

Progress in Essential Oils

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Fennel Oil

There are two commercial fennel oils that are produced in a variety of countries throughout the world. The most common one is bitter fennel whose taxonomic origin is *Foeniculum vulgare* Mill. subsp. vulgare. This also includes Florence fennel (finocchio) [F. vulgare subsp. vulgare var. azoricum (Mill.) Thell.] and sweet fennel [F. vulgare subsp. vulgare var. dulce Bett. et Trab.], which includes Bronze fennel (cultivars 'Rubrum,' 'Nigra,' 'Purpureum,' etc.) There is also a wild pepper fennel [F]. vulgare subsp. piperitum (Ucria) Cout., which is rarely encountered as seed or a collected wild plant.

A survey of the recent literature reveals that fennel oil (both sweet and bitter) has been the subject of review 12 times (Lawrence, 1979, 1981, 1984, 1989, 1992, 1994, 1996, 1998 and 2007). As has been seen in the past it is sometimes difficult to differentiate between sweet and bitter fennel oils. In this reviewer's experience the lower oil content and low level of fenchone is associated with sweet fennel oil while high oil and fenchone contents are associated with bitter fennel oil. In this review, the differentiation between the two oils will be attempted, as there does not appear to be a simple chemical point of difference. As most of the published studies have been on bitter fennel oil this review will commence with it.

Bitter Fennel Oil and Extract

The fruit oils of bitter fennel produced from plants collected from the wild in different regions of Italy and one region of Cyprus were examined by Bellomaria et al. (1999) using GC/MS only. The results of this study are reported in **T-1**.

Diaz-Maroto et al. (2006) collected 42 samples of wild fennel from two different geographical locations in central Spain. Each sample was dried at room temperature and ground prior to introduction into an automatic thermal desorption apparatus which was coupled to a GC/MS system (DTD-GC/MS). The volatiles determined from the 16 samples collected from the Madrid area (Middle Spain) can be seen summarized in T-2. Also the volatiles determined from the 26 samples collected from the Castilla-La Mancha area (Middle-South Spain) are summarized in T-3. As can be seen the oils varied in their α -pinene, α -phellandrene 1,8-cineole, fenchone, methyl chavicol and (E)-anethole contents. Furthermore it was interesting to note that the volatiles from the samples from the Madrid area varied considerably more than those from the Castilla-La Mancha area.

Zorca et al. (2006) compared the composition of a lab-distilled bitter fennel oil with the volatiles of the same batch of fruit with a supercuritical fluid CO_2 extraction using GC/MS as their method of analysis. The results of this study can be seen in **T-4**.

Bitter fennel seeds (fruit) that were purchased at a local market in Gorakhpur (GP) by Singh et al. (2006) were powdered and subjected to 6-hr hydrodistillation to produce an oil in 1.2% yield. Analysis of this oil using both GC-FID and GC/MS revealed that it contained the following constituents:

isovaleraldehyde (0.1%) α -pinene (0.2%) β -pinene (0.2%)myrcene (0.1%) δ -3-carene (0.1%)p-cymene (3.1%)limonene (3.1%)1,8-cineole (0.1%) (E)- β -ocimene (0.1%) γ -terpinene (2.1%)fenchone (8.6%)linalool (1.2%)camphor (0.3%) terpinen-4-ol (0.2%) α -terpineol (0.2%)methyl chavicol (4.7%) α -fenchyl acetate (0.2%)cuminaldehyde (0.4%)p-anisaldehyde (0.5%)(E)-anethole (70.1%)thymol (0.1%) α -copaene (0.1%) β -caryophyllene (0.2%)

Trace amounts (<0.01%) of ethanol, ethyl acetate, 2-methylbutanal, α -thujene, camphene, sabinene, α -terpinene, β -terpineol isomer, α -humulene and δ -cadinene were also characterized in this oil.

Nine lab-distillations of the same batch of bitter fennel seed (fruit) of Spanish origin were analyzed by Cerpa Chavez (2007). He found that the main components varied as follows:

 $\begin{array}{l} \alpha \text{-pinene} \ (1.0-7.9\%) \\ \beta \text{-pinene} \ (0.1-0.8\%) \\ myrcene \ (0.4-1.1\%) \\ \alpha \text{-phellandrene} \ (0.3-6.9\%) \\ limonene \ (1.1-2.3\%) \\ fenchone \ (5.8-14.9\%) \\ methyl \ chavicol \ (3.0-4.7\%) \\ (Z)\text{-anethole} \ (0.1-0.2\%) \\ (E)\text{-anethole} \ (63.1-85.2\%) \\ anisaldehvde \ (0.1-0.2\%) \end{array}$

Pour mortazavi and Hajimirsa deghi (2007) determined that supercritical fluid $\rm CO_2$ extracts of Iranian bitter fennel that were produced at 45 °C for 30–45 min at 200–350 bar possessed the following range of composition:

α-pinene (0.9–1.3%)
sabinene (0–0.9%)
limonene (7.2–9.3%)
(Z)-β-ocimene (0–1.4%)
γ-terpinene (0–0.8%)
fenchone (8.4–9.9%)
methyl chavicol (2.8–3.1%)
(E)-anethole (72.3–77.7%)
germacrene D (0–1.8%)

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An oil produced from bitter fennel seed grown in Iran was determined by Hadian et al. (2008) to possess the following major components:

