%)         |
| sabinene (1.34%)                 | nerol (0.14%)               |
| β-pinene (7.79%)                 | neral (0.05%)               |
| myrcene (1.08%)                  | geraniol (0.05%)            |
| α-phellandrene (0.07%)           | geranial (0.14%)            |
| α-terpinene (0.42%)              | thymol (8.13%)              |
| p-cymene (8.62%)                 | undecanal (0.04%)           |
| limonene (4.42%)                 | citronellyl acetate (0.13%) |
| (Z)-β-ocimene (0.08%)            | neryl acetate (0.23%)       |
| β-phellandrene (0.09%)           | geranyl acetate (0.03%)     |
| (E)-β-ocimene (1.55%)            | β-elemene (0.02%)           |
| γ-terpinene (39.90%)             | β-caryophyllene (0.22%)     |
| octanol (0.03%)                  | (Z)-β-farnesene (0.67%)     |
| <i>cis</i> -sabinene hydrate (t) | α-humulene (0.06%)          |
| <i>cis</i> -linalool oxide† (t)  | germacrene B (0.12%)        |
| α-p-dimethylstyrene (1.49%)      | δ-cadinene (0.04%)          |
| terpinolene (1.77%)              | elemol (0.08%)              |
| linalool (9.75%)                 | (E)-nerolidol (0.28%)       |
| isopulegol (0.39%)               | spathulenol (0.26%)         |
| citronellal (0.60%)              | caryophyllene oxide (0.10%) |
| terpinen-4-ol (0.15%)            |                             |

† furanoid form

t = trace (<0.01%)

The same authors found that the leaf oil of the Goutou cultivar possessed an oil that contained the following constituents:

**Table IV. Comparative percentage composition of three isolates of bitter orange leaves**

**T-4**

| Compound           | Oil   | SFE   | Ether Extract |
|--------------------|-------|-------|---------------|
| α-thujene          | 0.73  | 0.05  | 0.12          |
| α-pinene           | 1.21  | 0.40  | 1.13          |
| β-pinene           | 0.34  | 0.08  | 0.05          |
| myrcene            | 0.59  | 0.02  | t             |
| limonene           | 1.55  | 0.20  | 0.32          |
| terpinolene        | 0.34  | t     | t             |
| linalool           | 37.38 | 1.24  | 4.04          |
| α-terpineol        | 6.34  | 0.01  | t             |
| linalyl acetate    | 40.28 | 92.05 | 87.87         |
| neryl acetate      | 1.87  | 0.06  | 0.02          |
| geranyl acetate    | 3.77  | 0.14  | t             |
| β-caryophyllene    | 2.18  | 2.78  | 2.17          |
| β-bisabolene       | 0.96  | 1.32  | 1.25          |
| t = trace (<0.01%) |       |       |               |

|                                      |                             |
|--------------------------------------|-----------------------------|
| α-thujene (0.43%)                    | linalool (10.70%)           |
| α-pinene (2.14%)                     | citronellal (4.15%)         |
| camphene (0.16%)                     | terpinen-4-ol (0.41%)       |
| sabinene (5.25%)                     | α-terpineol (0.85%)         |
| β-pinene (26.56%)                    | citronellal (0.87%)         |
| myrcene (1.18%)                      | nerol (0.59%)               |
| α-phellandrene (0.09%)               | neral (2.37%)               |
| δ-3-carene (3.12%)                   | geraniol (0.68%)            |
| α-terpinene (0.35%)                  | geranial (3.50%)            |
| p-cymene (5.24%)                     | citronellyl acetate (0.66%) |
| limonene (6.90%)                     | α-terpinyl acetate (0.18%)  |
| 1,8-cineole (1.13%)                  | neryl acetate (0.95%)       |
| (Z)-β-ocimene (0.17%)                | geranyl acetate (2.64%)     |
| β-phellandrene (0.52%)               | β-elemene (0.05%)           |
| (E)-β-ocimene (4.67%)                | β-caryophyllene (0.45%)     |
| γ-terpinene (6.57%)                  | α-humulene (0.15%)          |
| octanol (0.03%)                      | germacrene B (0.24%)        |
| <i>cis</i> -sabinene hydrate (0.04%) | δ-cadinene (0.04%)          |
| <i>cis</i> -linalool oxide† (0.05%)  | (E)-nerolidol (0.39%)       |
| terpinolene (0.67%)                  | spathulenol (0.41%)         |
| nonanal (0.08%)                      | caryophyllene oxide (0.19%) |

† furanoid form

Finally, Huang et al. analyzed the leaf oil of the Jiangjin cultivar of *C. aurantium* grown in China. The composition of this oil was found to be as follows:

|                       |                             |
|-----------------------|-----------------------------|
| α-thujene (0.14%)     | decanal (0.03%)             |
| α-pinene (3.04%)      | citronellol (0.41%)         |
| camphene (0.19%)      | nerol (0.08%)               |
| sabinene (8.15%)      | neral (t)                   |
| β-pinene (49.78%)     | geraniol (t)                |
| myrcene (0.48%)       | geranial (t)                |
| δ-3-carene (t)        | thymol (t)                  |
| α-terpinene (0.07%)   | undecanal (0.07%)           |
| p-cymene (0.04%)      | citronellyl acetate (0.45%) |
| limonene (2.61%)      | neryl acetate (0.72%)       |
| (Z)-β-ocimene (0.30%) | δ-elemene (0.89%)           |



|                                     |                                    |
|-------------------------------------|------------------------------------|
| $\beta$ -phellandrene (0.94%)       | $\beta$ -elemene (0.75%)           |
| (E)- $\beta$ -ocimene (11.46%)      | $\beta$ -caryophyllene (2.80%)     |
| $\gamma$ -terpinene (0.18%)         | (Z)- $\beta$ -farnesene (0.35%)    |
| octanol (0.04%)                     | $\alpha$ -humulene (0.68%)         |
| <i>cis</i> -sabinene hydrate (t)    | (E,E)- $\alpha$ -farnesene (1.24%) |
| <i>cis</i> -linalool oxide† (0.06%) | germacrene B (1.17%)               |
| terpinolene (0.08%)                 | $\delta$ -cadinene (0.49%)         |
| nonanal (t)                         | elemol (1.91%)                     |
| linalool (1.52%)                    | (E)-nerolidol (3.98%)              |
| citronellal (0.89%)                 | spathulenol (0.81%)                |
| terpinen-4-ol (0.29%)               | caryophyllene oxide (0.78%)        |
| $\alpha$ -terpineol (0.08%)         |                                    |

† furanoid form

t = trace (<0.01%)

Lota et al. (2001) subjected the leaf oils of 26 cultivars and four hybrids of bitter orange to analysis using both GC and GC/MS. The compositions of the oils of seven country specific cultivars are shown in Table 5. In addition, the range of composition of the leaf oils of 18 of the other cultivars was found to be as follows:

|                                      |                                        |
|--------------------------------------|----------------------------------------|
| $\alpha$ -thujene (t)                | <i>trans</i> -linalool oxide† (0-0.1%) |
| $\alpha$ -pinene (0.1-0.3%)          | citronellal (0-t)                      |
| camphene (0-t)                       | linalool (27.7-37.7%)                  |
| $\beta$ -pinene (2.1-5.9%)           | linalyl acetate (21.7-30.1%)           |
| sabinene (0.3-0.8%)                  | <i>cis</i> -p-menth-2-en-1-ol (0-t)    |
| myrcene (2.2-2.8%)                   | $\beta$ -caryophyllene (0-0.3%)        |
| $\alpha$ -phellandrene (0-t)         | terpinen-4-ol (0-0.2%)                 |
| $\alpha$ -terpinene (0-0.1%)         | citronellyl acetate (0-t)              |
| limonene (0.6-1.2%)                  | $\alpha$ -humulene (0-t)               |
| $\beta$ -phellandrene (0-0.1%)       | neral (0-0.1%)                         |
| 1,8-cineole (0-t)                    | $\alpha$ -terpinyl acetate (0-0.2%)    |
| (Z)- $\beta$ -ocimene (0.9-1.1%)     | $\alpha$ -terpineol (9.1-11.1%)        |
| $\gamma$ -terpinene (0-0.1%)         | (Z)- $\alpha$ -bisabolene (0-0.2%)     |
| (E)- $\beta$ -ocimene (2.5-3.5%)     | neryl acetate (2.3-2.9%)               |
| p-cymene (0-t)                       | geranial (0-0.2%)                      |
| terpinolene (0.4-0.6%)               | geranyl acetate (4.3-5.5%)             |
| allo-ocimene* (t)                    | nerol (1.8-2.1%)                       |
| nonanal (0-t)                        | geraniol (5.2-6.5%)                    |
| <i>cis</i> -linalool oxide† (0-0.1%) | (E)-nerolidol (0.1%)                   |
| <i>trans</i> -sabinene hydrate (0-t) |                                        |

\*correct isomer not identified

† furanoid form

t = trace (<0.1%)

The authors further reported that the composition of the leaf oil of the Goutou cultivar was dissimilar to that of the others. Its composition was as follows:

|                               |                                       |
|-------------------------------|---------------------------------------|
| $\alpha$ -thujene (0.3%)      | allo-ocimene* (t)                     |
| $\alpha$ -pinene (2.2%)       | <i>cis</i> -linalool oxide† (0.2%)    |
| camphene (0.2%)               | <i>trans</i> -sabinene hydrate (0.2%) |
| $\beta$ -pinene (36.7%)       | <i>trans</i> -linalool oxide† (0.1%)  |
| sabinene (5.7%)               | citronellal (1.0%)                    |
| $\delta$ -3-carene (1.8%)     | linalool (22.6%)                      |
| myrcene (0.7%)                | $\beta$ -caryophyllene (0.2%)         |
| $\alpha$ -phellandrene (0.2%) | terpinen-4-ol (0.8%)                  |
| $\alpha$ -terpinene (0.3%)    | neral (0.7%)                          |
| limonene (4.0%)               | $\alpha$ -terpineol (1.3%)            |
| 1,8-cineole (2.4%)            | neryl acetate (0.1%)                  |
| (Z)- $\beta$ -ocimene (0.2%)  | geranial (1.0%)                       |
| $\gamma$ -terpinene (7.7%)    | geranyl acetate (0.5%)                |
| (E)- $\beta$ -ocimene (6.2%)  | nerol (0.1%)                          |
| p-cymene (0.3%)               | geraniol (0.2%)                       |

|                    |                      |
|--------------------|----------------------|
| terpinolene (0.7%) | (E)-nerolidol (0.4%) |
| octanal (t)        |                      |

\*correct isomer not identified

† furanoid form

t = trace (<0.1%)

Recently, an oil of petitgrain bigarade (ex. *C. aurantium*) of European origin was analyzed by Kubeczka and Formacek (2002) using a combination of GC and  $^{13}\text{C}$ -NMR. They found that the oil possessed the following composition:

|                                       |                                                |
|---------------------------------------|------------------------------------------------|
| $\alpha$ -pinene (0.22%)              | <i>cis</i> -linalool oxide† (0.08%)            |
| camphene (0.11%)                      | linalool (26.62%)                              |
| $\beta$ -pinene (1.57%)               | linalyl acetate (50.81%)                       |
| sabinene (0.30%)                      | $\beta$ -caryophyllene + terpinen-4-ol (0.67%) |
| $\delta$ -3-carene (0.39%)            | $\alpha$ -humulene (0.04%)                     |
| myrcene (1.96%)                       | neral (0.04%)                                  |
| limonene (1.05%)                      | $\alpha$ -terpineol (5.10%)                    |
| $\beta$ -phellandrene (0.10%)         | neryl acetate (1.69%)                          |
| (Z)- $\beta$ -ocimene (0.52%)         | geranial acetate (2.89%)                       |
| (E)- $\beta$ -ocimene (1.29%)         | citronellol (0.09%)                            |
| p-cymene (0.07%)                      | nerol (0.95%)                                  |
| terpinolene (0.19%)                   | geraniol (2.24%)                               |
| 6-methyl-5-hepten-2-one (0.05%)       |                                                |
| (Z)-3-hexenol (0.13%)                 |                                                |
| <i>trans</i> -linalool oxide† (0.11%) |                                                |

† furanoid form

- I. Calvarano, *Le essenze italiane di petitgrain. Nota II. Petitgrain bigarade e bergamotto*. Essenz. Deriv. Agrum., 38, 31-48 (1968).; cited in: *Citrus, The Genus Citrus*. Edits., G. Dugo and A. DiGiacomo, 425-460, Taylor and Francis, London (2002).
- M. S. Karawya, S. I. Balbaa and M. S. Hifnawy, *Study of the leaf essential oils of bitter orange and bergamot growing in Egypt*. Amer. Perfum., 85(11), 29-32 (1970).
- J. C. Urbeita-Rehnfeld and W. G. Jennings, *Paraguayan petitgrain oil*. Chem. Mikrobiol. Technol. Lebensm., 3, 36-38 (1974).
- L. R. de Vottero, G. Tonarelli, E. R. de Krasnoger and J. A. Retamar, *Petitgrains from bitter orange, lemon and mandarin leaves*. Essenz. Deriv. Agrum., 48, 150-156 (1978).
- A. Baaliouamer and B. Y. Meklati, *Analysis of bitter orange petitgrain essential oil by combined gas chromatography-mass spectrometry*. Agric. Biol. Chem., 50, 2111-2114 (1986).
- Z-K. Lin, Y-F. Hua and Y-H. Gu, *The chemical constituents of the essential oil from the flowers, leaves and peel of Citrus aurantium*. Acta Bot. Sinica, 28, 635-640 (1986).
- M. A. Germana, F. DePasquale, E. Bazan and E. Palazzolo, *Essential oil of the flowers, leaves and buds of five species of Citrus*. Essenz. Deriv. Agrum., 60, 297-313 (1990).
- O. Bussaada, *Variation of essential oil yield and composition of Citrus aurantium var. amara*. M. Sc. thesis, Mediterranean Agronomic Institute, Chania, Greece (1995).

## Percentage composition of the leaf oils of bitter orange cultivars of specific country origins

T-5

| Compound                                  | 1    | 2    | 3    | 4    | 5    | 6    | 7    |
|-------------------------------------------|------|------|------|------|------|------|------|
| $\alpha$ -thujene                         | -    | t    | t    | t    | t    | t    | 0.5  |
| $\alpha$ -pinene                          | 0.3  | 0.4  | 0.2  | 0.2  | 0.2  | 0.2  | 1.9  |
| camphene                                  | t    | t    | t    | t    | t    | t    | 0.1  |
| $\beta$ -pinene                           | 4.2  | 5.9  | 3.9  | 3.8  | 3.2  | 2.8  | 4.4  |
| sabinene                                  | 0.5  | 0.7  | 0.5  | 0.5  | 0.4  | 0.4  | 52.6 |
| $\delta$ -3-carene                        | -    | -    | -    | t    | -    | -    | 0.1  |
| myrcene                                   | 2.8  | 2.7  | 2.6  | 2.6  | 2.1  | 2.2  | 3.5  |
| $\alpha$ -phellandrene                    | -    | -    | t    | -    | -    | -    | 0.1  |
| $\alpha$ -terpinene                       | t    | 0.1  | t    | t    | -    | t    | 2.0  |
| limonene                                  | 0.7  | 0.8  | 2.2  | 0.7  | 0.6  | 0.8  | 2.3  |
| $\beta$ -phellandrene                     | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.8  |
| 1,8-cineole                               | t    | t    | t    | t    | t    | t    | -    |
| (Z)- $\beta$ -ocimene                     | 1.1  | 1.1  | 1.0  | 1.1  | 0.9  | 0.9  | 0.5  |
| $\gamma$ -terpinene                       | 0.1  | 0.1  | t    | 0.1  | t    | 0.1  | 3.2  |
| (E)- $\beta$ -ocimene                     | 3.2  | 3.4  | 3.0  | 3.1  | 2.6  | 2.7  | 15.1 |
| p-cymene                                  | -    | -    | -    | -    | -    | -    | 0.1  |
| terpinolene                               | 0.6  | 0.6  | 0.5  | 0.6  | 0.5  | 0.5  | 0.8  |
| octanal                                   | -    | -    | 0.1  | -    | -    | -    | -    |
| 6-methyl-5-hepten-2-one                   | -    | -    | -    | -    | -    | -    | -    |
| allo-ocimene*                             | -    | -    | t    | t    | t    | t    | t    |
| nonanal                                   | -    | -    | t    | -    | -    | -    | -    |
| <i>cis</i> -linalool oxide <sup>‡</sup>   | t    | 0.1  | 0.1  | t    | t    | 0.1  | t    |
| <i>trans</i> -sabinene hydrate            | -    | -    | -    | -    | -    | -    | 0.6  |
| <i>trans</i> -linalool oxide <sup>‡</sup> | -    | -    | t    | t    | t    | t    | -    |
| citronellal                               | -    | -    | t    | t    | t    | -    | -    |
| decanal                                   | -    | -    | -    | -    | -    | -    | -    |
| linalool                                  | 33.2 | 32.7 | 32.7 | 36.7 | 32.7 | 32.2 | 1.0  |
| linalyl acetate                           | 22.5 | 24.4 | 26.9 | 21.9 | 31.2 | 30.3 | -    |
| <i>cis</i> -p-menth-2-en-1-ol             | -    | -    | -    | -    | -    | -    | 0.4  |
| $\beta$ -caryophyllene                    | 0.2  | -    | -    | 0.2  | 0.1  | 0.2  | 0.2  |
| terpinen-4-ol                             | 0.2  | 0.2  | 0.1  | 0.2  | -    | 0.1  | 7.0  |
| undecanal                                 | -    | -    | -    | -    | -    | -    | -    |
| citronellyl acetate                       | -    | -    | t    | -    | -    | -    | t    |
| $\alpha$ -humulene                        | -    | t    | -    | -    | -    | -    | -    |
| neral                                     | -    | -    | t    | t    | t    | t    | t    |
| $\alpha$ -terpinyl acetate                | 0.1  | -    | -    | 0.1  | 0.1  | 0.1  | -    |
| $\alpha$ -terpineol                       | 11.8 | 10.2 | 9.5  | 11.0 | 9.4  | 10.0 | 0.3  |
| (Z)- $\alpha$ -bisabolene                 | 0.2  | 0.2  | 0.3  | 0.1  | 0.2  | 0.2  | 0.2  |
| neryl acetate                             | 2.9  | 2.6  | 2.5  | 2.8  | 2.6  | 2.6  | 0.4  |
| geranial                                  | -    | -    | -    | -    | -    | -    | -    |
| piperitone                                | -    | -    | -    | -    | -    | -    | -    |
| geranyl acetate                           | 5.5  | 5.0  | 4.8  | 5.4  | 4.9  | 5.1  | 0.1  |
| nerol                                     | 2.3  | 2.0  | 1.9  | 2.1  | 1.9  | 2.0  | t    |
| geraniol                                  | 6.7  | 5.8  | 5.4  | 6.2  | 5.4  | 5.8  | -    |
| (E)-nerolidol                             | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | -    |
| spathulenol                               | -    | -    | -    | -    | -    | -    | 0.1  |

\*correct isomer not identified

‡ furanoid form

t = trace (&lt;0.1%)

cultivars: 1. Florida, USA, 2. Spanish, 3. Tunisian, 4. Brazilian, 5. Algerian, 6. Moroccan and 7. Australian

- A. Gurib-Fakim and F. Demarne, *Aromatic plants of Mauritius: volatile constituents of the leaf oils of Citrus aurantium L., Citrus paradisi Macfad. and Citrus sinensis (L.) Osbeck*. J. Essent. Oil Res., 7, 105-109 (1995).
- L. Mondello, G. Dugo, P. Dugo and K. D. Bartle, *Italian Citrus petitgrain oils. Part I. Composition of bitter orange petitgrain oil*. J. Essent. Oil Res., 8, 597-609 (1996).
- G. Dugo, L. Mondello, A. Cotroneo, I. Stagno d'Alcontres, A. Basile, P. Previti, P. Dugo and K. D. Bartle, *Characterization of Italian Citrus petitgrain oils*. Perfum. Flavor., 21(3), 17-28 (1996).
- L. Mondello, P. Dugo, G. Dugo and K. D. Bartle, *On-line HPLC-HRGC-MS for the analysis of natural complex mixtures*. J. Chromatogr. Sci., 34, 174-181 (1996).
- D. de Rocca Serra, M. L. Lota, F. Tomi and J. Casanova, *Essential oils and taxonomy among Citrus example of bergamot*. Rivista Ital. EPPOS, (Numero Speciale), 38-43 (1998).
- E. Protopapadakis and X. Papanikolaou, *Characterization of Citrus aurantium and C. taiwanica rootstocks by isoenzyme and essential oil analysis*. J. Hort. Sci., Biotech., 73, 81-85 (1998).
- M. Adami, L. Arcuri, G. DiGiacomo, D. Ferri, G. Gazzola, F. Gionfriddo and E. Piccinelli, *Estrazione di petitgrain con CO<sub>2</sub> supercritical*. Essenz. Deriv. Agrum., 70, 193-200 (2000).
- Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 100 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).
- M-L. Lota, D. de Rocca Serra, C. Jacquemond, F. Tomi and J. Casanova, *Chemical variability of peel and leaf essential oils of sour orange*. Flav. Fragr. J., 16, 89-96 (2001).
- K-H. Kubeczka and V. Formacek, *Essential oils analysis by capillary gas chromatography and carbon-13 NMR spectroscopy*. 2<sup>nd</sup> Edn., 225-260, J. Wiley & Sons, NY (2002).

