

Progress in Essential Oils

Brian M. Lawrence, Consultant

Genet Oil

An analysis of an oil produced from the flowers of *Spartium junceum* L. (genet) collected from their naturalized habitat in Tuscany, Italy, was performed by Miraldi et al. (2004). The components identified in this oil were as follows:

2-heptanone (0.2%) α -thujene (0.5%) camphene (0.1%) sabinene (0.2%) 1-octen-3-ol (0.9%) myrcene (0.1%) α -phellandrene (0.1%) δ-3-carene (0.3%) α -terpinene (0.2%) p-cymene (0.6%) limonene (0.2%) β -ocimene* (0.1%) linalool (0.1%) methyl chavicol (0.4%) hexyl 2-methylbutyrate (0.7%)methyl carvacrol (0.1%) (E)-anethole (0.3%) β-damascenone* (0.3%) hexyl hexanoate (0.3%) 3-dodecanone (0.9%) tetradecanone* (0.3%) (E,E)- α -farmesene (1.0%)ethyl dodecanoate (0.1%) ethyl tetradecanoate (0.8%) methyl hexadecanoate (0.2%) ethyl hexadecanoate (1.8%) methyl octadecanoate (2.0%) octadecyl acetate (3.7%) tricosane (22.9%) tetracosane (8.9%) pentacosane (16.1%)

*correct isomer not identified

Trace amounts (< 0.1%) of β -pinene, γ -terpinene, octanol, α -terpineol and tetradecanol also were found in this oil.

The data presented by Miraldi et al. is quite different from that reported earlier (Lawrence 1981 and 1993) for the composition of genet absolute. B.M. Lawrence, Progress in essential oils. Perfum. Flavor., 6(2), 59–63 (1981); 18(2), 43–58 (1993).

E. Miraldi, S. Ferri and G. Giorgi, *Identification of volatile constituents from the flower oil of* Spartium junceum. J. Essent. Oil Res., 16, 568–570 (2004).

Sambac Oil and Extracts

The flowers of *Jasminum sambac* (L.) Aiton are used to produce oils and extracts (primarily absolutes) that are valuable low-volume fragrance materials.

He et al. (1998) compared the compositions of a supercritical CO_2 extract of the flowers of *J. sambac* grown in China with a petroleum ether extract. The analyses were performed using a combination of GC (FID) and GC/MS. A summary of the results is shown in T-1.

Guo et al. (1998) collected flowers of J. sambac during their blossoming season from different areas in Fuzhou, China. Using GC (FID) and GC/MS as their methods of analysis, the authors examined the composition of the headspace, essential oil and absolute. Although the authors did not present a full comprehensive series of quantitative analyses, they did report on the contents of the main components in the oil and absolute, as can be seen in T-2. The authors reported that the absolute also contained α -muurolene, δ -cadinene, α -patchoulene, α -elemene, selina-4(15),7(11)-diene, aromadendrene, heptadecane, tetramethylpentadecane, tetramethylhexadecane, *cis*- and *trans*-linalool oxide (furanoid), a linalool oxide pyranoid isomer, geraniol, trimethylcyclohexanol, ethyl benzoate, (Z)-3-hexenyl butyrate, methyl salicylate, (Z)-4-hexenyl acetate, (E)-3-hexenyl butyrate, hexyl benzoate, benzyl benzoate, benzaldehyde, 2,2dimethyl-1-phenyl-1-propanone, phenol, benzoic acid and methyl anthranilate, although they did not present any quantitative data for these compounds.

Ramchandra Rao and Rout (2003) analyzed oils produced from *J. sambac* flowers by three different Indian distillers in Kannauj (Uttar Pradesh), Salura and Vijayawada (Andhra Pradesh). The oils were produced by the traditional method in which part of the oil was obtained by direct decanting from the condensate of water distillation, while the other part of the oil was obtained from cohobation. Both oils were combined to yield the oil of commerce from each location. The compositions of these three oils can be seen in T-3.

Vaze (2003) reported that an absolute of *J. sambac* flowers produced in India possessed the following major components:

 $\begin{array}{l} \alpha \text{-farnesene}^{\circ} \ (19.3\%) \\ \text{methyl anthranilate} \ (8.3\%) \\ \text{indole} \ (5.1\%) \\ (Z) \text{-} 3 \text{-hexenyl benzoate} \ (8.8\%) \\ \text{benzyl alcohol} \ (6.3\%) \\ \text{linalool} \ (11.0\%) \\ \text{nerolidol}^{\circ} \ (0.5\%) \\ (Z) \text{-} 3 \text{-hexenyl acetate} \ (1.3\%) \\ \text{methyl benzoate} \ (0.6\%) \\ \text{2-phenethyl acetate} \ (1.0\%) \\ \end{array}$

*correct isomer not identified

- C-M. He, Z-Y. Liang and H. Liu, Chemical constituents of jasmine absolute extracted by supercritical carbon dioxide. Nat. Prod. Res. Develop., 11(3), 53–57 (1998).
- Y-J. Guo, L. Dai, L-P. Yang and Q. Ren, A study on the chemical compositions of Jasminum sambac (L.) Aiton in various farming seasons during the blossom period in Fuzhou region. Fujian Fexxi Ceshi, 7(1), 785–792 (1998).
- Y. Ramchandra Rao and P.K. Rout, *Geographic location and harvest time dependent variation in the composition of essential oils of* Jasminum sambac (*L.*) *Aiton.* J. Essent. Oil Res., **15**, 398–401 (2003).
- K. Vaze, Lesser known essential oils of India their compositions and uses. FAFI, (3/4), 47–58 (2003).

