Phytochemistry 109 (2015) 111–124

Contents lists available at ScienceDirect

Phytochemistry

journal homepage: www.elsevier.com/locate/phytochem

# Comparative analysis of three Australian finger lime (*Citrus australasica*) cultivars: Identification of unique citrus chemotypes and new volatile molecules

Estelle Delort *, Alain Jaquier, Erik Decorzant, Christian Chapuis, Alessandro Casilli [1], Eric Frérot

*Firmenich SA, Corporate R&D Division, Geneva, Switzerland*

ARTICLE INFO

*Article history:*
Received 4 June 2014
Received in revised form 15 October 2014
Available online 11 November 2014

*Keywords:*
Alstonville
Judy's Everbearing
Durham's Emerald
6-Methyl-1-octylacetate
Isoascaridole
Citronellyl citronellate
1,2:5,6-Diepoxy-*p*-menthane
2,3-Epoxy-*p*-menthan-6-one
*p*-Menth-1-en-3-ol-6-one
1,2-Epoxy-*p*-methan-5-one
4-Hydroxy-6-isopropyl-3-methylcyclohex-2-enone

ABSTRACT

The volatile constituents of the peel of three cultivars of Australian finger lime (*Citrus australasica*) were investigated: Alstonville, Judy's Everbearing and Durham's Emerald. Both qualitative and quantitative GC–MS analyses were performed on their peel solvent extract. The results showed that the unique phenotypes of finger lime are also correlated to unique molecular compositions. Each cultivar revealed a different chemotype: limonene/sabinene for cv. Alstonville, limonene/citronellal/isomenthone for cv. Judy's Everbearing, and limonene/citronellal/ citronellol for cv. Durham's Emerald. To the best of our knowledge, these chemotypes have never been reported in any other citrus species. Furthermore, the amounts of some volatile constituents (γ-terpinene, α-pinene, β-pinene, citral), which are generally the major constituents besides limonene in lime species, were surprisingly low in the three cultivars. Comparative GC–MS analysis also showed that some volatile molecules tended to be specific to one cultivar and could therefore be considered as markers. Moreover six molecules were reported for the first time in a citrus extract and confirmed by synthesis. Heart-cutting enantioselective two-dimensional GC–MS was performed to determine the enantiomeric distribution of the major chiral constituents. The combined data on three finger lime cultivars gives evidence of their divergence from other citrus species.



## 1. Introduction

The Australian finger lime *Citrus australasica* is one of five native citrus species endemic to Australia. It is native to the rainforests of South East Queensland and Northern New South Wales. Finger limes are genetically diverse in shape, peel and pulp color, size and taste. All have in common the caviar-like pulp, which makes this fruit unique in the genus *Citrus*. Because of the increasing demand for finger limes, initially from the restaurant trade, some finger lime cultivars were selected from the wild and are currently commercially grown in Australia. For the time being, one finger lime variety has been registered with Plant Breeders' Rights (*C. australasica var. sanguinea*, also called "Rainforest Pearl"), and seven finger lime cultivars have been registered with the Australian Cultivar Registration Authority: Alstonville, Blunobia Pink Crystal, Durham's Emerald, Judy's Everbearing, Pink Ice, Byron Sunrise and Jali Red. In our previous study (Delort and Jaquier, 2009), the volatile composition of the peel extract of Australian finger lime of unknown cultivar was investigated by gas chromatography–mass spectrometry (GC–MS). The work highlighted a unique composition (limonene/isomenthone/citronellal). Six new terpenyl esters were identified and their structures confirmed by chemical synthesis. In the present study, three finger lime cultivars, namely Alstonville, Judy's Everbearing and Durham's Emerald, were investigated for the first time with the aim of comparing, both qualitatively and quantitatively, their volatile composition and identifying the molecular markers of the cultivars.

## 2. Results and discussion

### 2.1. Comparison of phenotypic and organoleptic characters of fresh fruits

As shown in Fig. 1, the different cultivars investigated in the present study were relatively close in terms of shape and size, but differed in their peel and pulp color. The cultivar Alstonville

* Corresponding author at: Firmenich SA, Corporate R&D Division, Route des Jeunes 1, CH-1211 Geneva 8, Switzerland. Tel.: +41 22 780 35 32; fax: +41 22 780 33 34.
*E-mail address:* estelle.delort@firmenich.com (E. Delort).
[1] Present address: Universidade Federal do Rio de Janeiro, Instituto de Química, Ilha do Fundão, Rio de Janeiro, RJ 21941-909, Brazil.

http://dx.doi.org/10.1016/j.phytochem.2014.10.023
0031-9422/

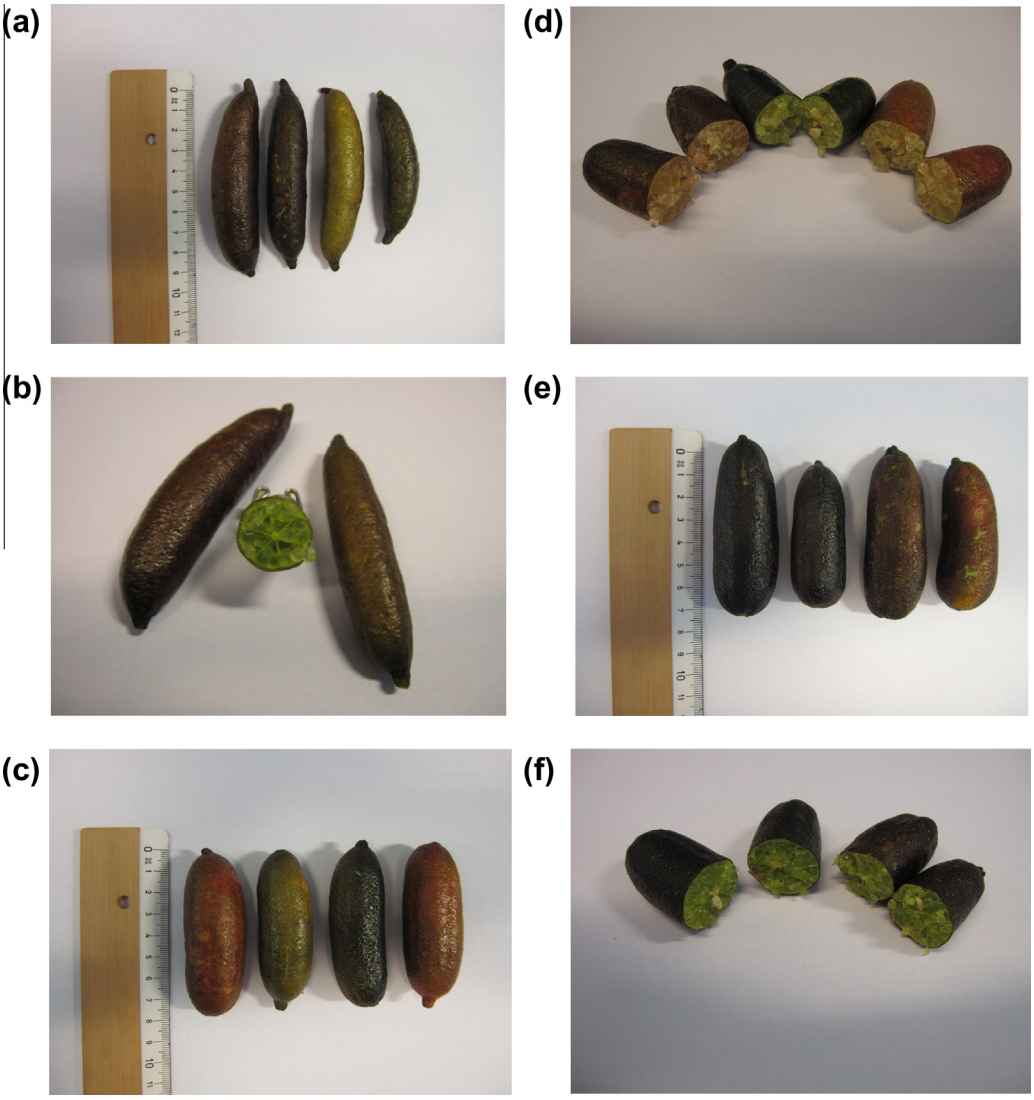



**Fig. 1.** Finger lime fruits investigated in the present study. (a, b) cv. Alstonville; (c,d) cv. Judy's Everbearing; (e,f) cv. Durham's Emerald (Photos: A. Jaquier, Firmenich S.A.).

was characterized by a pale to dark green peel and a pale green pulp. Judy's Everbearing fruits have a reddish to green and dark green peel with green to yellow rosy pulp. Durham's Emerald citrus has a green to dark green peel with green pulp, relatively close to the cultivar Alstonville, but with a size and shape closer to Judy's Everbearing.

The peel aroma and the juice taste of fresh fruits were evaluated by perfumers and flavorists, all experts in citrus. All of these experts noticed the organoleptic uniqueness of the peel. Compared to common lime varieties, namely Key lime (*Citrus aurantifolia*) and Tahiti lime (*Citrus latifolia*), the three cultivars were lime-like, but greener and less floral. Interestingly, the odor nuances of the peel were quite different from one cultivar to another. The peel of Alstonville was greener, more terpenic (myrcene-like, sabinene-like) and slightly minty. A clear citronellal-like character reminiscent of citronella was found in the peel of Judy's Everbearing. Its profile was also terpenic, but fresher, more minty-like, and associated with some spicy and fruity notes. The citronellal-like character was also perceived in Durham's Emerald, but it was distinctive for its woody lime character with phenolic (*p*-vinylguaiacol-like) and slightly smoky notes. The juice of these cultivars was less unique, being acidic and in-between lemon and lime juice with the following nuances: bitter and slightly resinous for Alstonville, green and citronellal-like for Judy's Everbearing, and citronellal-like with turpentine and vegetable notes for Durham's Emerald.

### 2.2. GC–MS comparative analysis of peel solvent extracts

The volatile composition of the peel extracts was analyzed by GC–MS. To perform a comparative analysis, the solvent extraction was repeated under strictly identical conditions for the three cultivars and the reported analytical procedure herein was followed for each peel extract. GC–MS files were first processed manually by using the MSD Chemstation software (Agilent). The deconvolution software AMDIS was then used as a support tool for the identification of additional trace compounds that were not easily detected manually because of coelutions. The additional identifications given by AMDIS, as well as the absence of molecules in some cultivars, were confirmed or rejected by using manual interpretation and extract ion mode. Then the percentages of the volatile components were determined by manual integration of GC-flame ionization detector (FID) areas with the use of an internal standard and the application of correction factors as reported earlier (de Saint Laumer et al., 2010). This meticulous analytical process allowed us to obtain a qualitative and quantitative comparative analysis of the peel extract of the three cultivars, as given in Table 1.

