

RESEARCH REPORT

## Italian *Citrus* Petitgrain Oils. Part IV. Composition of Lemon Petitgrain Oil<sup>1</sup>

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### Abstract

The composition of Italian industrial lemon petitgrain oil has been examined by HPLC-GC/MS (ITD), GC/MS (quadrupole) and GC using GC capillary SE-52 and Carbowax 20 M columns. A total of 66 compounds have been identified, which represent 98-99% of the whole oil. Among the oxygenated compounds identified, aldehydes were found in highest proportions. 1,8-Cineole, which is either absent or present only as trace in the other *Citrus* petitgrains, represented 1.1-2.1% of lemon petitgrain oil. Lemon petitgrain oil is more similar to lemon peel oil, than the other *Citrus* petitgrain oils to the correspondent peel oils.

### Key Word Index

*Citrus limon*, Rutaceae, Lemon leaf oil, Lemon petitgrain oil,  $\beta$ -pinene, limonene, neral, geranial.

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### Introduction

The composition of bitter orange (1), mandarin (2) and sweet orange (3) petitgrain oils have been previously determined by a combination of HPLC-GC/MS (ITD), GC/MS (quadrupole) and GC on SE-52 and Carbowax 20 M columns using some commercial libraries, e.g. NIST and Adams (4) and a home-made library equipped with Linear Retention Indices to be used interactively with MS data for peak identification (5). In this paper the results of the composition of Italian industrial lemon petitgrain oils determined using the same analytical techniques are reported.

A survey of the literature reveals that much has been written on the composition of lemon petitgrain oil (6-32). Most of the papers were reviewed by Lawrence (33). Most of the published data are directed towards true lemon petitgrain oil [*Citrus Limon* (L.) Burm.] (6,8-15,17,19-25,27,30,31), while a few papers dealt with the composition of the leaf oil of *C. jambhiri* Lush. (Rough lemon) (7,12,16,28,29), *C. limon* x *C. sinensis* (Meyer lemon) (18,24,26) and *C. volkameriana* (32).

Some papers refer to the composition of industrial lemon petitgrain oils (6,8,10,14,20,22,23), while most of the published data related to the analyses of laboratory steam distilled lemon petitgrain oil

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Table I. Quantitative composition of lemon [*Citrus limon* (L.) Burm.] petitgrain oil reported in the literature

| <b>Monoterpene hydrocarbons</b>   |                             |                           |                             |                             |                             |
|-----------------------------------|-----------------------------|---------------------------|-----------------------------|-----------------------------|-----------------------------|
| Camphene                          | 0.1 (9)                     | 0.09 (10)                 | 0-0.1 (11)                  | 0.08 (17)                   | tr-0.16 (19)                |
|                                   | 0.08-0.11 (20)              | 0.08 (21)                 | 0.12 (22)                   | 0.06-0.10 (24)              | 0.001 (25)                  |
| δ-3-Carene                        | 0.63 (10)                   | 1.08 (17)                 | 0.57-0.98 (19)              | 0.11-0.15 (20)              | 0.39 (21)                   |
| δ-4-Carene                        | 0.008 (21)                  |                           |                             |                             |                             |
| Cyclofenchene                     | 0.33 (21)                   |                           |                             |                             |                             |
| o-Cymene                          | 0.04-0.06 (20)              |                           |                             |                             |                             |
| p-Cymene                          | 0.5 (9)                     | 1.28 (10)                 | 0.3-0.6 (11)                | 0.04 (17)                   | tr (19)                     |
|                                   | 0.67-0.82 (20)              | 0.12 (21)                 | 0.91 (22)                   | 0.252 (25)                  |                             |
| α-Fenchene                        | 0.007 (21)                  |                           |                             |                             |                             |
| Limonene                          | 30 (8)                      | 23.1 (9)                  | 30.67 (10)                  | 22.2-28.9 (11)              | 13.00-14.70 (12)            |
|                                   | 38.63 (17)                  | 25.84-34.55 (19)          | 17.80-31.77 (20)            | 25.90 (21)                  | 30.71 (22)                  |
|                                   | 22.71-26.07 (24)            | 9.836 (25)                | 14.59-16.29 (27)            | 21.8 (30)                   | 38.20 (31)                  |
| Myrcene                           | 1.7 (9)                     | 1.01 (10)                 | 1.6-2.2 (11)                | 4.77-7.36 (12)              | 1.61 (17)                   |
|                                   | 1.15-1.64 (19)              | 1.02-1.80 (20)            | 0.94 (21) <sup>f</sup>      | 1.49 (22)                   | 0.98-1.03 (24)              |
|                                   | 0.660 (25)                  | 1.20 (31)                 |                             |                             |                             |
| β-Ocimene                         | 1.37 (10) <sup>d</sup>      | 2.90 (17) <sup>d</sup>    | 2.05-2.57 (19) <sup>d</sup> | 1.99 (21) <sup>d</sup>      | 1.67-1.96 (24) <sup>d</sup> |
| (E)-β-Ocimene                     | 0.750 (25)                  | 0.15 (31)                 |                             |                             |                             |
| (Z)-β-Ocimene                     | 0.10 (31)                   |                           |                             |                             |                             |
| α-Phellandrene                    | 0.08 (10)                   | 0.94 (21) <sup>f</sup>    | 0.16 (22)                   | 2.039 (25)                  | 0.19 (31) <sup>m</sup>      |
| β-Phellandrene                    | 0.55 (17)                   | 9.330 (25)                | 0.35 (31)                   |                             |                             |
| α-Pinene                          | 3.4 (9) <sup>a</sup>        | 2.29 (10)                 | 2.1-3.6 (11) <sup>a</sup>   | 0.19-0.27 (12)              | 1.58 (17)                   |
|                                   | 0.83-2.15 (19) <sup>a</sup> | 1.12-1.48 (20)            | 1.38 (21) <sup>e</sup>      | 1.21 (22) <sup>a</sup>      | 0.94-1.35 (24)              |
|                                   | 0.585 (25)                  | 1.66-2.23 (27)            | 0.16 (31)                   |                             |                             |
| β-Pinene                          | 12.4 (9) <sup>b</sup>       | 11.53 (10)                | 12.1-14.4 (11) <sup>b</sup> | 18.75 (17)                  | 9.79-26.86 (19)             |
|                                   | 15.63-19.86 (20)            | 17.11 (21)                | 13.59 (22)                  | 13.32-18.43 (24)            | 0.022 (25)                  |
|                                   | 3.97-5.22 (27)              | 0.10 (31)                 |                             |                             |                             |
| Sabinene                          | 12.4 (9) <sup>b</sup>       | 2.85 (10)                 | 12.1-14.4 (11) <sup>b</sup> | 2.06 (17)                   | 2.24-3.96 (19)              |
|                                   | 1.05-1.88 (20)              | 4.53 (21)                 | 3.56 (22)                   | 0.412 (25)                  | 0.32 (31)                   |
| α-Terpinene                       | tr (9)                      | 0.12 (10)                 | 0.08 (17)                   | tr-0.28 (19)                | 0.05 (21)                   |
|                                   | 0.19 (31) <sup>m</sup>      |                           |                             |                             |                             |
| γ-Terpinene                       | 3.3 (9)                     | 1.80 (10)                 | 2.1-3.5 (11)                | 2.39-2.49 (12)              | 0.22 (17)                   |
|                                   | 0.85-1.24 (19)              | 2.16-3.19 (20)            | 0.26 (21)                   | 2.32 (22)                   | 0.21-0.28 (24)              |
|                                   | 0.062 (25)                  | 1.48-1.91 (27)            | 0.50 (31)                   |                             |                             |
| Terpinolene                       | 0.30 (10)                   | 0.29 (17)                 | 0.25-0.31 (19)              | 0.18-0.22 (20)              | 0.16 (21)                   |
|                                   | 0.31 (22)                   | 0.035 (25)                | 0.16 (31)                   |                             |                             |
| α-Thujene                         | 3.4 (9) <sup>a</sup>        | 0.01 (10)                 | 2.1-3.6 (11) <sup>a</sup>   | 0.83-2.15 (19) <sup>a</sup> | 1.21 (22) <sup>a</sup>      |
|                                   | 0.008 (25)                  |                           |                             |                             |                             |
| β-Thujene                         | 1.38 (21) <sup>e</sup>      |                           |                             |                             |                             |
| Tricyclene                        | 0.008 (21)                  |                           |                             |                             |                             |
| <b>Sesquiterpene hydrocarbons</b> |                             |                           |                             |                             |                             |
| α-Bergamotene                     | 0.794 (21)                  | 0.059 (25)                |                             |                             |                             |
| Bicycloelemene                    | 0.62 (21)                   |                           |                             |                             |                             |
| β-Bisabolene                      | 0.09-0.10 (20)              | 2.78 (21)                 | 0.30-0.53 (24)              |                             |                             |
| δ-Cadinene                        | 0.028 (21)                  |                           |                             |                             |                             |
| β-Caryophyllene                   | 0.2 (9)                     | 0.2-2.3 (11)              | 0.66 (17)                   | 0.57-1.44 (19)              | 3.19-6.20 (20)              |
|                                   | 0.794 (21)                  | 0.95 (22)                 | 0.252 (25)                  | 0.58-0.89 (27)              |                             |
| β-Elemene                         | 0.4 (9) <sup>c</sup>        | 0.4-0.7 (11) <sup>c</sup> |                             |                             |                             |
| α-Farnesene                       | 0.033 (21)                  |                           |                             |                             |                             |
| γ-Gurjunene                       | 0.033 (21)                  |                           |                             |                             |                             |
| α-Humulene                        | 0.21 (17)                   | 9.38 (21) <sup>h</sup>    | 0.051 (25)                  |                             |                             |
| β-Selinene                        | 1.9 (9)                     | 1.4-2.0 (11)              | 1.03 (17)                   |                             |                             |