### **Citrus bergamia Risso et Poit.**

A sample of Calabrian bergamot petitgrain oil was determined by Calvarano (1968) to possess the following composition:

|                                      |                             |
|--------------------------------------|-----------------------------|
| $\alpha$ -thujene (t)                | terpinolene (0.42%)         |
| heptanal (0.01%)                     | linalool (18.82%)           |
| $\alpha$ -pinene (0.16%)             | nonanal (0.02%)             |
| camphene (0.01%)                     | citronellal (0.02%)         |
| sabinene (0.12%)                     | citronellol (0.50%)         |
| $\beta$ -pinene (1.11%)              | geraniol (0.09%)            |
| myrcene + $\delta$ -3-carene (2.04%) | nerol (1.74%)               |
| $\alpha$ -phellandrene (0.04%)       | terpinen-4-ol (0.21%)       |
| $\alpha$ -terpinene (0.09%)          | $\alpha$ -terpineol (5.69%) |
| p-cymene (1.02%)                     | neral (0.03%)               |
| limonene (2.80%)                     | geranial (0.14%)            |
| $\beta$ -ocimene* (0.18%)            | methyl N-methyl             |
| octanal (0.01%)                      | anthranilate (7.53%)        |
| $\gamma$ -terpinene (1.42%)          |                             |

\*correct isomer not identified  
t = trace (<0.01%)

In addition, the authors also identified a series of esters (51.02%) with linalyl acetate being the major one. The other esters identified for which no individual quantitative data were presented were octyl acetate, citronellyl acetate, geranyl acetate, neryl acetate and  $\alpha$ -terpinyl acetate.

Bergamot leaf oil produced in Egypt was analyzed by Karawya et al. (1970). The compounds identified in this oil were as follows:

|                             |                            |
|-----------------------------|----------------------------|
| $\alpha$ -pinene (3.16%)    | linalyl acetate (0.83%)    |
| $\beta$ -pinene (8.24%)     | neral (1.50%)              |
| camphene (0.25%)            | citronellol (2.17%)        |
| myrcene (0.83%)             | geranial (5.33%)           |
| limonene (10.91%)           | nerol + farnesol* (10.16%) |
| $\beta$ -ocimene* (3.25%)   | geraniol (0.92%)           |
| $\alpha$ -terpineol (0.67%) | geranyl acetate (1.17%)    |
| citronellal (1.33%)         |                            |
| linalool (1.33%)            |                            |

\*correct isomer not identified

As bergamot leaf oil is rich in linalool and linalyl acetate, this analysis should be disregarded. It is only included in this review for completeness.

An oil produced from the leaves of *C. bergamia* growing in China was analyzed by Huang et al. (1986) and found to possess the following composition:

|                                 |                                 |
|---------------------------------|---------------------------------|
| butyl acetate (t)               | terpinen-4-ol (0.11%)           |
| (Z)-3-hexenol (t)               | $\alpha$ -terpineol (7.89%)     |
| hexanol (t)                     | decanal (0.01%)                 |
| $\alpha$ -thujene (t)           | octyl acetate (0.02%)           |
| $\alpha$ -pinene (0.06%)        | nerol (1.92%)                   |
| camphene (t)                    | neral (0.84%)                   |
| 6-methyl-5-hepten-2-one (0.06%) | pulegone (0.06%)                |
| sabinene (0.17%)                | geraniol (22.51%)               |
| $\beta$ -pinene (0.81%)         | linalyl acetate (11.31%)        |
| myrcene (1.17%)                 | geranial (1.24%)                |
| $\alpha$ -phellandrene (t)      | $\alpha$ -terpinyl acetate (t)  |
| 1,4-cineole (t)                 | citronellyl acetate (0.14%)     |
| $\delta$ -3-carene (0.05%)      | neryl acetate (3.00%)           |
| p-cymene (t)                    | geranyl acetate (4.32%)         |
| limonene (1.16%)                | decyl acetate (0.03%)           |
| $\beta$ -ocimene* (0.32%)       | $\beta$ -caryophyllene (0.44%)  |
| $\gamma$ -terpinene (0.07%)     | (E)- $\beta$ -farnesene (0.04%) |
| cis-linalool oxide† (t)         | $\alpha$ -humulene (0.06%)      |
| sabinene hydrate* (0.07%)       | $\alpha$ -bergamotene* (0.06%)  |
| $\gamma$ -terpinene (0.06%)     | pentadecene (0.06%)             |
| linalool (41.24%)               | (Z)-nerolidol (0.03%)           |
| $\alpha$ -fenchol (0.01%)       | (E)-nerolidol (0.20%)           |
| citronellal (0.03%)             | $\beta$ -bisabolene (0.15%)     |
| isopulegol (0.03%)              | farnesol* (0.05%)               |

\*correct isomer not identified

† furanoid form

t = trace (<0.01%)

A sample of bergamot petitgrain oil was subjected to analysis by de Rocca Serra et al. (1998) by a combination of GC and  $^{13}\text{C}$ -NMR. The composition of the oil was found to be as follows:

|                              |                             |
|------------------------------|-----------------------------|
| $\beta$ -pinene (0.9%)       | linalyl acetate (19.9%)     |
| myrcene (2.6%)               | $\alpha$ -terpineol (12.1%) |
| limonene (1.0%)              | neryl acetate (3.3%)        |
| (Z)- $\beta$ -ocimene (1.1%) | geranyl acetate (5.7%)      |
| (E)- $\beta$ -ocimene (2.4%) | nerol (2.4%)                |
| terpinolene (0.6%)           | geraniol (6.8%)             |
| linalool (39.7%)             |                             |

The composition of a supercritical fluid  $\text{CO}_2$  extract of bergamot leaves of Italian origin was examined by Adami et al. (2000). The components identified in this extract were as follows:

|                               |                                     |
|-------------------------------|-------------------------------------|
| sabinene (t)                  | $\beta$ -caryophyllene (4.93%)      |
| $\beta$ -pinene (0.23%)       | cis-bergamotene* (0.09%)            |
| myrcene (0.09%)               |                                     |
| limonene (0.18%)              | $\beta$ -sesquiphellandrene (0.29%) |
| (Z)- $\beta$ -ocimene (0.08%) |                                     |
| linalool (1.09%)              | $\alpha$ -humulene (0.39%)          |
| nerol (0.04%)                 | nerolidol* (0.20%)                  |
| linalyl acetate (85.0%)       | germacrene B (1.85%)                |
| hydroxylinalool† (0.19%)      | $\delta$ -elemene† (1.64%)          |
|                               | isocaryophyllene† (0.08%)           |
| neryl acetate (0.94%)         | $\beta$ -bisabolene (0.52%)         |
| geranyl acetate (0.20%)       | spathulenol (0.59%)                 |
| $\beta$ -elemene (0.06%)      | caryophyllene oxide (0.08%)         |

\*correct isomer not identified

† component identity not proved

‡ incorrect identification based on elution order

I. Calvarano, *Le essenze italiane de petitgrain. Nota II. Petitgrain bigarade e bergamotto*. Essenz. Deriv. Agrum., 38, 31-48 (1968); cited in: *Citrus, The Genus Citrus*, Edits., G. Dugo and A. DiGiacomo, 425-460, Taylor and Francis, London (2002).

M. S. Karawya, S. I. Balbaa and M. S. Hifnawy, *Study of the leaf essential oils of bitter orange and bergamot growing in Egypt*. Amer. Perfum., 85(11), 29-32 (1970).

Y-Z. Huang, M-Z. Wen, S-C. Xiao, H. Zhao, W-J. Ren, Q-Y. Chen, H-D. Liu and T-C. Gui, *Studies on the chemical constituents of the steam distilled leaf and peel oils from Citrus bergamia*. Yunnan Zhiwu Yanjue, 8, 471-476 (1986).

D. de Rocca Serra, M. L. Lota, F. Tomi and J. Casanova, *Essential oils and taxonomy among Citrus example of bergamot*. Rivista Ital. EPPoS., (Numero Speciale), 38-43 (1998).

M. Adami, L. Arcuri, G. DiGiacomo, D. Ferri, G. Gazzola, F. Gionfriddo and E. Piccinelli, *Estrazione di petitgrain con  $\text{CO}_2$  supercritica*. Essenz. Deriv. Agrum., 70, 193-200 (2000).

### **Citrus hystrix DC**

The leaf oil, which is sometimes known as combava leaf or swangi leaf oil, is obtained from this species. The leaf oil of *C. hystrix* of Malaysian origin was analyzed using GC and GC/MS by Jantan et al.

(1996). They found that the oil contained the following constituents:

|                                |                                 |
|--------------------------------|---------------------------------|
| $\alpha$ -thujene (0.03%)      | citronellol (6.70%)             |
| $\alpha$ -pinene (0.10%)       | geraniol (0.16%)                |
| $\beta$ -pinene (1.93%)        | p-menthan-3-ol (0.26%)          |
| octanal (0.20%)                | $\delta$ -elemene (0.21%)       |
| myrcene (0.86%)                | citronellyl acetate (4.05%)     |
| $\alpha$ -phellandrene (0.02%) | neryl acetate (0.12%)           |
| $\delta$ -3-carene (0.14%)     | geranyl acetate (0.78%)         |
| $\alpha$ -terpinene (0.07%)    | $\beta$ -elemene (0.04%)        |
| limonene (0.14%)               | $\beta$ -cubebene (0.16%)       |
| (Z)- $\beta$ -ocimene (0.03%)  | $\beta$ -caryophyllene (0.93%)  |
| (E)- $\beta$ -ocimene (0.48%)  | $\alpha$ -bergamotene* (0.03%)  |
| $\gamma$ -terpinene (0.25%)    | $\alpha$ -humulene (0.23%)      |
| cis-linalool oxide‡ (0.36%)    | (Z)- $\beta$ -farnesene (0.11%) |
| trans-linalool oxide‡ (0.16%)  | $\alpha$ -cadinene† (0.44%)     |
| terpinolene (0.10%)            | (E)- $\beta$ -farnesene (0.21%) |
| trans-sabinene hydrate (1.46%) | $\delta$ -cadinene (0.38%)      |
| linalool (1.69%)               | hedycaryol (0.33%)              |
| citronellal (72.41%)           | (Z)-nerolidol (0.89%)           |
| p-menth-8-en-1-ol (0.17%)      | elemol (0.34%)                  |
| terpinen-4-ol (0.56%)          | $\beta$ -eudesmol (0.15%)       |
| $\alpha$ -terpineol (0.06%)    | $\alpha$ -eudesmol (0.21%)      |

† furanoid form

‡ incorrect identification based on elution order

\* correct isomer not identified

The leaf oil of *C. hystrix* produced from trees grown in China was analyzed by Huang et al. (2000). The components identified in this oil were as follows:

|                               |                                    |
|-------------------------------|------------------------------------|
| $\alpha$ -thujene (0.02%)     | terpinen-4-ol (0.05%)              |
| $\alpha$ -pinene (0.10%)      | $\alpha$ -terpineol (0.02%)        |
| camphene (t)                  | decanal (0.16%)                    |
| sabinene (2.42%)              | citronellol (5.99%)                |
| $\beta$ -pinene (0.17%)       | nerol (0.04%)                      |
| myrcene (0.72%)               | neral (t)                          |
| $\alpha$ -phellandrene (t)    | geraniol (0.12%)                   |
| $\delta$ -3-carene (0.04%)    | geraniol (0.05%)                   |
| $\alpha$ -terpinene (0.04%)   | undecanal (t)                      |
| p-cymene (t)                  | citronellyl acetate (3.75%)        |
| limonene (0.12%)              | neryl acetate (0.13%)              |
| (Z)- $\beta$ -ocimene (0.05%) | $\delta$ -elemene (0.05%)          |
| $\beta$ -phellandrene (0.03%) | geranyl acetate (0.75%)            |
| (E)- $\beta$ -ocimene (0.35%) | $\beta$ -caryophyllene (0.15%)     |
| $\gamma$ -terpinene (0.07%)   | $\alpha$ -humulene (0.04%)         |
| octanol (0.06%)               | (E,E)- $\alpha$ -farnesene (0.04%) |
| cis-sabinene hydrate (0.09%)  | germacrene B (0.07%)               |
| cis-linalool oxide‡ (0.33%)   | $\delta$ -cadinene (0.06%)         |
| terpinolene (0.05%)           | elemol (0.09%)                     |
| nonanal (0.17%)               | (E)-nerolidol (0.42%)              |
| linalool (3.66%)              | spathulenol (0.04%)                |
| citronellal (77.98%)          | caryophyllene oxide (0.09%)        |

† furanoid form

t = trace (<0.01%)

A leaf oil produced from *C. hystrix* grown in Malaysia was the subject of analysis by Taufiq-Yap et al. (2001). Using GC/MS as their method of analysis, the following components were identified:

|                                |                             |
|--------------------------------|-----------------------------|
| terpinolene (0.1%)             | $\alpha$ -armorphene (0.1%) |
| citronellal (83.3%)            | bicyclogermacrene (0.2%)    |
| citronellol (8.5%)             | $\delta$ -cadinene (0.2%)   |
| citronellyl propionate (1.4%)  | $\alpha$ -cadinol (0.1%)    |
| $\beta$ -caryophyllene (0.06%) |                             |

I. Jantan, A. S. Ahmad, A. R. Ahmad, N. A. Mohd Ali and N. Ayop, *Chemical composition of some Citrus oils from Malaysia*. J. Essent. Oil Res., 8, 627-632 (1996).

Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 100 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).

Y. H. Taufiq-Yap, T. H. Peh, G. C. L. Ee, A. M. Ali, M. Rahmani, M. A. Sukari and R. Muse,

*Chemical variability and some biological activities of leaf essential oils from five species of Malaysian Citrus*. Orient. J. Chem., 17, 387-390 (2001).

## Citrus latifolia Tanaka

Persian or Tahitian lime leaf oil is obtained from this species. Calvarano et al. (1982) subjected a leaf oil of *C. latifolia* to analysis. They found that the oil contained the following constituents:

|                             |                                    |
|-----------------------------|------------------------------------|
| $\alpha$ -thujene (t)       | citronellal (2.06%)                |
| $\alpha$ -pinene (0.23%)    | linalool (1.07%)                   |
| camphene (t)                | decanal (0.55%)                    |
| $\beta$ -pinene (0.22%)     | terpinen-4-ol (0.06%)              |
| sabinene (0.83%)            | linalyl acetate (0.21%)            |
| myrcene (0.93%)             | neral (14.95%)                     |
| limonene (34.47%)           | $\alpha$ -terpineol (0.47%)        |
| octanal (0.08%)             | geranial (19.54%)                  |
| $\beta$ -ocimene* (0.80%)   | geraniol (0.39%)                   |
| p-cymene (0.24%)            | neryl acetate (0.32%)              |
| $\gamma$ -terpinene (1.39%) | $\alpha$ -terpinyl acetate (0.40%) |
| terpinolene (0.04%)         | nerol† (6.48%)                     |
| nonanal (0.12%)             | geranyl acetate (3.64%)            |

\*correct isomer not identified

† tentative identification

t = trace (<0.01%)

A leaf oil from the Tahiti cultivar of *C. latifolia* (noted as *C. aurantifolia* by the authors) was analyzed by Jazet Dongmo et al. (1998) and found to contain the following components:

|                                 |                                      |
|---------------------------------|--------------------------------------|
| $\alpha$ -pinene (0.29%)        | neral (2.60%)                        |
| 6-methyl-5-hepten-2-one (2.25%) | nerol (11.24%)                       |
| sabinene (0.91%)                | geraniol (2.16%)                     |
| $\beta$ -pinene (0.34%)         | geranial (13.71%)                    |
| myrcene (1.26%)                 | thymol (0.06%)                       |
| p-cymene (0.23%)                | bornyl acetate (0.08%)               |
| limonene (49.72%)               | citronellyl acetate (0.19%)          |
| (E)- $\beta$ -ocimene (1.35%)   | $\delta$ -elemene (0.23%)            |
| $\gamma$ -terpinene (0.21%)     | $\alpha$ -terpinyl acetate (2.80%)   |
| terpinolene (0.06%)             | geranyl acetate (3.45%)              |
| linalool (1.39%)                | $\beta$ -elemene (0.13%)             |
| limonene oxide* (0.17%)         | trans- $\alpha$ -bergamotene (0.06%) |
| terpinen-1-ol (0.16%)           | $\alpha$ -humulene (0.07%)           |
| isopulegol (1.42%)              | germacrene D (0.13%)                 |
| menthone (0.37%)                | (E,E)- $\alpha$ -farnesene (0.08%)   |
| borneol (0.51%)                 | $\beta$ -bisabolene (0.12%)          |
| terpinen-4-ol (0.30%)           | germacrene B (0.17%)                 |
| $\alpha$ -terpineol (0.67%)     | spathulenol (0.10%)                  |
| $\gamma$ -terpineol† (0.15%)    | $\beta$ -eudesmol (0.08%)            |

† the natural origin of

$\gamma$ -terpineol is in question

The leaf oil of a Tahitian cultivar of lime that was grown in China was reported (Huang et al. 2000) to have a botanical origin of *C. aurantifolia*; however,

the normal origin of the Tahitian cultivar is *C. latifolia*. As a result, the oil composition reported by the Chinese researchers will be treated as a *C. latifolia* leaf oil. It was found to possess the following composition:

|                                 |                                    |
|---------------------------------|------------------------------------|
| $\alpha$ -thujene (t)           | nerol (1.89%)                      |
| $\alpha$ -pinene (0.19%)        | neral (13.77%)                     |
| camphene (t)                    | geraniol (0.84%)                   |
| 6-methyl-5-hepten-2-one (0.60%) | geranial (18.07%)                  |
| sabinene (0.64%)                | undecanal (0.07%)                  |
| $\beta$ -pinene (0.13%)         | methyl geranate (0.07%)            |
| myrcene (0.88%)                 | citronellyl acetate (0.24%)        |
| $\alpha$ -phellandrene (t)      | $\alpha$ -terpinyl acetate (0.10%) |
| $\delta$ -3-carene (0.03%)      | neryl acetate (7.70%)              |
| $\alpha$ -terpinene (t)         | geranyl acetate (4.31%)            |
| p-cymene (0.06%)                | dodecanal (0.05%)                  |
| limonene (35.35%)               | $\beta$ -elemene (0.17%)           |
| 1,8-cineole (0.99%)             | $\beta$ -caryophyllene (1.34%)     |
| $\beta$ -phellandrene (0.08%)   | cis- $\alpha$ -bergamotene (0.42%) |
| (E)- $\beta$ -ocimene (0.71%)   | (Z)- $\beta$ -farnesene (0.06%)    |
| $\gamma$ -terpinene (0.03%)     | $\alpha$ -humulene (0.16%)         |
| octanol (t)                     | $\gamma$ -muurolene (0.11%)        |
| cis-sabinene hydrate (t)        | (E,E)- $\alpha$ -farnesene (0.31%) |
| cis-linalool oxide‡ (t)         | germacrene B (0.06%)               |
| terpinolene (0.02%)             | $\beta$ -bisabolene (0.57%)        |
| nonanal (0.09%)                 | $\delta$ -cadinene (0.06%)         |
| linalool (1.02%)                | (E)-nerolidol (0.07%)              |
| isopulegol (0.30%)              | spathulenol (0.08%)                |
| citronellal (1.72%)             | caryophyllene oxide (0.23%)        |
| terpinen-4-ol (0.07%)           |                                    |
| $\alpha$ -terpineol (0.46%)     |                                    |
| decanal (0.25%)                 |                                    |
| citronellol (0.47%)             |                                    |

‡ furanoid form

t = trace (<0.01%)

The leaf oils of five Persian lime cultivars were analyzed by Lota et al. (2002) using GC and GC/MS techniques. The results of this comparative study are presented in T-6.

M. Calvarano, F. Salnitro and T. Sacco, *Essential oil from the leaves of the Tahiti lime (Citrus latifolia Tanaka) and Galego lime (Citrus aurantifolia Sw.) from Brazil*. Essenz. Deriv. Agrum., 52, 52-58 (1982).

P. M. Jazet Dongmo, P. H. Amvam Zollo, F. Fekam Boyom, C. Menuit, G. Lamaty and J. M. Bessiere, *Chemical composition of essential oils from Citrus species grown in Cameroon*. Rivista Ital. EPPOS, (Numero Speciale), 156-162 (1998).

Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 110 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).

M-L. Lota, D. de Rocca Serra, F. Tomi, C. Jacquemond and J. Casanova, *Volatile components of peel and leaf oils of lemon and lime species*. J. Agric. Food Chem., 50, 796-805 (2002).