**Table 1**
Volatile composition of finger lime solvent peel extracts.

| LRI $_{SPB-1}$ | Name | A % FID | JE % FID | DE % FID | Ident. |
|---|---|---|---|---|---|
| 617 | (*E*)-2-Butenal | tr* | tr* | tr* | LRI, MS |
| 627 | 3-Methylbutanal | tr* | tr* | – | LRI, MS |
| 636 | 2-Methylbutanal | tr* | – | – | LRI, MS |
| 654 | 1-Penten-3-one | tr* | tr | tr | LRI, MS |
| 657 | 1-Penten-3-ol | tr* | tr* | tr | LRI, MS |
| 668 | 3-Pentanone | tr* | tr* | tr | LRI, MS |
| 673 | 3-Hydroxy-2-butanone | – | tr* | tr* | LRI, MS |
| 716 | Tentative: (*Z*)-2-pentenal | tr* | tr | tr | MS |
| 725 | (*E*)-2-pentenal | tr* | tr | tr | LRI, MS |
| 746 | 1-Pentanol | – | tr | tr* | LRI, MS |
| 749 | (*Z*)-2-Penten-1-ol | tr* | tr | tr | LRI, MS |
| 753 | 3-methyl-2-butenal | tr* | tr* | tr* | LRI, MS |
| 773 | (*Z*)-3-Hexenal | tr | tr | tr | LRI, MS |
| 775 | Hexanal | tr | tr | tr | LRI, MS |
| 819 | (*Z*)-2-Hexenal | tr | tr | – | LRI, MS |
| 826 | (*E*)-2-Hexenal | tr | tr | tr | LRI, MS |
| 837 | (*Z*)-3-Hexen-1-ol | tr | tr | tr | LRI, MS |
| 847 | (*Z*)-2-Hexen-1-ol | – | tr* | tr* | LRI, MS |
| 850 | 1-Hexanol | tr | tr | – | LRI, MS |
| 861 | 2-Methylbutyl acetate | tr* | – | – | LRI, MS |
| 879 | Heptanal | tr* | – | tr* | LRI, MS |
| 880 | (*E*,*E*)-2,4-Hexadienal | tr* | tr* | – | LRI, MS |
| 903 | Unknown[b] | – | tr | – | |
| 927 | α-Thujene | 0.12 | tr | 0.01 | LRI, MS |
| 933 | Benzaldehyde | tr | tr* | tr* | LRI, MS |
| 936 | α-Pinene | 0.55 | 0.31 | 0.98 | LRI, MS |
| 948 | α-Fenchene | tr | tr | tr | LRI, MS |
| 950 | Camphene | tr | tr | tr | LRI, MS |
| 971 | Sabinene | 20.55 | 0.16 | 0.58 | LRI, MS |
| 977 | β-Pinene | 0.32 | tr | 0.03 | LRI, MS |
| 983 | Myrcene | 1.50 | 1.52 | 1.54 | LRI, MS |
| 986 | (*Z*)-3-Hexenyl acetate | tr* | tr | – | LRI, MS |
| 993 | Hexyl acetate | tr | – | tr* | LRI, MS |
| 995 | 2-Carene | – | tr | – | LRI, MS |
| 1001 | α-Phellandrene | 0.01 | 0.25 | 2.00 | LRI, MS |
| 1009 | δ-3-Carene | 0.09 | 0.19 | 0.36 | LRI, MS |
| 1012 | Phenylacetaldehyde | tr | tr | tr* | LRI, MS |
| 1013 | α-Terpinene | tr | tr* | tr | LRI, MS |
| 1016 | p-Cymene | tr | 0.16 | 0.32 | LRI, MS |
| 1026 | β-Phellandrene | 0.18[a] | 1.79[a] | 4.74[a] | LRI, MS |
| 1028 | Eucalyptol | tr[a] | – | – | LRI, MS |
| 1028 | Limonene | 61.66 | 64.38 | 66.27 | LRI, MS |
| 1031 | (*Z*)-β-Ocimene | 0.15 | 0.35 | 0.73 | LRI, MS |
| 1036 | 2,6-Dimethyl-5-heptenal | – | tr | tr | LRI, MS |
| 1039 | (*E*)-β-Ocimene | 0.21 | 0.08 | 0.19 | LRI, MS |
| 1053 | γ-Terpinene | 0.08 | 0.01 | 0.01 | LRI, MS |
| 1056 | 6-methyloctanal | tr | – | tr | LRI, MS |
| 1059 | *trans*-Sabinene hydrate | tr | tr | tr | LRI, MS |
| 1062 | *cis*-Linalyl oxide (furanoid) | – | tr | – | LRI, MS |
| 1073 | Methyl benzoate | tr* | tr | tr* | LRI, MS |
| 1076 | *trans*-Linalyl oxide (furanoid) | – | tr | tr* | LRI, MS |
| 1077 | p-Cymenene | tr | tr* | tr* | LRI, MS |
| 1084 | α-Terpinolene | 0.02 | 0.03 | 0.10 | LRI, MS |
| 1085 | Linalool | 0.03 | 1.94 | 0.21 | LRI, MS |
| 1088 | *cis*-Sabinene hydrate | tr | tr* | – | LRI, MS |
| 1092 | Heptyl acetate | tr | – | – | LRI, MS |
| 1099 | *cis*-Rose oxide | – | tr | tr* | LRI, MS |
| 1103 | Tentative: 1,3,8-*p*-menthatriene | tr | tr* | tr* | LRI, MS |
| 1108 | 2,6-Dimethyl-5-hepten-1-ol | – | – | tr* | LRI, MS |
| 1108 | *trans*-2,8-p-Menthadien-1-ol | tr | tr | – | LRI, MS |
| 1113 | *trans*-*p*-Menth-2-en-1-ol | – | tr | tr | LRI, MS |
| 1117 | *trans*-Rose oxide | – | tr* | tr | LRI, MS |
| 1119 | (4*E*,6*Z*)-Alloocimene | tr* | tr | tr | LRI, MS |
| 1122 | *cis*-1,2-Epoxy-8-*p*-menthene | tr* | tr* | tr | LRI, MS |
| 1126 | *trans*-1,2-Epoxy-8-*p*-menthene | tr | tr* | tr | LRI, MS |
| 1129 | *cis*-*p*-Menth-2-en-1-ol | – | tr | tr | LRI, MS |
| 1135 | Citronellal | – | 9.04 | 9.26 | LRI, MS |
| 1135 | Isopulegol | – | tr* | tr* | LRI, MS |
| 1136 | Neoisopulegol | – | tr* | tr* | LRI, MS |
| 1143 | Menthone | – | tr* | tr[a] | LRI, MS |
| 1144 | 4-Isopropenyl-2-cyclohexen-1-one | tr* | tr* | tr* | LRI, MS |
| 1148 | 4-Methylnonanal | – | – | tr | LRI, MS |
| 1149 | Ethyl benzoate | tr* | – | – | LRI, MS |
| 1151 | Isomenthone | – | 7.29 | 0.03 | LRI, MS |

(*continued on next page*)

**Table 1** (*continued*)

| LRI $_{SPB-1}$ | Name | A % FID | JE % FID | DE % FID | Ident. |
|---|---|---|---|---|---|
| 1152 | Phenylacetaldehyde (*E*)-O-methyl oxime | tr | tr | tr | LRI, MS |
| 1165 | Phenylacetaldehyde (*Z*)-O-methyl oxime | tr* | tr | tr | LRI, MS |
| 1159 | *trans*-Isopulegone | – | tr | tr | LRI, MS |
| 1159 | Tentative: thujenol | – | tr | tr | MS |
| 1164 | Tentative: 4-isopropyl-2-cyclohexen-1-one | – | tr | tr | LRI, MS |
| 1165 | *p*-Cymen-8-ol | tr* | tr | – | LRI, MS |
| 1169 | 4-Terpineol | 0.16 | 0.03 | 0.03 | LRI, MS |
| 1174 | *trans*-1(7),8-p-Menthadien-2-ol | tr | tr | tr | LRI, MS |
| 1176 | Methyl salicylate | tr* | – | tr | LRI, MS |
| 1178 | Neoisomenthol | – | 0.72[a] | – | LRI, MS |
| 1178 | Isomenthol | – | tr[a] | – | LRI, MS |
| 1179 | α-Terpineol | tr* | 0.21 | tr | LRI, MS |
| 1182 | 8-*p*-Menthen-2-ol | – | – | tr | LRI, MS |
| 1185 | Decanal | tr | tr* | tr | LRI, MS |
| 1187 | *cis*-Piperitol | – | tr | – | LRI, MS |
| 1191 | Octyl acetate | 0.10 | – | – | LRI, MS |
| 1195 | *trans*-Piperitol | – | tr | – | LRI, MS |
| 1199 | 4-Isopropylphenol | – | tr | tr | LRI, MS |
| 1202 | *trans*-Carveol | tr* | tr* | tr* | LRI, MS |
| 1206 | *cis*-1(7)-8-*p*-Menthadien-2-ol | tr | – | – | LRI, MS |
| 1207 | Unknown[c] | tr | tr | – | |
| 1210 | Citronellol | – | 2.00 | 5.18 | LRI, MS |
| 1211 | *trans*-Sabinene acetate | 0.43 | – | – | LRI, MS |
| 1216 | (*Z*)-3-Hexenyl 2-methylbutyrate | tr* | tr | tr* | LRI, MS |
| 1218 | neral | tr* | – | tr* | LRI, MS |
| 1222 | 4-Isopropylbenzaldehyde (cuminaldehyde) | – | – | tr* | LRI, MS |
| 1223 | Carvone | tr | tr | tr | LRI, MS |
| 1228 | Methyl thymol ether | – | – | tr* | LRI, MS |
| 1235 | Piperitone | tr | 0.96 | tr | LRI, MS |
| 1239 | (*E*)-2-Decenal | – | tr* | tr* | LRI, MS |
| 1240 | Linalyl acetate | tr | – | – | LRI, MS |
| 1243 | *cis*-Sabinene acetate | 0.25 | – | – | LRI, MS |
| 1245 | geranial | – | tr | tr | LRI, MS |
| 1247 | Isopiperitenone | tr* | – | tr* | LRI, MS |
| 1255 | Perillic aldehyde | tr | tr | tr | LRI, MS |
| 1259 | 1,2-Epoxy-*p*-menthan-5-one **7** | tr | tr | tr | LRI, MS |
| 1260 | 8-Methyldecanal | tr | – | tr | LRI, MS |
| 1263 | 6-Methyloctyl acetate **1** | tr* | – | – | LRI, MS |
| 1265 | Thymol | tr | – | – | LRI, MS |
| 1276 | Carvacrol | tr | tr | tr | LRI, MS |
| 1277 | Bornyl acetate | tr | – | – | LRI, MS |
| 1278 | *p*-Vinyl guaiacol | – | tr | tr | LRI, MS |
| 1283 | Citronellic acid | – | tr | tr | LRI, MS |
| 1291 | Terpinen-4-ol acetate | tr | – | – | LRI, MS |
| 1291 | Unknown[d] | tr | tr | – | |
| 1291 | *cis*-isoascaridole *cis*-**3a** | tr | – | tr* | LRI, MS |
| 1291 | Tentative: 2,6-dimethyl-7-octen-2,6-diol (2-hydroxydihydrolinalool) | – | tr | – | MS |
| 1297 | 2,3-Epoxy-*p*-menthan-6-one **5a** | – | 0.19[a] | 0.40[a] | LRI, MS |
| 1297 | Tentative: 3,7-dimethyl-5-octen-1,7-diol | – | 0.02[a] | 0.04[a] | MS |
| 1297 | Tentative: 3-oxo-*p*-menthen-1-en-7-al | – | – | tr | $LRI_{lit}$, MS |
| 1301 | 2,3-Epoxy-*p*-menthan-6-one **5b** | – | tr | 0.15 | LRI, MS |
| 1311 | Tentative: *p*-menthane-3,8-diol isomer 1 (8-hydroxymenthol) | – | 0.19 | 0.21 | MS |
| 1313 | 8-*p*-Menthene-1,2-diol isomer 1 | – | tr | tr* | LRI, MS |
| 1321 | Trans-piperitol acetate | tr | – | – | LRI, MS |
| 1324 | Citronellyl acetate | – | 0.04[a] | 0.04[a] | LRI, MS |
| 1324 | 1,2:5,6-Diepoxy-*p*-menthane **4a** | – | 0.20[a] | 0.20[a] | LRI, MS |
| 1324 | Unknown[e] | – | 0.01[a] | – | |
| 1324 | Tentative: *p*-menthane-3,8-diol isomer 2 | – | 0.01[a] | – | MS |
| 1331 | Tentative: 2-phenyl-2-hydroxypropanal | – | – | tr | MS |
| 1331 | 1,2:5,6-Diepoxy-*p*-menthane **4b** | – | 0.15[a] | 0.15[a] | LRI, MS |
| 1331 | Tentative: *p*-menthane-3,8-diol | – | tr | 0.05[a] | MS |
| 1334 | Eugenol | – | tr | – | LRI, MS |
| 1338 | α-Terpenyl acetate | 0.66 | tr | tr* | LRI, MS |
| 1341 | Neryl acetate | tr* | – | – | LRI, MS |
| 1345 | δ-Elemene | 0.61 | 0.58 | 0.16 | LRI, MS |
| 1358 | Geranyl acetate | tr* | – | – | LRI, MS |
| 1361 | (*Z*)-3-Hexenyl hexanoate | tr* | – | tr* | LRI, MS |
| 1362 | Vanillin | tr | tr | tr | LRI, MS |
| 1371 | Methyleugenol | – | tr | tr | LRI, MS |
| 1376 | *cis*-*p*-Menth-1-en-3-ol-6-one **6a** | – | tr | tr | LRI, MS |
| 1380 | *trans*-*p*-Menth-1-en-3-ol-6-one **6b** | – | tr | tr | LRI, MS |
| 1386 | (*E*)-7-Tetradecene | tr* | tr* | tr* | LRI, MS |
| 1389 | Decyl acetate | tr* | – | – | LRI, MS |
| 1389 | Dodecanal | – | tr* | tr* | LRI, MS |
| 1389 | 4-Hydroxypiperitone | – | tr | – | LRI, MS |