Table I. Continued

| <b>Alcohols</b>               |                         |                           |                             |                  |                        |
|-------------------------------|-------------------------|---------------------------|-----------------------------|------------------|------------------------|
| Borneol                       | 0.02 (17)               | 0.10-0.30 (19)            |                             |                  |                        |
| 2-Butyl octanol               | 0.041 (21)              |                           |                             |                  |                        |
| trans-Carveol                 | 0.022 (21)              |                           |                             |                  |                        |
| Cedrenol                      | 0.039 (21)              |                           |                             |                  |                        |
| Cedrol                        | tr (21)                 |                           |                             |                  |                        |
| Citronellol                   | 0.02 (17)               | 0.27-0.39 (19)            | 0.02-0.19 (20) <sup>l</sup> | 0.02 (21)        | 0.22 (22)              |
|                               | 1.40 (31)               |                           |                             |                  |                        |
| p-Cymol                       | 0.11-0.12 (24)          |                           |                             |                  |                        |
| 3,1,1-Dimethylethyl<br>phenol | 0.053 (21)              |                           |                             |                  |                        |
| Epiglobulol                   | 0.031 (21)              |                           |                             |                  |                        |
| Ethanol                       | 0.29 (21)               |                           |                             |                  |                        |
| Eucalyptol                    | 4.36 (21)               |                           |                             |                  |                        |
| Farnesol                      | 0.014 (21)              | 0.04-0.11 (24)            |                             |                  |                        |
| Geraniol                      | 2.8 (9)                 | 1.3-2.8 (11)              | 1.63 (17)                   | 0.99-1.63 (19)   | 0.43-1.05 (20)         |
|                               | 1.49 (21)               | 0.51 (22)                 | 0.173 (25)                  | 12.44-15.04 (27) | 3.00 (31)              |
| n-Hexanol                     | 0.02-0.09 (24)          |                           |                             |                  |                        |
| (E)-2-Hexenol                 | tr (9)                  |                           |                             |                  |                        |
| (E)-3-Hexenol                 | 0.026 (21)              |                           |                             |                  |                        |
| (Z)-3-Hexenol                 | 0.9 (9)                 | 0.12-0.20 (24)            |                             |                  |                        |
| Isogeraniol                   | 0.035 (21)              |                           |                             |                  |                        |
| Isopulegol                    | 0.017 (21)              | 0.519 (25)                |                             |                  |                        |
| Linalool                      | 24 (8)                  | 3.1 (9)                   | 1.7-3.2 (11)                | 1.75-2.11 (12)   | 1.20 (17)              |
|                               | 1.24-1.46 (19)          | 0.87-1.24 (20)            | 1.60 (21)                   | 1.77 (22)        | 0.89-1.03 (24)         |
|                               | 17.260 (25)             | 8.00 (31)                 |                             |                  |                        |
| Nerol                         | 2.0 (9)                 | 1.7-2.2 (11)              | 6.58-7.39 (12)              | 2.18 (17)        | 1.66-2.13 (19)         |
|                               | 2.66-3.10 (20)          | 1.54 (21)                 | 1.30 (22)                   | 4.466 (25)       | 3.50 (31)              |
| Nerolidol                     | 0.046 (21) <sup>d</sup> | 0.02-0.03 (24)            |                             |                  |                        |
| Nonanol                       | 1.17-2.39 (12)          |                           |                             |                  |                        |
| Octanol                       | 0.01-0.02 (24)          |                           |                             |                  |                        |
| Spathulenol                   | 0.043 (21)              |                           |                             |                  |                        |
| Terpinen-4-ol                 | 0.4 (9) <sup>c</sup>    | 0.4-0.7 (11) <sup>c</sup> | 0.21 (17)                   | 0.43-0.91 (19)   | 0.15-0.20 (20)         |
|                               | 0.15 (21)               | 0.24 (22)                 | 0.27-0.31 (24)              | 0.284 (25)       | 0.80 (31)              |
| $\alpha$ -Terpineol           | 0.1 (8)                 | 0.30 (17)                 | 0.63-1.00 (19)              | 0.38-0.45 (20)   | 9.38 (21) <sup>h</sup> |
|                               | 0.37 (22)               | 0.27-0.31 (24)            | 0.068 (25)                  | 3.00 (31)        |                        |
| $\beta$ -Terpineol            | 0.10 (31)               |                           |                             |                  |                        |
| trans- $\beta$ -Terpineol     | 0.105 (21)              |                           |                             |                  |                        |
| <b>Aldehydes</b>              |                         |                           |                             |                  |                        |
| (E)-2-Butenal                 | 0.23 (21)               | 0.07-0.15 (24)            |                             |                  |                        |
| Citronellal                   | 2.03-3.12 (12)          | 0.91 (17)                 | 1.06-1.90 (19)              | 1.11-1.89 (20)   | 1.075 (21)             |
|                               | 1.48 (22)               | 2.634 (25)                | 0.06 (31)                   |                  |                        |
| Decanal                       | tr-0.11 (19)            | 0.01-0.05 (20)            | 0.017 (21)                  | 0.06 (22)        | 0.07-0.10 (24)         |
|                               | 0.010 (25)              |                           |                             |                  |                        |
| 2,3-Dihydrofarnesal           | 0.01 (21)               |                           |                             |                  |                        |
| Dodecanal                     | 0.029 (25)              |                           |                             |                  |                        |
| Furfural                      | 0.001 (24)              |                           |                             |                  |                        |
| Geranial                      | 24.3 (9)                | 24.2-29.6 (11)            | 27.06-31.77 (12)            | 9.73 (17)        | 9.40-15.19 (19)        |
|                               | 10.91-17.27 (20)        | 11.11 (21)                | 10.93 (22)                  | 12.71-19.17 (24) | 21.306 (25)            |
|                               | 24.75-30.54 (27)        | 24.7 (30) <sup>i</sup>    | 15.20 (31)                  |                  |                        |

Table I. Continued

|                               |                         |                         |                             |                  |                 |
|-------------------------------|-------------------------|-------------------------|-----------------------------|------------------|-----------------|
| (E)-2-Hexanal                 | 2.0 (9)                 | 0.39-0.52 (24)          |                             |                  |                 |
| Neral                         | 16.4 (9)                | 16.0-18.2 (11)          | 18.14-22.54 (12)            | 5.97 (17)        | 7.60-12.10 (19) |
|                               | 8.30-12.63 (20)         | 1.42 (21)               | 6.48 (22)                   | 12.73-14.79 (24) | 13.958 (25)     |
|                               | 21.48-25.32 (27)        | 24.7 (30) <sup>i</sup>  | 10.20 (31)                  |                  |                 |
| Nonanal                       | 0.21-0.35 (19)          | 0.29-0.35 (20)          | 0.14 (21)                   | 0.019 (25)       |                 |
| Octanal                       | tr (19)                 | 0.037 (25)              |                             |                  |                 |
| Peryllaldehyde                | 0.01 (21)               |                         |                             |                  |                 |
| p-Toluyaldehyde               | 0.05 (21)               |                         |                             |                  |                 |
| Undecanal                     | tr-0.12 (19)            | 0.048 (25)              |                             |                  |                 |
| <b>Esters</b>                 |                         |                         |                             |                  |                 |
| Citronellyl acetate           | 0.11 (17)               | tr (19)                 | 9.38 (21) <sup>h</sup>      | 0.25 (22)        | 0.02 (24)       |
|                               | 0.372 (25)              |                         |                             |                  |                 |
| Citronellyl propionate        | tr (21)                 |                         |                             |                  |                 |
| Farnesyl acetate              | 0.031 (21)              |                         |                             |                  |                 |
| Geranyl acetate               | 5.38-7.98 (12)          | 2.58 (17)               | 2.30-3.31 (19)              | 0.19-0.88 (20)   | 1.75 (21)       |
|                               | 2.91 (22)               | 0.26-0.59 (24)          | 1.659 (25)                  | 2.71-4.03 (27)   |                 |
| Geranyl formate               | 2.57-3.32 (12)          | 0.208 (21)              |                             |                  |                 |
| Geranyl propanoate            | 0.028 (21)              |                         |                             |                  |                 |
| (Z)-3-Hexenyl acetate         | 0.01 (21)               |                         |                             |                  |                 |
| Linalyl acetate               | tr (8)                  | 0.21 (17)               | 0.02-0.19 (20) <sup>l</sup> | 0.23 (21)        | 6.50 (22)       |
|                               | 2.220 (25)              | 5.7 (30)                |                             |                  |                 |
| Methyl anthranilate           | tr (8)                  | 0.78 (22)               | 0.004-0.005 (24)            |                  |                 |
| Methyl N-methyl anthranilate  | 0.05 (8)                | 0.14-0.19 (19)          | 0.03-0.07 (20)              |                  |                 |
| Methyl salicylate             | 0.01 (21)               |                         |                             |                  |                 |
| Neryl acetate                 | 1.32-1.75 (12)          | 4.12-8.18 (19)          | 0.14 (21)                   | 7.44 (22)        | 0.18-0.39 (24)  |
|                               | 2.816 (25)              | 3.76-5.00 (27)          |                             |                  |                 |
| Neryl formate                 | 0.55-2.39 (12)          |                         |                             |                  |                 |
| Octyl acetate                 | tr-0.03 (20)            | 0.007 (21) <sup>g</sup> | 0.04 (22)                   | 0.008 (25)       |                 |
| Phytol                        | 0.22 (21)               |                         |                             |                  |                 |
| α-Terpinyl acetate            | 2.48-2.97 (12)          | tr (19)                 | 1.77-2.23 (20)              |                  |                 |
| <b>Oxides</b>                 |                         |                         |                             |                  |                 |
| Dipentene oxide               | 0.007 (21) <sup>g</sup> |                         |                             |                  |                 |
| Linalool oxide                | 1.80 (31) <sup>d</sup>  |                         |                             |                  |                 |
| cis-Linalool oxide            | 0.008 (25)              |                         |                             |                  |                 |
| trans-Linalool oxide          | 0.169 (25)              |                         |                             |                  |                 |
| <b>Others</b>                 |                         |                         |                             |                  |                 |
| Camphor                       | 0.017 (21)              |                         |                             |                  |                 |
| Carvone                       | 2.021 (25)              | 9.7 (30)                |                             |                  |                 |
| 1,4-Cineole                   | tr (25)                 |                         |                             |                  |                 |
| 1,8-Cineole                   | 0.70 (17)               |                         |                             |                  |                 |
| Dibutylphthalate              | 0.08-0.09 (24)          |                         |                             |                  |                 |
| 3-(1,1-Dimethyl-ethyl)-phenol | 0.053 (21)              |                         |                             |                  |                 |
| α-p-Dimethylstyrene           | 0.50 (31)               |                         |                             |                  |                 |
| Eneicosane                    | 0.19-0.20 (24)          |                         |                             |                  |                 |
| Epicamphor                    | 0.034 (21)              |                         |                             |                  |                 |
| p-Menthen-3-one               | 0.012 (21)              |                         |                             |                  |                 |
| Methanol-2-tetrahydroprane    | tr (21)                 |                         |                             |                  |                 |

