Progress in Essential Oils

Brian M. Lawrence, Consultant

Jasmin Absolute

A commercial sample of jasmin absolute of Indian origin was analyzed by Jirovetz et al. (2007 and 2007). The absolute was determined to possess the following composition:

benzyl alcohol (1.3%)
trans-linalool oxide[f] (0.5%)
cis-linalool oxide[f] (0.4%)
methyl benzoate (0.1%)
linalool (8.2%)
benzyl acetate (23.7%)
p-cresol (0.6%)
α-terpineol (0.9%)
methyl salicylate (0.1%)
2-phenethyl acetate (0.1%)
nerol (0.8%)
geraniol (1.0%)
indole (1.8%)
eugenol (2.5%)
(Z)-jasmone (1.9%)
methyl anthranilate (1.0%)
isoeugenol° (0.1%)
(E,E)-α-farnesene (1.1%)
δ-jasmin lactone† (1.1%)
(E)-nerolidol (0.3%)
(Z)-3-hexenyl benzoate (0.9%)
methyl (Z)-jasmonate (0.6%)
benzyl benzoate (20.7%)
benzyl salicylate (0.1%)
methyl hexadecanoate (1.4%)
phytol (10.9%)
isophytol (5.6%)
geranyl linalool (3.0%)
methyl linoleate (2.8%)
methyl oleate (0.8%)
phytyl acetate (5.3%)

° correct isomer not identified
[f] furanoid form
† also known as jasmolactone

Trace amounts (< 0.05%) of (Z)-3-hexenol, 6-methyl-2-heptanone, (Z)-3-hexenyl acetate, 2-phenethyl alcohol, chavicol and (E)-jasmone were also found in this absolute.

Joshi et al. (2002) analyzed the formation of fragrant components over a four-week period in internode ex-plant calli of Indian jasmin. The components monitored were (Z)-jasmone, methyl jasmonate, linalool, eugenol and benzyl acetate. The report showed that the internode ex-plants retain the biosynthetic pathways for essential oil accumulation.

Ranade et al. (2002) reported that the main constituents of jasmin absolute of Indian origin were:

linalool (15.0%)
benzyl acetate (65.0%)
α-terpineol (5.0%)
indole (2.5%)
(Z)-jasmone (3.0%)
methyl anthranilate (1.5%)
geraniol (1.0%)

Based on the extremely high benzyl acetate content it appears that the absolute reported by Ranade was adulterated.

Nidry and Srivastava (2007) analyzed the volatiles in jasmin absolute. The authors did not perform an exhaustive analysis; they merely characterized some of the constituents as follows:

methyl anthranilate (1.4%)
indole (3.7%)
benzyl acetate (13.6%)
benzyl benzoate (10.1%)
benzyl alcohol (13.6%)
linalool (5.0%)
(Z)-jasmone (9.0%)
eugenol (3.2%)
phytol (4.5%)
isophytol (9.3%)

Wei and Shibamoto (2007) determined that the major components of a commercial sample of jasmin oil were as follows:

linalool (6.4%)
benzyl acetate (22.5%)
benzyl alcohol (6.5%)
(Z)-jasmone (2.9%)
p-cresol (1.4%)
(Z)-3-hexenyl benzoate (1.1%)
eugenol (3.0%)
methyl hexadecanoate (1.2%)
isophytol (7.5%)
(Z)-phytol (15.0%)

L. Jirovetz, G. Buchbauer, G.A. Eller, I. Stoilova, A. Stoyanova, A. Krastanov, E.Schmidt and M.Geissler, *Chemical composition and antioxidant properties of* Jasminum grandiflorum *L. absolute from India.* In: *Aromatic Plants from Asia their Chemistry and Application in Food and Therapy.* Edits., L. Jirovetz, N–X. Dung and V.K. Varshney, pp. 37–48, Har Kishan Bhalla & Sons, Dehradun, India (2007).