 $\begin{array}{l} \alpha \text{-thujene} \; (4.3\%) \\ \beta \text{-pinene} \; (0.4\%) \\ \alpha \text{-phellandrene} \; (4.6\%) \\ p \text{-cymene} \; (0.3\%) \end{array}$

 $\begin{array}{l} \beta \text{-phellandrene (1.9\%)}\\ \gamma \text{-terpinene (0.5\%)}\\ \text{fenchone (7.2\%)}\\ \text{methyl chavicol (3.0\%)}\\ \text{(E)-anethole (75.8\%)} \end{array}$

Sharifi et al. (2008) screened two Iranian oils of the Apiaceae for their antifungal activity against postharvest

T-1. Comparative percentage composition of the fruit oils of *F. vulgare* var. *vulgare* from Italy and Cyprus

Compound	R.V.	S .	C.T.	P.L.
α-thujene	_	_	_	0.1
α -pinene	2.3	2.0	4.7	2.7
camphene	0.2	0.2	0.2	0.2
β-pinene	0.1	0.1	0.4	0.2
sabinene	0.4	0.4	0.3	0.3
myrcene	4.1	3.5	4.3	5.4
limonene	1.7	3.5	1.5	1.7
1,8-cineole	1.4	1.5	1.2	1.2
(Z)-β-ocimene	0.1	0.1	0.7	0.5
γ-terpinene	0.6	0.8	0.5	1.5
p-cymene	1.1	1.0	1.5	3.4
terpinolene	0.1	0.1	0.1	0.1
fenchone	19.7	18.4	16.7	14.0
lpha-fenchyl acetate	-	-	-	0.2
lpha-fenchyl alcohol	0.3	-	0.1	1.3
camphor	0.4	0.3	0.4	0.3
β-caryophyllene	-	-	0.1	0.1
methyl chavicol	59.8	65.0	64.9	65.8
(Z)-anethole	t	-	0.1	0.4
(E)-anethole	7.5	3.2	0.7	0.1
carvacrol	-	-	-	0.3

t=trace (<0.1%); R.V.=Rocca Varano (Camerino, Italy); S=Sentino (Camarino, Italy); C.T.=Colle Truscino (L'Aquita, Italy); P.L.=Pano Lefkara (Cyprus)

pathogens. One of the oils (bitter fennel), which was produced by 3-hr hydrodistillation in 2.6% yield, was analyzed by GC-FID and GC/MS. The composition of the oil was determined to be:

 α -thujene (0.1%) α -pinene (0.9%) camphene (0.1%)sabinene (0.2%) β -pinene (0.2%) myrcene (0.5%) p-cymene (0.1%) limonene (8.2%) (Z)- β -ocimene (0.9%) γ -terpinene (0.6%) fenchone (8.5%)camphor (0.1%)methyl chavicol (7.0%) α -fenchyl acetate (0.4%) (Z)-anethole (0.3%) (E)-anethole (71.2%)

Singh et al. (2008) reported that the constituents of the immature green seeds of an Indian bitter fennel (*F. vulgare*, according to the authors) were:

citronellal (1.8%) fenchone (8.2%) (E)-anethole (2.1%) geraniol (0.6%) cuminaldehyde (87.3%)

This study needs to be repeated as the cuminaldehyde was probably misidentified because it has only ever been characterized as a minor constituent of any fennel oil.

T-2. Comparative percentage composition of the volatiles of *F. vulgare* originating from the mid-Spain region

Compound	1	2	3	4	5	6	7
α-pinene	21.3	1.8–7.0	0.5-5.9	1.0-2.4	2.1	1.2-1.9	2.2
camphene	1.1	0.2-0.6	0.3–0.7	0.3–0.6	0.5	0.4-0.6	0.4
β-pinene	1.5	0.5-2.7	t–1.2	0.4-1.0	2.9	0.2-0.3	0.2
myrcene	7.8	2.7-3.8	2.9-4.3	4.6-5.8	2.2	1.7–1.8	1.9
α -phellandrene	0.4	14.9–39.5	24.9-33.3	25.8-31.4	0.2	0.3–3.5	0.5
1,8-cineole	46.1	0.6-8.9	6.6-8.4	23.5-27.2	21.7	11.6-41.2	2.5
limonene	12.4	0.4-5.2	3.2-6.6	t–6.5	0.4	1.3-4.0	0.1
β-phellandrene	0.5	t–1.5	0.1-0.3	t–1.5	t	t–0.1	t
p-cymene	0.1	1.8-6.7	0.8-2.2	1.3–1.4	0.1	1.0-4.1	0.1
fenchone	0.7	16.4-26.9	16.2-22.0	8.3-12.9	25.5	9.6-21.5	18.3
camphor	1.9	0.2-1.1	t–1.0	t	0.7	0.7-1.5	0.6
methyl chavicol	t	10.6-40.3	0.4-1.0	6.7–9.9	29.8	0.3–1.3	58.6
(E)-anethole	3.6	t8.5	23.1–37.3	11.5–15.5	13.6	34.9–55.9	14.2

t=trace (<0.1%); 1=oils rich in α-pinene, 1,8-cineole and limonene; 2=oils rich in α-phellandrene, fenchone and methyl chavicol; 3=oils rich in α-phellandrene, fenchone and (E)-anethole; 4=oils rich in α-phellandrene, 1,8-cineole, fenchone and (E)-anethole; 5=oils rich in 1,8-cineole, fenchone, methyl chavicol and (E)-anethole; 6=oils rich in 1,8-cineole, fenchone and (E)-anethole; 7=oils rich in fenchone, methyl chavicol and (E)-anethole Anwar et al. (2009a) examined the composition of oils produced by 3-hr hydrodistillation from fennel fruit (noted as being sweet fennel; however, with a high fenchone content it is undoubtedly bitter fennel) from three stages of maturity grown in the vicinity of Sangla Hill (Punjab, Pakistan). The oils were examined using both GC-FID and GC/ MS. The results of these analyses can be seen in **T-5**.