Table I. Continued

|                       |            |                |                |           |           |
|-----------------------|------------|----------------|----------------|-----------|-----------|
| Methylcyclopentane    | 0.011 (21) |                |                |           |           |
| 6-Methyl-5-hepten-    |            |                |                |           |           |
| 2-one                 | 2.30 (17)  | 0.57-0.80 (19) | 0.33-0.51 (20) | 1.06 (21) | 0.26 (22) |
|                       | 1.725 (25) | 24.4 (30)      | 3.20 (31)      |           |           |
| 3-(4-Methyl-3-        |            |                |                |           |           |
| pentenyl) furan       | 0.012 (21) |                |                |           |           |
| Pulegone              | 0.44 (21)  |                |                |           |           |
| Thymol methyl ether   | 0.03 (17)  |                |                |           |           |
| Toluene               | 0.007 (21) | 0.02 (24)      |                |           |           |
| 2,2,3-Trimethylbutane | tr (21)    |                |                |           |           |

a =  $\alpha$ -Pinene +  $\alpha$ -Thujene; b =  $\beta$ -Pinene + Sabinene; c =  $\beta$ -Elemene + Terpinen-4-ol; d = Correct isomer not characterized; e =  $\alpha$ -Pinene +  $\beta$ -Thujene; f = Myrcene +  $\alpha$ -Phellandrene; g = Dipentene oxide + Octyl acetate; h = Citronellyl acetate +  $\alpha$ -Terpineol +  $\alpha$ -Humulene; i = Neral + Geranial; l = Linalyl acetate + Citronellol; m =  $\alpha$ -Terpinene +  $\alpha$ -Phellandrene

#### Appendix to Table I

##### Details on the references on the composition of lemon leaf oil

Industry steam-distilled oils (6,8,10,14,20,22,23). Laboratory steam-distilled oils (12,15,19,21,24,27,30,31). Laboratory solvent extracted oils (9,11). Qualitative data (6,7,13,14,23). Quantitative data (8,9-12,15,17,19-22,24,25,27,30,31). Ontogenesis (11). Taxonomy (9,12,19,21,24,27,30,31). Influence of the distillation time (20). *Citrus limon* (L.)Burm (all). cv. Eureka (12,15,21,27,30). cv. Liston (12,19). cv. S. Fernando (12). cv. Verna, Villafranca, Fino (19). cv. Monachello (24,27). cv. Georgiana (24). cv. Femminello S. Giuseppe Larena, Femminello Favazzina (27). cv. Pant-lemon (31).

(12,15,19,21,24,27,30,31) or solvent extracted lemon petitgrain oils (9,11) for ontogenic (11) or taxonomic (9,12,19,21,24,27,30,31) studies.

Table I summarizes most of the quantitative results reported in literature on true lemon leaf oil, Table II summarizes the same results for Rough lemon, Mayer lemon and *C. volkameriana* leaf oils.

Some of the published data referred specifically to Italian lemon petitgrain oils (10,20,22,23). One of the studies (23) reported only qualitative results, while another (10) reported the relative composition of the different classes of compounds, so that only the content of monoterpene hydrocarbons could be obtained. In 1985, Di Giacomo et al. (20) established a relationship between the composition of lemon petitgrain oils and the time of distillation.

Some qualitative and/or quantitative differences among literature data reported in Table I may be due to the use of more or less advanced techniques, which sometimes allowed the identification of many minor components (21). In addition, other differences could be due to the oil isolation procedure (more or less drastic condition of the distillation, use of solvents) and especially to the cultivar or varietal and geographical origin of the leaves.

For example, values reported for  $\beta$ -pinene range from 0.10% (31) to 26.86% (19); for neral range from 1.42% (21) to 25.32% (27), for neryl acetate range from 0.14% (21) to 8.18% (19), and for linalool they range from 0.89% (24) to 17.26% (25).

## Experimental

The analyses were carried out on 6 samples of lemon petitgrain oil isolated under our supervision in a Sicilian oil processor in the Spring 1994. Each sample was distilled from 450 kg of leaves giving a yield of ca. 1.5 ‰. All the samples were analyzed by LC-GC/MS (ITD), GC/MS (quadrupole) and GC using the same experimental conditions as described previously for bitter orange (1), mandarin (2) and sweet orange (3) petitgrain oils.

As for bitter orange, mandarin and sweet orange petitgrain oils (1,2,3), the LC-GC/MS (ITD) system was equipped with a SE-52 column, 30 m x 0.32 mm; for the analyses with the GC/MS (quadrupole)

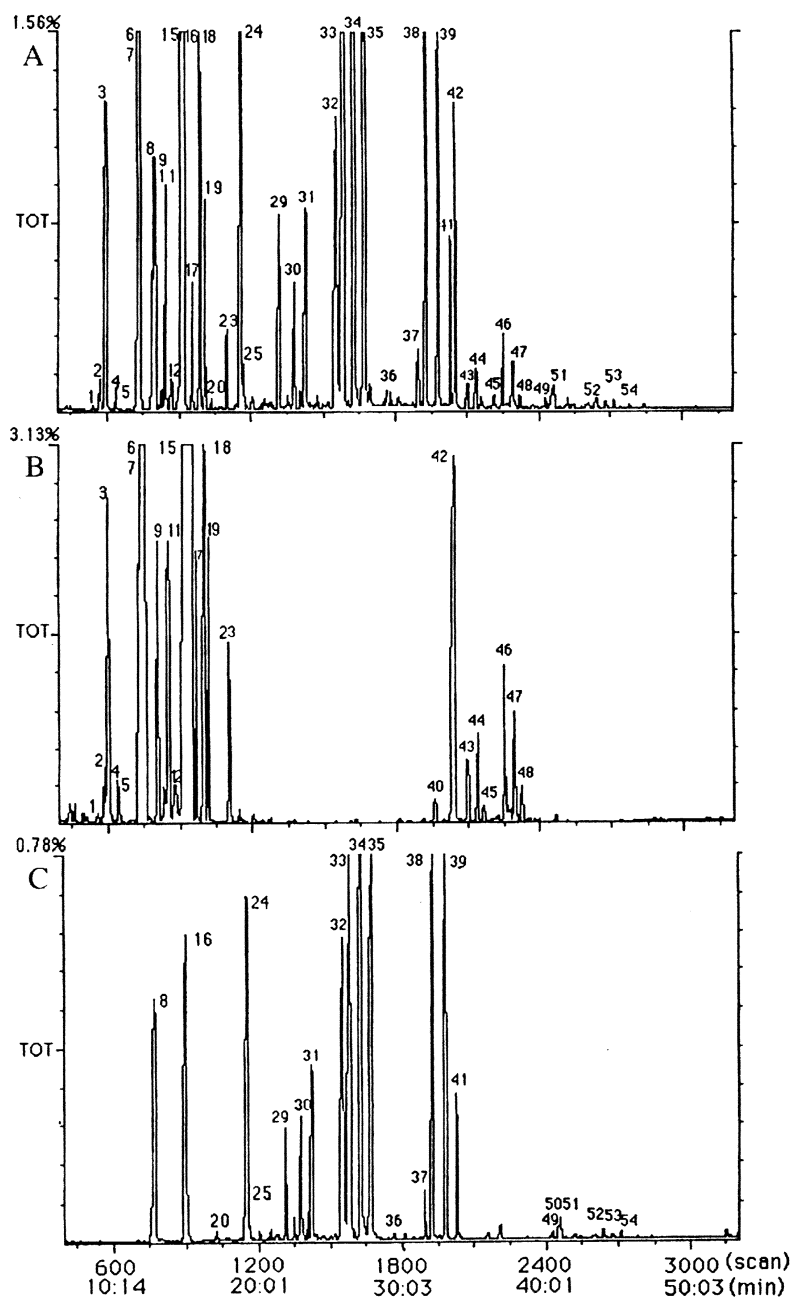


Figure 1. Total ion current chromatograms of a lemon petitgrain oil and of fractions from its LC-preseparation. GC column SE-52, 30 m. A = whole oil, B = hydrocarbons, C = oxygenated fraction. For peak identification see Table III

and GC systems, either a 60 m x 0.32 mm SE-52 or a Carbowax 20 M column was used.