**Table 1** (*continued*)

| LRI $_{SPB-1}$ | Name | A % FID | JE % FID | DE % FID | Ident. |
|---|---|---|---|---|---|
| 1398 | β-Elemene | tr | tr | tr | LRI, MS |
| 1413 | Perillic acetate | tr | – | – | LRI, MS |
| 1424 | Citronellyl propanoate | – | tr | tr* | LRI, MS |
| 1424 | (*E*)-Isoeugenol | – | – | tr* | LRI, MS |
| 1435 | trans-β-caryophyllene | tr | 0.38 | tr* | LRI, MS |
| 1438 | γ-Elemene | tr* | – | tr | LRI, MS |
| 1441 | *trans*-α-Bergamotene | – | – | tr | LRI, MS |
| 1446 | (*E*)-2-Dodecenal | – | – | tr* | LRI, MS |
| 1448 | β-Farnesene | – | – | tr | LRI, MS |
| 1450 | Geranyl propanoate | – | tr | – | LRI, MS |
| 1463 | Methyl isoeugenol | – | – | tr* | LRI, MS |
| 1468 | α-Humulene | 0.09 | 0.60 | tr* | LRI, MS |
| 1492 | Germacrene-D | 0.20 | 0.37 | 0.90 | LRI, MS |
| 1497 | (*E*,*E*)-α-Farnesene | tr | – | tr* | LRI, MS |
| 1498 | *cis*-α-Bisabolene | – | – | 0.74 | LRI, MS |
| 1508 | Bicyclogermacrene | 3.09 | 0.84 | 1.80 | LRI, MS |
| 1514 | Bornyl 3-methylbutanoate | – | tr | – | LRI, MS |
| 1517 | Elemicin | – | tr | – | LRI, MS |
| 1526 | δ-Cadinene | tr | – | tr* | LRI, MS |
| 1530 | (*Z*)-9-Dodecen-12-olide (yuzu lactone) | – | tr | tr | LRI, MS |
| 1538 | *trans*-α-Bisabolene | – | – | tr | LRI, MS |
| 1552 | (*Z*)-3-Hexenyl benzoate | tr | – | tr* | LRI, MS |
| 1559 | Hexyl benzoate | tr* | – | tr* | LRI, MS |
| 1560 | Citronellyl 2-methylbutanoate | – | tr | tr | LRI, MS |
| 1563 | Citronellyl 3-methylbutanoate | – | tr | – | LRI, MS |
| 1571 | Germacrene-B | – | tr | 0.12 | LRI, MS |
| 1582 | Spathulenol | 0.36 | 0.13 | 0.20 | LRI, MS |
| 1586 | geranyl 3-methylbutanoate | – | tr | – | LRI, MS |
| 1594 | Globulol | tr | – | – | LRI, MS |
| 1609 | Benzophenone | – | tr* | tr* | LRI, MS |
| 1627 | Tentative: germacrol | – | – | tr | MS |
| 1627 | Unknown[f] | 0.05[a] | tr | tr | |
| 1627 | Tentative: guaia-10(14),6-dien-4-ol | 0.05[a] | tr | tr | MS |
| 1627 | Tentative: valenca-1,9-dien-11-ol | – | tr | – | MS |
| 1647 | Citronellyl 3-methyl-2-butenoate | – | – | tr* | LRI, MS |
| 1655 | α-Cadinol | tr | tr | – | LRI, MS |
| 1676 | α-Bisabolol | – | – | tr* | LRI, MS |
| 1747 | Unknown[g] | 0.53 | 0.32 | tr | |
| 1837 | Neophytadiene | tr* | 0.22 | 0.23 | LRI, MS |
| 1879 | Tentative: neophytadiene isomer | tr | tr | tr* | MS |
| 1906 | Tentative: 8,13-epoxy-15,16-dinorlabd-12-ene | tr | tr | tr* | MS |
| 1909 | Citronellyl benzoate | – | tr | tr | LRI, MS |
| 1917 | 6,7-Dimethoxy-2H-chromen-2-one | – | tr | tr | LRI, MS |
| 1934 | Hexadecanoic acid | – | tr | tr | LRI, MS |
| 1936 | Sinapyl alcohol | tr | tr | tr | LRI, MS |
| 2022 | Citronellyl citronellate **2** | – | tr | tr | LRI, MS |
| 2057 | Unknown[h] | 0.21 | – | – | |
| 2101 | *trans*-Phytol | – | tr | tr* | LRI, MS |
| 2294 | Citronellyl decanoate | – | tr | tr* | LRI, MS |
| 2118 | Unknown[i] | – | 0.19 | – | |
| 2426 | Oxypeucedanin | 5.67 | 0.16 | – | LRI, MS |
| 2493 | Tentative: citronellyl dodecanoate | – | – | tr* | MS |
| 2643 | oxypeucedanin hydrate | tr | – | – | LRI, MS |

**A**: cv. Alstonville; **JE**: cv. Judy's Everbearing; **DE**: cv. Durham's Emerald. FID: flame ionization detector; LRI: linear retention index; tr: trace (<0.01%). tr*: Trace compound identified with AMDIS. $LRI_{lit}$: LRI obtained from the literature.

[a] Quantified on polar phase.

[b] *m*/*z* (%) = 140(19),125(10),112(9),111(67), 97(29), 82(51),81(20),79(12), 70(19),69(62),68(9), 67(89),59(23),55(16),53(13),**43**(**100**),41(36).

[c] *m*/*z* (%)=151(5),150(30),135(32),122(23),108(63),107(76), 95(20),94(14),93(54),91(17),82(21),81(47),80(33),**79**(**100**),77(18), 69(27),68(24),67(55),66(11),58(13), 55(21),54(36),53(64),52(8),51(13),43(10),41(65).

[d] *m*/*z*(%) = 137(36),134(34),123(11),121(42),119(30),110(14),109(69),107(11),105 (26),95(33),94(76),93(28),92(16),91(86),84(16),82(10),81(36),**79**(**100**),78(13),77(39),71 (13),69(20),67(23),65(13),55(17),53(16),51(12),43(50),41(34).

[e] *m*/*z*(%) = 168(7),117(12),97(10),**82**(**100**),79(13),71(71),68(10),67(46),58(14),55(12),50(10),45(11),44(28),43(75),41(18).

[f] *m*/*z* (%) = 202(37),187(26),162(22),159(87),149(25),147(31),145(32),135(21),134(19),133(62), 131(55),121(29),120(31),119(36),117(39),109(55),107(52),106(22), 105(77),95(33),93(57),**91**(**100**), 83(20),82(38),81(54),79(65),77(45),69(50),67(74),65(23),59(33),55(61),53(36),44(22),43(47), 41(91).

[g] *m*/*z* (%) = 202(25),159(56),147(21),145(31),133(62), 131(46), 123(26),121(24),120(23),119(34), 117(35),109(25), 107(43),105(81), 95(51),93(52),**91**(**100**), 82(32),81(45), 79(65), 77(51),69(36), 67(61),65(23),55(48),53(33),43(34),41(79).

[h] *m*/*z*(%) = 253(11),252(77),209(22),194(43),193(20),192(55),177(21),161(40),154(14),**149**(**100**),133(27),131(31),121(26),119(21),118(23),106(43),105(30),103(25), 91(53),89(25),78(42),77(48),65(22),60(36),51(21),45(49),43(94).

[i] *m*/*z*(%) = 231(10),230(82),216(16),**215**(**100**),213(12),201(15),187(78),176(11),175(90), 147(19),144(18),141(15),131(22),128(14),115(26),100(13),91(15),77(20),69(13),65(13),51(16),41(19).

As shown in Fig. 2, the volatile compositions of the three cultivars were very different. Each cultivar revealed a unique chemotype: limonene/sabinene for Alstonville, limonene/citronellal/isomenthone for Judy's Everbearing and limonene/citronellal/citronellol for Durham's Emerald. Recently, Lota et al. (2002) compared the chemical composition of peel and leaf oil of 43 lemon and lime

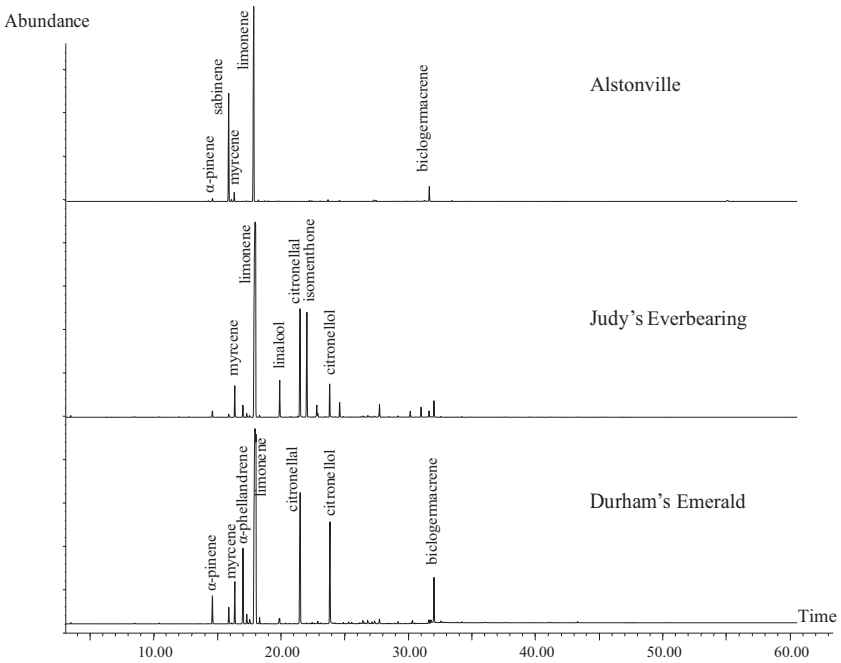



**Fig. 2.** GC profile of the peel solvent extract of the three cultivars on a non-polar column.

**Table 2**
Enantiomeric distribution obtained by enantioselective heart-cut 2D-GC–MS.

| | Alstonville | Judy's Everbearing | Durham's Emerald |
|---|---|---|---|
| Limonene (*R*)-(+)/(*S*)-(−) | 99.4/0.6 | 98.9/1.1 | 96.7/3.3 |
| Citronellal (*R*)-(+)/(*S*)-(−) | nd | 96.7/3.3 | 95.6/4.4 |
| Citronellol (*R*)-(+)/(*S*)-(−) | nd | 97.2/2.8 | 95.8/4.2 |
| Sabinene (*R*)-(+)/(*S*)-(−) | 5.3/94.7 | nd | nd |
| α-Phellandrene (*R*)-(−)/(*S*)-(+) | nd | 0/100 | 0/100 |

nd: Not determined due to their low abundance in the extract.

species/cultivars, all cultivated in similar environmental conditions. Results showed the existence of three chemotypes for lime peel extracts: limonene, limonene/β-pinene, and limonene/β-pinene/γ-terpinene. In that study, *C. australasica* (cultivar not mentioned) showed a unique pattern, with sabinene as the second major volatile constituent after limonene. To the best of our knowledge, the chemotypes of the three finger lime cultivars of the present study are not only unique in lime species, but also in the genus *Citrus*. Moreover, the three peel extracts had in common a surprisingly low amount of γ-terpinene (0.10%), α-pinene (<1.00%), β-pinene (<0.40%), neral (<0.01%) and geranial (<0.01%), which are generally the major volatile constituents of lime peel extracts besides limonene (Lota et al., 2002).

Comparing the three cultivars qualitatively and quantitatively highlighted the similarities and differences between them. Alstonville was characterized by the absence of citronellal and citronellol, both found in high amounts in the two other cultivars. On the other hand, its peel extract contained trace amounts of several aliphatic (heptyl acetate, octyl acetate) and terpenic acetates (linalyl acetate, *trans*- and *cis*-sabinene acetate, bornyl acetate), which were not detected in the two other cultivars. Such high amounts of various acetates, which has been reported in kumquat peel (Choi, 2000), is generally not common in lime. The use of AMDIS and extract ion mode on polar stationary phase allowed us to identify unambiguously eucalyptol (1,8-cineole) in this cultivar, which was absent in the other two cultivars. Eucalyptol, together with carvone, may contribute to the minty odor of the peel, while the higher amount of monoterpenes (e.g. sabinene, β-pinene, α-thujene) may explain the terpenic and green character.

Judy's Everbearing was characterized by an unusually high amount of citronellal and isomenthone. Many derivatives of these molecules were also identified: citronellyl acetate, citronellyl propanoate, citronellyl 2-methylbutanoate, citronellyl 3-methylbutanoate, citronellyl benzoate, citronellyl citronellate, citronellyl decanoate, neoisomenthol, isomenthol and menthone. Such a high amount of menthone derivatives is common in mint but not in citrus. They are probably responsible for the fresh minty odor perceived in the peel, while citronellal and citronellyl esters provide the citronella character and the fruity notes, respectively. Compared to those in the other cultivars, linalool and piperitone were also found in higher amounts. The spicy and slightly smoky notes of the peel may be explained by the high number of phenols in this cultivar: eugenol, carvacrol, 4-isopropylphenol, *p*-vinyl guaiacol and methyl eugenol.

Durham's Emerald had a profile that was closer to Judy's Everbearing than to Alstonville, with a high amount of citronellal and citronellol. However, both cultivars differed by the amount of some constituents like isomenthone, found in only trace amount in Durham's Emerald, and α-phellandrene, found in higher amount in Durham's Emerald. Several molecules were found only in this cultivar, in particular some aldehydes (4-methylnonanal, 4-isopropylbenzaldehyde, (*E*)-2-dodecenal), phenols (methyl isoeugenol,

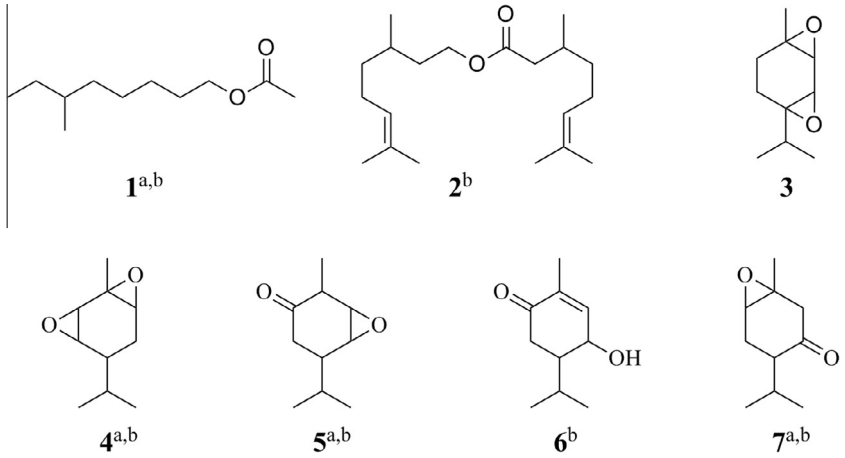



**Fig. 3.** Molecules newly identified in citrus. [a]Reported for the first time in a natural product; [b]reported for the first time in citrus.