L. Jirovetz, G. Buchbauer, T. Schweiger, Z. Denkova, A. Slavchev, A. Stoyanova, E. Schmidt and M.Geissler, *Chemical composition, olfactory evaluation and antimicrobial activities of* Jasminum grandiflorum *L. absolute from India.* Nat. Prod. Commun., **2**, 407–412 (2007).

A. Joshi, G.C. Nanawati, V. Sharma and G. Rajamani, Jasminum grandiflorum *internode explant callus: synthesis and accumulation of essential oils.* Indian Perfum., **46**, 217–223 (2002).

G.S. Ranade, *Essential Oil Profile Jasmine Absolute*. FAFAI, **4**(3), 63 (2002).

E.S.J. Nidry and H.C. Srivastava, *A comparative study of the antifungal activities of the absolutes of jasmine and tuberose and their constituents.* Indian Perfum., **51,** 53–55 (2007).

A. Wei and T. Shibamoto, *Antioxidant activities and volatile constituents of various essential oils.* J. Agric. Food Chem., **55,** 1737–1742 (2007).

Atlas Cedarwood Oil

Atlas cedar is the name given to the member of the Pinaceae found growing in the Atlas mountains of Morocco and northwestern Algeria. The oil is obtained by steam distillation of the sawdust of *Cedrus atlantica* (Endl.) G. Manetti ex Carrier (syn: *C. libani* A. Rich subsp. *atlantica* (Manetti) Holm.

A survey of the early literature (Gildemeister and Hoffman, 1956) reveals that acetone, 1-methyl-4-acetylcyclohex-1-ene, a cadinene, α-atlantone, γ-altantone and a number of sesquiterpene alcohols have been reported as constituents of the oil.

Plattier and Teisseire (1972) analyzed an oil of Atlas cedarwood, in which they confirmed the presence of 1-methyl-4-acetylcyclohex-1-ene, (Z)-α-atlantone, (E)-α-atlantone, α-himachalene and β-himachalene. In addition, using a combination of spectroscopic techniques, they structurally elucidated four new components: γ-dehydro-ar-himachalene, γ-himachalene, 6,7-epoxy-β-himachalene and dehydro-β-atlantone.

Teisseire and Plattier (1974) further reported that Atlas cedarwood oil also contained 10,11-dihydroatlantone (syn: bisabola-2,7-dien-9-one) and a ketone of himachalene.

Adams et al. (1975) examined a commercial sample of Atlas cedarwood oil. The components identified in the oxygenated fraction of the oil were as follows:

α-ionone* (0.1%)
4-(4-methylcyclohex-3-enyl) pent-3-en-2-one (0.8%)
α-caryophyllene alcohol (0.4%)
epoxy-β-himachalene (2.0%)
epi-epoxy-β-himachalene (2.0%)
epi-cubenol (2.2%)
deodarone (3.8%)
(Z)-α-atlantone (1.6%)
(E)-α-atlantone (4.6%)

* correct isomer not identified

Five separate lots of Atlas cedarwood oil were analyzed by Benjilali et al. (1992) (c.f Chalchat et al., 1994). The range in oil composition was found to be as follows:

α-pinene (0.1–0.3%)
camphene (t–0.1%)
β-pinene (t–0.2%)
undecane (t–0.1%)
limonene (0.1–0.2%)
p-cymene (0–0.1%)
α-cedrene (0.1–0.2%)
α-copaene (t–0.1%)
veratrole + α-gurjunene (1.4–3.9%)
allo-aromadendrene (0.6–0.7%)
caryophyllene* (0.3–0.6%)
α-himachalene (14.4–16.9%)
γ-curcumene (0.4–0.5%)
γ-himachalene (10.1–11.2%)
β-himachalene (41.3–46.0%)
himachalene* (0.1–1.3%)
δ-cadinene (1.8–2.1%)
curcumene* (t–0.1%)
curcumene* (t–0.2%)
ar-curcumene (0.6–1.0%)
dehydroaromadendrene (t– 0.1%)
β-spathulene (t–0.1%)
8,9-dehydro-isolongifolene (0.6–0.9%)
calamenene* (0.1–0.6%)
α-ar-himachalene (0.9–1.5%)
γ-ar-himachalene (0.7–1.2%)
calacorene* (0.6–0.8%)
calacorene* (t–0.1%)
epoxy-β-himachalene (0.3–0.6%)
cubenol (0.5–0.8%)
calamenen-1-ol (0.3%)
α-himachalol (0.2–0.3%)
β-atlantone (0.2–0.7%)
dihydrocalamenenol (t–0.2%)
(Z)-γ-atlantone (0.8–1.4%)
(E)-γ-atlantone + deodarone + deodarone* (1.4–2.8%)
(Z)-α-atlantone (0.4–0.6%)
(E)-α-atlantone (1.6–3.1%)
podocephalol† (0.1–0.5%)