LC-GC/MS (ITD) system was equipped with ADAMS library (4), while GC/MS (quadrupole) system was coupled with two commercial libraries (Nist and Adams) and an home-made FFC (Flavour and Fragrance Components) bank, provided with Linear Retention Indices, to be used interactively with MS data for compounds identification (5).

## Results and Discussion

Figure 1 shows the total ion current chromatograms of a lemon petitgrain oil and its correspondent fractions obtained by LC-pre-separation. Figures 2 and 3 report the GC/MS (quadrupole) chromatograms obtained using a Carbowax 20 M and SE-52 column, respectively. Table III reports peak identified by

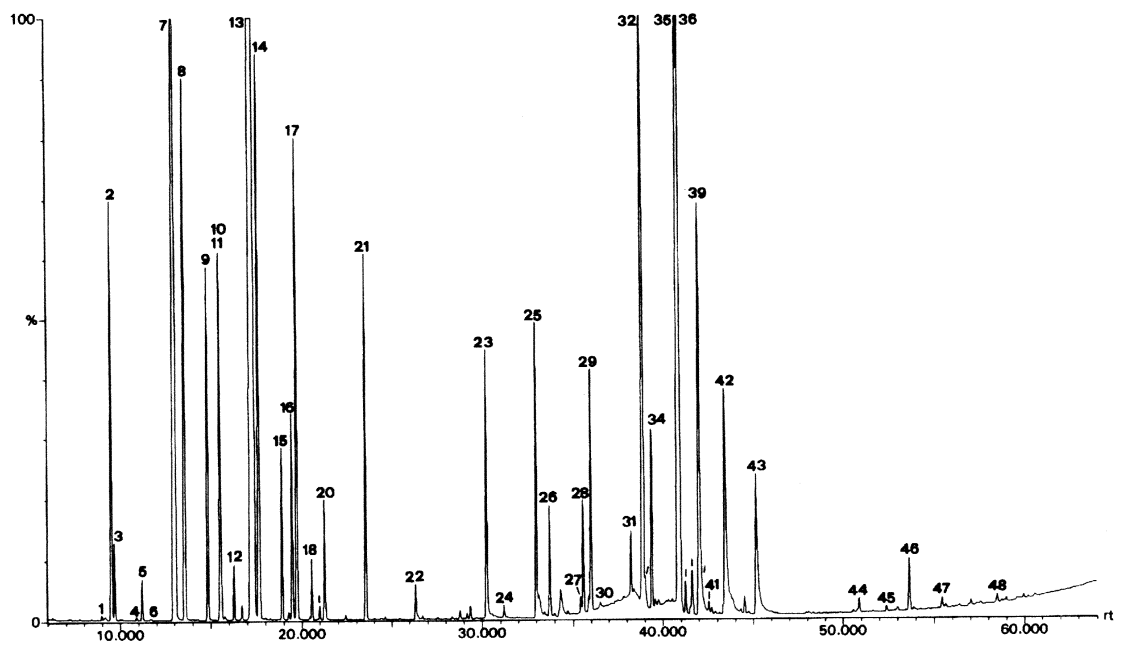


Figure 2. Total ion current chromatogram of a lemon petitgrain oil obtained by GC/MS (quadrupole). GC column Carbowax 20M, 60 m. For peak identification see Table III

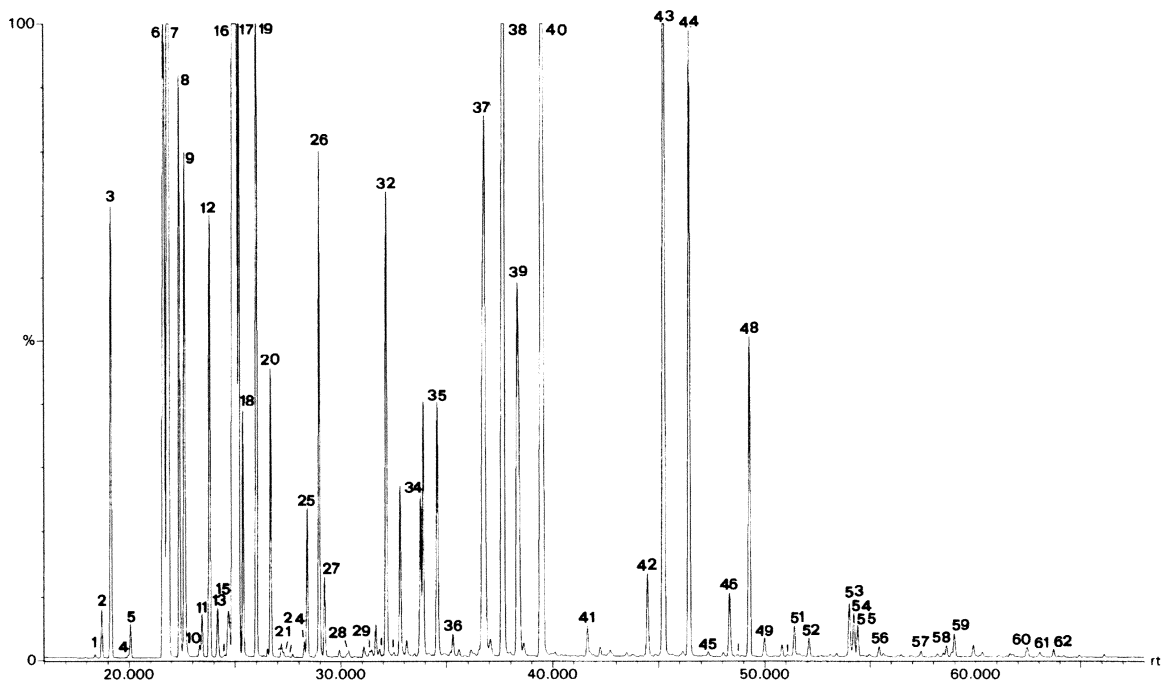


Figure 3. Total ion current chromatogram of a lemon petitgrain oil obtained by GC/MS (quadrupole). GC column SE-52, 60 m. For peak identification see Table III

Table II. Quantitative composition of *Citrus jambhiri* Lush. (Rough lemon),  
*Citrus limon* x *Citrus sinensis* (Meyer lemon) and *Citrus volkameriana*