Lemon Myrtle Oil

An oil of lemon myrtle is produced in limited quantities (less than 1 tonne) from the leaves of a medium-size rain forest tree *Backhousia citriodora* F.Muell. endemic to Queensland, Australia. A leaf oil

Comparative percentage composition of a supercritical CO₂ extract and petroleum ether extract of *Jasminum sambac*

Compound	CO ₂ extract	Petroleum ether extract
2-methylcyclopentanol**	0.44	1.03
benzaldehyde	0.77	_
6-methyl-5-hepten-2-one	0.25	0.04
(Z)-3-hexenyl acetate	0.10	0.08
benzyl alcohol	5.11	5.65
<i>cis</i> -linalool oxide [†]	0.85	0.07
<i>trans</i> -linalool oxide [†]	0.86	0.24
linalool	9.43	11.49
benzyl acetate	7.91	13.08
linalool oxide* [‡]	0.41	0.28
(Z)-3-hexenyl butyrate	0.31	0.14
citronellol	0.34	0.06
ethyl salicylate	0.23	0.26
piperonal	0.05	0.02
methyl anthranilate	0.11	0.11
safrole	0.85	4.43
lpha-cadinene***	0.29	12.27
γ-cadinene	0.12	0.57
δ-cadinene	0.24	0.14
(Z)-3-hexenyl benzoate	28.77	19.47
lpha-cadinol	1.42	0.11
α-muurolol	3.28	0.16
2,2-dimethyl-propyl benzoate**	2.54	3.01
benzyl benzoate	2.54	3.04
nerolidol*	0.48	0.48
benzyl salicylate	0.84	0.65
methyl hexadecanoate	0.65	0.30
butylcyclohexyl phthalate**	0.59	0.74
nerolidol*	0.95	1.01
(E)-5-eicosene	0.24	0.74
1,4-diphenyl-1,4-butanedione**	0.38	1.02
methyl limolenate	2.89	3.94
docosanol	0.36	0.17
(Z)-9-tricosene	0.53	0.76
tetracosanol	10.14	4.89

*correct isomer not identified; **not a naturally occurring constituent; ***incorrect identification based on GC elution order; [†]furanoid form; [†]pyranoid form

T-1

Comparative seasonal range in percentage composition of the main components of the oil and absolute of *Jasminum sambac* flowers

T-2

Compound	Seasonal percentage range		
	Oil	Absolute	
(Z)-3-hexenyl acetate	0.61-1.49	0.63-1.46	
benzyl alcohol	4.01-9.42	5.18-10.20	
methyl benzoate	0.05-0.28	0.15-0.36	
linalool	23.50-27.80	13.80-23.10	
benzyl acetate	5.03-11.20	4.19-9.20	
lpha-terpineol	0.17-0.19	0.12-0.16	
(Z)-3-hexenyl benzoate	13.60-21.60	15.80-22.40	

produced in the laboratory was analyzed by Brophy et al. (1995), and they identified the following components:

 $\begin{array}{l} \beta \text{-pinene (0.18\%)} \\ (E) \mbox{-}\beta \text{-ocimene (0.01\%)} \\ 6 \text{-methyl-5-hepten-2-one (0.71\%)} \\ linalool (0.02\%) \\ \beta \text{-elemene (0.09\%)} \\ \beta \text{-caryophyllene (0.04\%)} \\ neral (39.50\%) \\ geranial (57.78\%) \\ nerol (0.13\%) \\ geraniol (0.38\%) \\ globulol (0.09\%) \\ viridiflorol (0.05\%) \\ spathulenol (0.35\%) \end{array}$

Trace amounts (< 0.01%) of p-cymene and citronellal also were characterized in this oil.

Fergeus (2000) reported that the neral/geranial ratio in lemon myrtle oil was 35/65. The other minor components found in the oil were linalool, 6-methyl-5hepten-2-one, citronellal and small amounts of isomeric citrals. Fergeus noted that these isomeric citrals occur in litsea cubeba, lemongrass, melissa and other citral-rich oils. He believed that they probably were formed by the plant acid isomerization of neral and geranial during oil isolation by steam distillation. The structures of neral, geranial and their isomers can be seen in F-1.