Anwar et al. (2009b) examined the composition and some biological activities of bitter fennel fruit oil produced in 2.8% yield from mature fruit grown in Pakistan. The constituents characterized in this oil using GC-FID and GC/MS were as follows:

 α -pinene (0.6%) camphene (0.1%) sabinene (0.2%) β -pinene (0.1%) myrcene (0.9%) α -phellandrene (0.2%) limonene (5.1%)1,8-cineole (0.2%) (Z)- β -ocimene (0.6%) fenchone (10.2%) α-fenchyl alcohol (0.4%) methyl chavicol (5.5%) α -fenchyl acetate (0.1%) β -fenchyl acetate (0.5%) (Z)-anethole (0.3%)p-anisaldehyde (0.2%) (E)-anethole (69.9%) β -caryophyllene (0.3%) germacrene D (0.1%)

Trace amounts (< 0.05%) of p-cymene and (E)- β -ocimene were also found in this oil.

A commercial oil of bitter fennel was analyzed by De Martino et al. (2009) using GC-FID and GC/MS. The oil was found to contain the following constituents:

 $\begin{array}{l} \alpha \text{-pinene} \ (1.8\%) \\ \beta \text{-pinene} \ (0.5\%) \\ myrcene \ (0.2\%) \\ \alpha \text{-phellandrene} \ (0.3\%) \\ \delta \text{-}3\text{-carene} \ (0.3\%) \\ o \text{-cymene} \ (0.3\%) \\ limonene \ (1.5\%) \\ p \text{-cymene} \ (0.3\%) \\ \beta \text{-phellandrene} \ (0.4\%) \\ \gamma \text{-terpinene} \ (0.1\%) \\ fenchone \ (14.2\%) \\ dihydrocarveol \ (0.3\%) \\ myrtenal \ (0.1\%) \end{array}$

T-3. Comparative percentage volatiles of wild fennel originating from mid/south Spain

Compound	1	2	3	4
α-pinene	t–0.2	t–0.6	0.2-0.5	t–0.9
camphene	t	t–0.1	t–0.1	t–0.1
β-pinene	t–0.1	t-0.4	t0.8	0.1-0.7
myrcene	t–0.1	t–0.1	t0.4	0.1-0.2
lpha-phellandrene	t0.6	t-0.4	t–1.0	0.2–1.1
limonene	t–2.2	t-0.9	0.1–1.5	0.1-0.7
β -phellandrene	t	t	t–0.1	t–0.1
p-cymene	t0.2	t–0.5	t–1.4	0.2-0.7
fenchone	t0.8	1.5–16.1	6.3–19.0	15.5–27.0
camphor	t	t–0.1	t–0.2	t–0.2
methyl chavicol	0.1–0.8	0.1–0.7	0.1-0.6	31.4–55.2
(E)-anethole	95.9–98.1	89.6–96.6	68.9–88.0	13.4–50.5

t=trace (<0.1%); 1=oils rich in (E)-anthole; 2=oils rich in (E)-anthole and moderate amounts of ferchone; 3=oils rich in (E) anthole and ferchone; 4=oils rich in ferchone, methyl chavicol and (E)-anthole

T-4. Comparative percentage composition of the essential oil the volatiles of some supercritical fluid (CO_2) extracts of bitter fennel

Compound	Oil	Extract ^a
α -thujene	0.1	0.1-0.2
α-pinene	2.1	1.1–2.3
camphene	0.3	0.2-0.4
δ-3-carene	0.1	0–0.1
sabinene	0.2	0.1
β-pinene	0.1	0.1
myrcene	0.6	0.3–0.5
lpha-phellandrene	0.5	0.3
p-cymene	0.9	0.2-0.4
limonene	1.8	0.5-0.6
1,8-cineole	1.2	0.1–0.5
(Z)-a-ocimene	0.1	0–0.1
(E)-α-ocimene	0.1	0–0.1
α -terpinene	0.8	0.2-0.7
terpinolene	0.2	0.1
linalool	0.2	0.1–0.4
fenchone	20.3	23.3–25.4
α -thujone [†]	0.1	0.1
lpha-fenchyl alcohol	0.1	t–0.1
camphor	0.4	0.1-0.6
menthone [†]	0.1	0.1
isomenthone [†]	t	0–0.1
menthol [†]	-	0.1
terpinen-4-ol	0.3	0.1-0.1
dihydrocarveol	0.3	0.2
methyl chavicol	6.0	4.2-5.0
p-anisaldehyde	1.0	0.4-0.5
(Z)-anethole	0.5	0.5–0.7
(E)-anethole	59.1	61.2-64.1
dihydrocarvyl acetate	0.7	0.3-0.4
dihydrocarvyl acetate [*]	0.6	0.1–0.3
eugenol	0.5	0.3-0.6
methyl eugenol	0.2	0.1-0.2
β-caryophyllene	0.3	0.2-0.3
β-bisabolene	0.6	0.1–0.2