|                                   | Rough lemon           |                             | Meyer lemon            |                             | <i>Citrus volkameriana</i> |
|-----------------------------------|-----------------------|-----------------------------|------------------------|-----------------------------|----------------------------|
| <b>Monoterpene hydrocarbons</b>   |                       |                             |                        |                             |                            |
| Camphene                          | 0-1.58 (29)           |                             |                        |                             | 0.04 (32)                  |
| p-Cymene                          | 3.3 (16)              | 0-0.51 (29)                 | 0.13 (24)              | 0.02 (26)                   |                            |
| Limonene                          | 13.05-22.94 (12)      | 32.4 (16)                   | 73 (18)                | 57.03 (24)                  | 41.74 (32)                 |
|                                   | 26.7-41.0 (28)        | 18.40-29.00 (29)            | 35.63-48.03 (26)       |                             |                            |
| 1,3,8-p-Menthatriene              | 0-0.24 (29)           |                             |                        |                             |                            |
| Myrcene                           | 14.66-24.04 (12)      | 1.2 (16)                    | 1.3 (18)               | 1.20 (24)                   | 1.56 (32)                  |
|                                   | 1.1-2.4 (28)          | 0-0.10 (29)                 | 0.58-0.90 (26)         |                             |                            |
| β-Ocimene                         | 7.3 (16) <sup>a</sup> | 0.13-3.40 (29) <sup>a</sup> | 0.99 (18) <sup>a</sup> | 2.30 (24) <sup>a</sup>      |                            |
| (E)-β-Ocimene                     |                       |                             | 1.44-2.13 (26)         |                             | 3.88 (32)                  |
| α-Phellandrene                    |                       |                             | 0.01-0.14 (26)         |                             | 0.06 (32)                  |
| α-Pinene                          | 0.40-0.75 (12)        | 0-0.3 (28)                  | 0.21 (18)              | 0.22 (24)                   | 0.53 (32)                  |
|                                   | 0-0.86 (29)           |                             | 0.06-0.10 (26)         |                             |                            |
| β-Pinene                          | 0.09-1.62 (29)        |                             | 0.10 (24)              | 0.03-0.06 (26)              | 0.69 (32)                  |
| Sabinene                          | 7.4 (16)              | 24.1-31.4 (28)              | 0.27 (18)              | 0.26-0.42 (26)              | 16.16 (32)                 |
|                                   | 0-10.20 (29)          |                             |                        |                             |                            |
| α-Terpinene                       | 0.2 (16)              |                             | 0.08-0.12 (26)         | 0.13-0.26 (26)              | 0.11 (32)                  |
| γ-Terpinene                       | 3.17-5.75 (12)        | 7.4 (16)                    | 0.70 (18)              | 0.17 (24)                   | 0.27 (32)                  |
| Terpinolene                       | 0.2 (16)              |                             |                        |                             | 0.11 (32)                  |
| Thujene                           | 0-0.14 (29)           |                             |                        |                             |                            |
| α-Thujene                         | 0-0.67 (29)           |                             |                        |                             | 0.11 (32)                  |
| <b>Sesquiterpene hydrocarbons</b> |                       |                             |                        |                             |                            |
| α-Bergamotene                     |                       |                             |                        |                             | 0.06 (32)                  |
| β-Bisabolene                      | tr-0.69 (29)          |                             | 0.86 (24)              |                             | 0.31 (32)                  |
| δ-Cadinene                        |                       |                             | 0.46-0.56 (26)         |                             | 0.03 (32)                  |
| γ-Cadinene                        |                       |                             | 2.75-4.16 (26)         |                             |                            |
| β-Caryophyllene                   | 0.3 (16)              | 2.92-13.28 (29)             | 0.010 (18)             | 0.06 (26)                   | 0.36 (32)                  |
| β-Elemene                         | 0-0.79                |                             |                        |                             |                            |
| δ-Elemene                         |                       |                             |                        |                             | 0.05 (32)                  |
| Germacrene B                      |                       |                             |                        |                             | 0.15 (32)                  |
| Germacrene D                      |                       |                             |                        |                             | 0.04 (32)                  |
| α-Humulene                        | 0.31-0.65 (29)        |                             | 1.63-2.07 (26)         |                             | 0.04 (32)                  |
| Longifolene                       |                       |                             |                        |                             | 0.07 (32)                  |
| β-Selinene                        |                       |                             |                        |                             | 0.08 (32)                  |
| <b>Alcohols</b>                   |                       |                             |                        |                             |                            |
| 2-Buten-1-ol                      | 0-0.33 (29)           |                             |                        |                             |                            |
| δ-Cadinol                         |                       |                             |                        |                             | 0.03 (32)                  |
| Citronellol                       | 0-0.29 (29)           |                             | 0.002 (18)             |                             | 1.43 (32)                  |
| 1,2-Dihydrolinalool               |                       |                             |                        |                             | 0.05 (32)                  |
| Farnesol                          |                       |                             | 0.19 (24) <sup>a</sup> | 0.19-0.32 (26) <sup>a</sup> |                            |
| Geraniol                          | 2.4-3.0 (28)          | 0.08 (29)                   | 0.11-0.12 (26)         |                             | 0.04 (32)                  |
| Hexanol                           |                       |                             | 0.42 (24)              | 0.04-0.016 (26)             |                            |
| (Z)-3-Hexanol                     | 0.018 (16)            |                             | 0.62 (24)              |                             |                            |
| (E)-2-Hexenol                     |                       |                             | 0.14-0.18 (26)         |                             |                            |
| Isoborneol                        |                       |                             |                        |                             | 0.18 (32)                  |
| Iso-(iso)pulegol                  | 0.6 (16)              |                             | 0.16 (18)              |                             |                            |



Table II. Continued

|                                    | Rough lemon              |                        | Meyer lemon            |                | <i>Citrus<br/>volkameriana</i> |
|------------------------------------|--------------------------|------------------------|------------------------|----------------|--------------------------------|
| Isopulegol                         | 4.4 (16)                 | 0-0.57 (29)            | 3.0 (18)               | 0.11-0.16 (26) | 0.04 (32)                      |
| Linalool                           | 9.37-34.07 (12)          | 1.3 (16) <sup>b</sup>  | 0.23 (18)              | 1.51 (24)      | 3.12 (32)                      |
|                                    | 6.9-17.2 (28)            | 0-1.90 (29)            | 1.19-1.20 (26)         |                |                                |
| p-Mentha-1,4-dien-7-ol             |                          |                        | 0.01-0.02 (26)         |                |                                |
| cis-p-Mentha-2-en-1-ol             |                          |                        | 0.04-0.11 (26)         |                |                                |
| Nerol                              | 0.01-2.66 (12)           | 0-0.11 (29)            | 0.97-1.87 (26)         |                |                                |
| Nerolidol                          |                          |                        | 0.15 (24) <sup>a</sup> |                |                                |
| Nonanol                            | 1.07-2.16 (12)           | 1.3 (16) <sup>b</sup>  |                        |                | 0.17 (32)                      |
| Octadecanol                        | 0-0.48 (29)              |                        |                        |                |                                |
| Octanol                            |                          |                        | 0.01 (24)              |                |                                |
| Phytol                             |                          |                        |                        |                | 0.66 (32)                      |
| 2-Pentanol                         | 0.16-0.20 (29)           |                        |                        |                |                                |
| trans-Sabinene hydrate             |                          |                        |                        |                | 0.07 (32)                      |
| Sabinol                            | 0-0.92 (29)              |                        |                        |                |                                |
| Terpinen-4-ol                      | 0.022 (16)               | 0-0.80 (29)            | 0.05 (24)              | 0.05-0.06 (26) |                                |
| α-Terpineol                        | 1.0-2.7 (28)             | 0.38-0.44 (29)         | 0.23 (24)              | 0.07-0.14 (26) | 0.13 (32)                      |
| Thymol                             |                          |                        | 0.007 (18)             | 0.06 (24)      | 0.07 (32)                      |
|                                    |                          |                        | 0.06 (26)              |                |                                |
| <b>Aldehydes</b>                   |                          |                        |                        |                |                                |
| (Z)-2-Butenal                      |                          |                        | 0.25 (24)              |                |                                |
| Citronellal                        | 10.50-17.02 (12)         | 0.8 (16)               | 1.0 (18)               | 3.59-5.04 (26) | 22.21 (32)                     |
|                                    | 5.1-9.1 (28)             | 0-6.70 (29)            |                        |                |                                |
| Decanal                            | 0.10-0.69 (29)           |                        | 0.41-0.46 (26)         |                | 0.96 (32)                      |
| Furfural                           |                          |                        | 0.01 (24)              |                |                                |
| Geranial                           | 0.45-9.01 (12)           | 1.11 (16)              | 1.09 (24)              | 0.65-0.79 (26) | 1.26 (32)                      |
|                                    | 1.8-5.4 (28)             | 0-4.20 (29)            |                        |                |                                |
| (E)-2-Hexanal                      |                          |                        | 1.99 (24)              | 0.09-0.36 (26) |                                |
| Neral                              | 8.14-13.11 (12)          | 0.91 (16) <sup>c</sup> | 0.07 (18)              | 0.79 (24)      | 0.91 (32)                      |
|                                    | 1.2-3.6 (28)             | 0-6.50 (29)            | 0.51-0.61 (26)         |                |                                |
| Nonanal                            | 0-0.33 (29)              |                        |                        |                | 0.16 (32)                      |
| Octanal                            | 0.10-0.56 (29)           |                        |                        |                | 0.13 (32)                      |
| <b>Esters</b>                      |                          |                        |                        |                |                                |
| Citronellyl acetate                |                          |                        | 0.06 (18)              | 0.06 (24)      | 0.11 (32)                      |
|                                    |                          |                        | 0.71-1.37 (26)         |                |                                |
| Citronellyl butyrate               |                          |                        | 0.22-0.30 (26)         |                |                                |
| Geranyl acetate                    | 0.49-2.09 (12)           | 1.1 (16)               | 0.3 (18)               | 0.03 (24)      | 0.37 (32)                      |
|                                    | 0-0.80 (29) <sup>d</sup> |                        | 0.15-0.31 (26)         |                |                                |
| Geranyl butyrate                   |                          |                        | 0.11-0.14 (26)         |                |                                |
| Geranyl formate                    | 0.32-1.38 (12)           | 0.91 (16) <sup>c</sup> | 0.25-0.49 (26)         |                |                                |
|                                    | 0-0.15 (29) <sup>e</sup> |                        |                        |                |                                |
| (Z)-3-Hexenyl acetate              |                          |                        | 0-0.07 (26)            |                |                                |
| Linalyl acetate                    | 2.0-5.1 (28)             |                        |                        |                | 0.02 (32)                      |
| Methyl anthranilate                |                          |                        | 0.02 (24)              |                |                                |
| Methyl N-methyl-<br>anthranilate   | 7.70-40.0 (29)           |                        |                        |                |                                |
| Methyl-14-methyl<br>pentadecanoate | tr-0.72 (29)             |                        |                        |                |                                |
| Neryl acetate                      | 0.70-1.31 (12)           |                        |                        |                |                                |
|                                    | 0-0.80 (29) <sup>e</sup> | 0.8 (16)               | 0.11 (24)              | 0.61-1.19 (26) | 0.13 (32)                      |