Southwell et al. (2000) analyzed 68 samples of lemon myrtle leaf oil and found that the main constituents ranged as follows:

6-methyl-5-hepten-2-one (0.1–2.5%) myrcene (0.1–0.7%) linalool (0.3–1.0%) citronellal (0.1–0.9%) isoneral (0.6–2.7%) isogeranial (1.0–4.2%) neral (32.0–40.9%) geranial (46.1–60.7%)

Other constituents that were found in a single oil subjected to more detailed analysis were as follows:

 $\begin{array}{l} exo-isocitral (0.1\%) \\ nerol (0.2\%) \\ geraniol (0.8\%) \\ piperitone (0.2\%) \\ \beta-elemene (0.1\%) \\ \beta-caryophyllene (0.1\%) \end{array}$

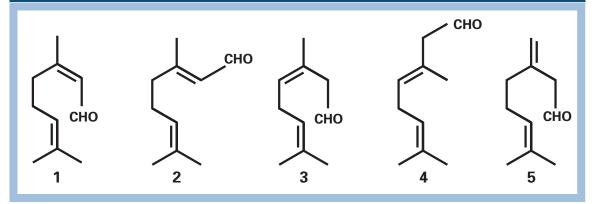
Comparative percentage composition of the flower oils of <i>Jasminum sambac</i> produced T-3 in three different locations in India				
Compound	Kannauj oil	Salura oil	Vijayawada oil	
ethyl acetate	-	0.2	0.5	
3-hexenol*	2.1	2.0	2.4	
hexanol	0.6	t	t	
benzaldehyde	0.4	t	0.2	
6-methyl-5-hepten-2-one	0.5	0.2	0.3	
(Z)-3-hexenyl acetate	3.5	1.0	1.8	
benzyl alcohol	1.4	1.5	1.5	
<i>cis</i> -linalool oxide [†]	1.1	t	0.4	
trans-linalool oxide [†]	0.9	t	0.5	
methyl benzoate	t	t	t	
linalool	26.0	41.3	42.5	
benzyl acetate	24.7	8.0	19.5	
ethyl benzoate	t 1	t	t	
hexenyl butyrate*	t	0.1	0.1	
α-terpineol	0.1	0.3	0.1	
methyl salicylate	3.2	1.5	0.9	
nerol	0.9	0.4	0.5	
(Z)-3-hexenyl isovalerate	0.5 t	0.4 t	0.1	
geraniol	0.8	0.9	0.3	
ethyl salicylate	0.9	0.3	t.5	
geranial	0.9 t		0.1	
•	0.7	t		
indole mathud anthronilate		0.2	t	
methyl anthranilate	0.6	0.6	0.4	
butyl benzoate	0.3	0.1	t	
β-elemene	1.2	0.4	0.4	
(Z)-jasmone	0.2	t	t	
isocaryophyllene	0.1	0.2	0.1	
(E)-β-farnesene	t	0.1	t	
germacrene D	0.4	0.4	0.1	
(Z,Z)-α-farnesene	0.1	0.2	1.2	
(E,E)-α-farnesene	1.0	10.1	7.2	
δ-cadinene	0.9	1.0	0.7	
cadina-1,4-diene	0.4	0.5	t	
(Z)-nerolidol	0.4	t	0.4	
(E)-nerolidol	0.3	0.3	0.3	
(Z)-3-hexenyl benzoate	15.0	21.8	15.1	
hexyl benzoate	t	0.2	0.2	
(E)-dihydroapofarnesol	t	0.2	0.1	
1-epi-cubenol	0.1	0.2	0.2	
T-cadinol	2.0	1.1	0.3	
T-muurolol	0.4	0.2	t	
lpha-cadinol	3.2	1.7	0.4	
hexyl salicylate	0.3	0.2	t	
nerolidyl acetate*	t	t	t	
oplopanone	t	t	t	
benzyl benzoate	0.6	0.9	0.2	
(Z)- <i>trans</i> -α-bergamotol	t	t	t	
benzyl salicylate	t	t	t	
methyl palmitoleate	t	t	t	
methyl hexadecanoate [‡]	0.1	0.1	t	
pimaradiene	t	t	t	
hexadecyl acetate	1.4	t	t	
methyl linoleate	t	t	t	
methyl octadecanoate**	t	0.1	-	
t = trace (< 0.1%); *correct isomer not identified	d: [†] furancid form: ‡ also known as m	ethyl palmitate: **also known as	mothyl stearate	

t = trace (< 0.1%); *correct isomer not identified; [†]furanoid form; [‡]also known as methyl palmitate; ^{**}also known as methyl stearate

The structures of neral, geranial and their isomers: 1) neral, 2) geranial, 3) isoneral, 4) isogeranial, 5) exo-isocitral

F-1

T-4



allo-aromadendrene (0.1%) bicyclogermacrene (0.3%) germacrene B (0.1%) spathulenol (0.1%)

The authors pointed out that lemon myrtle oil was a better source of citral (neral/geranial) than either litsea cubeba or lemongrass oils.