t = trace (< 0.05%)
* correct isomer not identified
† also known as himachala-1,3,5-trien-5-ol

In addition the oil contained trace (< 0.05%) amounts of decane,1,4-cineole, dodecane, tetradecane, pentadecane and cadalene. An unusual component such as 4,4-dimethyl-3-(3-methyl-2-buten-1-yliden)-2-methylidenebicyclo [4.1.0] heptanes (0.1–1.4%) was also identified in the oil.

Dahoun et al. (1993) compared the major components of some oils and extracts of Algerian Atlas cedarwood oils, the results of which are summarized in **T-1.**

Derriche et al. (1996) examined the effects of various parameters on the yield and composition of concretes obtained from Atlas cedarwood of Algerian origin.

The volatile components identified were α-himachalene, β-himachalene, γ-himachalene, α-calacorene, 7,8-dihydrohimachalene, epoxyhimachalene, γ-atlantone, (Z)-α-atlantone, (E)-α-atlantone, 2,7-dimethyloctanone, 2,7-dimethyloctanol and a number of uncharacterized sesquiterpenoid compounds. The variation of the major volatiles found in the concretes produced under different conditions was as follows:

α-himachalene (0.3–1.1%)
γ-himachalene (0.2–0.7%)
β-himachalene (0–1.5%)
7,8-dihydrohimachalene (3.4–8.2%)
expoxyhimachalene (9.5–20.7%)
γ-atlantone (0.3–1.5%)
(Z)-α-atlantone (0.3–0.7%)
(E)-α-atlantone (3.0–14.1%)

Aberchane et al. (2001) compared the composition of Atlas cedarwood oil produced either by steam distillation

Comparative main component composition of some oils and extracts of Moroccan Atlas cedarwood **T-1**

Compound	Oils	Extracts		
		Hexane	Diethyl ether	Methylene chloride
α-himachalene	3.1	2.3	0.4	1.5
γ-himachalene	4.0–10.8	12.2	6.9	3.4
β-himachalene	13.6–21.2	26.4	6.5	22.8
dehydrohimachalene*	0.5–1.1	1.1	0.7	2.0
epoxy-β-himachalene	3.3–8.7	8.0	11.1	5.6
γ-atlantone*	0.1–1.6	1.5	2.6	1.2
(Z)-α-atlantone	0.1–0.2	0.1	0.4	< 0.1
(E)-α-atlantone	4.5–10.8	5.5	12.2	6.8

* correct isomer not identified

or by hydrodistillation using wood collected in the Ouiouane forest, Khenifra (Morocco). The composition of the oils can be found in **T-2.** The authors also showed that hydrodistillation yielded oils richer in oxygenated sesquiterpenes, whereas steam distilled oils were richer in sesquiterpene hydrocarbons.