Table II. Continued

|                            | Rough lemon                                |                        | Meyer lemon                 | <i>Citrus<br/>volkameriana</i> |
|----------------------------|--|------------------------|-----------------------------|--------------------------------|
| Neryl formate              | 0.96-1.82 (12)<br>0-0.15 (29) <sup>e</sup> | 0.05 (16)              |                             |                                |
| Octyl acetate              |  |                        | 0.01-0.02 (26)              |                                |
| $\alpha$ -Terpinyl acetate | 0.52-1.58 (12)<br>0-3.50 (29)              | 0.91 (16) <sup>c</sup> | 0.10-0.12 (26)              |                                |
| <b>Oxides</b>              |  |                        |                             |                                |
| Caryophyllene oxide        | 0.2 (16)                                   |                        | tr (18)                     |                                |
| cis-Limonene oxide         |  |                        |                             | 0.07 (32)                      |
| Linalool oxide             | 0.03 (16)                                  |                        | 0.03-0.10 (26) <sup>a</sup> |                                |
| <b>Others</b>              |  |                        |                             |                                |
| Acetic acid                | 0.24-1.36 (29)                             |                        |                             |                                |
| Carvone                    | 0-0.95 (29)                                |                        |                             |                                |
| $\alpha$ -Collidine        | 0-1.24 (29)                                |                        |                             |                                |
| N,N-Dimethyl formamide     | 0.03-0.56 (29)                             |                        |                             |                                |
| Eneicosane                 |  |                        | 0.52 (24)                   |                                |
| 6-Methyl-5-hepten-2-one    | 0.10 (16)                                  | 0-0.16 (29)            |                             |                                |
| Methyl-2,4-pentadiene      | 0-7.00 (29)                                |                        |                             |                                |
| Pyridine                   | 0-2.72 (29)                                |                        |                             |                                |
| Thymol methyl ether        |  |                        |                             | 0.02 (32)                      |
| Toluene                    |  |                        | 0.06 (24)                   |                                |

a = Correct isomer not characterized; b = Linalool + Nonanol; c = Neral + Geranyl formate +  $\alpha$ -Terpinyl acetate; d = Neryl acetate + Geranyl acetate; e = Neryl formate + Geranyl formate

#### Appendix to Table II

##### Details on the references on the composition of lemon leaf oil

Industry steam-distilled oils (7,12,16,18,24,26,28,32). Laboratory solvent extracted oils (29). Qualitative data (7). Quantitative data (12,16,18,24,26,28,32). Biogenesis/Ontogenesis (7,28). Taxonomy (12,16,18,24,26,32). Treatment of the oil (29). cv. India, Jambhira CRC 3060, Stow, Sour variant, Limoneira, Mazoe, South Africa, Florida, Gomiri (12).

LC-GC/MS (ITD), by GC/MS (quadrupole) on Carbowax column and by GC/MS (quadrupole) on SE-52 column. Table IV reports the composition of the analyzed samples. Data reported in Table IV were obtained considering results of GC analyses with SE-52 and Carbowax 20 M columns, and the identification by GC/MS (quadrupole) and LC-GC/MS (ITD).

The LC pre-separation and the further GC/MS (ITD) analyses allowed a more certain identification of the components present in small amount, such as tricyclene,  $\alpha$ -fenchene, o-cymene, cis-linalool oxide furanoid form, octanol, cis-limonene oxide, isopulegol,  $\beta$ -elemene, (Z)- $\beta$ -farnesene, which were either present as traces or partially co-eluted with other components in the GC-analysis on SE-52 column of the whole oil.

Analyses carried out on Carbowax column allowed the resolution of the pairs of compounds limonene/ $\beta$ -phellandrene, geraniol/linalyl acetate, co-eluted in the GC analysis on SE-52 column of the whole oil and of the LC fractions.

As can be seen from the figures and the tables, 66 components have been identified, representing about 98-99% of the oil. cis-Sabinene hydrate, p-mentha-(2,4)8-diene, cis-p-menth-2-en-1-ol, cis- and trans-limonene oxide, iso(iso)pulegol, (Z)- $\beta$ -farnesene, bicyclogermacrene, caryophyllene oxide,

Table III. Compound identification by LC-GC/MS (ITD), by GC/MS (quadrupole) on Carbowax column and by GC/MS (quadrupole) on SE-52 column

| Compounds                     | 1  | 2  | 3  | Compounds                    | 1  | 2  | 3  |
|-------------------------------|----|----|----|------------------------------|----|----|----|
| hexanal                       |    | 6  |    | iso-(iso)pulegol             |    |    | 33 |
| tricyclene                    | 1  | 1  | 1  | terpinen-4-ol                | 30 | 28 | 34 |
| $\alpha$ -thujene             | 2  | 3  | 2  | $\alpha$ -terpineol          | 31 | 34 | 35 |
| $\alpha$ -pinene              | 3  | 2  | 3  | decanal                      |    | 24 | 36 |
| $\alpha$ -fenchene            | 4  | 4  | 4  | citronellol                  |    | 40 |    |
| camphene                      | 5  | 5  | 5  | nerol                        | 32 | 42 | 37 |
| sabinene                      | 6  | 8  | 6  | neral                        | 33 | 32 | 38 |
| $\beta$ -pinene               | 7  | 7  | 7  | geraniol                     |    | 43 | 39 |
| 6-methyl-5-hepten-2-one       | 8  | 21 | 8  | linalyl acetate              | 34 | 26 |    |
| myrcene                       | 9  | 10 | 9  | geranial                     | 35 | 36 | 40 |
| octanal                       |    |    | 10 | undecanal                    | 36 |    | 41 |
| $\alpha$ -phellandrene        | 10 | 11 | 11 | citronellyl acetate          | 37 | 31 | 42 |
| $\delta$ -3-carene            | 11 | 9  | 12 | neryl acetate                | 38 | 35 | 43 |
| $\alpha$ -terpinene           | 12 | 12 | 13 | geranyl acetate              | 39 | 39 | 44 |
| o-cymene                      | 13 |    | 14 | $\beta$ -elemene             | 40 |    | 45 |
| p-cymene                      | 14 | 18 | 15 | methyl N-methyl anthranilate | 41 | 46 | 46 |
| limonene                      | 15 | 13 | 16 | cis- $\alpha$ -bergamotene   |    |    | 47 |
| $\beta$ -phellandrene         |    | 14 |    | $\beta$ -caryophyllene       | 42 | 29 | 48 |
| 1,8-cineole                   | 16 |    | 17 | trans- $\alpha$ -bergamotene | 43 | 27 | 49 |
| (Z)- $\beta$ -ocimene         | 17 | 15 | 18 | (Z)- $\beta$ -farnesene      | 45 |    | 50 |
| (E)- $\beta$ -ocimene         | 18 | 17 | 19 | $\alpha$ -humulene           | 44 | 33 | 51 |
| $\gamma$ -terpinene           | 19 | 16 | 20 | geranyl propanoate           |    |    | 52 |
| cis-sabinene hydrate          | 20 |    | 21 | bicyclogermacrene            | 46 | 38 | 53 |
| octanol                       | 22 |    | 22 | (E,E)- $\alpha$ -farnesene   | 47 |    | 54 |
| cis-linalool oxide (furanoid) | 21 |    | 23 | $\beta$ -bisabolene          |    | 37 | 55 |
| p-mentha-(2,4)8-diene         |    | 19 | 24 | $\delta$ -cadinene           | 48 | 41 | 56 |
| terpinolene                   | 23 | 20 | 25 | (E)-nerolidol                | 49 | 45 | 57 |
| linalool                      | 24 | 25 | 26 | spathulenol                  | 50 | 47 | 58 |
| nonanal                       | 25 | 22 | 27 | caryophyllene oxide          | 51 | 44 | 59 |
| cis-p-menth-2-en-1-ol         | 27 | 30 | 28 | 2,3-dimethyl-3-(4-methyl-3-  |    |    |    |
| cis-limonene oxide            | 26 |    | 29 | pentenyl)-2-norbornanol      | 52 |    | 60 |
| trans-limonene oxide          |    |    | 30 | campherenol                  | 53 |    | 61 |
| isopulegol                    | 28 |    | 31 | $\alpha$ -bisabolol          | 54 | 48 | 62 |
| citronellal                   | 29 | 23 | 32 |                              |    |    |    |

1 = LC-GC/MS Peak in Figure 1; 2 = GC/MS on Carbowax column, Peak in Figure 2; GC/MS on SE-52 column, Peak in Figure 3

2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol, campherenol and  $\alpha$ -bisabolol have been identified in lemon petitgrain oil for the first time.

In lemon petitgrain the monoterpene hydrocarbons ranged from ca. 52-60% with limonene (28-35%) being the main component, and  $\beta$ -pinene (12-16%) the other major monoterpene hydrocarbon. Although the sesquiterpene content ranged only from 1.1-2.6%,  $\beta$ -caryophyllene was the main component of this fraction as was found in the other *Citrus* petitgrain oils. Aldehydes (18-27%) were the most abundant oxygenated compounds with neral and geranial being the predominant compounds as was found in the peel oil. Finally, the alcohol content of lemon petitgrain ranged from 7-14%, while esters ranged from 7-10%.