^asummary of three SFE extractions using different CO₂ flow rates; t=trace (<0.05%); *correct isomer not identified; [†]collaboration is needed for these unusual constituents

T-5. Comparative percentage composition of fennel fruit oils produced from different maturity stages

Compound	Immature fruit oil	Intermediate fruit oil	Mature fruit oil
α -thujene	0.5	0.3	0.1
lpha-pinene	0.9	0.6	0.4
camphene	0.1	0.1	0.1
sabinene	0.2	0.2	0.1
β-pinene	0.1	0.1	0.1
myrcene	0.7	0.9	0.8
lpha-phellandrene	1.2	0.8	0.2
p-cymene	t	t	t
limonene	7.8	4.7	3.5
1,8-cineole	0.3	0.4	0.2
$lpha$ -ocimene †	0.6	0.6	0.2
β-ocimene [‡]	1.0	t	t
γ-terpinene	1.1	0.1	0.1
fenchone	8.8	10.0	11.0
linalool	0.1	0.1	0.1
lpha-fenchyl alcohol	-	-	t
lpha-thujone	0.1	0.1	t
camphor	0.5	0.5	0.5
terpinen-4-ol	0.1	0.1	-
methyl chavicol	6.9	6.9	7.2
lpha-fenchyl acetate	0.1	t	0.1
β-fenchyl acetate	0.3	0.1	0.2
carvone	-	0.2	-
(Z)-anethole	0.5	0.5	0.7
p-anisaldehyde	0.3	0.4	0.2
(E)-anethole	65.2	69.7	72.6
piperitenone oxide [†]	-	-	0.3
lpha-copaene	0.1	0.2	0.1
anise ketone	t	0.1	-
β-bourbonene	t	t	-
β-caryophyllene	0.1	0.1	0.1
germacrene D	t	t	0.1
methyl (Z)-isoeugenol	0.1	0.1	0.1
elemicin	0.1	t	-
dillapiole	0.1	t	_
oil content	2.8	3.2	3.5
[†] probably (7)-ß-ocimene: probab	ly (F)-B-ocimene		

[†]probably (Z)- β -ocimene; probably (E)- β -ocimene

methyl chavicol (0.8%)

 $^{\mathrm{a}}\mathrm{should}$ be (E)-anethole

Trace amounts (< 0.05%) of α -thujene, sabinene, verbenene, α -terpinene, 1,8-cineole, (Z)- and (E)- β -ocimene, terpinolene, linalool, β -thujone, *trans*-pinocarveol, camphor, isopinocamphone, terpinene-4-ol, p-cymen-8-ol, carvacrol, methyl eugenol, α -copaene, isoledene, β -elemene, longifolene, β -caryophyllene, aromadendrene, α -humulene, allo-aromadendrene, γ -gurjunene, *cis*-muurola-4(14),5-diene and 7-epi- α -selinene were also listed as being found in this oil; however, the accuracy of their identifications requires corroboration before they can all be considered as true constituents of bitter fennel oil.

Cosge et al. (2009) collected the stems, leaves, leaf stalks and fruits of mature bitter fennel grown in an experimental garden in Ankara (Turkey). Hydrodistillation for 3 hr of each produced oils in the following yields: leaf (0.75%), leaf stalk (0.86%), stem (0.38%) and fruit (7.3%). The oils were analyzed using GC/MS only, the results of which can be seen in **T-6**.

Bankar et al. (2011) examined the composition of two commercial samples of Indian bitter fennel oil of Kanpur and Delhi origins. The results of this study are shown in **T-7**.

Saharkhiz and Tarakeme (2011) compared the main component composition of water distilled bitter fennel oils produced from fruit (seed) harvested at different stages of maturity when grown in Shiraz (Iran). The three ontogenetical stages of the fruit harvested were the 'pasty' stage (70% H_2O), the 'waxy' stage (52% H2O) and the 'fully ripe' stage (10–12% H_2O). The comparative composition of the oils that were analyzed by GC-FID and GC/MS can be seen in **T-8**. It is interesting to note that the oil yield was fairly constant irrespective of the maturity of the fruit.

Shalaby et al. (2011) examined the main constituents of two bitter fennel oils that were produced in Egypt from plants grown from seed imported from Germany and India. The main constituents of these oils are shown in **T-9**.

A commercial sample of bitter fennel oil was screened by Serban et al (2011) for its antimicrobial activity. The constituents characterized in this oil were α -pinene (10.3%), fenchone (48.5%) and (E)-anethole (26.8%). To date, no bitter fennel oil has ever been found with a fenchone content exceeding 30%.