## Percentage composition of the leaf oils of Persian lime cultivars

T-6

| Compound                     | 1    | 2    | 3    | 4    | 5    |
|------------------------------|------|------|------|------|------|
| $\alpha$ -thujene            | t    | t    | t    | t    | t    |
| $\alpha$ -pinene             | 0.2  | 0.3  | 0.2  | 0.2  | 0.2  |
| $\beta$ -pinene              | 0.3  | 0.3  | 0.2  | 0.2  | 0.2  |
| sabinene                     | 1.1  | 0.8  | 0.7  | 0.9  | 0.8  |
| $\delta$ -3-carene           | t    | t    | t    | t    | t    |
| myrcene                      | 0.9  | 1.5  | 1.0  | 1.0  | 1.1  |
| $\alpha$ -terpinene          | t    | t    | t    | t    | t    |
| limonene                     | 38.1 | 53.4 | 37.5 | 37.3 | 46.3 |
| $\beta$ -phellandrene        | -    | -    | -    | -    | 1.2  |
| 1,8-cineole                  | 1.3  | 1.3  | 2.1  | 2.5  | -    |
| (Z)- $\beta$ -ocimene        | 0.3  | 0.3  | 0.2  | 0.2  | 0.3  |
| $\gamma$ -terpinene          | 0.3  | 0.2  | 0.1  | 0.1  | 0.2  |
| (E)- $\beta$ -ocimene        | 1.5  | 2.2  | 1.5  | 1.3  | 1.9  |
| p-cymene                     | t    | t    | t    | t    | t    |
| terpinolene                  | t    | 0.1  | t    | -    | -    |
| octanal                      | t    | t    | t    | t    | 0.1  |
| 6-methyl-5-hepten-2-one      | 1.1  | 1.3  | 2.2  | 1.4  | 1.9  |
| allo-ocimene*                | -    | t    | -    | -    | -    |
| nonanal                      | 0.2  | 0.1  | -    | 0.1  | 0.2  |
| cis-limonene oxide           | -    | t    | -    | 0.1  | -    |
| trans-sabinene hydrate       | t    | t    | t    | t    | t    |
| octyl acetate                | -    | -    | t    | -    | -    |
| citronellal                  | 2.7  | 0.9  | 1.5  | 1.0  | 1.8  |
| decanal                      | 0.4  | 0.1  | 0.1  | 0.2  | 0.1  |
| linalool                     | 1.4  | 0.9  | 1.5  | 1.4  | 1.4  |
| cis-p-menth-2-en-1-ol        | t    | t    | -    | -    | -    |
| trans- $\alpha$ -bergamotene | t    | -    | t    | -    | -    |
| $\beta$ -elemene             | -    | 0.2  | t    | -    | 0.1  |
| $\beta$ -caryophyllene       | 0.1  | 0.3  | 0.1  | 0.1  | 0.2  |
| terpinen-4-ol                | 0.1  | 0.2  | 0.2  | 0.1  | 0.2  |
| undecanal                    | 0.1  | 0.1  | -    | -    | 0.1  |
| citronellyl acetate          | 0.2  | 0.2  | 0.1  | 0.1  | 0.2  |
| (E)- $\beta$ -farnesene      | t    | t    | t    | t    | t    |
| neral                        | 13.6 | 8.3  | 14.2 | 16.1 | 10.4 |
| $\alpha$ -terpinyl acetate   | -    | -    | -    | -    | t    |
| $\alpha$ -terpineol          | 0.8  | 0.6  | 0.9  | 0.8  | 0.9  |
| germacrene D                 | -    | t    | t    | t    | t    |
| neryl acetate                | 6.1  | 4.8  | 4.6  | 3.5  | 5.9  |
| geranial                     | 19.5 | 11.8 | 20.3 | 22.5 | 14.9 |
| (E,E)- $\alpha$ -farnesene   | -    | -    | -    | t    | -    |
| geranyl acetate              | 4.5  | 4.2  | 3.2  | 2.7  | 3.3  |
| citronellol                  | 0.6  | 0.3  | 0.7  | 0.5  | 0.5  |
| nerol                        | 1.1  | 1.4  | 2.4  | 1.9  | 1.8  |
| geraniol                     | 1.3  | 1.6  | 2.5  | 1.7  | 1.7  |
| caryophyllene oxide          | 0.1  | t    | t    | t    | t    |
| (E)-nerolidol                | 0.1  | t    | t    | t    | t    |
| santal-10-en-2-ol            | t    | t    | -    | -    | t    |
| $\beta$ -sinensal            | -    | t    | t    | -    | -    |

\* correct isomer not identified

t = trace (&lt;0.1%)

cultivars: 1. El Kseur, 2. IAC, 3. Bearss, 4. De Perse and 5. Tahiti

## ***Citrus limon* (L.) N. L. Burm.**

Nine samples of lemon leaf oil that were produced in Calabria (Italy) were subjected to analysis by Calvarano (1967). The average amounts of constituents found in these oils was as follows:

|                                |                             |
|--------------------------------|-----------------------------|
| $\alpha$ -pinene (2.29%)       | $\gamma$ -terpinene (1.80%) |
| heptanal (0.09%)               | terpinolene (0.30%)         |
| camphene (0.09%)               | linalool (6.30%)            |
| sabinene (2.85%)               | nonanal (0.16%)             |
| $\beta$ -pinene (11.53%)       | citronellal (0.34%)         |
| myrcene (1.01%)                | citronellol (0.84%)         |
| $\delta$ -3-carene (0.63%)     | nerol (2.20%)               |
| $\alpha$ -terpinene (0.12%)    | geraniol (1.95%)            |
| $\alpha$ -phellandrene (0.08%) | terpinen-4-ol (2.65%)       |
| p-cymene (1.28%)               | $\alpha$ -terpineol (2.65%) |
| limonene (30.67%)              | decanal (0.09%)             |
| $\beta$ -ocimene* (1.37%)      | neral (5.80%)               |
| octanal (0.41%)                | geranial (10.30%)           |

\*correct isomer not identified

In addition, the authors found that  $\alpha$ -terpinyl acetate, geranyl acetate, linalyl acetate and neryl acetate (compounds listed in decreasing order of concentration) which combined comprised 10.12% of the oil.

As part of a study of the leaf oils of various *Citrus* species grown in Japan, Kamiyama (1967) examined the composition of lemon leaf oil produced from leaves harvested from a single tree. The components identified in this oil were as follows:

|                                             |
|---------------------------------------------|
| $\alpha$ -thujene + $\alpha$ -pinene (3.4%) |
| camphene (0.1%)                             |
| $\beta$ -pinene + sabinene (12.4%)          |
| myrcene (1.7%)                              |
| $\alpha$ -terpinene (t)                     |
| limonene (23.1%)                            |
| (E)-2-hexenal (2.0%)                        |
| $\gamma$ -terpinene (3.3%)                  |
| p-cymene (0.5%)                             |
| (Z)-3-hexenol (0.09%)                       |
| (E)-2-hexenol (t)                           |
| linalool (3.1%)                             |
| $\beta$ -elemene + terpinen-4-ol (0.4%)     |
| $\beta$ -caryophyllene (0.2%)               |
| neral (16.4%)                               |
| geranial (24.3%)                            |
| $\beta$ -selinene (1.9%)                    |
| nerol (2.0%)                                |
| geraniol (2.8%)                             |

However, it should be noted that the levels of (E)-2-hexenal and (Z)-3-hexenol are high because the GC peak that was integrated was mixed. It would be expected that a  $\beta$ -ocimene was mixed with (E)-2-hexenal and a sabinene hydrate with (Z)-3-hexenol.

Lemon leaf oil produced in Argentina was determined by de Vottero et al. (1978) to contain  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, limonene,

p-cymene, citronellal, linalool, neral, geranial,  $\alpha$ -terpineol, citronellol, geraniol and geranyl acetate. Unfortunately, the authors did not present any quantitative data.

Wen et al. (1989) analyzed an oil of lemon leaves produced in China using GC/MS. The oil was found to possess the following composition:

|                                       |                                |
|---------------------------------------|--------------------------------|
| $\alpha$ -thujene (0.01%)             | citronellal (2.63%)            |
| $\alpha$ -pinene (0.59%)              | isopulegol (0.52%)             |
| camphene (t)                          | nonanal (0.92%)                |
| 6-methyl-5-hepten-2-one (1.73%)       | terpinen-4-ol (0.28%)          |
| sabinene (0.41%)                      | $\alpha$ -terpineol (0.07%)    |
| $\beta$ -pinene (0.02%)               | octyl acetate (0.01%)          |
| octanal (0.04%)                       | decanal (0.01%)                |
| myrcene (0.66%)                       | nerol (4.47%)                  |
| $\alpha$ -phellandrene (2.04%)        | neral (13.96%)                 |
| 1,4-cineole (t)                       | carvone (2.02%)                |
| p-cymene (0.25%)                      | geraniol (0.17%)               |
| $\beta$ -phellandrene (9.33%)         | linalyl acetate (2.22%)        |
| limonene (9.84%)                      | geranial (21.31%)              |
| (E)- $\beta$ -ocimene (0.75%)         | undecanal (0.05%)              |
| $\gamma$ -terpinene (0.06%)           | citronellyl acetate (0.37%)    |
| <i>cis</i> -linalool oxide† (0.01%)   | neryl acetate (2.82%)          |
| <i>trans</i> -linalool oxide‡ (0.17%) | geranyl acetate (1.66%)        |
| terpinolene (0.04%)                   | dodecanal (0.03%)              |
| nonanal (0.02%)                       | $\beta$ -caryophyllene (0.25%) |
|                                       | $\alpha$ -humulene (0.05%)     |
|                                       | $\alpha$ -bergamotene*         |

linalool (17.26%) (0.06%)

\*correct isomer not identified

† furanoid form

t = trace (<0.01%)

The leaf oil of lemon grown in Italy was found by Germana et al. (1990) to contain the following constituents:

|                                |                             |
|--------------------------------|-----------------------------|
| $\alpha$ -pinene (0.29%)       | benzaldehyde (0.50%)        |
| $\beta$ -pinene (6.72%)        | $\alpha$ -terpineol (4.59%) |
| sabinene (0.58%)               | neryl acetate (4.46%)       |
| myrcene (1.04%)                | neral (12.22%)              |
| limonene (28.39%)              | geranyl acetate (16.37%)    |
| $\alpha$ -terpinene (3.41%)    | geranial (19.27%)           |
| $\beta$ -caryophyllene (0.22%) | nerol (0.07%)               |
| linalool (1.64%)               |                             |

This occurrence of benzaldehyde in lemon leaf oil should be considered to be a misidentification.

The main components of the leaf oils of the Eureka cultivar of *C. limon* grown in China were determined by Lin and Hua (1992) to be:

|                                 |
|---------------------------------|
| limonene (21.8%)                |
| 6-methyl-5-hepten-2-one (24.4%) |
| linalyl acetate (5.7%)          |
| neral + geranial (24.7%)        |
| carvone (9.7%)                  |

This analysis was atypical particularly with the identification of such large amounts of 6-methyl-5-hepten-2-one and carvone.

An oil produced from the leaves of lemon trees growing in Turkey was the subject of an investigation by Verdi et al. (1993). Analysis of the oil was done by combining GC and GC/MS. The oil composition was found to be as follows:

|                                                  |                                                     |
|--------------------------------------------------|-----------------------------------------------------|
| 1-methyl-3-(1-methyl-ethyl)-cyclopentane (0.01%) | limonene oxide* (0.02%)                             |
|                                                  | limonene oxide* (0.01%)                             |
| 3,3,5-trimethyl-1,4-hexadiene* (0.01%)           | <i>trans</i> -sabinene hydrate (0.08%)              |
| $\alpha$ -pinene (1.36%)                         | citronellal (1.18%)                                 |
| camphene (0.12%)                                 | decanal (0.04%)                                     |
| $\beta$ -pinene (19.42%)                         | linalool (0.96%)                                    |
| sabinene (4.22%)                                 | linalyl acetate (0.05%)                             |
| $\delta$ -3-carene (0.44%)                       | citronellyl acetate (0.07%)                         |
| myrcene (1.17%)                                  | neral (11.27%)                                      |
| limonene (30.22%)                                | $\alpha$ -terpineol (0.41%)                         |
| 1,8-cineole (2.07%)                              | piperitone (0.04%)                                  |
| (Z)- $\beta$ -ocimene (0.43%)                    | geranial† + 2,7-dimethyl-2,6-octadien-1-ol* (16.6%) |
| $\gamma$ -terpinene (0.17%)                      | geranyl acetate (1.33%)                             |
| (E)- $\beta$ -ocimene (2.30%)                    | citronellol (0.19%)                                 |
| p-cymene (0.02%)                                 | nerol (0.80%)                                       |
| terpinolene (0.13%)                              | <i>trans</i> -carveol (0.01%)                       |
| 6-methyl-5-hepten-2-one (0.61%)                  | geraniol (0.30%)                                    |
| nonanal (0.27%)                                  |                                                     |

\* correct isomer not identified

† major component of mixed GC peak

On deterpenation of this oil the authors found that the neral and geranial levels increased to 26.97% and 45.38%, respectively.

The leaf oil of lemon trees grown in Benin was the subject of analysis by Ayedoun et al. (1996). This oil was found to possess the following composition:

|                              |                                             |
|------------------------------|---------------------------------------------|
| $\alpha$ -thujene (0.1%)     | decanal (0.4%)                              |
| $\alpha$ -pinene (1.5%)      | citronellol (2.3%)                          |
| camphene (0.1%)              | neral (0.3%)                                |
| sabinene (3.8%)              | geraniol (t)                                |
| $\beta$ -pinene (18.5%)      | geranial (0.3%)                             |
| octanal (0.1%)               | undecanal (0.1%)                            |
| myrcene (1.5%)               | citronellyl acetate (0.7%)                  |
| $\alpha$ -terpinene (t)      | neryl acetate (0.2%)                        |
| p-cymene (0.1%)              | geranyl acetate (0.3%)                      |
| 1,8-cineole (2.9%)           | dodecanal (t)                               |
| limonene (40.8%)             | $\beta$ -caryophyllene (0.8%)               |
| (Z)- $\beta$ -ocimene (0.8%) | <i>trans</i> - $\alpha$ -bergamotene (0.1%) |
| melonal (0.1%)               | $\alpha$ -humulene (0.1%)                   |
| (E)- $\beta$ -ocimene (3.1%) | germacrene D (t)                            |
| $\gamma$ -terpinene (0.8%)   | (E,E)- $\alpha$ -farnesene (0.2%)           |
| terpinolene (0.1%)           | $\beta$ -bisabolene (0.3%)                  |
| nonanal (0.2%)               | $\delta$ -cadinene (t)                      |
| linalool (0.9%)              | (E)-nerolidol (t)                           |
| isopulegol (0.3%)            | caryophyllene oxide (0.1%)                  |
| citronellal (16.5%)          |                                             |
| terpinen-4-ol (0.6%)         |                                             |
| $\alpha$ -terpineol (0.6%)   |                                             |

t = trace (<0.1%)

It should be noted that the occurrence of melonal (2,6-dimethyl-5-heptenal) and citronellal in lemon petitgrain oil are very unusual and require corroboration before their natural occurrence in lemon leaf oil be accepted.

Lemon leaf oil of Italian origin was analyzed by Mondello et al. (1996) and it was found to possess the following composition:

|                                      |                                              |
|--------------------------------------|----------------------------------------------|
| tricyclene (t)                       | citronellal (0.78%)                          |
| $\alpha$ -thujene (0.07%)            | terpinen-4-ol (0.51%)                        |
| $\alpha$ -pinene (0.87%)             | $\alpha$ -terpineol (0.96%)                  |
| $\alpha$ -fenchene (0.01%)           | nerol (2.66%)                                |
| camphene (0.05%)                     | neral (8.13%)                                |
| sabinene (3.01%)                     | linalyl acetate (5.44%)                      |
| $\beta$ -pinene (12.57%)             | geranial (11.67%)                            |
| 6-methyl-5-hepten-2-one (1.06%)      | undecanal (0.04%)                            |
| myrcene (0.83%)                      | citronellyl acetate (0.21%)                  |
| $\alpha$ -phellandrene (0.03%)       | neryl acetate (5.89%)                        |
| $\delta$ -3-carene (0.75%)           | geranyl acetate (2.92%)                      |
| $\alpha$ -terpinene (0.04%)          | $\beta$ -elemene (0.03%)                     |
| o-cymene (0.01%)                     | methyl N-methyl anthranilate (0.24%)         |
| p-cymene (0.51%)                     | $\beta$ -caryophyllene (0.96%)               |
| limonene (30.66%)                    | <i>trans</i> - $\alpha$ -bergamotene (0.06%) |
| 1,8-cineole (1.34%)                  | $\alpha$ -humulene (0.09%)                   |
| (Z)- $\beta$ -ocimene (0.30%)        | (Z)- $\beta$ -farnesene (0.02%)              |
| (E)- $\beta$ -ocimene (1.50%)        | bicyclogermacrene (0.17%)                    |
| $\gamma$ -terpinene (0.42%)          | (E,E)- $\alpha$ -farnesene (0.14%)           |
| <i>cis</i> -sabinene hydrate (0.03%) | $\delta$ -cadinene (0.02%)                   |
| <i>cis</i> -linalool oxide† (0.01%)  | (E)-nerolidol (0.01%)                        |
| octanol (0.01%)                      | spathulenol (0.04%)                          |
| terpinolene (0.19%)                  | caryophyllene oxide (0.05%)                  |
| linalool (3.09%)                     |                                              |

|                                       |                               |
|---------------------------------------|-------------------------------|
| nonanal (0.08%)                       | 2,3-dimethyl-3-(4-methyl-3-   |
| <i>cis</i> -limonene oxide (t)        | pentyl)-2-norbornanol (0.02%) |
| <i>cis</i> -p-menth-2-en-1-ol (0.02%) | campherenol (0.01%)           |
| isopulegol (t)                        | $\alpha$ -bisabolol (0.01%)   |

t = trace (<0.01%)

† furanoid form

Six samples of lemon petitgrain oil that were produced in Sicily were the subject of study by Dugo et al. (1996) and Mondello et al. (1997). The range of composition of these oils is summarized as follows:

|                                               |                                                      |
|-----------------------------------------------|------------------------------------------------------|
| tricyclene (t-0.01%)                          | iso(iso)pulegol (t)                                  |
| $\alpha$ -thujene (0.06-0.09%)                | terpinen-4-ol (0.25-0.59%)                           |
| $\alpha$ -pinene (0.84-1.13%)                 | $\alpha$ -terpineol (0.53-1.00%)                     |
| $\alpha$ -fenchene (0-t)                      | decanal (0.03-0.09%)                                 |
| camphene (0.05-0.07%)                         | citronellol (t)                                      |
| sabinene (2.99-3.81%)                         | nerol (1.90-3.14%)                                   |
| $\beta$ -pinene (11.96-16.03%)                | neral (6.64-10.78%)                                  |
| 6-methyl-5-hepten-2-one<br>(0.67-1.61%)       | geraniol (0.87-6.25%)                                |
| myrcene (0.79-1.60%)                          | linalyl acetate (0.31-0.42%)                         |
| octanal (0.01-0.04%)                          | geranial (9.87-14.07%)                               |
| $\alpha$ -phellandrene (0.03-0.09%)           | undecanal (0.02-0.08%)                               |
| $\delta$ -3-carene (0.63-1.08%)               | citronellyl acetate (0.13-0.23%)                     |
| $\alpha$ -terpinene (0.04-0.11%)              | neryl acetate (3.75-6.74%)                           |
| o-cymene (t-0.01%)                            | geranyl acetate (2.17-2.92%)                         |
| p-cymene (0.04-0.51%)                         | $\beta$ -elemene (t-0.03%)                           |
| limonene (28.41-34.82%)                       | methyl N-methylanthranilate<br>(t-0.39%)             |
| $\beta$ -phellandrene (2.22-2.60%)            | <i>cis</i> - $\alpha$ -bergamotene (t)               |
| 1,8-cineole (1.12-2.13%)                      | $\beta$ -caryophyllene (0.60-1.54%)                  |
| (Z)- $\beta$ -ocimene (0.30-0.44%)            | <i>trans</i> - $\alpha$ -bergamotene<br>(0.03-0.20%) |
| (E)- $\beta$ -ocimene (1.50-2.43%)            | (Z)- $\beta$ -farnesene (t-0.03%)                    |
| $\gamma$ -terpinene (0.34-0.70%)              | $\alpha$ -humulene (0.06-0.13%)                      |
| <i>cis</i> -sabinene hydrate (0.02-0.06%)     | geranyl propionate (0.03-0.04%)                      |
| octanol (t-0.01%)                             | bicyclogermacrene (0.06-0.23%)                       |
| <i>cis</i> -linalool oxide† (t-0.01%)         | (E,E)- $\alpha$ -farnesene (0.03-0.14%)              |
| p-mentha-2,4(8)-diene<br>(0.01- 0.03%)        | $\beta$ -bisabolene (0.07-0.33%)                     |
| terpinolene (0.19-0.31%)                      | $\delta$ -cadinene (0.02-0.05%)                      |
| linalool (0.88-3.87%)                         | (E)-nerolidol (0.01-0.03%)                           |
| nonanal (0.08-0.22%)                          | spathulenol (0.01-0.09%)                             |
| <i>cis</i> -p-menth-2-en-1-ol<br>(0.01-0.03%) | caryophyllene oxide (0.04-0.14%)                     |
| <i>cis</i> -limonene oxide (0.01-0.05%)       | 2,3-dimethyl-3-(4-methyl-3-                          |
| <i>trans</i> -limonene oxide<br>(0.01-0.06%)  | pentyl)-2-norbornanol<br>(0.02-0.06%)                |
| isopulegol (t-0.03%)                          | campherenol (0.01-0.02%)                             |
| citronellal (0.61-1.41%)                      | $\alpha$ -bisabolol (0.01-0.03%)                     |

t = trace <0.01%)

† furanoid form

An oil of lemon leaves produced from lemon trees grown in Egypt was the subject of study by Haggag et al. (1998). They found that the major constituents of the oil were as follows:

|                          |                              |
|--------------------------|------------------------------|
| $\alpha$ -pinene (3.95%) | $\alpha$ -terpineol (18.93%) |
| $\beta$ -pinene (9.72%)  | citronellol (22.95%)         |
| limonene (20.05%)        | geraniol (3.20%)             |
| p-cymene (0.29%)         | thymol (0.23%)               |
| citronellal (2.16%)      | carvacrol (0.12%)            |
| linalool (1.50%)         | eugenol (0.21%)              |
| nerol (1.24%)            |                              |

The composition of this oil is so vastly different to that found for lemon petitgrain oil the analysis should be ignored. Its inclusion is only for completeness of the review.