(*E*)-isoeugenol), and sesquiterpenes (*trans*-α-bergamotene, *cis*-and *trans*-α-bisabolene). These sesquiterpenes are typical in lime and may provide the woody lime character perceived in the fresh peel of this cultivar.

### 2.3. Chirality of major components

The enantiomeric distribution of the major compounds (limonene, sabinene, citronellol and citronellal) was determined by using heart-cutting enantioselective two-dimensional GC–MS. The principle was to transfer the compound of interest during its elution in the first dimension, a non-polar phase, into a second chiral column. Compared to the monodimensional approach, this multidimensional approach has the advantage of reducing coelutions that may lead to wrong enantiomeric ratios. The results are given in Table 2. The chirality of limonene was the same as that already reported in citrus oils (Mondello et al., 2011), with (*S*)-(−) as the major isomer. In Alstonville, the major enantiomer of sabinene was (*S*)-(−), as already reported in Persian lime and Key lime by the same authors. However, for citronellal, the (*R*)-(+) was the major isomer, which is not common in lime. Indeed, the major enantiomer of citronellal was reported to be (*S*)-(−) in Persian lime and Key lime, as well as in other citrus in which it occurs at a significant level, such as bergamot, kaffir lime and lemon (Mondello et al., 2011). The (*R*)-(+) is generally the major isomer in citronella oil (Nhu-Trang et al., 2006), as well as in tangerine, sweet orange, grapefruit and mandarin (Mondello et al., 2011).

### 2.4. Identification of new molecules

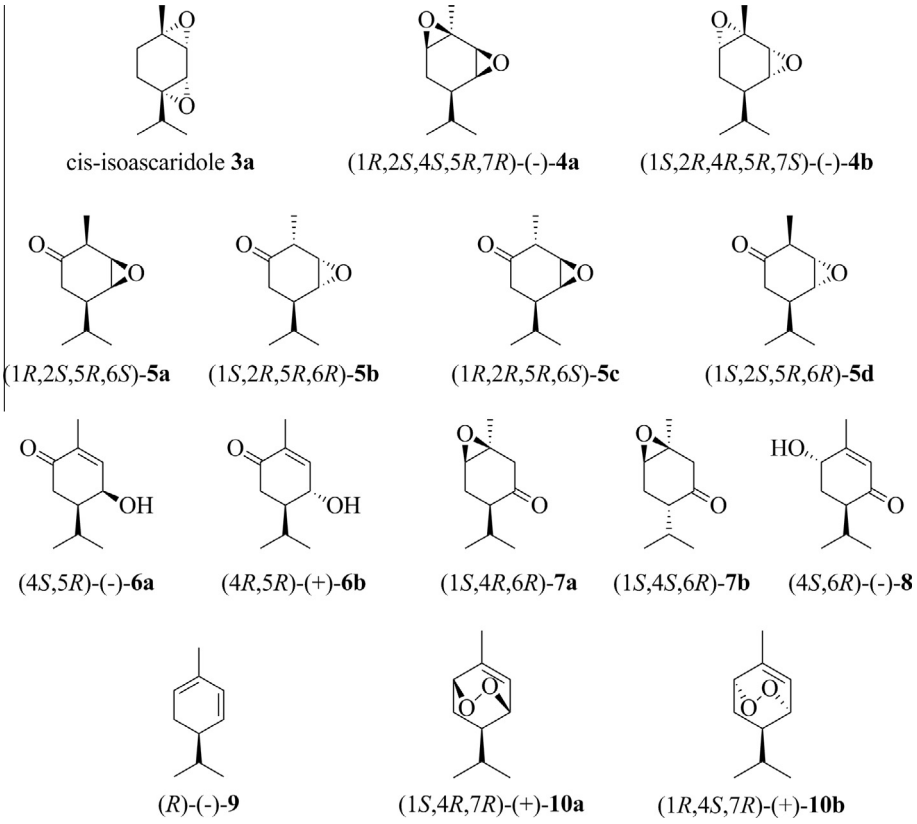
As reported in Table 1, several peaks detected in trace amounts remained unknown after GC–MS analysis. Although identification of the structure of unknowns based solely on mass spectra interpretation is challenging, seven unknowns could be elucidated during this work via high resolution mass spectra interpretation. Their structures were confirmed after comparison of their MS and LRIs with those of the seven corresponding freshly prepared standards (Fig. 3). To the best of our knowledge, six of them had never been found in a citrus extract, and four of them are reported for the first time in a natural product.

6-Methyloctyl acetate **1** (LRI 1263) was detected in the peel extract of the cultivar Alstonville and identified here for the first time in a natural product. The occurrence in citrus was not surprising, as its corresponding aldehyde was also found in trace amounts in the same extract and was already known in yuzu (Tajima et al., 1990) and orange peel oil (Widder et al., 2003). Citronellyl citronellate **2** (LRI 2022) had never been reported in citrus, but was identified in natural products that are rich in citronellal, such as citronella (Glichitch, 1926) and *Eucalyptus citriodora* (Vernin et al., 2004). It was identified in Judy's Everbearing and Durham's Emerald extracts, which indeed both contain a significant amount of citronellal. Isoascaridole of undetermined stereochemistry was recently reported for the first time in orange and bergamot essential oil (Tranchida et al., 2013). In the present study, both the *cis* and *trans* isomers were synthesized, and the presence of the *cis*-isoascaridole **3a** (LRI 1291) in finger lime could be confirmed. 1,2:5,6-Diepoxy-*p*-menthane **4** (2 isomers, LRI 1324 and 1331) and 2,3-epoxy-*p*-menthan-6-one **5** (2 isomers, LRI 1297 and 1301) are reported for the first time in a natural product. *Cis* and *trans*-*p*-menth-1-en-3-ol-6-one, *cis*-**6a** (LRI 1376) and *trans*-**6b** (LRI 1380), were identified in the peel extract of the cultivars Judy's Everbearing and Durham's Emerald. The MS of both isomers of **4** and **6** were detected in our previous analysis, but could not be identified at that time (Delort and Jaquier, 2009). To the best of our knowledge, **6** was reported in some natural products but never in citrus. 1,2-Epoxy-*p*-Methan-5-one **7** (LRI 1259) is reported here for the first time in a natural extract.

### 2.5. Confirmation by synthesis

All molecules mentioned above were confirmed after comparison of their MS spectra and LRIs with those of freshly prepared standards. 6-Methyloctyl acetate **1** and citronellyl citronellate **2** were synthesized via standard esterification. *Cis*-isoascaridole **3a** was obtained from ascaridole via thermal rearrangement. The molecules **4**, **5**, **6** and **7** were prepared from α-phellandrene, as shown in Table 3. The syntheses were carried out on the only commercially available enantiomer, (*R*)-(−)-α-phellandrene **9**, although its chirality in finger lime was determined as pure (*S*)-(+) (Table 2). Following the work of Schenck et al. (1953), (*R*)-(−)-α-phellandrene **9** was photo-oxygenated to produce a 57:43 mixture of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b**. Chromatographic purification allowed us to isolate an 83:17 enriched quality of (1*S*,4*R*,7*R*)-(+)-**10a**, as well as diastereoisomerically pure (1*R*,4*S*,7*R*)-(+)-**10b**. A small sample of pure (1*R*,4*S*,7*R*)-(+)-**10b** was treated with a catalytic amount of $[(Ph_3P)_3RuCl_2]$ in $CH_2Cl_2$ at 20 °C following methods of Suzuki et al. (1989) to afford the diastereoisomerically pure diepoxide (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** (Turner and Herz, 1977) in 80% yield, which proved to be thermally stable after 4 h in refluxing toluene. (1*R*,2*S*,4*S*,5*R*,7*R*)-(−)-**4a** was isolated after purification of the crude material obtained under the same

**Table 3**
Syntheses of new α-phellandrene derivatives. In table: **3a**: cis-isoascaridole; **4a**: (1*R*,2*S*,4*S*,5*R*,7*R*)-(−)-**4a**; **4b**: (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b**; **5a**: (1*R*,2*S*,5*R*,6*S*)-**5a**; **5b**: (1*S*,2*R*,5*R*,6*R*)-**5b**; **6a**: (4*S*,5*R*)-(−)-**6a**; **6b**: (4*R*,5*R*)-(+)-**6b**; **7b**: (1*S*,4*S*,6*R*)-**7b**; **8**: (4*S*,6*R*)-(−)-**8**; **10a**: (1*S*,4*R*,7*R*)-(+)-**10a**; **10b**: (1*R*,4*S*,7*R*)-(+)-**10b**. Conditions: *i*) a) $O_2$, *hv*, *i*PrOH, methylene blue, 40 h, 20 °C; *ii*) cat $[(Ph_3P)_3RuCl_2]$, $CH_2Cl_2$, 20 °C, 4 h; *iii*) toluene, 110 °C, 4 h; *iv*) toluene, 110 °C, 18 h; *v*) GC–MS injection on SPB-1 non-polar column (injector temperature 250 °C).




| Reagent | Cond. | 10a | 10b | 3a | 4a | 4b | 5a | 5b | 6a | 6b | 7b | 8 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (*R*)-(−)-**9** | *i* | 57% | 43% | | | | | | | | | |
| **10b** | *ii* | | | | | 80% | | | | | | |
| **10a**/**10b** 83:17 | *ii* | | | 12% | 38% | 22% | 22% | | 6% | | | |
| **10a**/**10b** 83:17 | *iii* | | | 17% | 32% | 25% | 18% | 4%[a] | | | 4%[a] | |
| **10b** | *iv* | | | | | 56% | | 11%[a] | | 5% | 15% | 15% |
| **10b** | *v* | | | | | 48% | | 27% | | | 11% | |

[a] Tentative identification.

conditions starting from the 83:17 mixture of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b**.

The keto-epoxides **5a** and **5b** were obtained after thermal treatment of the endoperoxides **10a** and **10b**. Indeed, the heating of the 83:17 mixture of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** in refluxing toluene for 4 h afforded, according to $^{13}C$ NMR analysis, a mixture of (1*R*,2*S*,4*S*,5*R*,7*R*)-**4a** (32%)/(1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** (25%), *cis*-isoascaridole **3a** (17%), the major keto-epoxide (1*R*,2*S*,5*R*,6*S*)-**5a** (18%), and two other very minor keto-epoxides tentatively assigned to (1*S*,2*R*,5*R*,6*R*)-**5b** (4%) and (1*S*,4*S*,6*R*)-**7b** (4%). The presence of isoascaridole *cis*-**3a** may come from thermal rearrangement of ascaridole found in the 83:17 mixture (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** obtained after photo-oxidation. As shown in Table 3, epoxy-cyclohexanone **5** may exist as four diastereoisomers. According to STO 6-31G** calculations (Frisch et al., 1998; Luft et al., 2007), both (1*R*,2*S*,5*R*,6*S*)-**5a** (0.41 kcal/mol) and (1*S*,2*R*,5*R*,6*R*)-**5b** (1.10 kcal/mol) may eventually epimerize into the thermodynamically more stable diastereoisomers (1*R*,2*R*,5*R*,6*S*)-**5c** (0.00 kcal/mol) and (1*S*,2*S*,5*R*,6*R*)-**5d** (0.95 kcal/mol), respectively. For these reasons, the stereochemistry of **5a** was further investigated for confirmation via successive reduction, separation and oxidation, as described in Supplementary information. (1*R*,2*S*,5*R*,6*S*)-**5a** was isolated from the above mixture by flash chromatography and obtained only in analytical quantity, as it degraded during purification on silica gel into the hydroxy-enone (4*S*,5*R*)-(−)-**6a**. Similarly, thermal treatment in refluxing toluene (18 h, 110 °C) of (1*R*,4*S*,7*R*)-(+)-**10b** afforded a mixture containing (1*S*,2*R*,5*R*,6*R*)-**5b** (11%), from which it could be characterized. (4*R*,5*R*)-(+)-**6b** was obtained in analytical quantity during the attempted chromatographic purification (cyclohexane/AcOEt 9:1) of this mixture.

Finally, taking into account the pure (*S*)-(+) enantiomer form in finger lime, as well as the LRIs (both on non-polar and polar columns) of the above standards, we suggest the following

configuration for the α-phellandrene derivatives in the finger lime extracts: (1*S*,2*R*,4*R*,5*S*,7*S*)-**4a**, (1*R*,2*S*,4*S*,5*S*,7*R*)-**4b**, (1*S*,2*R*,5*S*,6*R*)-**5a**, (1*R*,2*S*,5*S*,6*S*)-**5b**, (4*R*,5*S*)-**6a** and (4*S*,5*S*)-**6b**.

However, the natural occurrence of di-epoxides **4**, keto-epoxides **5** and hydroxy-enone **6** in finger lime should be considered with the utmost circumspection, in view of the photo and thermal lability of the endoperoxides **10**, readily affording mixtures of **4** and **5**, as well as the chromatographic instability of **5** leading to **6**. The thermal lability of endoperoxide **10** was confirmed, as the injection of pure (1*R*,4*S*,7*R*)-(+)-**10b** into a GC–MS revealed its degradation into the di-epoxide (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** and the keto-epoxides (1*S*,2*R*,5*R*,6*R*)-**5b** and (1*S*,4*S*,6*R*)-**7b**, which may occur in the injector (Table 3). Consequently, these molecules may come from the thermal rearrangement during GC–MS of **10**, in analogy to the reported conversion of ascaridole into its corresponding diepoxide iso-ascaridole (Nitz et al., 1989). For these reasons, the presence of new oxygen derivatives from α-phellandrene in two cultivars, not yet reported in any citrus, may rather indicate the presence of the corresponding endoperoxide as an intermediate metabolite during the biosynthesis of volatile molecules. The endoperoxide **10** had already been reported in the essential oil or extract of some plants, such as *Chenopodium multifidum* (De Pascual-Teresa et al., 1981) and *Alpinia densibracteata* (Sy and Brown, 1997), but never in citrus. Its presence in the cultivars Judy's Everbearing and Durham's Emerald could be explained by the significant amount of α-phellandrene in these cultivars, which may undergo a 1,4-cycloaddition of singlet oxygen, as reported to explain the generation of ascaridole from α-terpinene or the degradation of 1,3,8-*p*-menthatriene in parsley (Nitz et al., 1989).