A water distilled oil of the wood of *C. atlantica,* which was produced from trees harvested in the Bainem forest near Algiers (Algeria), was analyzed by Boudarene et al. (2004) using GC-FID and GC/MS. The components characterized in this oil were as follows:

α-pinene (5.6%)
α-thujene (0.3%)
camphene (0.4%)
verbenene (0.1%)
β-pinene (0.7%)
myrcene (0.1%)
o-cymene (0.1%)
p-cymene (0.1%)
limonene (0.5%)
1,8-cineole (0.3%)
cis-linalool oxide[f] (0.1%)
fenchone (0.4%)
α-campholenic aldehyde (0.2%)
cis-β-terpineol (1.7%)
pinocamphone (0.1%)
α-terpineol (0.8%)
myrtenal (0.1%)
mytenol (0.8%)
verbenone (0.1%)
carvone (0.1%)
α-copaene (0.3%)
α-ylangene (0.2%)
longifolene (0.3%)
β-caryophyllene (6.0%)
aromadendrene (3.3%)
α-himachalene (2.1%)
α-humulene (1.3%)
(E)-β-farnesene (1.4%)
γ-himachalene (2.3%)
γ-curcumene (0.4%)
β-himachalene (3.7%)
α-dehydro-ar-himachalene (0.2%)
δ-cadinene (0.8%)
γ-dehydro-ar-himachalene (0.6%)
β-vetivenene (0.2%)
α-calacorene (0.1%)
oxido-himachalene (1.2%)
spathulenol (0.7%)
himachalol (28.1%)
cadalene (0.9%)
(E)-γ-atlantone (0.1%)
cis-calamenene (0.1%)
(Z)-α-atlantone (0.4%)
(E)-α-atlantone (1.6%)
14-hydroxy-δ-cadinene (1.0%)
pimara-8(14),15-diene (0.1%)
manoyl oxide (0.8%)
abietatriene (1.3%)
abietadiene (1.5%)
dehydroabietal (0.8%)
methyl dehydroabietate[t] (0.9%)

[f] furanoid form
[t] tentative identification

Comparative percentage composition of Atlas cedarwood oils produced by different distillation methods **T-2**

Compound	Steam-distilled oil	Water-distilled oil
trans-rose oxide	0.6	0.7
α-himachalene	15.8	5.3
γ-himachalene	9.6	3.8
6-methyl-γ-ionone	0.4	0.7
β-himachalene	39.7	14.6
δ-cadinene	1.6	1.3
β-sesquiphellandrene	0.9	1.1
α-calacorene	1.6	1.0
furfuryl octanoate	0.4	1.9
carotol	0.7	1.2
epi-cedrol	0.6	3.3
cedranone	1.1	1.6
cubenol	0.4	2.5
himachalol	2.5	6.5
5-isocedrol	0.9	1.5
(Z)-α-*trans*-bergamotol	1.1	0.1
deodarone	1.4	4.4
cedroxyde	1.8	1.3
(Z)-α-atlantone	2.0	5.2
khusimol	0.5	1.1
(E)-α-atlantone	9.2	30.8
hinesol acetate	0.6	1.3

Trace amounts (< 0.1%) of sabinene, perillene, 6-camphenol, *trans*-pinocarveol, thuj-3-en-10-al, *trans*-carveol and caryophyllene oxide were also found in this oil.

Atlas cedarwood oils produced from trees harvested in seven different Moroccan provenances were the subject of analyses by Abarchane et al. (2004). The range in composition of the oils was determined to be as follows:

4-acetyl-1-methylcyclohexane (0–0.6%)
isoledene (0.1–0.4%)
longifolene (0–0.5%)
tetradecane (0–0.8%)
himachala-2,4-diene (0.3–0.7%)
α-himachalene (7.4–16.4%)
(Z)-β-farnesene (0–0.2%)
thujopsadiene (0–0.4%)
8,9-dehydroisolongifolene (0–0.5%)
γ-himachalene (5.1–9.7%)
γ-curcumene (0.7–1.5%)
(E)-β-ionone (0–0.4%)
β-himachalene (23.4–40.4%)
cuparene (0–0.6%)
α-dehydro-ar-himachalene (0.4–1.2%)
δ-cadinene (0.5–2.6%)
γ-dehydro-ar-himachalene (0–0.9%)
β-vetivenene (0–1.4%)
α-calacorene (0.5–1.6%)
elemicin (0–0.7%)
oxido-himachalene (0.4–1.0%)
carotol (0–0.8%)
longiborneol (0–1.0%)
β-himachalene oxide (0–1.6%)
cedranone (0.7–2.3%)
1-epi-cubenol (1.1–2.5%)
3-isothujopsanone (0–0.6%)
himachalol (1.7–3.7%)
isocedranol (1.2–3.1%)
cadalene (0–1.4%)
acorenone (0–0.3%)
(Z)-*trans*-α-bergamotol (0–0.2%)
deodarone (1.2–7.7%)
(E)-γ-atlantone (1.2–4.2%)
(Z)-α-atlantone (1.0-5.9%)
khusimol (0–0.6%)
benzyl benzoate (0–0.5%)
(E)-α-atlantone (5.2–29.5%)
14-hydroxy-α-muurolene (0.2–1.0%)