Lemon petitgrain oil was characterized by a significant amount of 1,8-cineole (1.1-2.1%), while it is only present as a trace component in bitter orange (1), mandarin (2) and sweet orange (3) petitgrain oils. Lemon petitgrain is also characterized by the occurrence of three sesquiterpene alcohols:

Table IV. Quantitative composition of lemon petitgrain oils

| Compounds*                    | 1     | 2     | 3     | 4     | 5     | 6     | Min   | Max   |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| tricyclene                    | 0.01  | 0.01  | 0.01  | t     | t     | t     | t     | 0.01  |
| $\alpha$ -thujene             | 0.07  | 0.09  | 0.07  | 0.07  | 0.07  | 0.06  | 0.06  | 0.09  |
| $\alpha$ -pinene              | 1.07  | 1.13  | 0.93  | 0.87  | 0.97  | 0.84  | 0.84  | 1.13  |
| $\alpha$ -fenchene            | -     | t     | t     | t     | t     | t     | -     | t     |
| camphene                      | 0.07  | 0.07  | 0.06  | 0.05  | 0.06  | 0.06  | 0.05  | 0.07  |
| sabinene                      | 3.81  | 3.04  | 2.99  | 3.01  | 3.15  | 3.28  | 2.99  | 3.81  |
| $\beta$ -pinene               | 16.03 | 14.63 | 12.55 | 12.57 | 12.26 | 11.96 | 11.96 | 16.03 |
| 6-methyl-5-hepten-2-one       | 0.67  | 1.29  | 1.23  | 1.06  | 1.61  | 0.72  | 0.67  | 1.61  |
| myrcene                       | 0.79  | 0.89  | 0.86  | 0.83  | 1.60  | 1.28  | 0.79  | 1.60  |
| octanal                       | 0.02  | 0.02  | 0.02  | 0.01  | 0.02  | 0.04  | 0.01  | 0.04  |
| $\alpha$ -phellandrene        | 0.04  | 0.04  | 0.06  | 0.03  | 0.09  | 0.07  | 0.03  | 0.09  |
| $\delta$ -3-carene            | 0.63  | 0.74  | 0.82  | 0.75  | 1.08  | 0.73  | 0.63  | 1.08  |
| $\alpha$ -terpinene           | 0.07  | 0.09  | 0.11  | 0.04  | 0.11  | 0.09  | 0.04  | 0.11  |
| o-cymene                      | 0.01  | 0.01  | t     | 0.01  | t     | t     | t     | 0.01  |
| p-cymene                      | 0.31  | 0.38  | 0.22  | 0.51  | 0.14  | 0.04  | 0.04  | 0.51  |
| limonene                      | 30.40 | 33.09 | 29.43 | 28.41 | 34.82 | 28.33 | 28.41 | 34.82 |
| $\beta$ -phellandrene         | 2.31  | 2.28  | 2.22  | 2.25  | 2.48  | 2.60  | 2.22  | 2.60  |
| 1,8-cineole                   | 1.12  | 2.13  | 1.53  | 1.34  | 1.50  | 1.70  | 1.12  | 2.13  |
| (Z)- $\beta$ -ocimene         | 0.35  | 0.32  | 0.36  | 0.30  | 0.42  | 0.44  | 0.30  | 0.44  |
| (E)- $\beta$ -ocimene         | 1.86  | 1.67  | 1.92  | 1.50  | 2.43  | 2.08  | 1.50  | 2.43  |
| $\gamma$ -terpinene           | 0.47  | 0.58  | 0.70  | 0.42  | 0.60  | 0.34  | 0.34  | 0.70  |
| cis-sabinene hydrate          | 0.03  | 0.04  | 0.03  | 0.03  | 0.02  | 0.06  | 0.02  | 0.06  |
| octanol                       | t     | t     | t     | 0.01  | t     | 0.01  | t     | 0.01  |
| cis-linalool oxide (furanoid) | t     | t     | t     | 0.01  | t     | t     | t     | 0.01  |
| p-mentha-(2,4)8-diene         | 0.03  | 0.02  | 0.03  | 0.01  | 0.03  | 0.03  | 0.01  | 0.03  |
| terpinolene                   | 0.21  | 0.24  | 0.29  | 0.19  | 0.31  | 0.22  | 0.19  | 0.31  |
| linalool                      | 1.72  | 1.16  | 3.87  | 3.09  | 1.26  | 0.88  | 0.88  | 3.87  |
| nonanal                       | 0.14  | 0.10  | 0.12  | 0.08  | 0.13  | 0.22  | 0.08  | 0.22  |
| cis-p-menth-2-en-1-ol         | 0.02  | 0.03  | 0.03  | 0.03  | 0.01  | 0.01  | 0.01  | 0.03  |
| cis-limonene oxide            | 0.03  | 0.05  | 0.01  | 0.05  | 0.02  | 0.01  | 0.01  | 0.05  |
| trans-limonene oxide          | 0.06  | 0.06  | 0.03  | 0.06  | 0.02  | 0.01  | 0.01  | 0.06  |
| isopulegol                    | 0.01  | 0.02  | 0.02  | 0.03  | 0.02  | t     | t     | 0.03  |
| citronellal                   | 0.91  | 0.62  | 0.75  | 0.78  | 1.08  | 1.41  | 0.61  | 1.41  |
| iso-(iso)pulegol              | t     | t     | t     | t     | t     | t     | t     | t     |
| terpinen-4-ol                 | 0.29  | 0.59  | 0.51  | 0.51  | 0.36  | 0.25  | 0.25  | 0.59  |
| $\alpha$ -terpineol           | 0.53  | 0.91  | 1.00  | 0.96  | 0.59  | 0.58  | 0.53  | 1.00  |
| decanal                       | 0.04  | 0.09  | 0.04  | 0.03  | 0.05  | 0.06  | 0.03  | 0.09  |
| citronellol                   | t     | t     | t     | t     | t     | t     | t     | t     |
| nerol                         | 1.90  | 2.84  | 2.40  | 2.66  | 2.81  | 3.14  | 1.90  | 3.14  |
| neral                         | 6.64  | 7.72  | 7.69  | 8.13  | 7.68  | 10.78 | 6.64  | 10.78 |
| geraniol                      | 4.42  | 1.04  | 6.25  | 5.08  | 1.16  | 0.87  | 0.87  | 6.25  |
| linalyl acetate               | 0.35  | 0.29  | 0.33  | 0.36  | 0.42  | 0.31  | 0.31  | 0.42  |
| geranial                      | 9.89  | 10.45 | 10.97 | 11.67 | 9.89  | 14.07 | 9.87  | 14.07 |
| undecanal                     | 0.06  | 0.04  | 0.02  | 0.04  | 0.05  | 0.08  | 0.02  | 0.08  |
| citronellyl acetate           | 0.23  | 0.13  | 0.16  | 0.21  | 0.16  | 0.13  | 0.13  | 0.23  |
| neryl acetate                 | 6.74  | 4.62  | 3.75  | 5.89  | 4.96  | 5.57  | 3.75  | 6.74  |
| geranyl acetate               | 2.42  | 2.17  | 2.40  | 2.92  | 2.29  | 2.27  | 2.17  | 2.92  |
| $\beta$ -elemene              | 0.02  | t     | 0.03  | 0.03  | 0.01  | t     | t     | 0.03  |
| methyl N-methyl anthranilate  | t     | 0.03  | 0.39  | 0.24  | 0.11  | 0.03  | t     | 0.39  |
| cis- $\alpha$ -bergamotene    | t     | t     | t     | t     | t     | t     | t     | t     |
| $\beta$ -caryophyllene        | 1.17  | 1.54  | 1.16  | 0.96  | 0.80  | 0.60  | 0.60  | 1.54  |
| trans- $\alpha$ -bergamotene  | 0.09  | 0.20  | 0.07  | 0.06  | 0.04  | 0.03  | 0.03  | 0.20  |
| (Z)- $\beta$ -farnesene       | t     | 0.01  | 0.01  | t     | 0.02  | 0.03  | t     | 0.03  |

Table IV. Continued

| Compounds*   | 1     | 2     | 3     | 4     | 5     | 6     | Min   | Max   |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| $\alpha$ -humulene                                 | 0.11  | 0.13  | 0.11  | 0.09  | 0.07  | 0.06  | 0.06  | 0.13  |
| geranyl propanoate                                 | 0.04  | 0.04  | 0.04  | 0.04  | 0.03  | 0.04  | 0.03  | 0.04  |
| bicyclogermacrene                                  | 0.16  | 0.23  | 0.22  | 0.06  | 0.13  | 0.13  | 0.06  | 0.23  |
| (E,E)- $\alpha$ -farnesene                         | 0.06  | 0.07  | 0.06  | 0.03  | 0.10  | 0.14  | 0.03  | 0.14  |
| $\beta$ -bisabolene                                | 0.14  | 0.33  | 0.12  | 0.11  | 0.07  | 0.07  | 0.07  | 0.33  |
| $\delta$ -cadinene                                 | 0.04  | 0.05  | 0.03  | 0.03  | 0.02  | 0.02  | 0.02  | 0.05  |
| (E)-nerolidol                                      | 0.03  | 0.01  | 0.02  | 0.02  | 0.01  | 0.01  | 0.01  | 0.03  |
| spathulenol  | 0.08  | 0.05  | 0.03  | 0.09  | 0.01  | 0.02  | 0.01  | 0.09  |
| caryophyllene oxide                                | 0.09  | 0.09  | 0.06  | 0.14  | 0.04  | 0.05  | 0.04  | 0.14  |
| 2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol | 0.06  | 0.03  | 0.04  | 0.04  | 0.02  | 0.05  | 0.02  | 0.06  |
| campherenol  | 0.02  | 0.02  | 0.01  | 0.01  | 0.01  | 0.02  | 0.01  | 0.02  |
| $\alpha$ -bisabolol                                | 0.03  | 0.01  | 0.02  | 0.02  | 0.02  | 0.03  | 0.01  | 0.03  |
| monoterpene hydrocarbons                           | 58.54 | 59.32 | 53.63 | 51.82 | 60.62 | 53.45 | 51.82 | 60.62 |
| sesquiterpene hydrocarbons                         | 1.79  | 2.56  | 1.81  | 1.37  | 1.26  | 1.08  | 1.08  | 2.56  |
| aldehydes  | 17.70 | 19.04 | 19.61 | 20.74 | 18.90 | 26.66 | 17.70 | 26.66 |
| alcohols   | 9.14  | 6.75  | 14.23 | 12.58 | 6.30  | 5.93  | 6.75  | 14.23 |
| esters   | 9.78  | 7.28  | 7.07  | 9.66  | 7.97  | 8.35  | 7.07  | 9.68  |
| others   | 1.97  | 3.62  | 2.86  | 2.66  | 3.19  | 2.49  | 1.87  | 3.62  |