The main constituents of the fruit oil of bitter *F. vulgare* of Thai origin that was produced in 0.57% yield were determined using GC/MS only by Intirach et al. (2012). They were as follows:

limonene (2.1%) fenchone (8.9%) methyl chavicol (5.7%) p-anisaldehyde (16.3%) (E)-anethole (63.0%) anise ketone^a (1.2%)

^aalso known as acetanisole or p-methoxyphenylacetone

Foeniculum vulgare plants were collected in the autumn from the Evora region, (Alentejo, Portugal). Hydrodistillation of the leaves for 3 hr produced an oil in 0.5% yield. Analysis of this oil by Martins et al. (2012) using GC-FID and GC/MS revealed that the oil possessed the following composition:

 $\begin{array}{l} \alpha \text{-pinene} \; (4.1\%) \\ \text{camphene} \; (0.2\%) \\ \alpha \text{-fenchene} \; (0.6\%) \end{array}$

⁽Z)-anethole^a (76.3%)

 $\begin{array}{l} \beta \text{-pinene } (0.5\%) \\ myrcene \, (5.2\%) \\ \alpha \text{-phellandrene } (2.2\%) \\ \text{limonene } (24.8\%) \\ 1,8\text{-cineole } (0.7\%) \\ (Z)\text{-}\beta\text{-ocimene } (0.1\%) \\ \gamma \text{-terpinene } (1.5\%) \\ (E)\text{-}\beta\text{-ocimene } (0.5\%) \\ \text{p-cymene } (1.1\%) \\ \text{terpinolene } (0.3\%) \\ \text{fenchone } (11.9\%) \\ \text{sabinene hydrate}^* (0.1\%) \\ \alpha \text{-copaene } (0.3\%) \\ \text{methyl chavicol } (2.8\%) \\ (E)\text{-anethole } (41.2\%) \end{array}$

°correct isomer not identified

A laboratory produced oil of *F. vulgare* of Tunisian origin was analyzed using GC-FID and GC/MS by Jilani et al. (2014). The main constituents of this oil were found to be as follows:

 α -pinene (1.4%) sabinene (0.5%) myrcene (0.3%) p-cymene (0.5%) limonene (11.2%) (E)- β -ocimene (0.4%) γ -terpinene (0.4%) fenchone (5.8%) camphor (0.2%) methyl chavicol (77.3%) carvone (0.3%) p-anisaldehyde (0.2%) (E)-anethole (6.4%)

El Ouariachi et al. (2014) examined the composition of bitter fennel leaf oil that was produced by 4-hr hydrodistillation from plants collected in full bloom from Al Hoceima (Morocco) using GC-FID and GC/MS. The oil was found to contain the following constituents:

 α -thujene (0.1%) α-pinene (8.0%) sabinene (1.0%) β -pinene (17.8%) myrcene (15.0%) α -phellandrene (0.3%) δ -3-carene (0.7%) p-cymene (1.5%) limonene (20.8%) γ -terpinene (0.8%) fenchone (12.5%) terpinolene (2.4%) linalool (0.3%) camphor (0.1%)trans-pinocarveol (0.2%) terpinen-4-ol (0.4%) α -terpineol (0.3%)

T-6. Comparative percentage composition of the oils produced from leaf, leaf stalk, stem and fruit of bitter fennel of the Turkish origin

Compound	Leaf oil	Leaf stalk oil	Stem oil	Fruit oil
α -pinene	31.8	2.4	1.8	1.8
camphene	0.1	-	_	-
β-pinene	3.0	0.4	_	_
myrcene	2.8	0.6	_	0.6
α -phellandrene	38.2	7.4	18.2	0.3
p-cymene	2.0	0.6	2.3	-
limonene	-	-	-	1.4
sabinene [†]	6.3	1.6	3.6	_
β-ocimene [*]	0.3	0.1	_	_
γ-terpinene	0.1	0.1	_	0.3
fenchone	1.0	1.7	_	15.1
camphor	_	0.1	_	0.2
methyl chavicol	0.4	3.9	3.4	5.2
α -fenchyl acetate	0.2	0.1	_	_
bicyclo [2.2.1] heptane [†]	_	0.2	1.4	
(E)-anethole	7.4	75.6	64.1	75.1
thymol	0.2	0.7	_	_
phenol [†]	_	0.1	_	_
α-copaene	0.1	0.2	_	_
germacrene D	2.0	2.0	3.9	_
naphthalene [†]	0.1	0.1	_	_
neophytadiene [†]	3.1	2.1	-	-

[†]incorrect identification; ^{*}correct isomer not identified

T-7. Percentage composition of two commercial bitter fennel oils of Indian origin

Compound	Kanpur oil	Delhi oil
α-pinene	0.9	0.5
camphene	0.1	0.1
β-pinene	0.1	_
β -phellandrene [†]	0.1	_
myrcene	0.4	0.3
limonene	6.3	2.7
1,8-cineole	0.2	0.2
(E)-β-ocimene	0.2	0.4
p-cymene	0.2	0.1
fenchone	9.4	10.9
lpha-fenchyl acetate	0.1	_
camphor	0.2	0.8
methyl chavicol	3.5	3.8
(E)-anethole	72.8	79.1
p-anisaldehyde	5.0	0.2
[†] incorrect identification		

 $\begin{array}{l} \mbox{piperitenone}^{\dagger} \ (1.0\%) \\ \mbox{piperitenone} \ \mbox{oxide}^{\dagger} \ (12.5\%) \\ \mbox{geranyl acetate} \ \ (0.2\%) \end{array}$

geranyl acetate (0.2%)nepetalactone[†] (0.7%)

[†]incorrect identification

B.M. Lawrence, Fenneloil. In: Progress in Essential oils. Perfum. Flavor., 4(2), 54–56 (1979); 4(5), $\begin{array}{l} 10\,(1979); {\bf 6}(2), 59-60\,(1981); {\bf 6}(3), 47\,(1981);\\ {\bf 9}(1), \, 59-60\,\,(1984);\, {\bf 9}(2), \, 24\,\,(1984);\, {\bf 14}(2),\\ 47-49\,\,(1989);\, {\bf 17}(2),\,\, 44-46\,\,(1992);\,\, {\bf 19}(1),\\ 31-32\,\,(1994);\, 21(2),\, 28,\, 30-31\,\,(1996);\, 23(2),\\ 52-55\,\,(1998);\, 32(1),\, 48-56\,\,(2007). \end{array}$

B. Bellomaria, G. Valentini and N. Arnold, *L'oLio essenziale di* Foeniculum vulgare *Mill. ssp.* vulgare. Rivista Ital., **27**, 43–48 (1999).