E. Gildemeister and Fr. Hoffman, *Die Atherischen Ole.* Revised W. Triebs and K.Bournot, Vol 4, pp. 234–236, Akademic Verlag, Berlin, Germany (1956).

M. Plattier and P. Teisseire, *Isolement et syntheses de Constituents de l'essence de Cedre de l'Atlas.* An. Acad. Bras. Cienc., 44 (supl.) 392–404 (1972).

P. Teisseire and M. Plattier, *New bicyclic sesquiterpenic ketone isolated from Atlas cedarwood oil.* Recherches, (19), 167–172 (1974).

D. R Adams, S.P. Bhatnagar and R.C. Cookson, *Structure and Synthesis of a new ketone from* Cedrus *species; some new constituents of* C. atlantica Manet. J. Chem. Soc. Perkin 1 (15), 1502–1506 (1975).

B. Benjilali, J–C. Chalchat and R–Ph. Garry, *Huiles essentielles de* Cedrus atlantica *valorisation des sciures.* Rivista Ital. EPPOS (num. speciale), 562–570 (1992).

A. Dahoun, R. Derriche and R. Belabbes, *Influence du mode d' extraction et de la composition de l'huile essentielle et de la concrete du bois de cedre de l'Atlas Algerien.* Rivista Ital. EPPOS, (10), 29–32 (1993).

J–C. Chalchat, R–Ph. Garry, A. Michet and B. Benjilali, *Essential oil components in sawdust of* Cedrus atlantica *from Morocco*. J. Essent. Oil Res., **6,** 323–325 (1994).

R.Derriche, E.H. Benyoussef, J.M. Bessiere and R.Belabbes, *Influence de la variation de quelques parameters operatoires sur l'extraction des concretes de bois de cedre de l' Atlas Algerien*. Rivista Itlal. EPPOS, (18), 11–17 (1996).

M. Aberchane, M. Fechtal, A. Chaouch and T. Bouayoune, *Influence de la duree el de la technique d'extraction sur le rendement et la qualite des huiles essentielles du Cedre' de l'Atlas* (Cedrus atlantica *Manetti)* Ann. Rech. For. Maroc., **34,** 110–118 (2001).

L.Boudarene, L. Rahim, A. Baaliouamer and B.V.Meklati, *Analysis of Algerian essential oils from twigs, needles and wood of* Cedrus atlantica *G.Manetti by GC/MS.* J. Essent. Oil Res., **16,** 531–534 (2004).

M. Aberchane, M.Fechtal and A. Chaouch, *Analysis of Moroccan Atlas cedarwood oil (*Cedrus atlantica *Manetti).* J. Essent. Oil Res., **16**, 542–547 (2004).

Canadian Hemlock Oil

Canadian hemlock oil can be obtained either from the steam distillation of the needles and twigs of *Tsuga canadensis* (L.) Carr. (eastern hemlock), *T. heterophylla* (Raf.) Sarg. (western hemlock) or *T. mertensiana* (Bong.) Carr. (mountain hemlock); however, the commercially available hemlock oil of Canadian origin is obtained exclusively from *T. canadensis*.