\* the compounds are listed according to the elution order on SE-52 columns, 60 m

2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol, campherenol and  $\alpha$ -bisabolol, which are absent in the other three *Citrus* petitgrains oils previously studied. It is of interest to note that these same three sesquiterpene alcohols are present also in the lemon peel oil. On the whole, lemon petitgrain oil better resembles the corresponding peel oil than the other *Citrus* petitgrain oils.

Our results offer a more detailed description of composition of Italian lemon petitgrain oil than those previously published (10,20,22). Even though the data agree closely with the previously published data, some differences are evident. For example, the ester contents of our oils were similar to those found by Goretti (22), but substantially different from those obtained by Di Giacomo et al. (20). Di Giacomo et al. did not find any neryl acetate, and they found only very small amounts of geranyl acetate and linalyl acetate, and more substantial amounts of  $\alpha$ -terpinyl acetate. This latter compound was not found in the lemon petitgrain oil samples analyzed in this work or in those analyzed by Goretti (22); however, it was also reported as being present in lemon petitgrain oil by Scora (12) and Malenderas et al. (19).

## References

1. L. Mondello, A. Cotroneo, P. Dugo and G. Dugo, *Italian Citrus petitgrain oils. Part I. Composition of bitter orange petitgrain oil*. J. Essent. Oil Res., **8**, 597-609 (1996).
2. L. Mondello, A. Basile, P. Previti and G. Dugo, *Italian Citrus petitgrain oils. Part II. Composition of mandarin petitgrain oil*. J. Essent. Oil Res., **9**, 255-266 (1997).
3. 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).
4. R. P. Adams, *Identification of essential oil components by gas chromatography-mass spectroscopy*. Allured Publ. Corp., Carol Stream, Illinois, USA (1995).
5. L. Mondello, P. Dugo, A. Basile, G. Dugo and K. D. Bartle, *Interactive use of linear retention indices, on polar and apolar columns, with a MS-library for reliable identification of complex mixtures*. J. Microcol. Sep., **7**, 581-591 (1995).
6. L. Peyron, *Petitgrain oils in perfumery*. Soap Perfum. Cosmet., **38**, 769-780 (1965).
7. J. A. Attaway, A. P. Pieringer and L. J. Barabas, *The origin of Citrus flavor components. I. The analysis of Citrus leaf oils using gas-liquid chromatography, thin layer chromatography and mass spectrometry*. Phytochemistry, **5**, 141-151 (1966).

8. G. Vernin, *Détection and évaluation de l'antranilate de méthyle et de ses dérivés méthyles dans différents échantillons naturels et de synthèse par C.C.M. et G.L.C.* La France et ses Parfums, **9**, 429-448 (1966).
9. S. Kamiyama, *Studies on the leaf oils of Citrus species. Part I. Composition of leaf oil from Citrus unshiu, Citrus natsudaikai, Citrus kokitsu and Citrus limon.* Agric. Biol. Chem., **31**, 1091-1096 (1967).
10. I. Calvarano, *Le essenze italiane di petitgrain. Nota I. I petitgrain di limone e mandarino.* Essenz. Deriv. Agrum., **37**, 27-54 (1967).
11. S. Kamiyama, *Studies on the leaf oil of Citrus species. II. An examination of the seasonal variation of leaf oil composition.* Bull. Brew. Sci., **14**, 43-47 (1968).
12. R. W. Scora, A. B. England and D. Chang, *Taxonomic affinities within the rough lemon group (Citrus jambhiri Lusb.) as aided by gas chromatography of their essential leaf oils.* Proc. First Int. Citrus Symp., (1968), **1**, 441-450, Riverside, Calif. 1969. In Reference 33.
13. A. Di Giacomo, *Gli oli essenziali degli agrumi.* Rivista Ital. EPPOS., Milano (1974).
14. M. J. Prager and M. A. Miskiewicz, *Gas chromatographic-mass spectrometric analysis, identification and detection of adulteration of perfumery products from bitter orange trees.* J. Assoc. Off. Anal. Chem., **64**, 131-138 (1981).
15. A. Baaliouamer and B. Y. Meklati, *Analyse qualitative par chromatographie gaz-liquide sur colonnes capillaires de verre de type WCOT des huiles essentielles d'écorce de fruit et de petitgrain du citronnier 'Eureka' cultivé en Algérie.* Fruits, **35**, 561-572 (1980).
16. E. D. Lund, P. E. Shaw and C. L. Kirkland, *Composition of Rough lemon leaf oil.* J. Agric. Food Chem., **29**, 490-494 (1981).
17. Y. S. Cheng and C. S. Lee, *Composition of leaf essential oils from ten Citrus species.* Proc. Natl. Sci. Council. B. Roc, **5**, 278-283 (1981). In reference 33.
18. E. D. Lund, P. E. Shaw and C. L. Kirkland, *Composition of Meyer lemon leaf oil.* J. Agric. Food Chem., **30**, 95-97 (1982).
19. F. A. Malenderas, A. J. Laeina, J. Flores and G. Guzman, *Aceites esenciales en hojas de variedades de limonero (Citrus limon L. Burm.).* An. Edafol. Agrobiol., **43**, 1161-1180 (1984). In Reference 33.
20. A. Di Giacomo, I. Calvarano, M. Calvarano and G. Belmusto, *Petitgrain di limone: composizione e tecnologia.* Essenz. Deriv. Agrum., **55**, 251-267 (1985).
21. A. Baaliouamer, B. Y. Meklati, D. Fraisse and C. Scharff, *Qualitative and quantitative analysis of petitgrain Eureka lemon essential oil by fused silica capillary column gas chromatography mass spectrometry.* J. Sci. Food Agric., **36**, 1145-1154 (1985).
22. G. Goretti, M. V. Russo, A. Liberti and G. Belmusto, *Valutazione gas cromatografica degli oli essenziali mediante campionamento dello spazio di testa.* Essenz. Deriv. Agrum., **56**, 345-358 (1986).
23. G. P. Cartoni, G. Goretti and M. V. Russo, *Capillary columns in series for the gas chromatographic analysis of essential oils.* Chromatographia, **23**, 790-795 (1987).
24. N. Adeishvili and L. G. Khrarebava, *Volatile components of lemon leaves.* Subtropicheskie Kul'tury, **6**, 63-66 (1987).
25. M. Wen, S. Xiao, H. Zhao, W. Ren and Y. Huang, *A study on the chemical components of the essential oil from leaves of Citrus limon (L.) Burm. f.* Tianran Chanwu Yanjiu Yu Kaifa, **1**(2), 18-22 (1989).
26. A. A. Nikolaishvili and L. G. Khrarebava, *Volatile compounds in leaves of Meyer lemon affected by red Citrus mite.* Subtropicheskie Kul'tury, **2**, 98-102 (1989).
27. F. G. Crescimanno, F. De Pasquale, M. A. Germanà, E. Bazan and E. Palazzolo, *Annual variation of essential oils in the leaves of four lemon (Citrus limon (L.) Burm. f.) cultivars.* Proc. Vith Int. Citrus Congress (Middle East, 1988), 583-588, Margraf Scientific Books, Weikersheim, Germany (1989).
28. S. G. Agarwal, S. Lal, R. K. Thappa, B. K. Kapahi and Y. K. Sarin, *Seasonal studies on Indian Citrus jambhiri Lush leaf oil - A new chemotype.* Flav. Fragr. J., **4**, 33-36 (1989).
29. S. Nemeo and E. Lund, *Leaf volatiles of mycorrhizal and nonmycorrhizal Citrus jambhiri Lush.* J. Essent. Oil Res., **2**, 287-297 (1990).
30. Z. K. Lin and Y. F. Hua, *Systematic evolutionary relation of chemical components of the essential oils from 11 taxa of Citrus leaves.* Acta Botanica Sinica, **34**, 133-139 (1992).
31. U. Kumar, B. Ram, A. K. Pant, K. G. Gupta and J. J. Brophy, *Volatile constituents of the distilled leaf and peel oils of Citrus limon Burm. cv. "Pant lemon-1,"* J. Essent. Oil Res., **4**, 643-644 (1992).
32. 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., **697**, 501-513 (1995).
33. B. M. Lawrence, *Progress in essential oils.* Perfum. Flavor., **18**(5), 43-68 (1993).