- M.C. Diaz-Maroto, M.S. Perez-Coello, J. Esteban and J. Sanz, Comparison of the volatile composition of wild fennel samples (Foeniculum vulgare Mill.) from Central Spain. J. Agric. Food Chem., 54, 6814–6818 (2006).
- M. Zorca, I. Gäinar and D. Bala, Influence of the process parameters on supercritical extraction of fennel essential oil. Anal. Univ. Bucharest, Chim., 15, 107–111 (2006).
- G. Singh, S. Maurya, M.P. de Lampasona and C. Catalan, *Chemical constituents, antifungal* and antioxidant potential of Foeniculum vulgare volatile oil and its acetone extract. Food Control, **17**, 745–752 (2006).
- M.G. Cerpa Chavez, *Hidrodestilacion de aceites* esenciales: Modelado y caracterizacion. Phd Thesis, Univ. Valladolid, Vallodolid, Spain (2007).
- S.M. Pourmortazavi and Hajimirsadeghi, Supercritical fluid extraction in plant essential and volatile oil analysis. J. Chromatogr., A, 1163, 2–24 (2007).
- J. Hadian, M. Ghasemnezhad, H. Ranjbar, M. Frazane and M. Ghorbanpour, Antifungal potency of some essential oils in control of postharvest decay of strawberry caused by Botrytis cinerea, Rhizopus stolonifer and Aspergillus niger. J. Essent. Oil Bear. Plants, 11, 553–562 (2008).
- R. Sharifi, H. Kiani, M. Farzaneh and M. Ahmadzadeh, Chemical composition of essential oils of Iranian Pimpinella anisum L. and Foeniculum vulgare Miller and their antifungal activity against postharvest pathogens. J. Essent. Oil Bear. Plants, 11, 514–522 (2008).
- V. Singh, M. Ali, D. Katiyar, S. Dubey, D. Anand and A. Malik, Volatile constituents and antimicrobial activity of immature green seeds of Foeniculum vulgare Miller. J. Essent. Oil Res., 11, 655–658 (2008).
- F. Anwar, M. Ali, A.I. Hussain and M. Shahid, Antioxidant and antimicrobial activities of essential oil and extracts offennel (Foeniculum vulgare Mill.) seeds from Pakistan. Flav. Fragr. J., 24, 170–176 (2009a).
- F. Anwar, A.I. Hussain, S. Tufail, H. Sherazi and M.I. Bhanger, *Changes in composition and* antioxidant and anti-microbial activities of essential oil of fennel (Foeniculum vulgare Mill.)fruit at different maturity stages. J. Herbs Spices Med. Plants, 15, 188–203 (2009b).
- L. De Martino, V. De Feo, F. Fratianni and F. Nazzaro, Chemistry, antioxidant, antibacterial and antifungal activities of volatile oils and their components. Nat. Prod. Commun., 4, 1741–1750 (2009).
- B. Cosge, A. Ipele and B. Gurbuz, Gas chromatography/mass spectrometry analysis of essential oil from different vegetative organs and fruits of Foeniculum vulgare Mill. var. vulgare growing in Turkey. Asian J. Chem., 21, 4081–4087 (2009).
- R. Bankar, A. Kumar and S. Puri, Comparative studies of the major components present in essential oils of commercial fennel. J. Med. Arom. Plant Sci., 33, 295–298 (2011).

T-8. Comparative percentage composition of bitter fennel fruit oils produced from different maturity stages

Compound	'Pasty' stage oil	'Waxy' stage oil	'Ripe' stage oil
lpha-pinene	0.3	0.2	0.2
sabinene	-	-	t
myrcene	0.2	0.2	0.1
lpha-phellandrene	-	-	t
limonene	3.3	3.0	3.3
1,8-cineole	0.5	0.5	0.4
γ-terpinene	-	0.1	0.1
fenchone	8.9	8.8	7.1
camphor	0.1	0.1	0.1
methyl chavicol	2.5	2.7	2.6
lpha-fenchyl acetate	0.1	0.1	0.1
(E)-anethole	84.1	84.3	86.1
oil yield (%)	1.3	1.2	1.3
t=trace (<0.05%)			

T-9. Percentage composition of the main constituents of German and Indian seed origin oils of bitter fennel grown in Egypt

Compound	German seed oil	Indian seed oil
lpha-pinene	4.0	2.6
β-pinene	0.5	0.7
myrcene	2.4	1.8
limonene	12.2	13.0
1,8-cineole	2.0	0.3
fenchone	10.9	14.6
methyl chavicol	4.8	8.7
(E)-anethole	62.1	50.3