## 3. Conclusions

Australian native finger limes (*C. australasica*) are known to be unique for their caviar-like pulp and diverse shape, peel and pulp color, and flavor. This study on three cultivars shows that these distinctive observed characteristics are also observed on the molecular level. Indeed, the analytical data obtained during this work showed that the three cultivars possess unique chemical compositions with unusual ratios of major volatile metabolites: limonene/sabinene in cv. Alstonville, limonene/citronellal/isomenthone in cv. Judy's Everbearing and limonene/citronellal/citronellol in cv. Durham's Emerald. Finger limes also differ from common lime species with their low amounts of γ-terpinene, α- and β-pinene, and citral, as well as their opposite enantiomeric distribution of citronellal. Variations in volatile compositions between cultivars were also observed. Some constituents seem to be specific to one cultivar (e.g. aliphatic and terpenyl acetates in Alstonville; citronellyl esters in Judy's Everbearing; 4-methylnonanal, cumin aldehyde and methyl thymol ether in Durham's Emerald). The combined data assess the divergence of finger limes from other *Citrus* genotypes. Considering the difficulty in tracing the origin of citrus species, further chemotaxonomic should be carried out to understand the origin of these native species and their divergence from other citrus species.

## 4. Experimental

### 4.1. General experimental procedures

Abbreviations: cv., cultivar; DIEA, diisopropylethylamine; DMAP, 4-dimethylaminopyridine; DS, Deans Switch; EI, electron ionization; EPC, electronic pneumatic control; LTM, low thermal mass; MSD; mass selective detector; LRI, linear retention index.

$^{1}$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 400 spectrometer at 25 °C with tetramethylsilane as the internal standard. Standard gradient-selected COSY, HSQC and HMBC experiments were carried out on a Bruker Avance 500 or on a Bruker Avance 600 spectrometer, and signal assignment was achieved by using Bruker NMR software TopSpin 2.0.

Infra-red measurements were done on a Perkin Elmer Spectrum One FT-IR, ν in $cm^{-1}$.

Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20 °C, $\lambda_{Na}$ = 589 nm; $\lambda_{Hg}$ = 578, 546, 436, 365 nm; conc. in g/100 mL.

Oxypeucedanin was purchased from ChromaDex® (Irvin, CA, USA). For the syntheses, the chemicals were supplied as follows: dichloromethane (Atrasol, SDS, France); 6-methyloctanoic acid (SynInnova, Edmonton, Canada); lithium aluminum hydride (Acros, Gent, Belgium); diethylether (Carlo Erba, Val de Rueil, France); methyl octanoate, acetyl chloride, diisopropylethylamine (DIEA) and 4-dimethylaminopyridine (DMAP) (Fluka, Buchs, Switzerland); (*R*)-(-)-α-phellandrene, methylene blue solution (Sigma Aldrich, Steinheim, Germany); $[(Ph_3P)_3RuCl_2]$ (Strem Chemicals, Bischeim, France); dicyclohexylcarbamide (Alfa Aesar, Karlsruhe Germany); ascaridole (City Chemical, West Haven, CT, USA); citronellic acid and citronellol (available in-house).

For the chirality study, (*R*)-(+)-limonene and (*S*)-(−)-limonene were available in-house; (*R*)-(+)-citronellal, (*S*)-(−)-citronellal, (*R*)-(+)-citronellol, (*S*)-(−)-citronellol and (*R*)-(−)-α-phellandrene were from Sigma Aldrich; (*S*)-(+)-α-phellandrene was found in rosemary oil (available in-house); (*R*)-(+)-sabinene was found in nutmeg oil (SAFC, Sigma Aldrich); and (*S*)-(−)-sabinene was found in bergamot oil (available in-house).

### 4.2. Plant material

Three cultivars of fresh finger lime fruits, Alstonville, Judy's Everbearing and Durham's Emerald, were purchased from Global Fresh Marketing PTY LTD (Hawthorn East, Australia) and delivered by express air freight courier. They arrived in very good shape and their peel extracts were immediately prepared. These three cultivars have been previously registered by the Australian Cultivar Registration Authority with the following registration numbers: ACC1123, ACC1122 and ACC1156.

### 4.3. Preparation of the finger lime peel extracts

The peel of 2.4 kg of finger limes (cv. Judy's Everbearing) was removed using a grater (Micropane, Betty Bossy) to give 77.5 g of peel, which was immediately covered with dichloromethane (400 mL) and left at room temperature for 24 h. The mixture was filtered through cotton wool. The peel was covered again with dichloromethane (300 mL), left at room temperature for 24 h and then filtered as before. The combined extracts were dried over $MgSO_4$ and concentrated using a Vigreux column at atmospheric pressure to give 7.4 g of peel extract. The same procedure was repeated with 4.5 kg of finger limes (cv. Alstonville) and 4.8 kg of finger limes (cv. Durham's Emerald) to give peel extracts of 15.6 g and 15.3 g, respectively.

### 4.4. Manual identification by GC–MS

GC–MS analyses were performed on a GC–MS 7890A/5975C (Agilent, Santa Clara, USA) operating in electron ionization (EI) mode equipped with a split/splitless injector (250 °C); transfer line temperature 280 °C; split ratio 1:50; equipped with a non-polar column (SPB-1 capillary column, 30 m × 0.25 mm, film thickness 1 μm, Supelco); oven temperature program: 60 °C for 5 min, increased to 250 °C at a rate of 5 °C/min; carrier gas: helium (He), constant flow rate 1 mL/min; injection volume: 0.5 μL.

GC–MS analyses were also carried out on a GC–MS 6890 N/5973 (Agilent) operating in the same configuration but equipped with a polar column (SUPELCOWAX 10 capillary column, 30 m × 0.25 mm, film thickness 0.25 μm, Supelco); oven temperature program: 50 °C for 5 min, increased to 240 °C at a rate of 5 °C/min; carrier gas: helium (He), constant flow rate 1 mL/min; injection volume: 0.5 μL. Total ion current (TIC) GC–MS profiles and mass spectra were obtained with Data Analysis MSD ChemStation software (Agilent). Mass spectra were generated at 70 eV from *m*/*z*: 27 to 350 with a scan rate of 2.29 scan/s. Linear retention indices (LRIs) were determined after injection of a series of *n*-alkanes under identical conditions.

The compounds were identified by comparison of their mass spectra and LRIs obtained from a proprietary database. This database is composed of analytical data obtained from synthesized or commercially available compounds that were all unequivocally characterized by NMR spectroscopy. The NIST05 MS database (National Institute of Standards and Technology, USA) and MassFinder3 (Dr. Hochmut, Scientific Consulting, Germany) were also used when necessary.

### 4.5. Automated mass spectral deconvolution and identification system (AMDIS)

GC–MS files were processed with the free version 2.69 of AMDIS software (available from http://chemdata.nist.gov/mass-spc/amdis/downloads/). To increase the accuracy of our identifications, we used both mass spectra and LRIs in the settings/algorithm of the software (Norli et al., 2010), with the following parameters: minimum match factor, 60; use retention index data; RI window, 10; match factor penalty, very strong; maximum penalty, 20; no RI in library, 20.

### 4.6. Quantitation by GC-FID

The finger lime extracts were injected into a GC 6890 (Agilent) equipped with a double injector and two DB-1 capillary columns (60 m × 0.25 mm, film thickness 0.25 μm, J&W). One column was connected to an MS 5973 N (Agilent) for identification, the other to an FID for quantitation. The temperature program was as follows: 50 °C for 5 min, increased to 120 °C at a rate of 3 °C/min, then increased to 250 °C at a rate of 5 °C/min, 5 min isothermal, then increased to 300 °C at a rate of 15 °C/min, and then 20 min isothermal; split ratio, 1:50; injection volume, 0.2 μL; injector and detector temperature, both 250 °C; carrier gas helium at a constant flow rate of 1.8 mL/min (FID) and 2.1 mL/min (MS). For the quantitative data given in Table 1, peel extract (452.2 mg) of finger lime Alstonville was diluted 10 times in dichloromethane with methyl octanoate (15.5 mg) as an internal standard. The percentages of the volatile constituents were obtained from the FID area corrected with the use of the response factors as described by Delort and Jaquier (2009). The same experiment was done with Judy's Everbearing peel extract (448.9 mg) with an internal standard of 15.4 mg, and Durham's Emerald peel extract (433.5 mg) with an internal standard of 14.5 mg.

### 4.7. Enantioselective heart-cut 2D-GC–MS

#### 4.7.1. Configuration 1 (for limonene, sabinene, citronellol and citronellal)

The 2D-GC–MS system consisted of a GC–MS 7890A/5973 (Agilent) retrofitted with one Deans Switch (DS) (Agilent), one 3-way splitter (Agilent), and one low thermal mass (LTM) II module (Agilent). The GC was equipped with a split/splitless injector, with an additional pneumatic control module (PCM). The PCM constant flow channel was connected to the Deans Switch and the PCM constant pressure channel was connected to the three-way splitter. The three-way splitter was connected to the MS using deactivated fused silica (0.90 m × 0.10 mm, Agilent) and to an olfactometry port using deactivated fused silica (0.90 m × 0.25 mm, Agilent).

The first dimension (1D) was a non-polar column (DB1-MS, 20 m × 0.18 mm, film thickness 0.18 μm, J&W) connected to the DS, and deactivated fused silica (0.45 m × 0.1 mm, Agilent) was installed to connect the DS to the three-way splitter. The second chiral dimension (2D) was installed as an LTM II module between the DS and the three-way splitter. For limonene and sabinene, the 1D temperature program was as follows: 50 °C to 250 °C at 10 °C/min, 100 min isotherm; carrier gas: helium (He), flow program: from 1.0 mL/min (for 30 min) to 0.2 mL/min (for 90 min) at 100 mL/min; split ratio 1:50. The second dimension (2D) was HP-CHIRAL (20% β-cyclodextrin in (35%-phenyl)-methylpolysiloxane, 30 m × 0.25 mm, film thickness 0.25 μm, Agilent). 2D temperature program: 30 °C, 30 min isotherm, then 3 °C/min to 220 °C, 26.6 min isotherm; carrier gas: helium, flow program: from 2.5 mL/min (for 30 min) to 1.2 mL/min (for 90 min) at 100 mL/min. For citronellol and citronellal, the 1D temperature program was as follows: 50 °C to 250 °C at 10 °C/min, 86.6 min isotherm; carrier gas: helium (He), flow program: from 0.8 mL/min (for 30 min) to 0.2 mL/min (for 76.6 min) at 100 mL/min; split ratio 1:10. The second dimension (2D) was MEGA-DEX-DAC (diacetyl tertbutylsilyl-β-cyclodextrin, 30 m × 0.25 mm, film thickness 0.25 μm, MEGA S.N.C., Legnano, Italy). 2D temperature program: 30 °C, 30 min isotherm, then 3 °C/min to 220 °C, 13.3 min isotherm; carrier gas: helium, flow program: from 2.5 mL/min (for 30 min) to 1.2 mL/min (for 76.6 min) at 100 mL/min.

#### 4.7.2. Configuration 2 (for α-phellandrene)

The 2D-GC–MS system consisted of a GC–MS 7890A/5973 (Agilent) retrofitted with one DS (Agilent), one three-way splitter (Agilent), and one LTM II module (Agilent). The GC was equipped with a split/splitless injector and two additional pneumatic control module (PCM) devices. The constant flow channel of each PCM was connected to the DS and to the three-way splitter, respectively. The second chiral dimension (2D) was installed as an LTM II module between the DS and the three-way splitter. The three-way splitter was connected to the MS using deactivated fused silica (0.90 m × 0.10 mm, Agilent) and to an olfactometry port using deactivated fused silica (0.90 m × 0.25 mm, Agilent).

The first dimension (1D) was a non-polar column (SPB1, 30 m × 0.25 mm, film thickness 1 μm, Supelco) connected to the DS, and deactivated fused silica (0.60 m × 0.1 mm, Agilent) was installed to connect the DS to the three-way splitter. 1D temperature program: 60 °C, 5 min isotherm, then 10 °C/min to 250 °C, 72.33 min isotherm; carrier gas: helium (He), flow program: from 1.5 mL/min (for 30 min) to 0.1 mL/min (for 66.33 min) at 100 mL/min; split ratio 1:5. The second dimension (2D) was MEGA-DEX DMP Beta (dimethyl pentyl-β-cyclodextrin, 30 m × 0.25 mm, film thickness 0.25 μm, MEGA S.N.C.). 2D temperature program: 40 °C, 30 min isotherm, then 3 °C/min to 230 °C, 3 min isotherm; flow program: from 3.0 mL/min (for 30 min) to 1.2 mL/min (for 66.33 min) at 100 mL/min.