Doimo (2001) compared the leaf oil and dried leaf headspace of two samples of lemon myrtle. The results of this comparative study can be seen in T-4. It is worth noting that *B. citriodora* exists in two chemotypic forms—the commercially important one possessing an oil rich in neral and geranial, while another more rare form possesses an oil rich in citronellal (Doran et al. 2001). However, as *B. citriodora* for oil production is being treated as a cultivated plantation crop, there should be no reason to have oils produced either from mixed or the wrong chemotypes.

Hayes and Markovic (2002) determined that a sample of lemon myrtle oil produced in Queensland, Australia, contained the following major components:

6-methyl-5-hepten-2-one (0.5%) citronellal (0.5%) isoneral (1.7%) isogeranial (2.6%) neral (40.9%) geranial (51.4%) geraniol (0.7%)

Comparative percentage composition of the leaf oil and headspace of lemon myrtle oil

Compound	Oil	Headspace
myrcene	0.2–0.9	0.8–1.4
6-methyl-5-hepten-2-one	0.2–0.3	-
linalool	0.5–1.6	0.6
isopulegol	0.2-0.9	0.4
citronellal	0.2	0.3
exo-isocitral (5)	0.1	-
isoneral (3)	2.5–2.6	1.5
isogeranial (4)	3.6–3.7	2.5-2.6
<i>trans</i> -pulegol	0.2-0.5	0.1
citronellol	0.2-0.3	0.1
nerol	0–0.3	0.2
isonerol	0.6	-
neral	37.2–39.3	37.2–38.6
geraniol	0.9–1.4	0.6
isogeraniol	0.1–0.3	-
geranial	44.0–48.8	48.3-50.7
neric acid	0.2–0.1	0–0.1

Trace amounts (< 0.1%) of myrcene and linalool also were found in this oil.

Hirobe et al. (2002) reported on the composition of a typical oil of lemon myrtle of Australian origin. They found that it contained the following constituents:

6-methyl-5-hepten-2-one (0.5%) myrcene (0.4%) linalool (0.5%) exo-isocitral (0.1%) citronellal (0.3%) isoneral (1.2%) isogeranial (2.3%) nerol (0.2%) neral (42.5%) geraniol (0.8%) piperitone (0.2%) geranial (48.5%) β -elemene (0.1%) β -caryophyllene (0.1%) allo-aromadendrene (0.1%) bicyclogermacrene (0.3%) germacrene B (0.1%) spathulenol (0.1%)

Interestingly enough, this was the same data as that reported by Southwell et al. (2000).

- J.J. Brophy, R.J. Goldsack, C.J.R. Fookes and P.I. Forster, *Leaf oils of the genus* Backhousia(*Myrtaceae*). J. Essent. Oil Res., 7, 237–254 (1995).
- J. Fergeus, What will be the next big oil from Australia? In: Asia—The Global Challenge. Proceed. IFEAT, International Conference on Essential Oils and Aromas, Oct. 31–Nov. 4, 1999, Edit., C. Green, pp 105–117, IFEAT London (2000).
- I.A. Southwell, M. Russell, R.L. Smith and D.W. Archer, Backhousia citriodora *F.Muell.* (Myrtaceae), a superior source of citral. J. Essent. Oil Res., **12**, 735–741 (2000).
- L. Doimo, Iso-citrals and iso-geraniols in lemon myrtle (Backhousia citriodora F.Muell.) essential oils. J. Essent. Oil Res., 13, 236–237 (2001).
- J.C. Doran, J.J. Brophy, E.V. Lassak and A.P.N. House, Backhousia citriodora F.Muell. – Rediscovery and chemical characterization of the L-citronellal form and aspects of its breeding system. Flav. Fragr. J., 16, 325–328 (2001).
- A.J. Hayes and B. Markovic, Toxicity of Australian essential oil Backhousia citriodora (lemon myrtle). Part I. Antimicrobial activity and in vitro cytotoxicity. Food Chem. Toxicol., 40, 535–543 (2002).
- C. Hirobe, E. Nakagaki and M. Nakagaki, Lemon myrtle, a wonderful present from Oceania. Shokuhin Kogyo, 45(7), 61–65 (2002).

Tangerine Oil

The name "tangerine," "mandarin" or "mandarin orange" is used to connote all citrus fruits that possess similar characteristics, such as being easy to peel because it separates readily from the fruit (flesh). The tree also possesses flowers that are either singly formed or in clusters without ever forming branched inflorescences as other *Citrus* species (Jackson and Davies 1999).

The taxonomic origin of the mandarin or tangerine is *Citrus reticulata* Blanco. It originally was used to describe the Ponkan and Suntura mandarins of Taiwan and India, respectively. However, reference to the treatise of Reuther et al. (1967) revealed that Tanaka proposed species recognition for tangerine (*Citrus tangerina* Horto ex Tanaka). Although this species recognition has not been accepted universally, recently Ortiz (2002) confirmed his acceptance of the name. For the purpose of this review, the name *C. tangerina* will be used exclusively for the Dancy cultivar of tangerine. All other so-called tangerine cultivars are of hybrid origin, and when reference is made to them, their hybrid origins will be noted (if known).