- M.J. Sarkarkhiz and A. Tarakeme, Essential oil content and composition offennel (Foeniculum vulgare L.) fruits at different stages of development. J. Essent. Oil Bear. Plants, 14, 605–609 (2011).
- A.S. Shalaby, S.F. Hendawy and M.Y. Khalil, Evaluation of some types of fennel (Foeniculum vulgare Mill.) newly introduced and adapted in Egypt. J. Essent. Oil Res., 23, 35–41 (2011).
- E.S. Serban, M. Ionescu, D. Matinca, C.S. Maier and M.T. Bojita, *Screening of the antibacterial* and antifungal activity of eight volatile essential oils. Farmacia, **59**, 440–446 (2011).
- J. Intirach, A. Junkum, B. Tuetun, W. Choochote, U. Chaithong, A. Jitpakdi, D. Riyong, D. Champakaew and B. Pitasawat, *Chemical* constituents and combined larvicidal effects of selected essential oils against Anipheles cracens (Diptera: Culicidae). Psyche, 1–11 (2012).
- M.R. Martins, M.T. Tinoco, A.S. Almeida and J. Cruz-Morais, *Chemical composition, antioxidant* and antimicrobial properties of three essential oils from Portuguese flora. J. Pharmacognosy, 3(1), 39–44 (2012). I. Ben Haj Jilani, S. Chebil, R. Khiari, I. Melki, S. Limam-Ben Saad, A. Daoud–Bouattour and Z. Gammar–Ghrabi, Allelopathic potential of some essential oils

vis-a-vis three noxious weed species invading cereals. Internat. J. Agron. Agric. Res., 4(3), 77–97 (2014).

E. El Ouariachi, N. Lahhit, A. Bouyanzer, B. Hammouti, J. Paolini, L. Majidi, J-M. Desjobeit and J. Costa, *Chemical composition* and antioxidant activity of essential oils and solvent extracts of Foeniculum vulgare Mill. from Morocco. J. Chem. Pharmaceut. Res., 6, 743–748 (2014).

Other Fennel Oils

In addition to the other varieties of *Foeniculum vulgare*, a number of the studies did not adequately describe the taxonomic identity of the fennel examined. Hence, they will be included in this section.

Perez et al. (2007) characterized the volatile components of an aqueous extract of fennel plants using a PDMS-DVB SPME fiber combined with GC/ MS. The characterized components were as follows:

T-10. Comparative percentage composition of the stem, leaf and inflorescence	ļ
oils of <i>F. vulgare</i>	

Compound	Stem oil	Leaf oil	Inflorescence oil
α-pinene	10.9	13.4	7.0
camphene	0.4	0.6	0.4
sabinene	t	t	2.4
β-pinene	4.3	5.0	t
myrcene	5.0	5.5	2.6
δ-2-carene	t	4.2	t
lpha-phellandrene	14.6	1.3	8.7
p-cymene	t	17.5	t
limonene	12.9	5.7	9.5
(Z)-β-ocimene	2.0	t	1.2
(E)-β-ocimene	0.2	t	t
α -terpinene	0.4	t	2.2
fenchone	3.0	4.8	9.0
lpha-pinene oxide	t	0.5	-
isoanyl isovalerate	-	0.5	-
camphor	-	0.7	-
methyl chavicol	32.7	27.4	49.8
lpha-fenchyl acetate	1.4	4.3	0.1
β-fenchyl acetate	7.9	4.5	0.9
(E)-anethole	1.0	t	5.3
bornyl acetate	0.2	0.6	t
lpha-copaene	0.2	t	t
β-caryophyllene	0.6	0.3	t
<i>trans</i> -α-bergamotene	0.2	-	-
<i>cis</i> -muurola-4(14), 5-diene	1.3	1.0	0.8
t=trace (<0.1%)			

 $\begin{array}{l} \alpha \text{-pinene } (4.0)^a \\ \text{limonene } (21.1) \\ \gamma \text{-terpinene } (7.2) \\ \text{fenchone } (9.7) \\ (Z) \text{-anethole } (2.7) \\ \alpha \text{-fenchyl acetate } (7.5) \\ (E) \text{-anethole } (153.0) \\ \text{apiole } (13.5) \end{array}$

^aµg/g

While screening a sample of fennel oil produced in the lab from seeds (fruit) purchased at a local Egyptian market, Dawidar et al. (2008) determined that the major constituents of the oil were as follows:

limonene (34.6%) 1,8-cineole (2.0%) cis-sabinene hydrate (5.9%) fenchone (3.9%) carvone (11.0%) (E)-anethole (13.6%) β -longipinene[†] (2.5%) apple (1.2%)

[†]incorrect identification

It should be noted that the level of (E)-anethole is very low; this level is generally only encountered when the methyl chavicol chemotype is examined. In addition, the level of carvone is much higher than previously encountered.

Manolakou et al. (2009) collected the aerial parts of Foeniculum vulgare at the end of its flowering stage from a planting on the campus of the University of Athens (Greece). The fresh and dried stems, fresh leaves and fresh inflorescences were separated, cut into small pieces and separately hydrodistilled for 3 hr. The oil yields were 1.25% (fresh stems), 1.41% (fresh leaves) and 2.46% (fresh inflorescences). Analysis of these oils was conducted using GC-FID, GC/ MS and retention indices on both polar and non-polar capillary columns. The constituents characterized in these oils can be seen in summary form in T-10.