For each compound, the chiral phase was first tested with standard compounds to ensure good separation of both enantiomers. The injection volume was 1.0 μL of neat citrus sample; injector temperature 250 °C; MS parameters: mass range, *m*/*z* from 29 to 350; ionization, 70 eV; transfer line temperature, 250 °C; source temperature, 230 °C; quadrupole temperature, 150 °C.

### 4.8. High-resolution GC-TOF-MS

Time-of-flight GC–MS analyses were performed on a GCT Premier (Waters, Milford, USA) with a SPB-1 column

(30 m × 0.25 mm, film thickness 1.0 μm, Supelco). Oven program: 60 °C, 5 min; 5 °C/min to 250 °C; constant helium flow, 1.0 mL/min; injection volume, 0.1 μL; injector temperature, 250 °C; split ratio, 1:50. The acquisition time was set to 0.49 s with an interscan delay of 0.01 s over a mass range of 1–300 Da. Spectra were recorded using the following parameters: electron energy, 70 eV; emission current, 594.6 μA: trap current, 200 μA; source temperature, 200 °C. Calibration was performed by using heptacosa (perfluorotributylamine, Mass Spec Std, Alfa Aesar, Karlsruhe, Germany). Calibration data were collected for 1 min in centroid mode. A total of 60 spectra were summed to generate a 23-point calibration curve from *m*/*z* 69 to 502 Da. The curve was fitted to a second-order polynomial such that the standard deviation of the residuals was 0.001 amu or lower. Heptacosa was continuously introduced into the ion source and the ion *m*/*z* 218.9856 was used as a lock mass. Mass spectra and molecular formula were obtained by using MassLynx software (Waters). The difference between the exact mass calculated ($M_{calc}$) from the measured mass ($M_{meas}$) is expressed in ppm ($(M_{meas.} - M_{calc.})/M_{calc.} \times 10^6$).

### 4.9. Synthesis

#### 4.9.1. 6-Methyloctyl acetate **1**

6-Methyloctanoic acid (10 g, 63 mmol) was reduced by lithium aluminum hydride (2.4 g, 1.0 eq.) in dry diethylether (150 mL) at 0 °C and then left at room temperature overnight to yield after work-up the corresponding alcohol (7.4 g, GC purity 97%). Acetylation of 6-methyloctanol (2.4 g, 16.6 mmol) was performed by using acetyl chloride (1.57 g, 1.2 eq.) and DIEA (4.3 g, 2.0 equiv.) in ethyl acetate (50 mL). After the usual work-up, the crude product was distilled under vacuum (~84 °C, ~5 mmHg) to yield 6-methyloctyl acetate (2.2 g, 72%, GC purity 98.7%).

$^1$H NMR (400 MHz, $CDCl_3$): 4.05 (t, *J* = 6.7, 2H); 2.05 (s, 3H); 1.59–1.66 (m, 2H); 1.25–1.38 (m, 7H); 1.08–1.16 (m, 2H); 0.86 (t, *J* = 7.1, 3H); 0.85 (d, *J* = 6.5, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 171.2 (C); 64.7 ($CH_2$); 36.5 ($CH_2$); 34.3 (CH); 29.5 ($CH_2$); 28.7 ($CH_2$); 26.7 (CH2); 26.3 ($CH_2$); 21.0 ($CH_3$); 19.2 ($CH_3$); 11.4 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 186 (0, $M^+$); 98 (22); 97 (100); 83 (17); 71 (15); 70 (54); 69 (39); 68 (11); 61 (41); 57 (27); 56 (31); 55 (75); 43 (72); 42 (10); 41 (29); 29 (10). LRI (SPB-1) 1264; LRI (SWax) 1544. In *cv.* Alstonville extract, LRI (SPB-1) 1263; LRI (SWax) 1543.

#### 4.9.2. Citronellyl citronellate **2**

Dicyclohexylcarbamide (2.67 g, 12.92 mmol, 1.1 eq.) was added to a solution of citronellic acid (2.00 g, 11.75 mmol, 1 eq.), citronellol (1.84 g, 11.75 mmol, 1 eq.) and DMAP (0.15 g, 1.18 mmol) in dichloromethane (20 mL) and stirred at room temperature for 6 h. The mixture was poured on water and extracted with diethyl ether. The combined organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed to give 3.91 g of crude product. The residue was purified by flash-chromatography using 2% diethyl ether in pentane, yielding pure product (2.63 g, 73%, GC–MS purity 97%) after bulk-to-bulk distillation (160 °C, 0.056 mbar).

$^1$H NMR (400 MHz, CDCl3): $\delta$ 5.09 (br t, *J* = 7.05, 2 H); 4.04–4.17 (m, 2 H); 2.30 (dd, *J* = 5.9, 14.5, 1 H); 2.10 (dd, *J* = 8.2, 14.5, 1H); 1.98 (m, 1.89–2.07, 5 H); 1.68 (s, 6 H); 1.60 (s, 6 H); 1.49–1.72 (m, 2 H); 1.13–1.48 (m, 5 H); 0.94 (d, *J* = 6.5, 3 H); 0.91 (d, *J* = 6.5, 3 H). 13C NMR (100 MHz, CDCl3): $\delta$ 173.3 (C), 131.5 (C), 131.3 (C), 124.6 (CH), 124.3 (CH), 62.7 (CH2), 41.9 (CH2), 37.0 (CH2), 36.8 (CH2), 35.6 (CH2), 30.1 (CH), 29.5 (CH), 25.7 (2CH3), 25.4 (CH2), 25.4 (CH2), 19.6 (CH3), 19.4 (CH3), 17.6 (2 CH3). MS (EI, 70 eV), *m*/*z* (%): 308 (2, M+); 170 (2); 153 (10); 152 (8); 139 (5); 138 (42); 136 (5); 124 (5); 123 (45); 110 (19); 109 (42); 97 (7); 96 (11); 95 (49); 94 (12); 83 (26); 82 (33); 81 (54); 80 (6); 71 (5); 70 (9); 69 (100); 68 (8); 67 (20); 57 (9); 56 (6); 55 (26); 53 (5); 43 (7); 41 (32). HR-GC-TOF-MS: 308.2713 (C20H36O, −0.6 ppm). LRI (SPB-1) 2025; LRI (SWax) 2360. In cv. Judy's Everbearing and Durham's Emerald extracts: LRI (SPB-1) 2022; LRI (SWax) 2352.

#### 4.9.3. Isoascarisole **3**

*4.9.3.1. Cis-isoascaridole cis-**3a**.* Ascaridole (100.2 mg, 0.596 mmol) in xylene (15 mL) was heated at reflux for 18 h. The cold reaction mixture was concentrated and purified by flash chromatography (cyclohexane/AcOEt 99:1 to 6:4) to afford *cis*-**3a** in 85% yield. IR: 2961, 2935, 2874, 1465, 1443, 1419, 1380, 1366, 1310, 1264, 1226, 1208, 1747, 1097, 1065, 1039, 1014, 996, 928, 901, 877, 850, 804, 778, 718, 693, 656, 616. $^1$H NMR (600 MHz, $CDCl_3$): 3.13 (*d*, *J* = 3.0, 1H); 3.10 (*d*, *J* = 3.0, 1H); 1.86–1.81 (*m*, 1H); 1.79–1.73 (*m*, 1H); 1.67–1.58 (*m*, 1H); 1.53 (*hept*, *J* = 6.9, 1H); 1.36 (*s*, 3H); 0.98 (*d*, *J* = 6.8, 3H); 0.93 (*d*, *J* = 6.8, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): 59.9 (C); 56.0 (C); 54.6 (CH); 54.2 (CH); 34.3 (CH); 27.7 ($CH_2$); 22.0 ($CH_3$); 21.1 ($CH_2$); 17.9 ($CH_3$); 17.4 ($CH_3$).

MS (EI, 70 eV), *m*/*z* (%): 168 (7, $M^+$), 150 (10); 140 (12); 139 (29); 135 (25); 126 (11); 125 (52); 119 (32); 110 (14); 109 (13); 107 (39); 105 (10); 99 (11); 98 (15); 97 (97); 95 (34); 93 (11); 91 (29); 85 (22); 83 (22); 82 (29); 81 (24); 79 (36); 77 (17); 71 (33); 70 (13); 69 (66); 67 (26); 65 (10); 60 (12); 57 (10); 55 (48); 53 (19); 43 (100); 42 (10); 41 (68); 39 (29); 29 (11); 27 (17). HR-GC-TOF-MS: 168.1153 ($C_{10}H_{16}O_2$, +1.8 ppm). LRI (SPB-1) 1287; LRI (SWax) 1867. In *cv.* Alstonville and Durham's Emerald extracts: LRI (SPB-1) 1291; LRI (SWax) 1869.

*4.9.3.2. Trans-isoascaridole trans-**3b**.* Isolated in analytical amount from commercially available ascaridole by flash chromatography (cyclohexane/AcOEt 99:1 to 6:4). $^1$H NMR (600 MHz, $CDCl_3$): 3.17 (*s*, 2H); 1.85–1.71 (*m*, 4H); 1.50 (*hept*, *J* = 7.0, 1H); 1.29 (*s*, 3H); 0.96 (*d*, *J* = 7.0, 3H); 0.93 (*d*, *J* = 7.0, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): 64.0 (C); 58.6 (C); 57.2 (CH); 56.2 (CH); 34.1 (CH); 25.3 ($CH_2$); 22.7 ($CH_3$); 19.4 ($CH_2$); 18.0 ($CH_3$); 17.6 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (1, $M^+$), 125 (15), 110 (10), 107 (18), 97 (94), 95 (27), 85 (17), 82 (24), 79 (28), 71 (31), 69 (28), 67 (17), 60 (10), 55 (31), 53 (12), 43 (100), 41 (51), 39 (21), 27 (15). LRI (SPB-1) 1291; LRI (SWax) 1888. Not detected in finger lime extracts.

#### 4.9.4. Phellandrene endoperoxyde 10

*4.9.4.1. (+)-(1S,4R,7R)-7-Isopropyl-5-methyl-2,3-dioxabicyclo[2.2.2]oct-5-ene ((1S,4R,7R)-(+)-**10a**).* A solution of (*R*)-(-)-α-phellandrene **9** ($[\alpha]_D^{20} = -170$, conc. = 4.1, $CHCl_3$; 16.6 g, 122 mmol) in *i*PrOH (90 mL) was irradiated at 20 °C for 40 h (125 W equivalent daylight-balanced; color temperature 6500 °K; LED camera light) in the presence of a few drops of methylene blue solution, while air was bubbled through a glass frit into the mixture at a rate of 480 mL/min. Every 8 h, both the level of solvent and the blue color were readjusted. The reaction mixture of 57:43 (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** was then concentrated under vacuum and purified by flash chromatography (cyclohexane/AcOEt 97:3 to 95:5) to afford a 70:30 mixture of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** in 23% yield (4.71 g). During an additional purification by flash chromatography, an enriched 83:17 (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** fraction (800 mg, 3.9% yield) was obtained and used for analytical and synthetic purposes. $[\alpha]_D^{20} = +43.0$, conc. = 4.0, $CHCl_3$. IR: 3047, 2958, 2871, 1661, 1470, 1443, 1385, 1369, 1206, 1121, 1065, 1006, 961, 943, 909, 795, 726, 676. $^1$H NMR (500 MHz, $CDCl_3$): 6.33 (*dq*, *J* = 1.7, 6.5, 1H); 4.57 (*dt*, *J* = 1.5, 6.5, 1H); 4.38 (*dq*, *J* = 1.8, 3.6, 1H); 2.35 (*ddd*, *J* = 4.3, 8.6, 13.1, 1H); 1.94 (*s*, 3H); 1.82 (*dt*, *J* = 4.2, 13.2, 1H); 1.70 (*ddd*, *J* = 2.5, 11.0, 13.2, 1H); 1.12–1.07 (*m*, 1H); 0.99 (*d*, *J* = 6.6, 3H); 0.98 (*d*, *J* = 6.6, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): 141.4 (C); 126.0 (CH); 76.2 (CH); 73.1 (CH); 41.6 (CH); 30.5 (CH); 27.8 ($CH_2$); 21.3 ($CH_3$); 20.8 ($CH_3$); 18.6

($CH_3$). Because of its thermal instability, the MS and LRI analyses could not be measured and its presence in the extracts could not be studied.

*4.9.4.2. (+)-(1R,4S,7R)-7-Isopropyl-5-methyl-2,3-dioxabicyclo[2.2.2] oct-5-ene ((+)-(1R,4S,7R)-**10b**).*. During purification by flash chromatography described above, an enriched 4:96 (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** fraction (100 mg, 0.5% yield) was obtained and used for analytical and synthetic purposes. $[\alpha]_D^{20}$ = + 62.8, conc. = 4.1, $CHCl_3$. IR: 2958, 2938, 2871, 1470, 1443, 1385, 1368, 1207, 1065, 1006, 982, 960, 942, 905, 795, 726, 676. $^1$H NMR (600 MHz, $CDCl_3$): 6.19 (*dq*, *J* = 2.0, 6.1, 1H); 4.60 (*ddd*, *J* = 1.5, 3.5, 5.7, 1H); 4.43 (*dq*, *J* = 1.7, 3.6, 1H); 2.35 (*ddd*, *J* = 4.3, 8.7, 13.0, 1H); 1.94 (*s*, 3H); 1.91 (*ddt*, *J* = 4.0, 5.7, 9.5, 1H); 1.09 (*ddd*, *J* = 1.7, 4.7, 13.0, 1H); 1.06–1.01 (*m*, 1H); 0.90 (*d*, *J* = 6.5, 3H); 0.85 (*d*, *J* = 6.5, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): 142.2 (C); 122.8 (CH); 75.6 (CH); 73.9 (CH); 41.7 (CH); 32.6 (CH); 28.5 ($CH_2$); 20.4 ($CH_3$); 19.8 ($CH_3$); 18.6 ($CH_3$). Because of its thermal instability, the MS and LRI analyses could not be measured and its presence in the extracts could not be studied.