According to Jackson and Davies (1999), until 1945 the word "tangerine" in Florida was synonymous with the Dancy cultivar. More recently, this cultivar has been replaced primarily with mandarin hybrids, such as Robinson and Sunburst.

It should be noted that the several fruits grown in Florida and sold as tangerines are man-made hybrids that resemble the Dancy tangerine and usually have *C. tangerina* or *C. clementina* Hort. ex Tanaka as one of their parents (Jackson and Davies 1999).

In 1987, Cartoni et al. used a combination of two capillary columns coupled in the following order, Carbowax 20M-SE54, and a temperature program of 50°C (10 min), 50–120°C (2°C/min) and 120–170°C (4°C/min) to produce a chromatogram for tangerine oil in which the components were well-resolved. The compounds characterized by Cartoni et al. were α -thujene, α -pinene, camphene, β -pinene, myrcene, α - and β -phellandrene, limonene, p-cymene, octanal, γ -terpinene, terpinolene, decanal, linalool, terpinen-4-ol, α -terpineol, β -caryophyllene, a bergamotene isomer, citronellol, α -humulene and thymol. The authors did not present any quantitative data, although from the chromatogram presented it is possible to estimate the relative amounts of most of the components.

An oil of tangerine peel produced in China was the subject of analysis by Li and Qi (1997). The constituents identified in this oil were as follows:

 α -pinene (0.62%) sabinene (0.22%) β-pinene (1.18%) α -terpinene (0.06%) limonene (91.72%) β-ocimene* (0.07%) terpinolene (2.82%) linalool (1.14%) citronellal (0.05%) terpinen-4-ol (0.03%) α -terpineol (0.08%) methyl thymol (0.05%) citronellol (0.05%) neral (0.01%) perillaldehyde (0.02%) citronellyl acetate (0.01%)neryl propionate[†] (0.01%) α -copaene (t) elemene* (t) α -bisabolene[†] (0.01%) β -caryophyllene (0.01%) α -cubebene[†] (0.03%) valencene (t) farnesene* (0.01%) β -cadinene[†] (t) β -selinene[†] (0.04%) α -sinensal (0.26%)

°correct isomer not identified; [†]incorrect identification based on GC elution order; t = trace (< 0.01%)</p> Analysis of 35 samples of tangerine oil by Barrett and Nelson (1998) revealed that the coumarin and psoralen levels were as follows:

herniarin (< 2 ppm) citropten (15–75 ppm) bergapten (< 5 ppm) isopimpinellin (< 5 ppm)

A cold-pressed oil of tangerine produced in China was the subject of analysis by Huang and Wu (1998). They found that the composition of this oil was as follows:

Lota et al. (2001). The components found in these oils were as follows:

 $\begin{array}{l} \alpha \text{-thujene} \ (0.1 - 0.2\%) \\ \alpha \text{-pinene} \ (0.5 - 0.9\%) \\ \beta \text{-pinene} \ (0.3 - 0.4\%) \\ \text{sabinene} \ (0.1 - 0.2\%) \\ \text{myrcene} \ (1.5 - 1.7\%) \\ \alpha \text{-terpinene} \ (0.1\%) \\ \text{limonene} \ (87.1 - 90.9\%) \\ \beta \text{-phellandrene} \ (0 - 0.3\%) \\ \gamma \text{-terpinene} \ (3.9 - 5.2\%) \\ (E) - \beta \text{-ocimene} \ (t - 0.2\%) \\ \text{p-cymene} \ (0.1 - 0.4\%) \end{array}$

(Z)-3-hexenol (0.03%) α-pinene (0.89%) sabinene (0.15%) myrcene (1.94%) β -pinene (0.30%) α-phellandrene (0.40%) limonene (89.15%) (Z)- β -ocimene (0.27%) β -phellandrene (0.11%) (E)- β -ocimene (0.07%) p-cymene (3.32%) γ-terpinene (0.03%) cis-sabinene hydrate (0.18%) terpinolene (1.32%) linalool (0.03%)trans-sabinene hydrate (0.02%) citronellal (0.07%) decanal (0.12%) α -terpineol (0.10%) citronellol (0.08%) methyl thymol (0.11%) geranial (0.02%) δ -elemene (0.07%) thymol (0.09%) citronellyl acetate (0.04%) perillaldehyde (0.03%) α-copaene (0.03%) nervl acetate (0.02%) β -elemene (0.04%) dodecanal (0.03%) β -caryophyllene (0.06%) β-farnesene* (0.02%) α -humulene (0.02%) α -farnesene* (0.04%) γ -muurolene (0.07%) α -sinensal (0.12%)

*correct isomer not identified

Trace amounts (< 0.01%) of hexanol, camphene, octanol, terpinen-4-ol, nerol, geraniol, neral, undecanal, geranyl acetate, γ -elemene and δ -cadinene also were found in this same oil.