The leaf oils of the Lisbon and Eureka cultivars of lemon, which were produced in Cameroon, were analyzed by Jazet Dongmo et al. (1998) and found to contain the following component range:

|                                        |                                                |
|----------------------------------------|------------------------------------------------|
| $\alpha$ -thujene (0.08-0.12%)         | p-cymen-8-ol (0-0.06%)                         |
| $\alpha$ -pinene (1.15-1.32%)          | $\gamma$ -terpineol (0.05-0.06%)               |
| camphene (0.08%)                       | neral (2.71-4.60%)                             |
| 6-methyl-5-hepten-2-one (2.76-2.93%)   | nerol (7.79-7.85%)                             |
| sabinene (2.60-3.38%)                  | geraniol (1.82-3.43%)                          |
| $\beta$ -pinene (13.14-14.85%)         | geranial (9.36-9.49%)                          |
| myrcene (1.49-1.64%)                   | methyl naphthalene (0-0.08%)                   |
| $\alpha$ -phellandrene (0.07%)         | thymol (0-0.06%)                               |
| $\delta$ -3-carene (0.75-1.06%)        | $\delta$ -elemene (0.06-0.09%)                 |
| $\alpha$ -terpinene (0.10-0.15%)       | $\alpha$ -terpinyl acetate (0.79-1.22%)        |
| p-cymene (0.24-0.30%)                  | geranyl acetate (1.02-1.14%)                   |
| limonene (38.77-42.43%)                | $\alpha$ -copaene (0-0.06%)                    |
| (E)- $\beta$ -ocimene (1.88-1.99%)     | $\beta$ -elemene (0.11-0.17%)                  |
| $\gamma$ -terpinene (0.26-0.51%)       | $\beta$ -caryophyllene (0.35-0.65%)            |
| <i>cis</i> -sabinene hydrate (0-0.08%) | <i>trans</i> - $\alpha$ -bergamotene (0-0.06%) |
| terpinolene (0.25-0.26%)               | linalool (1.81-1.88%)                          |
| limonene oxide* (t-0.09%)              | $\alpha$ -humulene (0.10-0.11%)                |
| limonene oxide* (0-t)                  | bicyclogermacrene (0.15-0.19%)                 |
| terpinen-1-ol (0.12-0.14%)             | isopulegol (0.61-0.65%)                        |
| menthone (0.16-0.27%)                  | (E,E)- $\alpha$ -farnesene                     |

|                                  |                               |
|----------------------------------|-------------------------------|
| $\beta$ -terpineol* (0-0.06%)    | (0-0.08%)                     |
| borneol (0.28-0.39%)             | $\beta$ -bisabolene (0-0.08%) |
| terpinen-4-ol (0.84-1.06%)       | spathulenol (0.12-0.20%)      |
| $\alpha$ -terpineol (0.77-1.29%) | $\beta$ -eudesmol (0-0.06%)   |

\* correct isomer not identified  
t = trace (<0.01%)

The leaf oil of the Barum cultivar of lemon was examined by de Rocca Serra et al. (1998) using a combination of GC and  $^{13}\text{C}$ -NMR. The components found in this oil were as follows:

|                              |                             |
|------------------------------|-----------------------------|
| myrcene (2.6%)               | linalyl acetate (18.4%)     |
| limonene (3.2%)              | neral (0.7%)                |
| (Z)- $\beta$ -ocimene (1.1%) | $\alpha$ -terpineol (11.4%) |
| $\gamma$ -terpinene (0.4%)   | neryl acetate (3.4%)        |
| (E)- $\beta$ -ocimene (2.4%) | geranial (1.0%)             |
| terpinolene (0.5%)           | geranyl acetate (5.1%)      |
| citronellal (0.9%)           | nerol (2.4%)                |
| linalool (38.9%)             | geraniol (6.4%)             |

In contrast, a leaf oil from the Eureka cultivar of lemon was found to contain the following components:

|                              |                            |
|------------------------------|----------------------------|
| $\alpha$ -pinene (0.9%)      | terpinen-4-ol (0.7%)       |
| $\beta$ -pinene (13.9%)      | neral (10.9%)              |
| sabinene (2.2%)              | $\alpha$ -terpineol (0.7%) |
| $\delta$ -3-carene (0.7%)    | neryl acetate (3.0%)       |
| myrcene (1.1%)               | geranial (16.4%)           |
| limonene (27.9%)             | geranyl acetate (2.0%)     |
| 1,8-cineole (0.9%)           | citronellol (1.0%)         |
| (E)- $\beta$ -ocimene (2.0%) | nerol (3.4%)               |
| citronellal (1.7%)           | geraniol (2.4%)            |
| linalool (1.9%)              |                            |

The composition of the leaf oils of the Eureka, Lisbon, Verna and Botswana cultivars of lemon grown in China were the subject of analysis by Huang et al. (2000). They found that the oils contained the following compositional range:

|                                           |                                                 |
|-------------------------------------------|-------------------------------------------------|
| (E)-2-hexenal (0-0.08%)                   | $\alpha$ -terpineol (0.35-0.70%)                |
| (Z)-3-hexenol (0-0.02%)                   | decanal (0.10-0.15%)                            |
| $\alpha$ -thujene (0.05-0.07%)            | citronellol (0.33-1.35%)                        |
| $\alpha$ -pinene (0.64-1.16%)             | nerol (2.09-6.38%)                              |
| camphene (0.04-0.10%)                     | neral (12.22-15.56%)                            |
| 6-methyl-5-hepten-2-one (0.35-1.01%)      | geraniol (1.34-3.76%)                           |
| sabinene (1.70-3.24%)                     | geranial (15.88-20.00%)                         |
| $\beta$ -pinene (8.21-12.11%)             | thymol (0-t)                                    |
| myrcene (0.97-1.13%)                      | undecanal (0.10-0.13%)                          |
| $\alpha$ -phellandrene (t-0.08%)          | methyl geranate (0.06-0.24%)                    |
| $\delta$ -3-carene (0.17-1.46%)           | citronellyl acetate (0.17-0.41%)                |
| $\alpha$ -terpinene (t-0.04%)             | neryl acetate (5.62-6.85%)                      |
| p-cymene (0.05-0.16%)                     | geranyl acetate (2.79-4.53%)                    |
| limonene (20.52-25.75%)                   | dodecanal (t)                                   |
| 1,8-cineole (0.26-1.59%)                  | $\beta$ -elemene (t-0.03%)                      |
| (Z)- $\beta$ -ocimene (0.20-0.32%)        | $\beta$ -caryophyllene (0.67-1.10%)             |
| $\beta$ -phellandrene (0.25-0.32%)        | <i>cis</i> - $\alpha$ -bergamotene (0.10-0.17%) |
| (E)- $\beta$ -ocimene (0.90-1.67%)        | (Z)- $\beta$ -farnesene (0.04-0.06%)            |
| $\gamma$ -terpinene (0.10-0.11%)          | $\alpha$ -humulene (0.08-0.14%)                 |
| octanol (t-0.03%)                         | (E,E)- $\alpha$ -farnesene (0.05-0.06%)         |
| <i>cis</i> -sabinene hydrate (0.05-0.07%) | germacrene B (0.07-0.18%)                       |
| <i>cis</i> -linalool oxide† (0-0.05%)     | $\beta$ -bisabolene (0.19-0.32%)                |
| terpinolene (0.04-0.25%)                  | $\delta$ -cadinene (0.02-0.06%)                 |
| nonanal (0.17-0.25%)                      | (E)-nerolidol (t-0.05%)                         |



linalool (0.94-1.75%)  
isopulegol (0.05-0.12%)  
citronellal (1.51-1.92%)  
terpinen-4-ol (0.16-0.23%)

† furanoid form  
t = trace (<0.01%)

spathulenol (0.06-0.20%)  
caryophyllene oxide  
(0.14-0.24%)

γ-terpinene (2.2-3.7)  
terpinolene (1.4-2.6)  
linalool (8.0-24.6)  
nonanal (1.5-2.9)  
citronellal (7.2-17.2)  
cis-isocitral (2.5-4.7)  
trans-isocitral (2.8-3.8)  
terpinen-4-ol (4.2-6.7)

bergamotene\* (0-1.2)  
α-humulene (0.7-1.8)  
neryl propionate (0.6-1.2)  
geranyl propionate  
(0.6-3.4)  
farnesene\* (0-1.1)  
caryophyllene oxide  
(0-1.0)

<sup>a</sup> = mg/kg oil  
<sup>\*</sup>correct isomer not identified

The authors also reported that the leaf oil of the Ponderosa cultivar possessed a different composition which can be seen as follows:

|                                 |                             |
|---------------------------------|-----------------------------|
| (E)-2-hexenal (t)               | decanal (0.13%)             |
| (Z)-3-hexenol (t)               | citronellol (1.04%)         |
| α-thujene (0.26%)               | nerol (0.61%)               |
| α-pinene (1.24%)                | neral (5.30%)               |
| camphene (0.04%)                | geraniol (0.31%)            |
| 6-methyl-5-hepten-2-one (0.20%) | geranial (7.27%)            |
| sabinene (32.11%)               | thymol (0.02%)              |
| β-pinene (2.20%)                | undecanal (0.04%)           |
| myrcene (2.56%)                 | methyl geranate (0.04%)     |
| α-phellandrene (0.05%)          | citronellyl acetate (0.60%) |
| δ-3-carene (0.03%)              | neryl acetate (0.71%)       |
| α-terpinene (0.16%)             | geranyl acetate (1.20%)     |
| p-cymene (0.53%)                | dodecanal (0.07%)           |
| limonene (5.12%)                | β-elemene (1.48%)           |
| 1,8-cineole (0.03%)             | β-caryophyllene (1.33%)     |
| (Z)-β-ocimene (0.32%)           | cis-α-bergamotene (0.02%)   |
| β-phellandrene (0.41%)          | (Z)-β-farnesene (0.37%)     |
| (E)-β-ocimene (6.48%)           | α-humulene (0.43%)          |
| γ-terpinene (0.56%)             | (E,E)-α-farnesene (0.07%)   |
| octanol (0.07%)                 | germacrene B (0.26%)        |
| cis-sabinene hydrate (0.59%)    | δ-cadinene (0.08%)          |
| cis-linalool oxide† (0.12%)     | (E)-nerolidol (0.15%)       |
| terpinolene (0.17%)             | spathulenol (0.26%)         |
| nonanal (0.23%)                 | caryophyllene oxide (0.29%) |
| linalool (7.56%)                | β-sinensal (2.14%)          |
| isopulegol (0.11%)              |                             |
| citronellal (7.35%)             |                             |
| terpinen-4-ol (1.85%)           |                             |
| α-terpineol (0.50%)             |                             |

t = trace (<0.01%)  
† furanoid form

Leaves from the Zambetakis cultivar of lemon grown in Crete (Greece) were harvested December 1996, March 1997, May 1997, June 1997, November 1997 and April 1998 from oils which were produced by Vekiari et al. (2002) using hydrodistillation. The yield of oil was found to vary from 0.65-1.74% v/w with the highest yield obtained from leaves harvested in November. The oil composition from each of the oils was found to vary as follows:

|                                |                               |
|--------------------------------|-------------------------------|
| α-thujene (0-0.8) <sup>a</sup> | α-terpineol (5.2-12.1)        |
| α-pinene (6.1-10.8)            | decanal (0.5-1.4)             |
| camphene (0-0.8)               | neral (108.0-148.3)           |
| β-pinene (81.8-107.3)          | geranial (103.9-164.9)        |
| myrcene (11.6-17.3)            | undecanal (0.4-1.9)           |
| α-terpinene (0.7-1.4)          | citronellyl acetate (1.4-4.9) |
| δ-3-carene (4.2-10.4)          | neryl acetate (32.6-61.7)     |
| limonene (162.9-197.4)         | geranyl acetate (22.5-41.8)   |
| (Z)-β-ocimene (3.9-5.4)        | β-caryophyllene (3.4-7.3)     |
| (E)-β-ocimene (19.9-26.5)      | dodecanal (0-0.7)             |

The leaf oils of nine lemon cultivars were examined by Lota et al. (2002) using a combination of GC and GC/MS. The composition of these oils is shown in T-7. The authors also found that the composition of the leaf oil of the Barum cultivar of lemon was unusual as can be seen as follows:

|                                |                         |
|--------------------------------|-------------------------|
| α-thujene (t)                  | citronellal (0.9%)      |
| α-pinene (t)                   | decanal (t)             |
| β-pinene (t)                   | linalool (38.9%)        |
| sabinene (t)                   | linalyl acetate (18.5%) |
| myrcene (2.6%)                 | trans-α-bergamotene (t) |
| α-terpinene (t)                | β-caryophyllene (0.1%)  |
| limonene (3.2%)                | terpinen-4-ol (0.1%)    |
| β-phellandrene (t)             | α-humulene (t)          |
| (Z)-β-ocimene (1.1%)           | neral (0.7%)            |
| γ-terpinene (0.4%)             | α-terpineol (11.4%)     |
| (E)-β-ocimene (2.4%)           | neryl acetate (3.4%)    |
| p-cymene (t)                   | geranial (1.0%)         |
| terpinolene (0.5%)             | geranyl acetate (5.1%)  |
| 6-methyl-5-hepten-2-one (0.1%) | citronellol (0.1%)      |
| allo-ocimene* (t)              | nerol (2.4%)            |
| cis-linalool oxide† (t)        | geraniol (6.4%)         |
| trans-limonene oxide (t)       | (E)-nerolidol (t)       |

\*correct isomer not identified  
† furanoid form  
t = trace (<0.1%)

I. Calvarano, *Le essenze italiane di petitgrain Notal. petitgrain limone e mandarino*. Essenz. Deriv. Agrum., 37, 27-54 (1967); cited In:

*Citrus, The Genus Citrus*. Edits., G. Dugo and A. DiGiacomo, 425-460, Taylor and Francis, London (2002).

S. Kamiyama, *Studies on the leaf oils of Citrus species. Part I. Composition of leaf oils from Citrus unshiu, Citrus natsudaoidai, Citrus kokitsu and Citrus limon*. Agric. Biol. Chem., 31, 1091-1096 (1967).

L. R. de Vottero, G. Tonarelli, E. R. de Krasnogor and J. A. Retamar, *Petitgrains from bitter orange, lemon and mandarin leaves*. Essenz. Deriv. Agrum., 48, 150-156 (1978).

M-H. Wen, S-C. Xiao, H. Zhao, W-J. Ren and Y-Z. Huang, *A study on the chemical components of the essential oil from leaves of the Citrus limon (L.) Burm. f.* Tianvan Chanwu Yanjiu and Yukai, 1(2), 18-22 (1989).

M. A. Germana, F. DePasquale, E. Bazan and E. Palazzolo, *Essential oils of the flowers, leaves and buds of five species of Citrus*. Essenz. Deriv. Agrum., 60, 297-212 (1990).

| Compound                     | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|------------------------------|------|------|------|------|------|------|------|------|------|
| $\alpha$ -thujene            | -    | 0.1  | t    | 0.1  | t    | 0.1  | 0.1  | 0.1  | 0.1  |
| $\alpha$ -pinene             | 1.7  | 1.5  | 0.7  | 1.2  | 0.7  | 1.1  | 1.0  | 1.0  | 1.2  |
| camphene                     | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  |
| $\beta$ -pinene              | 25.1 | 23.8 | 10.5 | 16.8 | 13.9 | 18.0 | 18.2 | 15.9 | 18.5 |
| sabinene                     | 4.4  | 5.1  | 1.9  | 3.6  | 2.2  | 2.9  | 3.3  | 3.1  | 2.7  |
| $\delta$ -3-carene           | 0.4  | 0.1  | 0.6  | 0.5  | 0.7  | 0.3  | 0.2  | 0.4  | 0.4  |
| myrcene                      | 1.0  | 0.9  | 1.0  | 1.1  | 1.1  | 0.9  | 0.8  | 1.0  | 0.9  |
| $\alpha$ -phellandrene       | 0.1  | t    | t    | t    | t    | t    | t    | t    | t    |
| $\alpha$ -terpinene          | 0.2  | 0.2  | t    | 0.1  | 0.1  | t    | t    | 0.1  | 0.1  |
| limonene                     | 19.2 | 19.1 | 24.2 | 28.9 | 27.9 | 21.8 | 22.0 | 21.4 | 23.8 |
| $\beta$ -phellandrene        | -    | -    | -    | -    | -    | -    | -    | -    | 0.8  |
| 1,8-cineole                  | 2.6  | 5.2  | 0.8  | 1.6  | 0.9  | 0.8  | 1.0  | 2.1  | -    |
| (Z)- $\beta$ -ocimene        | 0.3  | 0.4  | 0.2  | 0.4  | 0.4  | 0.3  | 0.3  | 0.4  | 0.3  |
| $\gamma$ -terpinene          | 0.4  | 0.6  | 0.2  | 0.4  | 0.3  | 0.3  | 0.3  | 0.4  | 0.3  |
| (E)- $\beta$ -ocimene        | 1.5  | 2.2  | 1.2  | 2.1  | 2.0  | 1.6  | 1.5  | 2.0  | 1.8  |
| p-cymene                     | t    | t    | 0.1  | t    | -    | 0.1  | 0.1  | t    | t    |
| terpinolene                  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.1  | 0.1  | 0.2  | 0.2  |
| octanal                      | t    | t    | 0.1  | t    | t    | 0.1  | 0.1  | t    | t    |
| 6-methyl-5-hepten-2-one      | 1.8  | 1.2  | 1.0  | 1.4  | 3.2  | 0.9  | 0.7  | 1.3  | 1.7  |
| allo-ocimene*                | -    | t    | -    | -    | -    | -    | -    | -    | -    |
| nonanal                      | -    | 0.2  | 0.4  | 0.2  | -    | 0.3  | 0.3  | 0.1  | 0.2  |
| cis-limonene oxide           | -    | -    | 0.1  | t    | -    | 0.1  | -    | -    | -    |
| trans-limonene oxide         | -    | t    | -    | -    | -    | -    | -    | -    | -    |
| trans-sabinene hydrate       | 0.1  | 0.1  | 0.1  | 0.1  | t    | 0.1  | 0.1  | 0.1  | t    |
| citronellal                  | 0.7  | 0.5  | 1.2  | 1.7  | 1.7  | 1.8  | 1.6  | 1.4  | 1.5  |
| decanal                      | -    | -    | 0.1  | t    | -    | t    | 0.1  | t    | t    |
| linalool                     | 1.6  | 1.9  | 1.5  | 1.4  | 1.9  | 1.6  | 1.8  | 1.8  | 2.1  |
| cis-p-menth-2-en-1-ol        | t    | 0.1  | -    | -    | -    | -    | -    | -    | -    |
| trans- $\alpha$ -bergamotene | -    | -    | -    | -    | t    | -    | -    | -    | t    |
| $\beta$ -caryophyllene       | 0.1  | 0.3  | 0.4  | 0.2  | 0.2  | 0.2  | 0.1  | 0.1  | 0.1  |
| terpinen-4-ol                | 0.7  | 1.0  | 0.2  | 0.4  | 0.7  | 0.3  | 0.4  | 0.5  | 0.5  |
| citronellyl acetate          | t    | t    | 0.2  | 0.2  | 0.1  | 0.1  | 0.1  | 0.1  | -    |
| (E)- $\beta$ -farnesene      | -    | t    | -    | -    | -    | -    | -    | -    | 0.1  |
| $\alpha$ -humulene           | t    | -    | t    | -    | t    | -    | -    | -    | t    |
| neral                        | 12.4 | 11.6 | 16.1 | 10.4 | 10.9 | 13.2 | 12.8 | 14.7 | 13.6 |
| $\alpha$ -terpineol          | 1.0  | 1.8  | 0.5  | 0.7  | 0.7  | 0.4  | 0.6  | 0.9  | 0.6  |
| $\beta$ -bisabolene          | -    | -    | t    | -    | -    | t    | -    | -    | -    |
| $\alpha$ -bisabolene*        | -    | -    | 0.1  | -    | -    | -    | -    | -    | -    |
| neryl acetate                | 1.0  | 0.7  | 4.2  | 3.0  | 3.0  | 5.0  | 5.1  | 2.9  | 1.8  |
| geranial                     | 16.8 | 15.9 | 22.6 | 14.3 | 16.4 | 19.1 | 18.1 | 20.1 | 18.9 |
| (E,E)- $\alpha$ -farnesene   | 0.1  | -    | -    | -    | -    | -    | -    | -    | 0.1  |
| geranyl acetate              | 1.2  | 0.8  | 2.5  | 2.4  | 2.0  | 3.2  | 2.3  | 2.5  | 2.0  |
| citronellol                  | 0.6  | 0.4  | 0.5  | 0.6  | 1.0  | 0.3  | 0.5  | 0.6  | 0.6  |
| nerol                        | 1.8  | 1.2  | 2.7  | 2.4  | 3.4  | 2.2  | 3.3  | 2.1  | 2.0  |
| geraniol                     | 1.5  | 1.1  | 1.7  | 1.8  | 2.4  | 0.8  | 1.1  | 1.4  | 1.6  |
| caryophyllene oxide          | -    | -    | 0.1  | 0.1  | -    | t    | -    | -    | -    |
| (E)-nerolidol                | -    | t    | t    | t    | -    | -    | t    | t    | t    |