*4.9.5. 1,2:5,6-Diepoxy-p-menthane **4***

*4.9.5.1. (−)-(1R,2S,4S,5R,7R)-5-Isopropyl-1-methyl-3,8-dioxatricyclo[5.1.0.02,4]octane ((1R,2S,4S,5R,7R)-(-)-**4a**).* A 83:17 mixture of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** (1500 mg, 8.93 mmol) was treated with $[(Ph_3P)_3RuCl_2]$ (13.8 mg) in $CH_2Cl_2$ (2 mL) at 20 °C for 4 h to obtain, according to 13C NMR analysis, a mixture of (1*R*,2*S*,4*S*,5*R*,7*R*)-(−)-**4a** (38%), (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** (22%), keto-epoxides (1*R*,2*S*,5*R*,6*S*)-**5a** (22%), hydroxy-enone (4*S*,5*R*)-(-)-**6a** (6%), and *cis*-isoascaridole **3a** (12%), from which (*1R*,*2S*,4*S*,5*R*,7*R*)-(−)-**4a** could be isolated in analytical amount by flash chromatography (cyclohexane/AcOEt 9:1). $[\alpha]_D^{20}$ = −13.9, conc. = 0.4, $CHCl_3$. IR: 2959, 2931, 2873, 1464, 1445, 1416, 1369, 1220, 1109, 1096, 1062, 920, 905, 891, 859, 838, 810, 776, 718, 701, 628. $^1$H NMR (500 MHz, $CDCl_3$): 3.13 (*d*, *J* = 4.1, 1H); 3.11 (*dd*, *J* = 0.6, 4.2, 1H); 2.88 (*dd*, *J* = 2.9, 7.0, 1H); 1.82–1.74 (*m*, 4H); 1.47 (*s*, 3H); 0.98 (*d*, *J* = 6.6, 3H); 0.975 (*d*, *J* = 6.6, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): 54.7 (CH); 53.7 (C); 53.5 (CH); 50.5 (CH); 39.0 (CH); 30.9 (CH); 22.6 ($CH_2$); 20.7 ($CH_3$); 20.0 ($CH_3$); 19.7 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (1, $M^+$); 153 (8); 135 (10); 126 (15); 125 (20); 119 (15); 111 (13); 110 (10); 109 (20); 107 (29); 98 (25); 97 (100); 95 (25); 93 (22); 91 (19); 85 (18); 83 (28); 82 (12); 81 (24); 79 (21); 77 (13); 71 (26); 70 (35); 69 (37); 67 (18); 57 (14); 55 (60); 53 (18); 43 (90); 42 (11); 41 (53); 39 (35); 29 (14); 27 (17). (1*R*,2*S*,4*S*,5*R*,7*R*)-(−)-**4a**: LRI (SPB-1) 1326; LRI (SWax) 1949. HR-GC-TOF-MS: 168.1151 ($C_{10}H_{16}O_2$, +0.6 ppm). In Judy's Everbearing and Durham's Emerald extracts, **4a**: LRI (SPB-1) 1324; LRI (SWax) 1945.

*4.9.5.2. (−)-(1S,2R,4R,5R,7S)-5-Isopropyl-1-methyl-3,8-dioxatricyclo[5.1.0.02,4]octane ((1S,2R,4R,5R,7S)-(-)-**4b**).* $[(Ph_3P)_3RuCl_2]$ (67 mg, 0.07 mmol) was added to a solution of pure stereoisomer (1*R*,4*S*,7*R*)-(+)-**10b** (309 mg, 1.84 mmol) in $CH_2Cl_2$ (10 mL). After 4 h at 20 °C, the reaction mixture was concentrated, and then purified by flash chromatography (cyclohexane/AcOEt 9:1) to afford pure (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** in 80% yield. $[\alpha]_D^{20}$ = −41.8, conc. = 1.5, $CHCl_3$. IR: 2959, 2932, 2874, 1465, 1448, 1416, 1379, 1369, 1298, 1264, 1252, 1203, 1093, 1075, 1015, 931, 912, 892, 868, 808, 775, 696, 665. $^1$H NMR (500 MHz, $CDCl_3$): 3.13 (*d*, *J* = 4.0, 1H); 2.91 (*t*, *J* = 3.3, 1H); 2.88 (*dd*, *J* = 2.2, 4.0, 1H); 1.88 (*dt*, *J* = 3.1, 12.5, 1H); 1.70–1.67 (*m*, 3H); 1.53 (*s*, 3H); 1.00 (*d*, *J* = 6.5, 3H); 0.96 (*d*, *J* = 6.5, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): 56.3 (CH); 53.1 (C); 52.0 (CH); 51.9 (CH); 37.0 (CH); 30.3 (CH); 24.3 ($CH_2$); 21.0 ($CH_3$); 20.4 ($CH_3$); 20.1 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (1, $M^+$); 153 (9); 135 (13); 125 (19); 119 (30); 111 (13); 110 (10); 109 (20); 107 (30); 98 (19); 97 (91); 95 (25); 93 (20); 91 (22); 85 (33); 83 (29); 82 (13); 81 (25); 79 (24); 77 (14); 71 (15); 70 (13); 69 (35); 67 (16); 57 (12); 55 (46); 53 (16); 43 (100); 41 (47); 39 (28); 29 (12); 27 (15). (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b**: LRI (SPB-1) 1333; LRI (SWax) 1963. HR-GC-TOF-MS: 168.1157 ($C_{10}H_{16}O_2$, +4.2 ppm). In Judy's Everbearing and Durham's Emerald extracts, **4b**: LRI (SPB-1) 1331; LRI (SWax) 1957.

*4.9.6. 2,3-Epoxy-p-menthan-6-one **5***

*4.9.6.1. (1R,2S,5R,6S)-5-Isopropyl-2-methyl-7-oxabicyclo[4.1.0]heptan-3-one ((1R,2S,5R,6S)-**5a**).* Thermal treatment in refluxing toluene (4 h, 110 °C) of the 83:17 mixture of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** afforded, according to 13C NMR analysis, a mixture of (1*R*,2*S*,4*S*,5*R*,7*R*)-**4a**(32%)/(1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b**(25%), together with *cis*-isoascaridole **3a** (17%), the major keto-epoxide (1*R*,2*S*,5*R*,6*S*)-**5a** (18%), and two other very minor keto-epoxides tentatively assigned, from spectroscopic data, to (1*S*,2*R*,5*R*,6*R*)-**5b** (4%) and (1*S*,4*S*,6*R*)-**7b** (4%). (1*R*,2*S*,5*R*,6*S*)-**5a** could only be isolated in analytical quantity, as its purification by flash chromatography (cyclohexane/AcOEt 9:1) resulted in its transformation into the hydroxy-enone (4*S*,5*R*)-(−)-**6a**.

IR: 2960, 2930, 2874, 1711, 1463, 1378, 1370, 1247, 1204, 1177, 1111, 1096, 1064, 1015, 921, 893, 858, 833, 778, 730, 699, 654. $^1$H NMR (500 MHz, $CDCl_3$): 3.37 (*d*, *J* = 4.2, 1H); 3.20 (*dd*, *J* = 2.0, 4.2, 1H); 2.59 (*ddq*, *J* = 0.8, 1.9, 7.2, 1H); 2.27, (*dd*, *J* = 13.0, 16.5, 1H); 2.17–2.15 (*m*, 1H); 2.15–2.12 (*m*, 1H); 1.87 (*dsept*, *J* = 5.1, 6.8, 1H); 1.31 (*d*, *J* = 7.2, 3H); 1.03 (*d*, *J* = 6.8, 3H); 1.01 (*d*, *J* = 6.8, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): 210.7 (C); 54.7 (CH); 54.4 (CH); 41.7 (CH); 39.7 (CH); 37.4 ($CH_2$); 31.3 (CH); 19.6 ($CH_3$); 19.4 ($CH_3$); 14.1 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (7, $M^+$); 153 (16); 135 (10); 126 (49); 125 (30); 111 (22); 98 (37); 97 (40); 95 (11); 83 (14); 81 (15); 79 (12); 71 (62); 70 (100); 69 (43); 68 (10); 67 (11); 57 (18); 56 (10); 55 (71); 53 (11); 43 (24); 42 (19); 41 (46); 39 (28); 29 (10); 27 (12). HR-GC-TOF-MS: 168.1149 ($C_{10}H_{16}O_2$, -0.6 ppm). (1*R*,2*S*,5*R*,6*S*)-**5a**: LRI (SPB-1) 1299; LRI (SWax): degrades on polar phase. In Judy's Everbearing and Durham's Emerald extracts, **5a**: LRI (SPB-1) 1297; LRI (SWax) not detected.

*4.9.6.2. (1S,2R,5R,6R)-5-Isopropyl-2-methyl-7-oxabicyclo[4.1.0]heptan-3-one ((1S,2R,5R,6R)-**5b**).* When pure endoperoxide (1*R*,4*S*,7*R*)-(+)-**10b** was heated in refluxing toluene for 18 h, a mixture containing, according to 13C NMR analysis, (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** (56%)/(1*R*,4*R*,6*S*)-**7b** (15%)/(−)-(4*S*,6*R*)-**8** (13%)/(1*S*,2*R*,5*R*,6*R*)-**5b** (or eventually the thermodynamically more stable (1*S*,2*S*,5*R*,6*R*)-**5d**) (11%)/(4*R*,5*R*)-(+)-**6b** (5%)) was obtained. The spectroscopic data given for (1*S*,2*R*,5*R*,6*R*)-**5b** were deduced from the mixture. These are tentative attributions, as they could refer eventually to the thermodynamically more stable stereoisomer (1*S*,2*S*,5*R*,6*R*)-**5d**. $^1$H NMR (500 MHz, $CDCl_3$): 3.31–3.30 (*m*, 1H); 3.25 (*d*, *J* = 3.3, 1H); 2.67 (*q*, *J* = 7.1, 1H); 2.40–1.60 (*m*, 4H); 1.29 (*d*, *J* = 7.1, 3H); 1.03 (*d*, *J* = 6.7, 3H); 0.98 (*d*, *J* = 6.7, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): 210.8 (C); 57.8 (CH); 55.6 (CH); 42.6 (CH); 41.4 (CH); 38.2 ($CH_2$); 30.7 (CH); 20.3 ($CH_3$); 19.8 ($CH_3$); 13.6 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (5, $M^+$); 153 (19); 126 (49); 125 (37); 111 (24); 98 (33); 97 (42); 95 (10); 83 (18); 81 (11); 79 (11); 71 (62); 70 (100); 69 (58); 67 (12); 57 (17); 56 (11); 55 (84); 53 (11); 43 (26); 42 (21); 41 (51); 39 (27); 29 (12); 27 (12). HR-GC-TOF-MS: 168.1157 ($C_{10}H_{16}O_2$,+4.2 ppm). (1*S*,2*R*,5*R*,6*R*)-**5b**: LRI (SPB-1) 1304; LRI (SWax): degrades on polar phase. In Judy's Everbearing and Durham's Emerald extracts, **5b**: LRI (SPB-1) 1301, LRI (SWax) not detected.

*4.9.7. p-Menth-1-en-3-ol-6-one 6*

*4.9.7.1. (−)-(4S,5R)-4-Hydroxy-5-isopropyl-2-methylcyclohex-2-enone ((4S,5R)-(-)-**6a**).* (4*S*,5*R*)-(−)-**6a** was obtained in 8% yield during the attempted chromatographic purification of

(1*R*,2*S*,5*R*,6*S*)-**5a** from the mixture obtained after thermal treatment (4 h, 110 °C in toluene) of (1*S*,4*R*,7*R*)-(+)-**10a**/(1*R*,4*S*,7*R*)-(+)-**10b** (reported above) and could be characterized. $[\alpha]_D^{20} = -108.0$, conc. = 2.1, $CHCl_3$. IR: 3426, 2959, 2923, 2871, 1660, 1473, 1448, 1418, 1384, 1366, 1245, 1183, 1139, 1113, 1088, 1042, 1021, 947, 925, 887, 834, 721, 707, 654. $^1$H NMR (600 MHz, $CDCl_3$): 6.78 (*dq*, *J* = 1.5, 6.0, 1H); 4.42 (*br s*, 1H); 2.56 (*dd*, *J* = 4.0, 16.6, 1H); 2.45 (*dd*, *J* = 13.0, 16.6, 1H); 2.04 (*br s*, 1 OH); 1.81 (*br s*, 3H); 1.80–1.77 (*m*, 1H); 1.67–1.62 (*m*, 1H); 1.03 (*d*, *J* = 6.6, 3H); 0.96 (*d*, *J* = 6.6, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): 200.1 (C); 142.8 (CH); 137.3 (C); 64.3 (CH); 45.9 (CH); 36.9 ($CH_2$); 28.5 (CH); 20.4 ($CH_3$); 20.2 ($CH_3$); 15.6 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (24, $M^+$); 135 (19); 126 (49); 125 (14); 111 (38); 107 (10); 98 (100); 97 (25); 82 (13); 79 (15); 77 (12); 70 (47); 69 (35); 55 (14); 43 (15); 42 (10); 41 (24); 39 (14). HR-GC-TOF-MS: 168.1153 ($C_{10}H_{16}O_2$, +1.8 ppm). (4*S*,5*R*)-(−)-**6a**: LRI (SPB-1) 1378; LRI (SWax) 2339. In Judy's Everbearing and Durham's Emerald extracts, **6a**: LRI (SPB-1) 1376; LRI (SWax) 2340.