The peel oils of the Vohangisahy, Beauty of Glen Retreat, Brickaville, Dancy, Redskin and Swatow cultivars of *C. tangerina* were analyzed by $\begin{array}{l} \mbox{terpinolene} \ (0.2\%) \\ \mbox{octanal} \ (0.1\mbox{-}0.2\%) \\ \mbox{trans-limonene} \ \mbox{oxide} \ (0\mbox{-}t) \\ \mbox{citronellal} \ (0\mbox{-}t) \\ \mbox{linalool} \ (0.4\mbox{-}2.2\%) \\ \mbox{linalool} \ (0.4\mbox{-}2.2\%) \\ \mbox{linalool} \ \mbox{actate} \ (0\mbox{-}t) \\ \mbox{\beta-elemene} \ (0\mbox{-}0.1\%) \\ \mbox{\alpha-terpineol} \ (t\mbox{-}0.1\%) \\ \mbox{\beta-bisabolene} \ (0\mbox{-}0.1\%) \\ \mbox{neryl} \ \mbox{actate} \ (0\mbox{-}t) \\ \mbox{geranyl} \ \mbox{actate} \ (0\mbox{-}t) \\ \mbox{geranyl} \ \mbox{actate} \ (0\mbox{-}t) \\ \mbox{geranyl} \ \mbox{actate} \ (0\mbox{-}t) \\ \mbox{citronellol} \ (0\mbox{-}t) \\ \mbox{actate} \ (0\mbox{-}t) \\ \mbox{geranyl} \ \mbox{actate} \ \mbox{a$

t = trace (< 0.1%)

Mitiku et al. (2001) determined the enantiomeric distribution of four monoterpene hydrocarbons in the cold-pressed oil of the Sabine tangerine cultivar of Kenyan origin that was produced in Japan. The results of this chiral GC analysis can be seen as follows:

- (4R)-(+)-limonene (99.31%):(4S)-(-)-limonene (0.69%) (1R,5R)-(+)-α-pinene (77.04%):(1S,5S)-(-)-α-pinene (22.96%)
- (1R,5R)-(+)-sabinene (100%):(1S,5S)-(-)-sabinene (0%) (1R,5R)-(+)-β-pinene (87.77%):(1S,5S)-(-)-β-pinene (12.23%)

Naef and Velluz (2001) characterized a number of fatty aldehydes in a methylene chloride extract of tangerine peel (taxonomic origin of the tangerine is unknown). The aldehydes found in the extract were (E)-2-hexenal, (E,E)-2,4-heptadienal, (E)-2-octenal, octanal, (E)-2-nonenal, nonanal, (E,Z,Z)-2,4,7-decatrienal, (E,E,Z)-2,4,7-decatrienal, (E,Z)-2,4-decadienal, (E,E)-2,4-decadienal, (Z)-4-decenal, (E)-2-decenal, decanal, undecanal, (E,Z)-2,6-dodecadienal, (Z)-2-dodecenal, (E)-2-dodecenal, dodecanal, (E)-2-tridecenal, tetradecanal, pentadecanal and hexadecanal. Furthermore, the authors found the following constituents in the extract:

α-pinene (0.6%) sabinene (0.1%) Trace amounts of β -pinene, p-cymene, β -caryophyllene, terpinen-4-ol, perillaldehyde, (E)-2-dodecenal and α -sinensal also were characterized in the extract.

A hand-pressed oil of tangerine produced from fruit grown in Vietnam was the subject of analysis by Minh Tu et al. (2002). They found that the oil comprised the following components:

 $\begin{array}{l} \alpha \text{-pinene} \ (0.5\%) \\ \beta \text{-pinene} \ (0.4\%) \\ \text{sabinene} \ (0.2\%) \\ \text{myrcene} \ (2.0\%) \\ \text{limonene} \ (95.1\%) \\ \beta \text{-phellandrene} \ (0.3\%) \\ \text{octanal} \ (0.2\%) \\ \text{tetradecane} \ (0.1\%) \\ \text{decanal} \ (0.1\%) \\ \text{linalool} \ (0.2\%) \\ \alpha \text{-terpineol} \ (0.1\%) \\ \text{nerol} \ (0.1\%) \end{array}$

In addition, trace amounts (< 0.1%) of camphene, α -phellandrene, (Z)- β -ocimene, (E)- β -ocimene, terpinolene, tridecane, *cis*-linalool oxide (furanoid), *cis*-limonene oxide, *trans*-limonene oxide, *trans*linalool oxide (furanoid), citronellal, octanol, β elemene, undecanal, *trans*-p-mentha-2,8-dien-1-ol, (E)-2-decenal, citronellyl acetate, α -humulene, neral, dodecanal, germacrene D, neryl acetate, geranial, carvone, geranyl acetate, citronellol, perillaldehyde, octadecane, *cis*-carveol, (E)-2-dodecenal and perillyl alcohol also were found in this same oil.