\* correct isomer not identified

t = trace (&lt;0.1%)

Cultivars: 1. Corpaci, 2. Lisbon, 3. Panaché, 4. Lapithou, 5. Eureka, 6. Berna, 7. Fino, 8. Menton and 9. Santa Teresa

- Z-K. Lin and Y-F. Hua, *Systematic evolutionary relation of chemical components of the essential oils from 11 taxa of Citrus leaves*. Acta Bot. Sinica, 34, 133-139 (1992).
- H. T. Verdi, C. Kunkar, T. ÷zek, S. Hakka Beis and K. H. Can Baser, *Petitgrain di limone Turco: Composizione dell' essenza del deterpenato e delle frazioni di testa*. Essenz. Deriv. Agrum., 63, 181-190 (1993).
- A. M. Ayedoun, P. V. Sossou, M. Mandarowicz and P. A. Leclercq, *Volatile constituents of the peel and leaf oils of Citrus limon L. Burm. f. from Benin*. J. Essent. Oil Res., 8, 441-444 (1996).
- L. Mondello, P. Dugo, G. Dugo and K. D. Bartle, *On-line HPLC-HRGC-MS for the analysis of natural complex mixtures*. J. Chromatogr. Sci., 34, 174-181 (1996).
- G. Dugo, L. Mondello, A. Cotroneo, I. Stagno d'Alcontres, A. Basile, P. Previti, P. Dugo and K. D. Bartle, *Characterization of Italian Citrus petitgrain oils*. Perfum. Flavor., 21(3), 17-28 (1996).
- L. Mondello, A. Cotroneo, G. Dugo and P. Dugo, *Italian Citrus petitgrain oils. Part IV. Composition of lemon petitgrain oil*. J. Essent. Oil Res., 9, 495-508 (1997).
- E. G. Haggag, S. M. A. Wahab, S. M. El-Zalabany, E. A. A. Moustafa, E. M. El-Kherasy and T. J. Mabry, *Volatile oils and pectins from Citrus auratifolia (lime) and Citrus limonia (lemon)*. Asian J. Chem., 10, 828-833 (1998).
- P. M. Jazet Dongmo, P. H. Amvam Zollo, F. Fekam Boyom, C. Menut, G. Lamaty and J. M. Bessiere, *Chemical composition of essential oils from Citrus species grown in Cameroon*. Rivista Ital. EPPOS, (Numero Speciale), 156-162 (1998).
- D. de Rocca Serra, M. L. Lota, F. Tomi and J. Casanova, *Essential oils and taxonomy amount Citrus example of bergamot*. Rivista Ital. EPPOS, (Numero Speciale), 38-43 (1998).
- Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 100 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).
- S. A. Vekiari, E. E. Protopapadakis, P. Papadopoulou, D. Papanicolaou, C. Panou and M. Vamvakias, *Compositional and seasonal variation of the essential oil from leaves and peel of a Cretan lemon variety*. J. Agric. Food Chem., 50, 147-153 (2002).
- M-L. Lota, D. de Rocca Serra, F. Tomi, C. Jacquemond and J. Casanova, *Volatile components of peel and leaf oils of lemon and lime species*. J. Agric. Food Chem., 50, 796-805 (2002).

### **Citrus paradisi Macfady.**

An oil produced from the leaves of the Marsh seedless grapefruit cultivars was subjected to analysis by Germana et al. (1990). The results of this analysis are summarized as follows:

|                                |                             |
|--------------------------------|-----------------------------|
| sabinene (10.22%)              | neral (3.07%)               |
| myrcene (1.25%)                | geranyl acetate (7.65%)     |
| limonene (2.12%)               | geranial (5.33%)            |
| $\alpha$ -terpinene (0.49%)    | nerol (3.49%)               |
| $\beta$ -caryophyllene (0.99%) | geraniol (3.74%)            |
| linalool (26.66%)              | methyl anthranilate (7.97%) |
| benzaldehyde (2.94%)           | farnesol* (5.63%)           |
| neryl acetate (3.92%)          |                             |

\*correct isomer not identified

The characterization of benzaldehyde and methyl anthranilate requires corroboration before full acceptance.

Gurib-Fakim and Demarne (1995) used a combination of GC and GC/MS to analyze a leaf oil of grapefruit produced from trees grown in Mauritius. The oil was found to contain the following components:

|                               |                             |
|-------------------------------|-----------------------------|
| (Z)-3-hexenol (t)             | $\alpha$ -terpineol (0.30%) |
| $\alpha$ -phellandrene (t)    | verbenone (0.36%)           |
| $\alpha$ -terpinene (t)       | cis-carveol (0.18%)         |
| $\beta$ -phellandrene (0.21%) | citronellol (8.60%)         |
| limonene (0.14%)              | neral (0.81%)               |
| (Z)- $\beta$ -ocimene (0.18%) | geraniol (2.73%)            |
| cis-linalool oxide†           | geranial (0.10%)            |
| (0.13%)                       | geranyl formate (0.23%)     |
| octanol (0.64%)               | carvacrol (0.22%)           |
| terpinolene (0.33%)           | cinnamaldehyde (11.11%)     |
| linalool (22.93%)             | cinnanyl formate (0.18%)    |

| Compound                          | Balady | Yussuf | Effendy | Dancy Maya |
|-----------------------------------|--------|--------|---------|------------|
| $\alpha$ -thujene                 | -      | 0.78   | 0.65    | -          |
| $\alpha$ -pinene                  | 1.34   | 1.83   | 1.31    | -          |
| $\beta$ -pinene                   | 0.72   | 1.51   | 1.18    | 0.11       |
| sabinene                          | -      | -      | 0.41    | 1.41       |
| myrcene                           | 0.31   | 0.34   | 0.11    | 0.25       |
| $\alpha$ -phellandrene            | 0.05   | t      | -       | -          |
| ethyl (E)-2-butenolate            | -      | -      | -       | 0.04       |
| $\alpha$ -terpinene               | 0.15   | 0.11   | 0.21    | 0.07       |
| limonene                          | 4.91   | 1.00   | 0.39    | 0.23       |
| $\beta$ -phellandrene             | 0.03   | -      | -       | 0.06       |
| (Z)- $\beta$ -ocimene             | 0.04   | -      | 0.10    | 2.31       |
| $\gamma$ -terpinene               | 12.60  | 4.57   | 3.11    | 2.12       |
| (Z)-3-hexenyl formate             | 0.11   | -      | -       | -          |
| p-cymene                          | 3.10   | 6.54   | 4.09    | 1.43       |
| terpinolene                       | 0.53   | 0.34   | -       | -          |
| (Z)-2-pentenol                    | t      | -      | -       | -          |
| (Z)-3-hexenol                     | 0.06   | 0.13   | 0.05    | 0.33       |
| ethyl octanoate                   | 0.01   | t      | -       | 0.02       |
| trans-sabinene hydrate            | 0.01   | -      | -       | 2.79       |
| ethyl nonanoate                   | 0.01   | -      | -       | -          |
| cis-linalool oxide <sup>†</sup>   | -      | 0.06   | 0.44    | -          |
| trans-linalool oxide <sup>†</sup> | -      | -      | 0.21    | -          |
| $\alpha$ -copaene                 | -      | -      | -       | 0.03       |
| decanal                           | -      | -      | -       | 0.03       |
| benzaldehyde                      | -      | -      | -       | 0.02       |
| linalool                          | 0.11   | 45.12  | 50.73   | 55.10      |
| trans- $\beta$ -bergamotene       | -      | -      | -       | 0.02       |
| $\beta$ -elemene                  | -      | -      | 0.10    | 0.04       |
| terpinen-4-ol                     | 1.63   | -      | -       | -          |
| $\beta$ -caryophyllene            | 0.14   | 5.44   | 0.24    | 2.00       |
| valencene                         | 0.05   | -      | -       | -          |
| methyl thymol                     | -      | -      | 4.63    | -          |
| terpinen-1-ol                     | 0.01   | t      | t       | -          |
| ethyl decanoate                   | 0.03   | t      | -       | -          |
| (E)- $\beta$ -farnesene           | -      | -      | t       | t          |
| $\alpha$ -humulene                | 0.08   | 0.51   | 0.25    | 0.11       |
| sabinol*                          | -      | -      | t       | -          |
| $\alpha$ -terpineol               | 0.24   | 0.33   | 0.58    | 1.30       |
| viridiflorene                     | t      | 0.31   | 0.18    | -          |
| $\alpha$ -muurolene               | -      | t      | t       | 0.02       |
| bicyclogermacrene                 | -      | -      | -       | 0.06       |
| (E,E)- $\alpha$ -farnesene        | -      | 0.71   | 0.50    | 1.00       |
| citronellol                       | -      | -      | -       | t          |
| $\gamma$ -cadinene                | -      | 0.06   | 0.02    | 0.06       |
| methyl salicylate                 | 1.00   | -      | -       | -          |
| ethyl phenylacetate               | 0.06   | -      | -       | 0.02       |
| anethole*                         | -      | -      | 0.02    | 0.01       |
| geraniol                          | -      | 0.02   | t       | 0.03       |
| ethyl dodecanoate                 | -      | 0.02   | t       | 0.03       |
| p-cymen-8-ol                      | 0.10   | 0.05   | t       | t          |
| 2-phenethanol                     | -      | t      | 0.02    | 0.03       |
| myrtenol                          | -      | t      | t       | t          |
| cis-carveol                       | 0.04   | t      | 0.01    | -          |
| humulene oxide*                   | -      | 0.03   | t       | -          |

| Compound                     | Balady | Yussuf | Effendy | Dancy Maya |
|------------------------------|--------|--------|---------|------------|
| caryophyllene oxide          | t      | 0.31   | 0.33    | -          |
| nerolidol*                   | -      | 0.04   | t       | 0.04       |
| ethyl tetradecanoate         | 0.18   | 0.11   | 0.14    | 0.05       |
| methyl N-methyl anthranilate | 65.71  | -      | -       | -          |
| thymol                       | 0.12   | 14.43  | 11.70   | 8.21       |
| <i>trans</i> -carveol        | 0.04   | -      | -       | -          |
| ethyl pentadecanoate         | 0.03   | -      | -       | -          |
| $\beta$ -sinensal            | -      | -      | 0.41    | 2.98       |
| ethyl hexadecanoate          | 1.83   | 2.31   | 2.79    | 6.08       |
| ethyl heptadecanoate         | 0.04   | 0.09   | 0.15    | 0.07       |
| $\alpha$ -sinensal           | -      | 0.93   | 0.24    | 0.72       |
| ethyl octadecanoate          | 0.06   | 0.09   | 0.15    | 0.07       |
| ethyl linoleate              | 0.74   | 0.78   | 0.39    | 1.06       |
| ethyl linolenate             | 2.64   | 2.86   | 0.68    | 6.88       |
| phytol                       | 0.14   | 0.19   | 0.12    | 1.29       |

\*correct isomer not identified; t=trace (<0.01%)  
‡ furanoid form

nonanal (0.36%)

*trans*-rose oxide (0.82%)

menthone (0.96%)

isomenthone (0.10%)

(Z)- $\beta$ -terpineol (6.98%)

bornyl acetate (1.17%)

 $\gamma$ -terpineol† (0.64%)

terpinen-4-ol (20.00%)

*trans*-piperitol (7.40%)

\*correct isomer not identified

t = trace (&lt;0.01%)

‡ furanoid form

† the natural origin of  $\gamma$ -terpineol is in question

citronellyl acetate (4.84%)

citronellic acid (0.41%)

 $\alpha$ -cubebene (0.30%)

geranyl acetate (0.29%)

 $\beta$ -copaene (0.62%)*trans*- $\beta$ -bergamotene (t)

nerolidol\* (t)

citronellyl tiglate (t)

(E)- $\beta$ -ocimene (9.23-10.47%) $\gamma$ -terpinene (1.20-1.68%)

octanol (t)

*cis*-sabinene hydrate (0.36-0.45%)*cis*-linalool oxide‡ (0.04-0.09%)

terpinolene (0.29-0.36%)

nonanal (0.02%)

linalool (8.18-8.51%)

isopulegol (0.06-0.12%)

citronellal (1.51-1.71%)

terpinen-4-ol (2.01-3.47%)

 $\alpha$ -terpineol (0.20-0.24%)

decanal (0.20-0.23%)

citronellol (0.22-0.26%)

nerol (0.05-0.06%)

neral (0.12-0.31%)

geraniol (0.09%)

linalyl acetate (0.09%)

geranial (0.24-0.46%)

thymol (0.04-0.07%)

carvacrol (0.06%)

citronellyl acetate (0.18-0.43%)

neryl acetate (0.11-0.28%)

geranyl acetate (0.10-0.15%)

dodecanal (0.05-0.07%)

 $\beta$ -elemene (0.69-1.44%) $\beta$ -caryophyllene (0.39-1.04%)*cis*- $\alpha$ -bergamotene (0-0.10%)(Z)- $\beta$ -farnesene (0.24-0.66%) $\alpha$ -humulene (0.22-0.53%) $\gamma$ -muurolene (0-0.04%)(E,E)- $\alpha$ -farnesene (0.07-0.09%)

germacrene B (0.13-0.33%)

 $\delta$ -cadinene (0.04-0.09%)

elemol (0.13-0.15%)

(E)-nerolidol (0.21-0.24%)

Grapefruit leaf oil was the subject of analysis by Huang et al. (2000). They used a combination of GC and GC/MS to examine the leaf oils of the Marsh and Duncan cultivars grown in China. The results of this study are summarized as follows:

 $\alpha$ -thujene (0.40-0.41%) $\alpha$ -pinene (1.25-1.70%)

camphene (0.05%)

6-methyl-5-hepten-2-one (0.04-0.07%)

sabinene (50.38-50.57%)

 $\beta$ -pinene (3.30-3.58%)

myrcene (3.18-3.53%)

 $\alpha$ -phellandrene (0.09%) $\delta$ -3-carene (t-0.02%) $\alpha$ -terpinene (0.61-0.67%)

p-cymene (0.09-0.21%)

limonene (2.60-2.82%)

(Z)- $\beta$ -ocimene (0.38-0.46%) $\beta$ -phellandrene (0.65-0.75%)



spathulenol (0.24-0.25%)  
 caryophyllene oxide (0.26-0.28%)  
 $\beta$ -eudesmol (0-0.31%)  
 $\beta$ -sinensal (2.22-2.39%)

† furanoid form  
 t = trace (<0.0.1%)

The volatiles found in an extract of the fresh leaves of the Star Ruby cultivar of grapefruit were the subject of study by Garcel et al. (2002). In the extract, the following components were found:

|                                    |                              |
|------------------------------------|------------------------------|
| $\alpha$ -pinene (40) <sup>a</sup> | $\beta$ -elemene (18)        |
| $\alpha$ -thujene (5)              | $\beta$ -caryophyllene (65)  |
| $\beta$ -pinene (68)               | undecanal (<1)               |
| sabinene (990)                     | $\alpha$ -humulene (19)      |
| $\delta$ -3-carene (<1)            | citronellyl acetate (<1)     |
| $\alpha$ -phellandrene (4)         | (E)- $\beta$ -farnesene (90) |
| myrcene (60)                       | neral (<1)                   |
| $\alpha$ -terpinene (1)            | germacrene D (5)             |
| limonene (33)                      | $\alpha$ -terpineol (<1)     |
| (Z)- $\beta$ -ocimene (5)          | $\gamma$ -cadinene (177)     |
| $\gamma$ -terpinene (1)            | geranyl acetate (<1)         |
| (E)- $\beta$ -ocimene (146)        | germacrene C (1)             |
| p-cymene (<1)                      | citronellol (2)              |
| terpinolene (1)                    | nerol (<1)                   |
| octanal (<1)                       | geraniol (<1)                |
| citronellal (17)                   | (E)-nerolidol (3)            |
| decanal (1)                        | $\beta$ -sinensal (73)       |
| linalool (134)                     | geranic acid (3)             |

<sup>a</sup> = mg/g (fresh weight)

- M. A. Germana, F. De Pasquale, E. Bazan and E. Palazzolo, *Essential oils of the flowers, leaves and buds of five species of Citrus*. Essenz. Deriv. Agrum., 60, 297-312 (1990).
- A. Gurib-Fakim and F. Demarne, *Aromatic plants of Mauritius: Volatile constituents of the leaf oils of Citrus aurantium L., Citrus paradisi Macfad. and Citrus sinensis (L.) Osbeck*. J. Essent. Oil Res., 7, 105-109 (1995).
- Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 110 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 56-66 (2000).
- A-L. Gancel, D. Oll  , P. Ollitrault, F. Luro and J-M. Brillouet, *Leaf and peel volatile compounds of an interspecific Citrus somatic hybrid [ Citrus aurantifolia (Christm.) Swing + Citrus paradisi Macfayden]*. Flav. Fragr. J., 17, 416-424 (2002).

## Citrus reticulata Blanco

An oil produced from the leaves of the mandarin tree grown in Argentina was found by de Vottero et al. (1978) to contain  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, limonene, p-cymene,  $\gamma$ -terpinene, linalool, linalyl acetate,  $\alpha$ -terpineol, citronellol, geranyl acetate and methyl N-methyl anthranilate although no quantitative data were given.