*4.9.7.2. (+)-(4R,5R)-4-Hydroxy-5-isopropyl-2-methylcyclohex-2-enone ((4R,5R)-(+)-**6b**).* (4*R*,5*R*)-(+)-**6b** was obtained in analytical quantity during the chromatographic purification (cyclohexane/AcOEt 9:1) of the mixture obtained after thermal treatment (18 h, 110 °C in toluene) of (1*R*,4*S*,7*R*)-(+)-**10b**, which contained, according to 13C NMR analysis, (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** (56%)/(1*R*,4*R*,6*S*)-**7b** (15%)/(−)-(4*S*,6*R*)-**8** (13%)/(1*S*,2*R*,5*R*,6*R*)-**5b** (or eventually the thermodynamically more stable (1*S*,2*S*,5*R*,6*R*)-**5d**) (11%)/(4*R*,5*R*)-(+)-**6b** (5%)). $[\alpha]_D^{20} = +67.0$, conc. = 0.9, $CHCl_3$. $[\alpha]_D^{20} = +92.2$, conc. = 0.6, EtOH. IR: 3418, 2958, 2928, 2873, 1661, 1466, 1448, 1421, 1386, 1369, 1356, 1256, 1143, 1117, 1090, 1048, 1007, 984, 927, 893, 754, 728. $^1$H NMR (600 MHz, $CDCl_3$): 6.65 (*quint*, *J* = 1.6, 1H); 4.35 (*br d*, *J* = 8.0, 1H); 2.46 (*dd*, *J* = 3.8, 16.0, 1H); 2.18 (*dhept*, *J* = 3.3, 7.0, 1H); 2.12 (*dd*, *J* = 13.2, 16.0, 1H); 1.96 (*ddt*, *J* = 3.3, 9.4, 13.2, 1H); 1.78 (*t*, *J* = 1.6, 3H); 1.55 (*br s*, 1OH); 0.97 (*d*, *J* = 7.0, 3H); 0.90 (*d*, *J* = 7.0, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): 199.8 (C); 148.3 (CH); 135.3 (C); 69.2 (CH); 50.1 (CH); 36.3 ($CH_2$); 26.4 (CH); 20.5 ($CH_3$); 16.6 ($CH_3$); 15.3 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (31, $M^+$); 150 (11); 135 (36); 126 (50); 125 (17); 111 (50); 107 (11); 98 (100); 97 (34); 95 (12); 91 (10); 79 (16); 77 (12); 70 (48); 69 (42); 55 (15); 43 (18); 42 (11); 41 (27); 39 (15). HR-GC-TOF-MS: 168.1150 ($C_{10}H_{16}O_2$, +0.0 ppm). (4*R*,5*R*)-(+)-**6b**: LRI (SPB-1) 1381; LRI (SWax) 2375. In Judy's Everbearing and Durham's Emrald extracts, **6b**: LRI (SPB-1) 1380; LRI (SWax) 2376.

*4.9.8. 1,2-Epoxy-p-menthan-5-one* **7**

*4.9.8.1. (1R,4R,6S)-4-Isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptan-3-one ((1S,4S,6R)-**7b**).* Constitutes 15% of the mixture obtained after thermal treatment of (1*R*,4*S*,7*R*)-(+)-**10b** (18 h, 110 °C in toluene), which contained (1*S*,2*R*,4*R*,5*R*,7*S*)-(−)-**4b** (56%)/(1*S*,4*S*,6*R*)-**7b** (15%)/(−)-(4*S*,6*R*)-**8** (13%)/(1*S*,2*R*,5*R*,6*R*)-**5b** (or eventually the thermodynamically more stable (1*S*,2*S*,5*R*,6*R*)-**5d**) (11%)/(4*R*,5*R*)-(+)-**6b** (5%)). The spectroscopic data were deduced from the mixture: $^1$H NMR (500 MHz, $CDCl_3$): 2.80 (*d*, *J* = 18.4, 1H); 2.55 (*d*, *J* = 18.4, 1H); 2.40–1.60 (*m*, 5H); 1.37 (*s*, 3H); 0.90 (*d*, *J* = 6.8, 3H); 0.83 (*d*, *J* = 6.8, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): 209.0 (C); 58.7 (CH); 57.2 (C); 48.2 (CH); 44.9 ($CH_2$); 26.3 (CH); 23.9 ($CH_2$); 22.5 ($CH_3$); 20.5 ($CH_3$); 18.4 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (27, $M^+$); 153 (27); 139 (16); 135 (17); 126 (84); 125 (34); 124 (18); 111 (32); 110 (13); 109 (20); 107 (13); 99 (10); 98 (92); 97 (49); 95 (10); 85 (13); 84 (61); 83 (34); 82 (23); 81 (31); 79 (18); 77 (10); 71 (15); 70 (46); 69 (93); 68 (42); 67 (28); 57 (24); 56 (16); 55 (76); 53 (17); 44 (10); 43 (100); 42 (17); 41 (68); 39 (43); 29 (14); 27 (21). HR-GC-TOF-MS: 168.1153 ($C_{10}H_{16}O_2$, +1.8 ppm). LRI (SPB-1) 1260; LRI (SWax): degrades on polar phase. In all finger lime extracts, LRI (SPB-1) 1259; LRI (SWax): not detected.

*4.9.8.2. (−)-(4S,6R)-4-Hydroxy-6-isopropyl-3-methylcyclohex-2-enone ((4S,6R)-(−)-**8**).* (−)-(4*S*,6*R*)-**8** constitutes 13% of the mixture obtained after thermal treatment of (1*R*,4*S*,7*R*)-(+)-**10b** (18 h, 110 °C in toluene). It was obtained pure in 9% yield after flash chromatography (cyclohexane/AcOEt 99:1 to 6:4). $[\alpha]_{589}^{20} = -34.5$, conc. = 3.1, $CHCl_3$. $[\alpha]_{589}^{20} = -58.8$, $[\alpha]_{578}^{20} = -62.0$, $[\alpha]_{546}^{20} = -72.0$, $[\alpha]_{436}^{20} = -145.7$, $[\alpha]_{365}^{20} = -147.9$, conc. = 1.8, MeOH. IR: 3408, 2958, 2872, 1651, 1464, 1439, 1370, 1309, 1248, 1208, 1072, 1034, 1009, 988, 976, 906, 879, 732, 685, 673. $^1$H NMR (600 MHz, $CDCl_3$): 5.81 (br *d*, *J* = 1.0, 1H); 4.36 (*t*, *J* = 4.8, 1H); 2.37 (*ddd*, *J* = 4.7, 5.9, 9.0, 1H); 2.26 (*dq*, *J* = 6.8, 7.0, 1H); 2.15 (*ddd*, *J* = 4.2, 9.0, 13.3, 1H); 2.05 (*dt*, *J* = 9.0, 5.3, 1H); 2.03 (*d*, *J* = 1.0, 3H); 1.96 (*br s*, 1 OH); 0.94 (*d*, *J* = 7.0, 3H); 0.89 (*d*, *J* = 6.8, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): 201.3 (C); 159.9 (C); 127.1 (CH); 67.1 (CH); 48.5 (CH); 32.3 ($CH_2$); 26.4 (CH); 21.0 ($CH_3$); 20.7 ($CH_3$); 19.1 ($CH_3$). MS (EI, 70 eV), *m*/*z* (%): 168 (12, $M^+$); 135 (26); 126 (53); 125 (32); 124 (34); 111 (34); 109 (20); 98 (100); 97 (13); 83 (10); 70 (31); 69 (34); 55 (13); 43 (11); 42 (13); 41 (22); 39 (13). LRI (SPB-1) 1390; LRI (SWax) 2444. Not detected in finger lime extracts.

## Acknowledgements

We are indebted to Alain Bagnoud, Claude-Alain Richard and Tim Vernet for their skillful experimental work; Fred Durham (Global Fresh Marketing) for supplying the finger limes; Florence Fouillet, Helen Claussen Jaquier, Josef Limacher and Matthis Van de Waal for the organoleptic evaluations of fruits and extracts; Dr. Jean-Yves de Saint Laumer for theoretical calculations; Robert Brauchli for NMR stereochemical elucidations; Anna Castelli for the bibliography; Giovanni Cipolla for helpful discussions on deconvolution software; Prof. Carlo Bicchi and Stefano Galli for their valuable advices on enantioselective GC analysis.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.phytochem.2014.10.023.

## References

Choi, H.-S., 2000. Characteristic odor components of kumquat (*Fortunella japonica Swingle*) peel oil. J. Agric. Food Chem. 48, 4868–4873.

de Pascual-Teresa, J., Bellido, I.S., Torres, C., Sastre, B.A., Grande, M., 1981. Phellandrene endoperoxides from the essential oil of *Chenopodium multifidum*. Phytochemistry 20, 163–165.

de Saint Laumer, J.-Y., Cicchetti, E., Merle, P., Egger, J., Chaintreau, A., 2010. Quantification in gas chromatography: prediction of flame ionization detector response factors from combustion enthalpies and molecular structures. Anal. Chem. 82, 6457–6462.

Delort, E., Jaquier, A., 2009. Novel terpenyl esters from *Citrus australasica* peel extract. Flavour Fragrance J. 24, 123–132.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery Jr., J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., Pople, J.A., 1998. Gaussian 98, Revision A.7. Gaussian, Inc., Pittsburgh, PA.

Glichitch, L.S., 1926. Some new constituents of Java oil of citronella. Parfums Fr. 4, 253–260.

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

Luft, J.A.R., Meleson, K., Houk, K.N., 2007. Transition structures of diastereoselective 1,3-dipolar cycloadditions of nitrile oxides to chiral homoallylic alcohols. Org. Lett. 9, 555–558.

Mondello, L., Costa, R., Sciarrone, D., Dugo, G., 2011. In: Dugo, G., Mondello, L. (Eds.), Medicinal and Aromatic Plants. Industrial Profiles, 49 (Citrus Oils), pp. 349–403.
Nhu-Trang, T.-T., Casabianca, H., Grenier-Loustalot, M.-F., 2006. Authenticity control of essential oils containing citronellal and citral by chiral and stable-isotope gas-chromatographic analysis. Anal. Bioanal. Chem. 386, 2141–2152.
Nitz, S., Kollmannsberger, H., Spraul, M.H., Drawert, F., 1989. Oxygenated derivatives of menthatriene in parsley leaves. Phytochemistry 28, 3051–3054.
Norli, H.R., Christiansen, A., Holen, B., 2010. Independent evaluation of a commercial deconvolution reporting software for gas chromatography mass spectrometry of pesticide residues in fruits and vegetables. Anal. Chem. A 1217, 2056–2064.
Schenck, G.O., Kinkel, K.G., Mertens, H.-J., 1953. Photochemische Reaktion I: Ueber die Photosynthese des Askaridols und verwandter Endoperoxyde. Just. Lieb. Ann. Chem. 584, 125–155.
Suzuki, M., Ohtake, H., Kameya, Y., Hamanaka, N., Noyori, R., 1989. Ruthenium(II)-catalyzed reactions of 1,4-epiperoxides. J. Org. Chem. 54, 5292–5302.
Sy, L.-K., Brown, G.D., 1997. Oxygenated bisabolanes from *Alpinia densibracteata*. Phytochemistry 45, 537–544.
Tajima, K., Tanaka, S., Yamaguchi, T., Fujita, M., 1990. Analysis of green and yellow yuzu peel oils (*Citrus junos Tanaka*). Novel aldehyde components with remarkably low odor thresholds. J. Agric. Food Chem. 38, 1544–1548.
Tranchida, P.Q., Zoccalia, M., Bonaccorsi, I., Dugo, P., Mondello, L., Dugo, G., 2013. The off-line combination of high performance liquid chromatography and comprehensive two-dimensional gas chromatography–mass spectrometry: a powerful approach for highly detailed essential oil analysis. J. Chromatogr. A 1305, 276–284.
Turner, J.A., Herz, W., 1977. Fe(II)-induced decomposition of epidioxides derived from α-phellandrene. J. Org. Chem. 42, 1895–1900.
Vernin, G.A., Parkanyi, C., Cozzolino, F., Fellous, R., 2004. GC/MS analysis of the volatile constituents of *Corymbia citriodora* Hook. from Reunion Island. J. Essential Oil Res. 16, 560–565.
Widder, S., Eggers, M., Pickenhagen, W., 2003. New flavor compounds from orange essence oil. In: Le Quéré, J.L., Etievant, P.X. (Eds.), Flavour Research at the Dawn of the Twenty-first Century. Lavoisier Editions, Paris, pp. 745–748.