Kryger (2002) reported that Dancy tangerine peel oil typically contained α -thujene, α -pinene, sabinene, β -pinene, myrcene, octanal, limonene, γ -terpinene, linalool, decanal and α -sinensal. The oil has been found to possess an aldehyde content of 1.0–1.2%. It lacks β -sinensal, which usually is found at higher levels than α -sinensal in orange oil. It also lacks the potent methyl N-methyl anthranilate characteristic of Italian mandarin oils.

The Sunburst tangerine cultivar (*Citrus clementina* Hort. ex Tanaka x *C. paradisi* Macf. x *C. tangerina* x *C. paradisi* x *C. tangerina*) has become the most widely grown tangerine in Florida (Jackson and Davies 1999). Kryger (2002) reported that the oil contained α -thujene, α -pinene, sabinene, β -pinene, myrcene, octanal, limonene, γ -terpinene, linalool, decanal and α -sinensal. The oil generally is found to contain lower levels of β -pinene, γ -terpinene and α -sinensal, as well as a total aldehyde (ca. 0.8%) less than Dancy tangerine oil, making it less intense than the Dancy oil.

The Robinson tangerine cultivar oil (*C. clementina* x *C. paradisi* x *C. tangerina*) is available commercially only occasionally (Jackson and Davies 1999). The oil composition is very similar to that of Sunburst oil, although the γ -terpinene content is reduced (Kryger 1999).

The Murcott, Honey tangerine or Honey Murcott tangerine cultivar oil (hybrid origin unknown) was found to contain α -thujene, α -pinene, sabinene, β -pinene, myrcene, octanal, limonene, γ -terpinene, linalool and decanal (Kryger 1999). Unlike the other so-called tangerine oils, it has very low β -pinene and γ -terpinene contents, a negligible amount of α -sinensal, but an aldehyde content of ca. 1.2%, which is similar to Dancy tangerine oil.

The Fallglo tangerine was developed by crossing the Bower citrus hybrid (origin unknown) with the Temple orange hybrid (*C. tangerina* x *C. sinensis* (L.) Osbeck) (Jackson and Davies 1999). Kryger (2002) found that the oil contained α -pinene, sabinene, β -pinene, myrcene, octanal, limonene, γ -terpinene, linalool, decanal, α -sinensal and β -sinensal.

The Orlando tangerine is actually a tangelo whose hybrid origin is *C. paradisi* (Duncan cultivar) x *C. tangerina* (Dancy cultivar). The oil of Orlando tangerine oil was found by Kryger (2002) to contain α -thujene, α -pinene, sabinene, β -pinene, myrcene, octanal, limonene, γ -terpinene, linalool, decanal, valencene, β -sinensal and α -sinensal. Because of the α -sinensal and valencene content, this oil appears very similar to that of an orange oil.

The temple hybrid orange (*C. tange-rina* x *C. sinensis*) (Jackson and Davies 1999) often is classified as being a hybrid tangerine. Kryger (2002) reported that the oil obtained from this hybrid contained

 α -pinene, sabinene, β -pinene, myrcene, octanal, limonene, γ -tepinene, linalool, decanal, valencene and α -sinensal. The level of octanal found in this oil was the highest of any of the hybrid tangerines known to date.

Cold-pressed oils of the Dancy tangerine produced from fruit collected from six different geographic regions were analyzed by Dugo et al. (2005). The composition of these oils ranged as follows:

nonane + heptanal (t-0.01%) α-thujene (0.14-0.16%) α-pinene (0.83–1.02%) camphene (t-0.01%) sabinene (0.14-0.18%) β-pinene (0.29-0.34%) myrcene (1.76-2.34%) octanal (0.08–0.12%) α -phellandrene (0.03–0.04%) α-terpinene (0.02-0.06%) p-cymene (t-1.12%) limonene (89.58-90.94%) (E)-β-ocimene (0.02-0.06%) γ-terpinene (2.15-3.46%) cis-sabinene hydrate + octanol (0.02–0.06%) terpinolene (0.12-0.18%) linalool (0.54-0.72%) nonanal (0.03-0.06%)