The authors also characterized a number of trace (<0.1%) constituents in one or all of the oils. They were α -thujene, α -terpinene, β -phellandrene,

1,8-cineole, *cis*-sabinene hydrate, α -fenchyl alcohol, *cis*-p-menth-2-en-1-ol, an allo-ocimene isomer, *cis*-pinene hydrate, β -pinene oxide, *trans*-verbenol, terpinen-4-ol, verbenone, hexyl isovalerate, cuminaldehyde, carvone, (E)-2-hexenyl isovalerate, (Z)-anethole, *trans*-sabinyl acetate, neryl acetate, β -cubebene, (E)- β -farnesene, bicyclogermacrene, α -cadinene, (E)-nerolidol, caryophyllene oxide, allo-aromadendrene epoxide and T-muurolol.

The main constituents of an oil produced in Egypt from the mature fruit of finocchio [*Foeniculum vulgare* Mill. var. *azoricum* (Mill.) Thell.] were found by Shalaby et al. (2011) to be:

 $\begin{array}{l} \alpha \text{-pinene (2.2\%)} \\ \beta \text{-pinene (0.2\%)} \\ \text{myrcene (0.4\%)} \\ \text{limonene (16.7\%)} \\ 1,8\text{-cineole (0.3\%)} \\ \text{fenchone (8.0\%)} \\ \text{methyl chavicol (4.5\%)} \\ \text{(E)-anethole (64.4\%)} \end{array}$

An oil produced by hydrodistillation for 3 hr from the flowering plants of *F. vulgare* var. *azoricum*, which was collected from a commercial cultivation near Bilbase City (Egypt), was analyzed by Shahat et al. (2012) using GC/MS only. The constituents characterized in this oil were:

 α -pinene (32.8%) camphene (0.5%)sabinene (0.3%) β -pinene (2.1%) myrcene (1.6%) p-cymene (0.3%) limonene (13.9%) (E)- β -ocimene (0.7%) sylvestrene^{\dagger} (1.0%) γ -terpinene (0.6%) fenchone (5.9%) terpinolene (1.1%) trans-limonene oxide (0.2%)camphor (0.1%)terpinen-4-ol (0.1%) methyl chavicol (15.3%) α -fenchyl acetate (0.5%) β -fenchyl acetate (7.8%) (E)-anethole (14.8%) β -caryophyllene (0.3%) germacrene D (0.1%)

[†]incorrect identification

Shahat et al. (2012) also collected wild fennel (*F. vulgare* subsp. *piperitum*)

during its flowering period from Marsa-Matroh province in Egypt. Analysis of the oil, which was produced by hydrodistillation for 3 hr, using GC/MS only revealed that it possessed the following composition:

 α -pinene (2.0%) camphene (0.1%)sabinene (0.1%) β -pinene (0.1%) myrcene (0.9%) limonene (84.5%) sylvestrene[†] (0.2%) trans-isolimonene[†] (0.4%) γ -terpinene (0.5%) fenchone (0.8%)terpinolene (0.4%) trans-limonene oxide (0.2%)terpinen-4-ol (< 0.1%) methyl chavicol (0.1%) α -fenchyl acetate (0.1%) β -fenchyl acetate (0.9%) (Z)-anethole (0.1%)(E)-anethole (6.2%) β -caryophyllene (0.1%) germacrene D (40.1%)

[†]incorrect identification

Finally, Khan et al. (2014) determined that the typical oil yield of Indian fennel was 0.38%, while the typical fenchone and (E)-anethole contents were 3.5% and 80.5%, respectively. Furthermore, the authors showed that growth regulators used in a controlled way could result in an increase in oil content to 0.49% with fenchone and (E)-anethole contents of 4.0% and 85.3%, respectively.

- R.A. Pérez, T. Navarro and C. de Lorenzo, HS-SPME analysis of the volatile compounds from spices as a source of flavour in 'Campo Real' table olive preparations. Flav. Fragr., J., 22, 265–273 (2007).
- A.M. Dawider, M.A. Mogib, A.H. El-Ghorab, M. Mahfouz, F.G. Elsaid and Kh. Hussien, Chemical composition and effect of photooxygenation on biological activities of Egyptian commercial anise and fennel essential oils. J. Essent. Oil Bear. Plants, 61, 124–136 (2008).
- A.S. Shalaby, S.F. Hendawy and M.Y. Khalil, Evaluation of some types of fennel (F. vulgare Mill.) newly introduced and adapted in Epypt. J. Essent. Oil Res., 23, 35–41 (2011).
- S. Manolakou, D. Pitarokili, G. Koliopoulos, A. Michaelakis and O. Tzakou, *Essential oil*

composition of different parts of Greek Foeniculum vulgare and larvicidal activity of the stem oil. In: Essential oils and aromas, green extractions and applications. Edit., F. Chemat, 271–283, Har Krishan Bhalla & Sons, Dehradun, India (2009).

- A.A. Shahat, F.M. Hammouda, K.A. Shams and M.A. Saleh, *Comparative chemical analysis of* the essential oil of wild and cultivated fennel (Foeniculum vulgare Mill.). J. Essent. Oil Bear. Plants, 15, 314–319 (2012).
- M.M.A. Khan, N. Hashmi Moinuddin and T.A. Dar, Changes in growth, yield, photosynthetic characteristics, enzyme activities and essential oil production of fennel (Foeniculum vulgare Mill.) under growth regulator treatments. J. Essent. Oil Res., 26, 105–113 (2014).

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