Mandarin leaf oil (ex. *C. reticulata*) produced in Italy was analyzed by Germana et al. (1990) and it was found to contain the following components:

|                                |                         |
|--------------------------------|-------------------------|
| $\alpha$ -pinene (0.96%)       | neryl acetate (0.17%)   |
| $\beta$ -pinene (0.96%)        | neral (0.03%)           |
| sabinene (0.54%)               | geranyl acetate (0.78%) |
| myrcene (8.03%)                | geranial (1.99%)        |
| limonene (24.24%)              | nerol (1.27%)           |
| $\alpha$ -terpinene (4.07%)    | geraniol (1.11%)        |
| $\beta$ -caryophyllene (0.06%) | methyl N-methyl         |
| linalool (4.37%)               | anthranilate (50.10%)   |
| benzaldehyde (0.11%)           | farnesol* (0.4%)        |

\*correct isomer not identified

| Compound                        | 1         | 2         | 3         | 4         | 5         | 6    |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|------|
| $\alpha$ -thujene               | 0.4-0.9   | 0.2-0.8   | 1.0-1.7   | 1.0-1.4   | 1.9-2.3   | t    |
| $\alpha$ -pinene                | 1.5-2.9   | 0.9-2.1   | 2.1-3.6   | 1.8-2.9   | 4.0-4.4   | 0.3  |
| $\beta$ -pinene                 | 2.1-3.4   | 1.9-3.1   | 2.6-3.8   | 2.1-2.9   | 4.9-10.7  | 0.1  |
| sabinene                        | 43.2-59.4 | 34.1-48.3 | 0.3-0.4   | 0.2-0.3   | 0.5-1.7   | 2.1  |
| $\delta$ -3-carene              | t-0.2     | 0-2.9     | 0-3.8     | -         | -         | -    |
| myrcene                         | 3.2-4.4   | 2.3-3.2   | 0.7-1.5   | 0.6-0.8   | 1.1-1.2   | 0.9  |
| $\alpha$ -phellandrene          | 0-0.3     | 0-0.3     | t-0.4     | t         | 0.1       | t    |
| $\alpha$ -terpinene             | 1.1-2.7   | 0.4-1.4   | 0.6-0.7   | 0.2-0.4   | 1.1-1.4   | 0.1  |
| limonene                        | 1.6-3.3   | 1.5-19.8  | 4.8-5.3   | 1.6-3.1   | 4.6-6.5   | 44.3 |
| $\beta$ -phellandrene           | 0.5-0.7   | 0.4-0.8   | t-0.2     | 0-t       | t-0.3     | 0.1  |
| (Z)- $\beta$ -ocimene           | 0.1-0.8   | 0-0.3     | 0.2-0.3   | 0.4-0.5   | 0.1-0.2   | 0.4  |
| $\gamma$ -terpinene             | 2.5-5.4   | 1.5-9.4   | 23.5-25.7 | 5.7-15.8  | 51.0-61.3 | 0.2  |
| (E)- $\beta$ -ocimene           | 2.8-13.7  | 2.8-10.5  | 4.8-8.1   | 7.5-11.4  | 1.5-5.0   | 2.3  |
| p-cymene                        | t-0.7     | t-2.3     | 14.6-20.4 | 2.5-4.1   | 0-1.9     | -    |
| terpinolene                     | 0.5-1.2   | 0.5-1.0   | 1.6-2.6   | 0.9-1.2   | 2.2-2.4   | 0.1  |
| p-cymenene                      | 0-0.5     | 0-0.4     | 3.8       | 0.4-2.0   | -         | -    |
| <i>trans</i> -sabinene hydrate  | 0.5-0.9   | 0.5-1.4   | -         | 0-t       | 0-t       | -    |
| citronellal                     | 0-2.2     | 0-0.7     | -         | -         | -         | -    |
| linalool                        | 5.3-14.8  | 16.7-34.0 | 12.5-34.1 | 40.9-54.3 | 10.5-12.3 | 0.5  |
| linalyl acetate                 | 0-t       | 0-0.3     | 0-0.1     | -         | -         | -    |
| <i>cis</i> -p-menth-2-en-1-ol   | 0.3-0.6   | 0-0.6     | t         | 0-t       | t         | -    |
| $\beta$ -elemene                | 0-0.5     | 0-0.7     | 0-1.3     | -         | -         | -    |
| $\beta$ -caryophyllene          | 0-0.3     | 0-0.3     | 0.1-0.6   | 0-0.4     | 0.2       | 0.3  |
| methyl thymol                   | 0-1.9     | 0-4.0     | -         | 0.2-7.0   | -         | -    |
| terpinen-4-ol                   | 4.3-10.6  | 3.3-6.2   | 0.2-0.3   | 0.1-0.2   | 0.3-0.4   | 0.4  |
| <i>trans</i> -p-menth-2-en-1-ol | 0.1-0.3   | 0.1-0.4   | t-0.1     | 0-t       | t         | -    |
| $\alpha$ -humulene              | 0-t       | 0-0.1     | 0-0.2     | 0-t       | 0-0.2     | 0.1  |
| neral                           | 0-0.4     | 0-0.4     | 0-0.3     | -         | -         | -    |
| $\alpha$ -terpineol             | 0.3-1.0   | 0.3-1.0   | 0.2-0.4   | 0.2-0.3   | 0-0.5     | 0.1  |
| germacrene D                    | 0-0.1     | 0-t       | -         | 0-t       | -         | -    |
| $\alpha$ -bisabolene*           | 0-0.4     | 0-0.3     | 0-0.2     | 0-0.1     | 0-t       | t    |
| neryl acetate                   | 0-0.3     | 0-0.7     | -         | -         | -         | -    |
| (E,E)- $\alpha$ -farnesene      | 0-0.1     | 0-0.1     | 0-0.1     | 0-0.1     | 0-0.1     | -    |
| geranial                        | 0-t       | 0-0.7     | 0-0.4     | -         | -         | -    |
| $\delta$ -cadinene              | 0-0.1     | 0-0.1     | -         | 0-t       | 0-t       | -    |
| geranyl acetate                 | 0-0.1     | 0-0.4     | 0-0.2     | -         | -         | -    |
| citronellol                     | 0-1.0     | 0-0.1     | 0-0.1     | -         | -         | -    |
| nerol                           | 0-0.9     | 0-0.3     | 0-0.3     | 0-t       | 0-t       | -    |
| geraniol                        | 0-0.2     | 0.7       | 0-0.1     | 0-0.2     | -         | -    |
| (E)-nerolidol                   | 0-0.1     | t-0.2     | 0-0.1     | 0-0.1     | t         | -    |
| methyl N-methyl anthranilate    | -         | 0-t       | 0-0.1     | -         | 0-0.1     | 46.6 |
| T-cadinol                       | 0-0.1     | 0.0.1     | -         | -         | -         | -    |
| thymol                          | 0-0.9     | 0-2.8     | 0-0.1     | 8.2-12.9  | t-0.1     | -    |
| $\beta$ -sinensal               | 0.4-1.8   | 0-1.5     | 0-1.0     | -         | 0-t       | -    |
| $\alpha$ -sinensal              | 0-1.2     | 0-1.3     | 0-1.0     | 0-t       | -         | 0.1  |

\* correct isomer not identified

t = trace (&lt;0.1%)

o = not detected

Cultivars: 1. Fewtrell, Cravo, Wallent, Ananas, Osceola, Lime sucrée, East India, Africa do Sul, Giant Palazzelli, Page, Bower, Macaque, C54-4-4, Nova, Batangas, Oneco, Lebon, Leroux, Antillaise, Ponkan Yoshida, Ponkan Changsha, Honey, Malvasio, Federici Scarlett, Hansen, Parson Special Warnurco, Zanzibar, Natal Tightskin, Improved Kara, Guyanan Carvalhal

In 1991, Fleisher and Fleisher examined the composition of petitgrain oils produced from four Mandarin (*Citrus reticulata*) cultivars (Balady, Yussuf Effendy, Dancy and Maya) that were grown in Israel. A summary of the oil compositions can be found in T-8. It is of interest to note that the leaf oils of Yussuf Effendy, Dancy and Maya were very similar while the Balady cultivar oil was quite different. This latter oil appears to be a very good source of natural methyl N-methyl anthranilate.

An oil of mandarin (*C. reticulata*) leaves that was produced in Colombia was analyzed by Blanco Tirado et al. (1995) and found to possess the following composition:

|                               |                                |
|-------------------------------|--------------------------------|
| $\alpha$ -thujene (1.26%)     | $\alpha$ -terpineol (0.06%)    |
| $\alpha$ -pinene (2.66%)      | neral (6.05%)                  |
| camphene (0.37%)              | geraniol (0.16%)               |
| sabinene (2.81%)              | geranial (7.45%)               |
| $\beta$ -pinene (0.86%)       | citronellyl acetate (0.43%)    |
| myrcene (0.05%)               | longifolene (0.23%)            |
| $\delta$ -3-carene (0.04%)    | $\delta$ -elemene (0.22%)      |
| 1,4-cineole (0.27%)           | $\beta$ -caryophyllene (0.24%) |
| $\alpha$ -terpineol (1.95%)   | $\alpha$ -bergamotene* (0.11%) |
| p-cymene (2.35%)              | $\alpha$ -humulene (0.08%)     |
| 1,8-cineole (0.70%)           | germacrene D (0.17%)           |
| limonene (8.32%)              | $\beta$ -selinene (1.01%)      |
| (E)- $\beta$ -ocimene (7.87%) | $\alpha$ -muurolene (0.08%)    |
| $\gamma$ -terpinolene (1.49%) | $\delta$ -cadinene (0.08%)     |
| linalool (52.66%)             | germacrene B (0.10%)           |
| cis-sabinene hydrate (0.08%)  | $\alpha$ -bisabolol (0.29%)    |
| cis-limonene oxide (0.59%)    | $\alpha$ -muurolol (0.06%)     |
| dihydrolinalool† (0.03%)      | $\alpha$ -sinensal (0.50%)     |
| nonanol (0.19%)               | phytol (0.13%)                 |

\*correct isomer not identified

† incorrect identification, dihydrolinalool does not occur naturally

An oil of Mandarin petitgrain of Sicilian origin was subjected to analysis by Mondello et al. (1996) using HPLC-GC/MS combinations. The composition of this oil was found to be as follows:

|                                 |                                        |
|---------------------------------|----------------------------------------|
| tricyclene (0.01%)              | terpinen-4-ol (0.24%)                  |
| $\alpha$ -thujene (0.98%)       | p-cymen-8-ol (0.02%)                   |
| $\alpha$ -pinene (2.16%)        | $\alpha$ -terpineol (0.26%)            |
| $\alpha$ -fenchene (0.01%)      | decanal (0.01%)                        |
| camphene (0.02%)                | citronellol (0.01%)                    |
| sabinene (0.30%)                | nerol (0.10%)                          |
| $\beta$ -pinene (2.31%)         | neral (0.06%)                          |
| 6-methyl-5-hepten-2-one (0.01%) | linalyl acetate (0.96%)                |
| myrcene (0.79%)                 | geranial (0.10%)                       |
| $\alpha$ -phellandrene (0.04%)  | thymol (0.11%)                         |
| $\delta$ -3-carene (0.02%)      | methyl anthranilate (0.01%)            |
| $\alpha$ -terpinene (0.24%)     | $\alpha$ -terpinyl acetate (0.01%)     |
| p-cymene (5.19%)                | neryl acetate (0.03%)                  |
| limonene (12.59%)               | geranyl acetate (0.05%)                |
| 1,8-cineole (0.02%)             | methyl N-methyl anthranilate (41.61%)  |
| (Z)- $\beta$ -ocimene (0.18%)   | $\beta$ -caryophyllene (0.92%)         |
| (E)- $\beta$ -ocimene (0.59%)   | $\alpha$ -humulene (0.07%)             |
| $\gamma$ -terpinene (27.64%)    | methyl N-dimethyl anthranilate (0.03%) |
| cis-sabinene hydrate (0.01%)    | $\alpha$ -selinene (0.04%)             |
| cis-linalool oxide† (t)         |                                        |
| octanol (t)                     |                                        |

# Comparative chemical composition (%) of the leaf oils of three sweet orange cultivars grown in Israel

T-10

| Compound                               | Valencia | Jaffa | Ruby  |
|----------------------------------------|----------|-------|-------|
| $\alpha$ -pinene                       | 1.75     | 0.88  | 1.02  |
| $\beta$ -pinene                        | 1.06     | 1.30  | 1.14  |
| sabinene                               | 18.66    | 32.58 | 15.81 |
| $\delta$ -3-carene                     | 2.52     | 4.34  | 3.06  |
| myrcene                                | 2.79     | 5.63  | 3.64  |
| ethyl (E)-2-butenolate                 | 0.10     | 0.08  | 0.11  |
| $\alpha$ -phellandrene                 | 0.05     | 0.08  | 0.06  |
| limonene                               | 1.70     | 1.25  | 2.96  |
| $\beta$ -phellandrene                  | 0.35     | 0.55  | 0.81  |
| (Z)- $\beta$ -ocimene                  | 0.18     | 0.06  | 0.50  |
| $\gamma$ -terpinene                    | 7.52     | 7.41  | 10.50 |
| p-cymene                               | 0.10     | 0.18  | 0.15  |
| terpinolene                            | 1.31     | 0.75  | 1.51  |
| 3-methyl-2-butenol                     | 0.02     | -     | t     |
| 6-methyl-5-hepten-2-one                | t        | t     | t     |
| (Z)-3-hexenol                          | 1.25     | 0.41  | 1.93  |
| ethyl octanoate                        | 0.11     | t     | 0.06  |
| trans-sabinene hydrate                 | 2.17     | 1.53  | 3.23  |
| citronellal                            | 1.82     | 1.32  | 1.65  |
| linalool                               | 8.21     | 5.13  | 20.92 |
| cis-sabinene hydrate                   | 2.17     | 1.53  | 3.23  |
| $\beta$ -elemene                       | 4.13     | 2.38  | 4.00  |
| terpinen-4-ol + $\beta$ -caryophyllene | 7.87     | 3.62  | 6.95  |
| ethyl benzoate                         | t        | t     | t     |
| $\alpha$ -humulene                     | 0.11     | 0.98  | 1.19  |
| $\alpha$ -terpineol                    | 0.13     | 0.09  | 0.18  |
| valencene                              | 0.03     | 0.02  | 0.04  |
| $\beta$ -selinene                      | 0.02     | t     | 0.03  |
| $\alpha$ -selinene                     | 0.01     | 0.02  | 0.01  |
| bicyclogermacrene                      | 0.06     | 0.08  | 0.06  |
| citronellol                            | 0.12     | 0.06  | 0.09  |
| ethyl phenylacetate                    | 0.09     | 0.08  | 0.11  |
| anethole*                              | 0.07     | 0.05  | 0.12  |
| ethyl dodecanoate                      | 0.05     | 0.04  | 0.05  |
| geraniol                               | t        | t     | t     |
| 2-phenthyl alcohol                     | 0.04     | t     | 0.02  |
| ethyl tetradecanoate                   | 0.03     | t     | 0.05  |
| $\beta$ -sinensal                      | 1.22     | 0.43  | 2.35  |
| ethyl hexadecanoate                    | 5.57     | 3.54  | 6.77  |
| $\alpha$ -sinensal                     | 0.03     | 0.02  | 0.07  |
| ethyl octadecanoate                    | 0.21     | 0.13  | 0.07  |
| ethyl linoleate                        | 0.60     | 0.47  | 0.61  |
| ethyl linolenate                       | 5.26     | 0.35  | 3.74  |
| phytol                                 | 2.04     | 0.91  | 1.07  |

\*correct isomer not identified

|                                         |                                |
|-----------------------------------------|--------------------------------|
| terpinolene (0.97%)                     | valencene (0.02%)              |
| linalool (0.93%)                        | (E,E)- $\alpha$ -farnesene (t) |
| nonanal (0.01%)                         | $\delta$ -cadinene (t)         |
| <i>cis</i> -limonene oxide (t)          | caryophyllene oxide            |
| <i>trans</i> -p-menth-2-en-1-ol (0.02%) | (0.02%)                        |

t = trace (<0.01%)

† furanoid form

Dugo et al. (1996) and Mondello et al. (1997) examined the composition of five mandarin petitgrain oils produced commercially in Sicily using a combination of the HPLC-GC/MS. The range of composition of the five oils are summarized as follows:

|                                              |                                             |
|----------------------------------------------|---------------------------------------------|
| tricyclene (t)                               | citronellal (0.02-0.08%)                    |
| $\alpha$ -thujene (0.78-1.04%)               | terpinen-4-ol (0.20-0.42%)                  |
| $\alpha$ -pinene (1.75-2.30%)                | p-cymen-8-ol (0.01-0.02%)                   |
| $\alpha$ -fenchene (t-0.01%)                 | $\alpha$ -terpineol (0.16-0.26%)            |
| camphene (0.01-0.02%)                        | decanal (0.01-0.02%)                        |
| sabinene (0.22-2.33%)                        | citronellol (t)                             |
| $\beta$ -pinene (1.90-2.45%)                 | nerol (0.01-0.03%)                          |
| 6-methyl-5-hepten-2-one (t-0.01%)            | methyl thymol (0.10-0.16%)                  |
| myrcene (0.62-0.82%)                         | geraniol (t)                                |
| octanal (t)                                  | linalyl acetate (0.02-0.96%)                |
| $\alpha$ -phellandrene (0.03-0.06%)          | geranial (t-0.10%)                          |
| $\delta$ -3-carene (0.01-0.29%)              | thymol (0.11-0.17%)                         |
| $\alpha$ -terpinene (0.19-0.33%)             | carvacrol (0.01%)                           |
| o-cymene (t)                                 | methyl anthranilate (t-0.03%)               |
| p-cymene (2.96-5.19%)                        | $\alpha$ -terpinyl acetate (t)              |
| limonene (7.18-12.59%)                       | neryl acetate (t-0.05%)                     |
| $\beta$ -phellandrene (0.03-0.05%)           | geranyl acetate (t-0.02%)                   |
| 1,8-cineole (0.01-0.02%)                     | $\beta$ -elemene (t-0.01%)                  |
| (Z)- $\beta$ -ocimene (0.15-0.20%)           | methyl N-methyl anthranilate (41.61-51.93%) |
| (E)- $\beta$ -ocimene (0.42-0.92%)           | $\beta$ -caryophyllene (0.92-1.40%)         |
| $\gamma$ -terpinene (23.94-28.48%)           | $\alpha$ -humulene (0.07-0.13%)             |
| <i>cis</i> -sabinene hydrate (0.01-0.05%)    | methyl N-dimethyl anthranilate (t-0.4%)     |
| octanol (t)                                  | $\alpha$ -selinene (t-0.02%)                |
| <i>cis</i> -linalool oxide† (t)              | bicyclogermacrene (0.03-0.13%)              |
| terpinolene (0.71-0.88%)                     | (E,E)- $\alpha$ -farnesene (t-0.03%)        |
| p-cymenene (0.10-0.18%)                      | $\beta$ -bisabolene (t-0.02%)               |
| linalool (0.27-1.10%)                        | $\delta$ -cadinene (t)                      |
| nonanal (t-0.01%)                            | (Z)-3-hexenyl benzoate (t-0.02%)            |
| p-mentha-1,3,8-triene (t-0.02%)              | spathulenol (t-0.02%)                       |
| <i>cis</i> -p-menth-2-en-1-ol (t)            | caryophyllene oxide (0.01-0.08%)            |
| <i>trans</i> -p-menth-2-en-1-ol (0.02-0.03%) |                                             |

† furanoid form

t = trace (<0.01%)

An oil of mandarin leaf produced from trees grown in Egypt was determined by Omer et al. (1997) to contain the following components:

|                                 |                                       |
|---------------------------------|---------------------------------------|
| $\alpha$ -pinene (3.22%)        | p-cymene (t)                          |
| $\beta$ -pinene (3.02%)         | citronellal (0.39%)                   |
| $\alpha$ -phellandrene (12.61%) | terpinen-4-ol (0.33%)                 |
| limonene (14.52%)               | methyl N-methyl anthranilate (63.68%) |
| $\alpha$ -terpinene (0.64%)     |                                       |

A supercritical CO<sub>2</sub> extract of mandarin leaves of Italian origin was analyzed by Adami et al. (2000). Although many of the expected constituents were identified in this extract, other than reporting that the methyl N-methyl anthranilate content was 67.54%, the other constituents were either not listed in elution order or there were a large number of misidentifications. As a result, the qualitative and quantitative data will not be included in this review.

The leaf oils of many mandarin cultivars were analyzed by Lota et al. (2000). A summary of the results of this study can be seen in T-9. In addition, the authors also identified camphene, octanal, nonanal, *cis*-linalool oxide (furanoid), *cis*- and *trans*-limonene oxide, octyl acetate, decanal, *cis*-dihydrocarvone, citronellyl acetate, (E)- $\beta$ -farnesene, carvone, myrtenol, *trans*-carveol, caryophyllene oxide, elemol, spathulenol and  $\alpha$ -cadinol in amounts between trace and 0.2%.

Three samples of mandarin leaf oil produced from Vietnamese, Jushaxianggan and Daxianggan cultivars grown in China were analyzed by Huang et al. (2000). The range of oil composition was determined to be as follows:

|                                           |                                         |
|-------------------------------------------|-----------------------------------------|
| (E)-2-hexenal (0-0.09%)                   | $\alpha$ -terpineol (0.18-0.38%)        |
| (Z)-3-hexenol (0-0.05%)                   | decanal (0.05-0.15%)                    |
| $\alpha$ -thujene (0.39-0.45%)            | thymol (0.02-1.04%)                     |
| $\alpha$ -pinene (1.60-1.79%)             | carvacrol (0.04-0.11%)                  |
| camphene (0.04-0.05%)                     | citronellyl acetate (0-0.02%)           |
| sabinene (34.49-43.69%)                   | $\alpha$ -terpinyl acetate (0-0.11%)    |
| $\beta$ -pinene (2.05-2.27%)              | neryl acetate (0-0.05%)                 |
| myrcene (2.45-3.35%)                      | $\delta$ -elemene (0.02-0.18%)          |
| $\alpha$ -phellandrene (0.08-0.10%)       | $\beta$ -elemene (0.02-1.21%)           |
| $\delta$ -3-carene (0-1.13%)              | $\beta$ -caryophyllene (0.50-1.16%)     |
| $\alpha$ -terpinene (0.67-0.75%)          | $\alpha$ -humulene (0.08-0.24%)         |
| p-cymene (0.08-0.40%)                     | $\gamma$ -muurolene (0-0.12%)           |
| limonene (1.59-2.96%)                     | (E,E)- $\alpha$ -farnesene (0.07-0.27%) |
| (Z)- $\beta$ -ocimene (0.37-0.48%)        | germacrene B (0.47-1.53%)               |
| $\beta$ -phellandrene (0.35-0.57%)        | valencene (0.04-0.09%)                  |
| (E)- $\beta$ -ocimene (6.37-10.48%)       | $\delta$ -cadinene (0.07-0.13%)         |
| $\gamma$ -terpinene (1.39-2.02%)          | elemol (0.03-0.08%)                     |
| <i>cis</i> -sabinene hydrate (0.57-0.90%) | (E)-nerolidol (0.07-0.10%)              |
| <i>cis</i> -linalool oxide† (0.08-0.10%)  | spathulenol (t)                         |
| $\alpha$ -p-dimethylstyrene (0.24-0.43%)  | caryophyllene oxide (t-0.06%)           |
| terpinolene (0.33-0.44%)                  | $\beta$ -eudesmol (0.10-0.17%)          |
| nonanal (0.06-0.08%)                      | $\beta$ -sinensal (t-0.84)              |
| linalool (22.03-32.63%)                   | $\alpha$ -sinensal (0.26-1.67%)         |
| citronellal (0.04-0.08%)                  |                                         |
| terpinen-4-ol (2.24-2.85%)                |                                         |

† furanoid form

t = trace (<0.01%)

L. R. de Vottero, G. Tonarelli, E. R. de Krasnogor and J. A. Retamar, *Petitgrains from bitter orange, lemon and mandarin leaves*. *Essenz. Deriv. Agrum.* 48, 150-156 (1978).