cis-limonene oxide (0.03-0.21%) trans-limonene oxide (0.03-0.14%) myroxide* (0.01-0.02%) citronellal (0.03-0.06%) terpinen-4-ol (0.01-0.02%) α-terpineol (0.07-0.24%) decanal (0.10-0.14%) cis-carveol (t-0.02%) citronellol (0.03-0.05%) methyl thymol (0.03-0.05%) neral (t-0.01%) carvone (0.01-0.03%) (E)-2-decenal (0.01-0.02%) geranial (0.01-0.02%) perillaldehyde (0.03-0.05%) thymol (0.05-0.07%) undecanal (0.01-0.02%) (E,E)-2,4-decadienal (0.02%) α -terpinyl acetate (0.01–0.04%) neryl acetate (0.01–0.03%) α -copaene (0.01%) geranyl acetate (t-0.01%) β -cubebene + β -elemene (0.02–0.04%) 1-tetradecene (t-0.01%) dodecanal (0.02-0.03%) β -caryophyllene (t-0.01%) γ -elemene (t-0.01%) α -humulene (0.01%) γ-muurolene (0.02-0.08%) (E,E)-α-farnesene (0.04–0.05%) δ-cadinene (0.01–0.02%) elemol (t-0.01%)

germacrene B (0.05–0.09%) spathulenol (0.03–0.04%) α-sinensal (0.11–0.20%)

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

In addition, trace amounts of octyl formate, geraniol, citronellyl acetate, (E)-2-dodecenal, tridecanol, tetradecanal and tetradecanol also were found in each of the six oils.

The enantiomeric distribution of three monoterpene hydrocarbons in six cold-pressed oils of Mexican Dancy tangerine was determined by Dugo et al. (2005) using chiral GC. A summary of the results obtained can be seen as follows:

(1R,5R)-(+)-β-pinene (97.6–98.7%):(1S,5S)-(-)-β-pinene (1.3–2.4%)
(1R,5R)-(+)-sabinene (90.1–92.7%):(1S,5S)-(-)-sabinene

(7.3 - 9.9%)

(4R)-(+)-limonene (99.2%):(4S)-(-)-limonene (0.8%)

Examination of the oxygenated heterocyclic fraction of six samples of cold-pressed Dancy tangerine oil obtained from different regions in Mexico was the subject of study by Dugo et al. (2005). A summary of the results can be seen as follows:

tangeritin (1990–4220)^a heptamethoxyflavone (330–730) nobiletin + tetra-O-methylscutellarein (1180–2470)

 $^{a} = ppm$

- W. Reuther, H. J. Webber and L. D. Batchelor, *The Citrus Industry*. Vol. 1, p 366, University of California, Riverside, CA (1967).
- 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).
- C. Li and C. Qi, Studies on the chemical constituents of the essential oil from fruit peel of Citrus tangerina Hort. ex Tanaka. Fujian Fenxi Ceshi, 6, 716–718 (1997).
- V.L. Barrett and D.B. Nelson, Characterization of coumarin and psoralen levels in California and Arizonacitrusoils. In: Flavor Analysis. Developments in isolation and characterization. Edits., C.J. Mussinan and M.J. Morello, pp. 233–238, ACS Symp. Series No 705, Amer. Chem. Soc., Washington DC (1998).
- Y-H. Huang and V-L. Wu, Chemical components of essential oils from peels of 25 Citrus species and cultivars. Tianran Chanwu Yanjiu Yu Kaifa, 10(4), 48–54 (1998).
- L.K. Jackson and F.S. Davies, *Citrus Growing in Florida*. 4th Edn., pp. 88–95, University Press of Florida, Gainesville, FL (1999).

- M-L. Lota, D. de Rocca Serra, F. Tomi and J. Casanova, *Chemical variability of peel and leaf essential oils of 15 species of mandarins*. Biochem. Syst. Ecol., **29**, 77–104 (2001).
- S.B. Mitiku, H. Ukeda and M. Sawamura, Enantiomeric distribution of α-pinene, β-pinene, sabinene and limonene in various citrus essential oils. In: Food Flavors and Chemistry. Advances of the New Millennium. Edits., A.M. Spanier, F. Shahidi, T.H. Parliament, C. Mussinan, C-T. Ho and E. Tratras Contis, pp. 216–231, Royal Soc. Chem., Cambridge (2001).
- R. Naef and A. Velluz, Volatile constituents in extracts of mandarin and tangerine peel. J. Essent. Oil Res., 13, 154–157 (2001).
- N.T. Minh Tu, L.X. Thanh, A. Une, H. Ukeda and M. Sawamura, Volatile constituents of Vietnamese pummelo, orange, tangerine and lime oils. Flav. Fragr. J., 17, 169–174 (2002).
- J.M. Ortiz, Botany: taxonomy, morphology and physiology of fruits leaves and flowers. In: Citrus, The Genus Citrus. Edits., G. Dugo and A. DiGiacomo, pp. 16–35, Taylor and Francis, London, UK (2002).
- R. Kryger, Florida tangerine peel oil the changing cultivar landscape. Perfum. Flavor., 27(1), 22–27 (2002).
- P. Dugo, L. Mondello, O. Favoino, L. Cicero, N.A. Rodriguez Zenteno and G. Dugo, *Characterization of cold-pressed Mexican Dancy tangerine oils*. Flav. Fragr. J., **20**, 60–66 (2005).

To get a copy of this article or others, visit the P&F magazine Article Archives at www.PerfumerFlavorist.com/articles