A commercial sample of hemlock oil was analyzed by Lawrence (1980). The oil was found to contain:

tricyclene (1.3%)
α-pinene (12.1%)
camphene (13.4%)
β-pinene (16.0%)
limonene (12.0%)
β-phellandrene (4.9%)
p-cymene (0.1%)
terpinolene (3.7%)
p-cymenene (0.2%)
bornyl acetate (37.6%)
terpinen-4-ol (0.1%)
β-caryophyllene (0.9%)
citronellyl acetate (0.1%)
α-terpineol (0.6%)
borneol (0.1%)
α-terpinyl acetate (0.1%)
piperitone (0.6%)
geranyl acetate (0.2%)

Kubeczka and Schultze (1987) examined the composition of the needle oils of a number of coniferous trees, among which was *T. canadensis*. They found that the oil contained the following components:

santene (0.2%)
tricyclene (6.8%)
α-pinene (20.1%)
camphene (17.5%)
β-pinene (2.62%)
sabinene (0.2%)
δ-3-carene (< 0.1%)
myrcene (4.5%)
α-phellandrene (1.5%)
α-terpinene (0.2%)
limonene (3.0%)
β-phellandrene (2.6%)
γ-terpinene (0.4%)
p-cymene (0.4%)
terpinolene (0.5%)
p-cymenene (< 0.1%)
bornyl acetate (28.4%)
terpinen-4-ol (0.8%)
citronellyl acetate (0.2%)
α-terpineol (0.5%)
borneol + α-terpinyl acetate (0.3%)
piperitone (1.8%)
geranyl acetate (0.1%)

Broeckling and Salom (2003) measured the emission of volatiles from *T. canadensis.* They found a significant increase in the emission of volatiles of trees that were infested with the hemlock wooly adelgid (a major pest of eastern hemlock). Although the authors did not present easily relatable quantitative data, they showed that the major volatiles of uninfested foliage, in a decreasing order of magnitude, were (+)-α-pinene, (-)-α-pinene, myrcene, (+)-camphene, α-phellandrene, β-phellandrene, (-)-β-pinene, bornyl acetate, tricyclene, limonene, (+)-camphene and terpinolene. They did, however, note that the total α-pinene content was 66% of the volatiles.

Lagalante et al. (2007) screened the needle volatiles of 13 cultivars of *T. canadensis* using SPME and GC/MS. The headspace volatiles of the cultivars were found to range as follows:

tricyclene (3.1–7.8%)
α-pinene (11.6–22.7%)
camphene (7.8–15.9%)
sabinene (0–0.7%)
β-pinene (1.2–4.3%)
myrcene (0.7–2.4%)
α-phellandrene (0–3.3%)
o-cymene (0–1.6%)
limonene (0.7–5.6%)
β-phellandrene (0.4–5.2%)
(Z)-β-ocimene (0.2–3.5%)
γ-terpinene (0–0.2%)
terpinolene (t–0.8%)
camphor (0–1.8%)
borneol (0–3.0%)
piperitone (0–5.1%)
isobornyl acetate† (33.3–50.7%)
β-caryophyllene (1.3–6.0%)
α-humulene (0–9.2%)
γ-muurolene (0.1–1.6%)
germacrene D (0–6.4%)
viridiflorene (0–0.5%)
γ-cadinene (0.2–2.2%)
δ-cadinene (0.4–3.2%)

t = trace (< 0.05%)
† should be bornyl acetate

B.M. Lawrence, unpublished data (1980)

K-H. Kubeczka and W. Schultze, *Biology and Chemistry of conifer oils*. Flav. Frag. J., **2**, 137–148 (1987).

C.D. Broeckling and S.M. Salom, *Volatile emissions of eastern hemlock,* Tsuga canadensis *and the influence of hemlock woolly adelgid*. Phytochemistry, **62**, 175–180 (2003).

A.F. Lagalante, M.E. Montgomery, F.C. Calvosa and M.N. Mirzabeigi, *Characterization of terpenoid volatiles from cultivars of eastern hemlock (*Tsuga canadensis*)*. J. Agric. Food Chem. **55**, 10850–10856 (2007).