- M. A. Germana, F. DePasquale, E. Bazan and E. Palazzolo, *Essential oils of the flowers, leaves and buds of five species of Citrus*. *Essenz. Deriv. Agrum.*, 60, 297-312 (1990).
- Z. Fleisher and A. Fleisher, *Citrus petitgrain oils of Israel*. *Perfum. Flavor.*, 16(1), 43-47 (1991).
- C. Blanco Tirado, E. E. Stashenko, M. Y. Combariza and J. R. Martinez, *Comparative study of Colombian Citrus oils by high resolution gas chromatography and gas chromatography-mass spectrometry*.
- J. Chromatogr., A697, 501-413 (1995). G. Dugo. L. Mondello, A. Cotroneo, I. Stagno d'Alcontres, A. Basile, P. Previti, P. Dugo and K. D. Bartle, *Characterization of Italian Citrus petitgrain oils*. *Perfum. Flavor.*, 21(3), 17-28 (1996).
- L. Mondello, P. Dugo, G. Dugo and K. D. Bartle, *On-line HPLC-HRGC-MS for the analysis of natural complex mixtures*. *J. Chromatogr. Sci.*, 34, 174-181 (1996).
- L. Mondello, A. Basile, P. Previti and G. Dugo, *Italian Citrus petitgrain oils. Part II. Composition of mandarin petitgrain*. *J. Essent. Oil Res.*, 9, 255-266 (1997).
- E. A. Omer, A. A. Youssef, E. N. Abo-Zeid and A. M. Sharaby, *Biochemical studies on the essential oils of Balady orange and mandarin*. *Egypt. J. Hort.*, 24, 207-218 (1997).
- M. Adami, L. Arcuri, G. DiGiacomo, D. Ferri, G. Gazzola, F. Gionfriddo and E. Piccinelli, *Estrazione di petitgrain con CO<sub>2</sub> supercritica*. *Essenz. Deriv. Agrum.*, 70, 193-200 (2000).
- M-L. Lota. D. de Rocca Serra, F. Tomi and J. Casanova, *Chemical variability of peel and leaf essential oils of mandarins from Citrus reticulata Blanco*. *Biochem. Syst. Ecol.*, 28, 61-78 (2000).
- Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 100 Citrus species, cultivars, hybrids and varieties of Chinese origin*. *Perfum. Flavor.*, 25(1), 53-66 (2000).

orange cultivars (Valencia, Jaffa and Ruby) grown in Israel. The results of this study are shown in T-10. As can be seen, the Jaffa petitgrain oil was much richer in sabinene than the oils of the other two cultivars. Also, it is interest to note the levels of  $\beta$ -sinensal especially in the Ruby cultivar oil. The Ruby oil was also considerably richer in linalool.

The main components of the leaf oil of the Glorious and Washington cultivars of sweet orange grown in China were found by Lin and Hua (1992) to be as follows:

sabinene (45.5-46.6%)  
 myrcene (4.1-4.3%)  
 limonene (3.8-4.1%)  
 $\gamma$ -terpinene (5.9-6.2%)  
 linalool (9.5-12.7%)  
 neral + geranial (6.4-8.8%)  
 $\alpha$ -sinensal +  $\beta$ -sinensal (0.9-1.3%)

Lin and Hua also reported that the leaf oil of the Hamlin sweet orange cultivar contained the following main components:

sabinene (27.2%)  
 $\beta$ -pinene (27.2%)  
 myrcene (4.6%)  
 limonene (4.6%)  
 $\gamma$ -terpinene (5.9%)  
 linalool (7.7%)

### ***Citrus sinensis* (L.) Osbeck**

The leaves of sweet orange grown in Italy were found by Germana et al. (1990) to possess the following composition:

$\alpha$ -pinene (0.59%)  
 $\beta$ -pinene (0.80%)  
 sabinene (27.86%)  
 myrcene (3.92%)  
 limonene (18.84%)  
 $\alpha$ -terpinene (2.43%)  
 $\beta$ -caryophyllene (0.09%)  
 linalool (18.28%)  
 benzaldehyde (0.99%)  
 $\alpha$ -terpineol (1.90%)  
 neryl acetate (5.87%)  
 neral (4.19%)  
 geranyl acetate (4.01%)  
 geranial (2.11%)  
 nerol (1.27)  
 geraniol (0.09%)  
 methyl anthranilate (4.18%)  
 farnesol\* (2.37%)

\* correct isomer not identified

The characterization of benzaldehyde and methyl anthranilate in orange leaf oil requires corroboration before it can be considered to be factual.

Fleisher and Fleisher (1991) compared the leaf oils of three sweet



| Compound                        | Valencia late | Biondo Commune | Moro  | Compound                           | Valencia late | Biondo Commune | Moro |
|---------------------------------|---------------|----------------|-------|------------------------------------|---------------|----------------|------|
| hexanal                         | t             | t              | t     | $\alpha$ -terpineol                | 0.93          | 0.36           | 0.38 |
| hexanol                         | 0.09          | 0.09           | 0.01  | <i>cis</i> -piperitol              | 0.06          | 0.05           | 0.06 |
| tricyclene                      | t             | t              | t     | decanal                            | 0.02          | 0.01           | 0.02 |
| $\alpha$ -thujene               | 0.34          | 0.34           | 0.33  | <i>trans</i> -piperitol            | 0.16          | 0.07           | 0.09 |
| $\alpha$ -pinene                | 1.59          | 1.76           | 1.65  | citronellol                        | 0.13          | 0.26           | 0.23 |
| $\alpha$ -fenchene              | 0.01          | 0.02           | 0.01  | nerol                              | 0.13          | 0.45           | 0.30 |
| camphene                        | 0.04          | 0.04           | 0.04  | neral                              | 1.04          | 1.75           | 1.79 |
| sabinene                        | 40.66         | 38.46          | 48.52 | geraniol                           | 0.16          | 0.24           | 0.15 |
| $\beta$ -pinene                 | 1.87          | 2.01           | 2.33  | linalyl acetate                    | 0.10          | 0.10           | 0.07 |
| 6-methyl-5-hepten-2-one         | 0.08          | 0.12           | 0.08  | geranial                           | 1.37          | 2.14           | 2.17 |
| myrcene                         | 3.49          | 4.40           | 3.72  | thymol                             | 0.02          | 0.02           | t    |
| octanal                         | t             | t              | t     | methyl geranate                    | 0.04          | 0.04           | 0.10 |
| $\alpha$ -phellandrene          | 0.37          | 0.69           | 0.22  | citronellyl acetate                | 0.03          | 0.05           | 0.10 |
| $\delta$ -3-carene              | 4.45          | 10.28          | 5.51  | neryl acetate                      | 0.04          | 0.11           | 0.15 |
| $\alpha$ -terpinene             | 1.16          | 0.74           | 0.48  | geranyl acetate                    | 0.04          | 0.16           | 0.15 |
| o-cymene                        | 0.03          | 0.06           | 0.08  | $\beta$ -elemene                   | 0.49          | 1.07           | 0.36 |
| p-cymene                        | 0.76          | 0.59           | 1.68  | methyl N-methyl                    |               |                |      |
| limonene                        | 2.90          | 3.67           | 4.04  | anthranilate                       | t             | t              | t    |
| $\beta$ -phellandrene           | 0.65          | 0.70           | 0.74  | <i>cis</i> - $\alpha$ -bergamotene | t             | -              | t    |
| (Z)- $\beta$ -ocimene           | 0.22          | 0.33           | 0.19  | $\beta$ -caryophyllene             | 0.28          | 0.83           | 0.27 |
| (E)- $\beta$ -ocimene           | 6.14          | 9.73           | 4.99  | (Z)- $\beta$ -farnesene            | 0.07          | 0.15           | 0.06 |
| $\gamma$ -terpinene             | 2.43          | 1.41           | 1.46  | $\alpha$ -humulene                 | 0.15          | 0.37           | 0.12 |
| <i>cis</i> -sabinene hydrate    | 0.06          | 0.12           | 0.10  | $\beta$ -santalene                 | -             | -              | 0.04 |
| <i>cis</i> -linalool oxide†     | 0.01          | t              | t     | valencene                          | t             | t              | t    |
| p-mentha-2,4(8)-diene           | 0.15          | 0.36           | 0.14  | $\alpha$ -selinene                 | t             | t              | t    |
| terpinolene                     | 1.32          | 2.14           | 0.95  | bicyclogermacrene                  | 0.05          | 0.09           | -    |
| linalool                        | 15.12         | 6.29           | 6.52  | (E,E)- $\alpha$ -farnesene         | 0.01          | 0.05           | -    |
| nonanal                         | t             | 0.01           | 0.05  | (E)-nerolidol                      | 0.04          | 0.01           | 0.02 |
| <i>cis</i> -p-menth-2-en-1-ol   | 0.25          | 0.16           | 0.19  | (Z)-3-hexenyl benzoate             | t             | 0.01           | t    |
| <i>trans</i> -p-menth-2-en-1-ol | 0.22          | 0.14           | 0.18  | caryophyllene oxide                | 0.04          | 0.07           | 0.10 |
| citronellal                     | 0.47          | 0.51           | 0.48  | $\beta$ -sinensal                  | 1.38          | 1.27           | 1.44 |
| terpinen-4-ol                   | 7.33          | 3.75           | 6.14  | $\alpha$ -sinensal                 | 0.27          | 0.46           | 0.08 |
| p-cymen-8-ol                    | 0.04          | 0.05           | 0.09  |                                    |               |                |      |

† furanoid form  
t = trace (<0.01%)

neral + geranial (3.2%)  
 $\alpha$ -sinensal +  $\beta$ -sinensal (1.1%)

Sweet orange leaf oil produced from trees grown in Colombia was analyzed by Blanco Tirado et al. (1995). This oil was found to possess the following composition:

|                                |                                    |
|--------------------------------|------------------------------------|
| $\alpha$ -thujene (0.30%)      | <i>cis</i> -limonene oxide (0.05%) |
| $\alpha$ -pinene (0.55%)       | dihydrolinalool† (0.02%)           |
| camphene (0.02%)               | citronellal (2.83%)                |
| sabinene (47.68%)              | isopulegol (0.13%)                 |
| $\beta$ -pinene (2.00%)        | isoborneol (0.20%)                 |
| octanal (0.04%)                | nonanol (0.37%)                    |
| myrcene (3.73%)                | $\alpha$ -terpineol (0.10%)        |
| $\alpha$ -phellandrene (0.69%) | decanal (0.15%)                    |
| $\delta$ -3-carene (7.38%)     | citronellol (0.53%)                |
| 1,4-cineole (0.48%)            |                                    |

|                                        |                                |
|----------------------------------------|--------------------------------|
| $\alpha$ -terpinene (0.12%)            | neral (1.87%)                  |
| p-cymene (0.02%)                       | geraniol (0.21%)               |
| 1,8-cineole (0.16%)                    | geranial (2.61%)               |
| limonene (5.95%)                       | linalyl acetate (0.03%)        |
| $\beta$ -phellandrene (0.33%)          | thymol (0.07%)                 |
| (E)- $\beta$ -ocimene (8.31%)          | citronellyl acetate (0.06%)    |
| $\gamma$ -terpinene (0.65%)            | neryl acetate (0.17%)          |
| <i>trans</i> -sabinene hydrate (0.16%) | geranyl acetate (0.16%)        |
| octanol (0.27%)                        | longifolene (0.04%)            |
| terpinolene (1.57%)                    | $\delta$ -elemene (0.63%)      |
| linalool (4.38%)                       | $\beta$ -caryophyllene (0.21%) |
| <i>cis</i> -sabinene hydrate (0.02%)   | $\alpha$ -humulene (0.06%)     |
| myrcenol (0.05%)                       | $\beta$ -bisabolene (0.03%)    |
| methyl octanoate (0.12%)               | germacrene B (0.12%)           |
|                                        | $\alpha$ -sinensal (0.13%)     |
|                                        | phytol (0.22%)                 |

† dihydrolinalool does not occur naturally

In 1995, Gurib-Fakim and Demarne determined that a leaf oil of *C. sinensis* produced from trees harvested in Mauritius contained the following constituents:

|                                     |                                     |
|-------------------------------------|-------------------------------------|
| hexanal (0.36%)                     | citronellol (0.64%)                 |
| butyl propionate (0.17%)            | $\alpha$ -fenchyl acetate (3.60%)   |
| $\alpha$ -pinene (0.94%)            | geraniol (0.10%)                    |
| heptanol (0.76%)                    | geranial (1.04%)                    |
| $\beta$ -pinene (0.32%)             | citronellyl formate (0.35%)         |
| 1,4-cineole (0.71%)                 | geranyl formate (0.20%)             |
| (Z)- $\beta$ -ocimene (0.33%)       | carvacrol (2.96%)                   |
| $\beta$ -phellandrene (0.34%)       | cinnamyl alcohol (1.97%)            |
| (E)- $\beta$ -ocimene (0.8%)        | cinnamyl formate (0.56%)            |
| <i>cis</i> -linalool oxide† (0.37%) | $\alpha$ -cubebene (0.40%)          |
| linalool (1.65%)                    | geranyl acetate (0.28%)             |
| 1-octen-3-ol (16.97%)               | $\alpha$ -copaene (4.52%)           |
| <i>cis</i> -rose oxide (1.34%)      | <i>trans</i> - $\beta$ -bergamotene |
| (1.15%)                             |                                     |
| <i>trans</i> -rose oxide (0.20%)    | allo-aromadendrene (0.20%)          |
| dihydroxylinalool† (1.50%)          | $\alpha$ -humulene (0.58%)          |
| citronellal (1.70%)                 | 3-methylcoumarin (0.10%)            |
| $\beta$ -terpineol* (0.74%)         | valencene (0.75%)                   |
| benzyl acetate (0.15%)              | $\beta$ -bisabolene (0.18%)         |
| isoborneol (0.40%)                  | (Z)-nerolidol (0.10%)               |
| menthol (0.25%)                     | 10-epi- $\gamma$ -eudesmol (0.13%)  |
| nonanol (0.19%)                     | citronellyl tiglate (0.37%)         |
| <i>cis</i> -piperitol (26.42%)      | (E,E)-farnesyl acetate (0.19%)      |
| $\alpha$ -terpineol (1.95%)         | $\alpha$ -sinensal (2.93%)          |
| dihydrocarveol (0.59%)              | $\beta$ -sinensal (1.14%)           |
| verbenone (0.50%)                   | elemol (0.13%)                      |
| linalyl formate (0.44%)             | geranyl tiglate (1.42%)             |
| neral (2.20%)                       |                                     |

\*correct isomer not identified

† furanoid form

† this compound does not occur naturally

It should be noted that this oil is atypical for sweet orange leaf oil.

A leaf oil produced from sweet orange trees growing in Sicily was the subject of analysis by Mondello et al. (1996). The composition of this oil was determined to be as follows:

|                                      |                                        |
|--------------------------------------|----------------------------------------|
| tricyclene (t)                       | citronellal (0.43%)                    |
| $\alpha$ -thujene (0.39%)            | terpinen-4-ol (2.36%)                  |
| $\alpha$ -pinene (1.51%)             | $\alpha$ -terpineol (0.21%)            |
| $\alpha$ -fenchene (0.01%)           | decanal (0.03%)                        |
| camphene (0.04%)                     | citronellol (0.03%)                    |
| sabinene (38.26%)                    | nerol (0.26%)                          |
| $\beta$ -pinene (2.62%)              | neral (0.28%)                          |
| 6-methyl-5-hepten-2-one (0.05%)      | linalyl acetate (0.40%)                |
| myrcene (2.88%)                      | geranial (0.59%)                       |
| octanal (0.01%)                      | thymol (0.05%)                         |
| $\alpha$ -phellandrene (0.23%)       | citronellyl acetate (0.25%)            |
| $\delta$ -3-carene (3.46%)           | $\alpha$ -copaene (0.01%)              |
| $\alpha$ -terpinene (0.65%)          | neryl acetate (0.38%)                  |
| o-cymene (0.05%)                     | $\beta$ -cubebene (0.10%)              |
| p-cymene (2.89%)                     | geranyl acetate (0.28%)                |
| limonene (5.85%)                     | $\beta$ -elemene (3.80%)               |
| 1,8-cineole (0.03%)                  | <i>cis</i> - $\alpha$ -bergamotene (t) |
| (Z)- $\beta$ -ocimene (0.21%)        | methyl N-methyl                        |
| (E)- $\beta$ -ocimene (4.49%)        | anthranilate (10.29%)                  |
| $\gamma$ -terpinene (2.62%)          | $\beta$ -caryophyllene (2.47%)         |
| <i>cis</i> -sabinene hydrate (0.23%) | $\alpha$ -humulene (0.60%)             |
|                                      | (Z)- $\beta$ -farnesene (0.58%)        |

|                                         |                                    |
|-----------------------------------------|------------------------------------|
| terpinolene (0.98%)                     | $\alpha$ -selinene (0.04%)         |
| linalool (4.34%)                        | valencene (0.02%)                  |
| nonanal (0.04%)                         | (E,E)- $\alpha$ -farnesene (0.12%) |
| <i>cis</i> -p-menth-2-en-1-ol (0.09%)   | (E)-nerolidol (0.05%)              |
| <i>trans</i> -p-menth-2-en-1-ol (0.07%) |                                    |
| t = trace (<0.01%)                      |                                    |

Dugo et al. (1996) and Mondello et al. (1997) used a combination of GC and GC/MS to also examine the composition of four commercial samples of Italian sweet orange leaf oil. They found that the range in composition of the oils was as follows:

|                                              |
|----------------------------------------------|
| hexanal (t)                                  |
| hexanol (t)                                  |
| tricyclene (t)                               |
| $\alpha$ -thujene (0.21-0.39%)               |
| $\alpha$ -pinene (0.99-1.51%)                |
| $\alpha$ -fenchene (0.01%)                   |
| camphene (0.03-0.04%)                        |
| sabinene (37.64-41.93%)                      |
| $\beta$ -pinene (1.89-2.62%)                 |
| 6-methyl-5-hepten-2-one (0.04-0.06%)         |
| myrcene (2.66-3.85%)                         |
| octanal (0.03-0.05%)                         |
| $\alpha$ -phellandrene (0.23-0.50%)          |
| $\delta$ -3-carene (3.46-5.91%)              |
| $\alpha$ -terpinene (0.27-0.96%)             |
| o-cymene (0.03-0.05%)                        |
| p-cymene (0.59-2.89%)                        |
| limonene (5.12-8.37%)                        |
| $\beta$ -phellandrene (0.78-1.06%)           |
| 1,8-cineole (0-0.05%)                        |
| (Z)- $\beta$ -ocimene (0.21-0.33%)           |
| (E)- $\beta$ -ocimene (4.53-9.21%)           |
| $\gamma$ -terpinene (2.19-2.98%)             |
| <i>cis</i> -sabinene hydrate (0.13-0.42%)    |
| <i>cis</i> -linalool oxide† (t-0.01%)        |
| p-mentha-2,4(8)-diene (0.09-0.22%)           |
| terpinolene (0.98-1.52%)                     |
| linalool (4.34-10.71%)                       |
| nonanal (t-0.03%)                            |
| <i>cis</i> -p-menth-2-en-1-ol (0.04-0.11%)   |
| <i>trans</i> -p-menth-2-en-1-ol (0.03-0.07%) |
| citronellal (0.43-4.44%)                     |
| terpinen-4-ol (0.55-2.59%)                   |
| p-cymen-8-ol (t-0.09%)                       |
| $\alpha$ -terpineol (0.21-0.30%)             |
| <i>cis</i> -piperitol (0.01-0.07%)           |
| decanal (0.02-0.07%)                         |
| <i>trans</i> -piperitol (t-0.05%)            |
| citronellol (0.10-0.22%)                     |
| nerol (0.13-0.26%)                           |
| methyl thymol (0-t)                          |
| neral (0.28-2.18%)                           |
| geraniol (0.06-0.29%)                        |
| linalyl acetate (0.02-0.12%)                 |
| geranial (0.59-3.11%)                        |
| thymol (0.01-0.05%)                          |
| methyl geranate (0.05-0.07%)                 |
| citronellyl acetate (0.21-0.65%)             |
| $\alpha$ -copaene (t-0.01%)                  |

## Enantiomeric distribution of selected compounds in petitgrain oils

T-12

| Compound                      | Petitgrain Oil | Commercial Oils |      |
|-------------------------------|----------------|-----------------|------|
|                               |                | 1               | 2    |
| (1R,5R)-(+)- $\alpha$ -pinene | 6.7-34.7       | 12.4            | 15.6 |
| (1S,5S)-(-)- $\alpha$ -pinene | 65.3-93.3      | 87.6            | 84.4 |
| (1R,5R)-(+)- $\beta$ -pinene  | 0.1-1.1        | 3.8             | 8.0  |
| (1S,5S)-(-)- $\beta$ -pinene  | 98.9-99.9      | 96.2            | 92.0 |
| (4R)-(+)-limonene             | 53.3-76.1      | 90.8            | 56.0 |
| (4S)-(-)-limonene             | 23.9-46.7      | 9.2             | 44.6 |
| (3S)-(+)-linalool             | 0.1-33.6       | 39.3            | 28.8 |
| (3R)-(-)-linalool             | 66.4-99.9      | 60.7            | 7.12 |
| (3S)-(+)-linalyl acetate      | 0.6-2.3        | 25.3            | 22.5 |
| (3R)-(-)-linalyl acetate      | 97.7-99.4      | 74.7            | 77.5 |
| (4S)-(+)-terpinen-4-ol        | 47.9-67.4      | 49.0            | 43.0 |
| (4R)-(-)-terpinen-4-ol        | 32.6-52.1      | 51.0            | 57.0 |
| (4R)-(+)- $\alpha$ -terpineol | 71.6-73.6      | 56.0            | 72.9 |
| (4S)-(-)- $\alpha$ -terpineol | 26.4-28.4      | 43.1            | 27.1 |

neryl acetate (0.29-0.38%)  
 $\beta$ -cubebene (t-0.10%)  
geranyl acetate (0.15-0.28%)  
 $\beta$ -elemene (0.04-3.80%)  
methyl N-methyl anthranilate (1.26-10.29%)  
*cis*- $\alpha$ -bergamotene (t)  
 $\beta$ -caryophyllene (0.13-2.47%)  
(Z)- $\beta$ -farnesene (0.01-0.58%)  
 $\alpha$ -humulene (0.05-0.60%)  
valencene (0-t)  
 $\alpha$ -selinene (0-t)  
bicyclogermacrene (0.01-0.24%)  
(E,E)- $\alpha$ -farnesene (0.02-0.13%)  
 $\beta$ -bisabolene (0-0.09%)  
(E)-nerolidol (0.01-0.05%)  
(Z)-3-hexenyl benzoate (0-t)  
caryophyllene oxide (0.02-0.24%)  
 $\beta$ -sinensal (0.23-1.29%)  
 $\alpha$ -sinensal (0.04-0.32%)

t = trace (<0.01%)

† furanoid form

In addition, the authors also compared the composition of three laboratory prepared leaf oils of sweet orange cultivars (Valencia late, Biondo commune and Moro). A summary of the oil compositions can be seen in T-11.

Huang et al. (2000) examined the leaf oil composition of eleven orange cultivars grown in China. The range of oil composition was found to be as follows:

|                                      |                              |
|--------------------------------------|------------------------------|
| (E)-2-hexenal (0-0.24%)              | neral (0.88-4.82%)           |
| (Z)-3-hexenol (0-0.03%)              | geraniol (0.09-0.86%)        |
| $\alpha$ -thujene (0.26-0.44%)       | geranial (1.14-6.03%)        |
| $\alpha$ -pinene (1.35-1.92%)        | thymol (0.03-0.23%)          |
| camphene (0.04-0.05%)                | undecanal (t-0.05%)          |
| 6-methyl-5-hepten-2-one (0.17-0.52%) | methyl geranate (0.08-0.29%) |

|                                           |                                      |
|-------------------------------------------|--------------------------------------|
| sabinene (30.19-52.11%)                   | citronellyl acetate (0.19-1.07%)     |
| $\beta$ -pinene (1.40-2.40%)              | $\alpha$ -terpinyl acetate (0-0.13%) |
| myrcene (3.59-4.23%)                      | neryl acetate (0.21-1.87%)           |
| $\alpha$ -phellandrene (0.23-0.61%)       | geranyl acetate (0.30-2.06%)         |
| $\delta$ -3-carene (2.87-10.27%)          | dodecanal (0.03-0.09%)               |
| $\alpha$ -terpinene (0.13-0.66%)          | $\beta$ -elemene (0.47-1.79%)        |
| p-cymene (0.07-0.83%)                     | $\beta$ -caryophyllene (0.23-1.09%)  |
| limonene (2.62-9.48%)                     | (Z)- $\beta$ -farnesene (0.11-0.42%) |
| (Z)- $\beta$ -ocimene (0.19-0.34%)        | $\alpha$ -humulene (0.14-0.41%)      |
| $\beta$ -phellandrene (0.52-0.92%)        | (E,E)- $\alpha$ -farnesene (t-0.08%) |
| (E)- $\beta$ -ocimene (4.99-10.16%)       | germacrene B (0.04-0.09%)            |
| $\gamma$ -terpinene (0.34-1.19%)          | $\delta$ -cadinene (t-0.04%)         |
| <i>cis</i> -sabinene hydrate (0.28-0.99%) | elemol (0.03-0.05%)                  |
| <i>cis</i> -linalool oxide† (0.09-0.32%)  | (E)-nerolidol (0.03-0.07%)           |
| terpinolene (0.68-1.78%)                  | spathulenol (0-0.10%)                |
| nonanal (0.14-0.35%)                      | caryophyllene oxide (0.02-0.07%)     |
| linalool (5.03-10.24%)                    | $\beta$ -sinensal (0.95-1.75%)       |
| citronellal (1.34-3.81%)                  | farnesol* (0.04-0.07%)               |
| terpinen-4-ol (0.82-2.17%)                | farnesal* (0.02-0.12%)               |
| $\alpha$ -terpineol (0.10-0.65%)          | $\alpha$ -sinensal (0.13-0.39%)      |
| decanal (0.05-0.25%)                      |                                      |
| citronellol (0.09-0.74%)                  |                                      |
| nerol (0.08-1.26%)                        |                                      |

\*correct isomer not identified

† furanoid form

t = trace (<0.01%)

The cultivars included in the above composition range were Taoyecheng, Huangbaipitiancheng, Gailiangcheng, Jincheng, Hamlin, Washington, Ruby Blood, Valencia, Liucheng, Xuegan and Xinhuicheng.

Taufiq-Yap et al. (2001) screened a number of leaf oils of *Citrus* species grown in Malaysia for their biological activity. As part of this study they deter-

mined that sweet orange leaf oil contained the following constituents:

|                              |                                |
|------------------------------|--------------------------------|
| $\alpha$ -terpinene (3.0%)   | $\beta$ -caryophyllene (3.0%)  |
| 1,8-cineole (5.4%)           | $\alpha$ -humulene (2.8%)      |
| (E)- $\beta$ -ocimene (7.2%) | bicyclogermacrene (2.0%)       |
| p-mentha-1,5,8-triene (1.5%) | germacrene B (1.1%)            |
| linalool (36.9%)             | germacrene A (3.8%)            |
| $\beta$ -elemene (22.4%)     | 4-vinyl-2-methoxyphenol (0.5%) |

Although the authors noted that the oil was analyzed using GC/MS, the analysis seems to be inaccurate based on what is known about sweet orange leaf oil. As a result, it was only included for completeness of the review.

- M. A. Germana, F. DePasquale, E. Bazan and E. Palazzolo, *Essential oils of the flowers, leaves and buds of five species of Citrus*. Essenz. Deriv. Agrum., 60, 297-312 (1990).
- Z. Fleisher and A. Fleisher, *Citrus petitgrain oils of Israel*. Perfum. Flavor., 16(1), 43-47 (1991).
- Z-K. Lin and Y-F. Hua, *Systematic evolutionary relation of chemical components of the essential oils from 11 taxa of Citrus leaves*. Acta Bot. Sinica, 34, 133-139 (1992).
- C. Blanco Tirado, E. E. Stashenko, M. Y. Combariza and J. R. Martinez, *Comparative study of Colombian citrus oils of high resolution gas chromatography and gas chromatography-mass spectrometry*. J. Chromatogr., A697, 501-513 (1995).
- A. Gurib-Fakim and F. Demarne, *Aromatic plants of Mauritius volatile constituents of the leaf oils of Citrus aurantium L., Citrus paradisi Macfad. and Citrus sinensis (L.) Osbeck*. J. Essent. Oil Res., 7, 105-109 (1995).
- L. Mondello, P. Dugo, G. Dugo and K. D. Bartle, *On-line HPLC-HRGC-MS for the analysis of natural complex mixtures*. J. Chromatogr. Sci., 34, 174-181 (1996).
- G. Dugo, L. Mondello, A. Cotroneo, I. Stagno d'Alcontres, A. Basile, P. Previti, P. Dugo and K. D. Bartle, *Characterization of Italian Citrus petitgrain oils*. Perfum. Flavor., 21(3), 17-28 (1996).
- L. Mondello, A. Cotroneo, I. Stagno d'Alcontres and G. Dugo, *Italian Citrus petitgrain oils. Part III. Composition of sweet orange petitgrain oil*. J. Essent. Oil Res., 9, 379-392 (1997).
- Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 110 Citrus species, cultivars, hybrids and*

*varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).

Y-H. Taufiq-Yap, T. H. Peh, G. C. L. Ee, A. M. Ali, M. Rahmani, M. A. Sukari and R. Muse, *Chemical variability and some biological activities of leaf essential oils from five species of Malaysian Citrus*. Orient. J. Chem., 17, 387-390 (2001).

## **Citrus tangerine Hort. ex Tanaka**

The leaf oil of the Dahongpao cultivar of tangerine grown in China was found by Lin and Hua (1992) to contain the following major components:

|                                        |
|----------------------------------------|
| sabinene (4.1%)                        |
| $\beta$ -ocimene* (5.3%)               |
| $\gamma$ -terpinene (6.6%)             |
| cis- and trans-linalool oxide* (12.2%) |
| linalool (35.9%)                       |

\*correct isomer not identified

Huang et al. (2000) compared the leaf oil compositions of the Chunaju, Dancy and Fuju cultivars of tangerine grown in China. They found that the oil composition ranged as follows:

|                                    |
|------------------------------------|
| (E)-2-hexenal (0-0.6%)             |
| (Z)-3-hexenol (t-0.02%)            |
| $\alpha$ -thujene (0.82-1.31%)     |
| $\alpha$ -pinene (1.81-2.87%)      |
| camphene (t-0.02%)                 |
| sabinene (0.27-0.29%)              |
| $\beta$ -pinene (2.29-2.71%)       |
| myrcene (0.71-0.78%)               |
| $\alpha$ -phellandrene (0.04%)     |
| $\alpha$ -terpinene (0.22-0.25%)   |
| p-cymene (2.19-2.98%)              |
| limonene (2.34-2.64%)              |
| (Z)- $\beta$ -ocimene (0.28-0.40%) |
| $\beta$ -phellandrene (0-t)        |
| (E)- $\beta$ -ocimene (6.42-8.22%) |
| $\gamma$ -terpinene (7.89-8.64%)   |

*cis*-sabinene hydrate (0.02-0.04%)  
*cis*-linalool oxide† (0.02-0.06%)  
 $\alpha$ -p-dimethylstyrene (1.12-1.32%)  
 terpinolene (0.59-1.27%)  
 nonanal (0.03-0.04%)  
 linalool (40.44-50.84%)  
 citronellal (0.39-0.43%)  
 terpinen-4-ol (0.11-0.14%)  
 $\alpha$ -terpineol (0.23-0.24%)  
 decanal (0-0.03%)  
 citronellol (0-0.10%)  
 methyl thymol (7.43-9.10%)  
 thymol (6.67-7.48%)  
 carvacrol (0.04-0.05%)  
 $\delta$ -elemene (0.07-0.18%)  
 $\beta$ -elemene (0.06-0.15%)

$\beta$ -caryophyllene (0.07-0.22%)  
 $\alpha$ -humulene (0.06-0.11%)  
 $\gamma$ -muurolene (0.06-0.22%)  
 (E,E)- $\alpha$ -farnesene (0.04-0.07%)  
 germacrene B (0.28-0.72%)  
 valencene (0-0.09%)  
 $\delta$ -cadinene (0.06-0.19%)  
 elemol (0.04-0.05%)  
 (E)-nerolidol (0.08-0.10%)  
 spathulenol (0.04-0.18%)  
 caryophyllene oxide (0.05-0.19%)  
 $\beta$ -eudesmol (0.04-0.13%)  
 $\alpha$ -sinensal (0.48-0.52%)

† furanoid form  
 t = trace (<0.01%)

Tangerine leaf oil produced from Brickaville, Vohangisahy, Beauty of Glen Retreat and Dancy cultivars were the subject of GC and GC/MS analysis by Lota et al. (2001). The range of composition of these oils was found to be as follows:

$\alpha$ -thujene (0.3-1.3%)  
 $\alpha$ -pinene (0.7-2.7%)  
 $\beta$ -pinene (1.1-2.9%)  
 sabinene (0.2-0.3%)  
 myrcene (0.4-0.8%)  
 $\alpha$ -terpinene (0.1-0.3%)  
 limonene (2.6-4.5%)  
 $\beta$ -phellandrene (t-0.5%)  
 (Z)- $\beta$ -ocimene (0.3-0.6%)  
 $\gamma$ -terpinene (3.0-14.5%)  
 (E)- $\beta$ -ocimene (4.1-11.0%)  
 p-cymene (2.7-3.6%)  
 terpinolene (0.7-1.2%)  
 $\alpha$ -p-dimethylstyrene (0.5-1.5%)  
*trans*-sabinene hydrate (t)  
 decanal (0-0.1%)  
 linalool (40.9-59.3%)  
*cis*-p-menth-2-en-1-ol (0-0.2%)  
 $\beta$ -elemene (0-t)  
 $\beta$ -caryophyllene (0-0.4%)  
 methyl thymol (0.4-8.8%)  
 terpinen-4-ol (0.1%)  
*trans*-p-menth-2-en-1-ol (0-0.1%)  
 citronellyl acetate (0-t)  
 $\alpha$ -humulene (0-t)  
 $\alpha$ -terpineol (0.1-0.3%)  
 $\alpha$ -bisabolene\* (0-0.1%)  
 bicyclogermacrene (0-0.2%)  
 citronellol (0-t)  
 nerol (0-0.1%)  
 geraniol (t-0.2%)  
 methyl N-methyl anthranilate (0-0.1%)  
 thymol (8.4-13.0%)  
 $\alpha$ -sinensal (0.5-1.8%)

\*correct isomer not identified  
 t = trace (<0.1%)

The authors also found that the leaf oils of the Redskin and the



Dancy cultivars of tangerine were dissimilar to that shown above. As a result, the range of oil composition for the leaf oils of these two cultivars was as follows:

$\alpha$ -thujene (0.5-1.2%)  
 $\alpha$ -pinene (1.4-1.6%)  
 $\beta$ -pinene (2.3-2.4%)  
sabinene (37.8-43.1%)  
 $\delta$ -3-carene (t)  
myrcene (2.8-2.9%)  
 $\alpha$ -terpinene (1.3-1.5%)  
limonene (2.0-2.4%)  
 $\beta$ -phellandrene (0.4-0.5%)  
(Z)- $\beta$ -ocimene (0.3%)  
 $\gamma$ -terpinene (2.9-3.3%)  
(E)- $\beta$ -ocimene (5.6-6.0%)  
p-cymene (0.5%)  
terpinolene (0.7%)  
 $\alpha$ -p-dimethylstyrene (0.3-0.5%)  
trans-sabinene hydrate (0.7-0.9%)  
citronellal (t)  
decanal (t-0.1%)  
linalool (22.1-25.6%)  
cis-p-menth-2-en-1-ol (0.4%)  
 $\beta$ -elemene (0.1%)  
methyl thymol (0.9-1.0%)  
terpinen-4-ol (6.1-6.2%)  
trans-p-menth-2-en-1-ol (0.2%)  
 $\alpha$ -humulene (0-t)  
neral (0-0.1%)  
 $\alpha$ -terpineol (0.3-0.5%)  
 $\alpha$ -bisabolene\* (0-0.4%)  
neryl acetate (0-0.3%)  
geranyl acetate (0-0.1%)  
nerol (0-t)  
geraniol (t)  
methyl N-methyl anthranilate (0-0.1%)  
thymol (0.1%)  
 $\beta$ -sinensal (1.2%)  
 $\alpha$ -sinensal (0.5-0.6%)

\*correct isomer not identified  
t = trace (<0.1%)

Z-K. Lin and Y-F. Hua, *Systematic evolutionary relation of chemical components of the essential oils from 11 taxa of Citrus leaves*. Acta Bot. Sinica, 134I, 133-139 (1992).

Y-Z. Huang, Z-L. Pu and Q-Y. Chen, *The chemical composition of the leaf essential oils from 110 Citrus species, cultivars, hybrids and varieties of Chinese origin*. Perfum. Flavor., 25(1), 53-66 (2000).

M-L. Lota, D. de Rocca Serra, F. Tomi and J. Casanova, *Chemical variability of peel and leaf essential oils of 15 species of mandarins*. Biochem. Syst. Ecol., 29, 77-104 (2001).

## Chirality

In 1990 Mosandl et al. used a combination of polar GC and chiral GC to determine the enantiomeric distribution of  $\alpha$ -pinene (1.3%),  $\beta$ -pinene (10.0%) and limonene (32.5%) in petitgrain oil. The authors found the following results:

(1R,5R)-(+)- $\alpha$ -pinene (18%) : (1S,5S)-(-)- $\alpha$ -pinene (82%)  
(1R,5R)-(+)- $\beta$ -pinene (2%) : (1S,5S)-(-)- $\beta$ -pinene (98%)

(4R)-(+)-limonene (88%) : (4S)-(-)-limonene (12%)

Three samples of petitgrain oil were subjected to multidimensional GC/MS-chiral GC by Bernreuther and Schreier (1991). They found that the enantiomeric distribution of linalool was as follows:

(3R)-(-)-(53.4-64.9%) : (3S)-(+)-(35.1-46.6%)

Ravid et al. (1994) determined that the enantiomeric distribution of linalyl acetate in petitgrain oil was as follows:

(3R)-(-)-linalyl acetate (92%) : (3S)-(+)-linalyl acetate (8%)

Although  $\alpha$ -terpineol is merely a minor constituent of a commercial sample of petitgrain oil (4.9%), Ravid et al. (1995) determined that it existed in the following enantiomeric ratio:

(4R)-(+)- $\alpha$ -terpineol (57%) : (4S)-(-)- $\alpha$ -terpineol (43%)

Juchelka et al. (1996) determined the enantiomeric distribution of a number of authentic oils and two commercially available petitgrain oils. The results of this study can be seen in T-12. From these results, it can be determined that the two commercial samples of petitgrain oil were probably adulterated with racemic linalyl acetate.

An authentic sample of petitgrain oil was determined by Mosandl and Juchelka (1997) to contain the following enantiomeric ratios for two constituents as shown below:

(3R)-(-)-linalyl acetate (97%) : (3S)-(+)-linalyl acetate (3%)

(1S,5S)-(-)- $\beta$ -pinene (91%) : (1R,5R)-(+)- $\beta$ -pinene (9%)

A. Mosandl, U. Hener, P. Kreis and H. G. Schmarr, *Enantiomeric distribution of l-a-pinene, l-b-pinene and limonene in essential oils and extracts. Part I. Rutaceae and Graminae*. Flav. Fragr. J., 5, 193-199 (1990).

A. Bernreuther and P. Schreier, *Multidimensional gas chromatography/mass spectrometry: A power tool for the direct chiral evaluation of aroma compounds in plant tissues. II. Linalool in essential oils and fruits*. Phytochem. Analysis, 2, 167-170 (1991).

U. Ravid, E. Putievsky and I. Katzir, *Chiral GC analysis of enantiomerically pure (R)-(-)-linalyl acetate in some Lamiaceae, Myrtle and Petitgrain essential oils*. Flav. Fragr. J., 9, 275-276 (1994).

U. Ravid, E. Putievsky and I. Katzir, *Determination of the enantiomeric composition of l-a-terpineol in essential oils*. Flav. Fragr. J., 10, 281-284 (1995).

D. Juchelka, A. Steil, K. Witt and A. Mosandl, *Chiral compounds of essential oils xx. Chirality evaluation and authenticity profiles of neroli and petitgrain oils*. J. Essent. Oil Res., 8, 487-497 (1996).

A. Mosandl and D. Juchelka, *Advances in the authenticity assessment of Citrus oils*. J. Essent. Oil Res., 9, 5-12 (1997). ■