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THE ESSENTIAL OIL OF TAURUS CEDAR (*Cedrus libani* A. RICH): RECENT RESULTS

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*Water and steam distilled essential oils from wood and roots of Taurus Cedar (*Cedrus libani *A. Rich) obtained from Antalya and Içel (Tarsus) provinces were analyzed by GC and GC/MS. 37 components were characterized representing 90-93% of the oils. Himachalenes (α-, β-, and γ-) constituted 58.6% of the oils. In order to isolate minor sesquiterpenes, the oils were subjected to fractional distillation and chromatographic techniques. The isolated constituents were characterized by spectral analysis (IR, MS, ^{1}H and ^{13}C-NMR). Cis- and trans-10,11-dihydroatlantones, cis- and trans-β-atlantones, 8,9-dehydroneoisolongifolene, longipinene, α-ylangene, camphor, sativene, α-gurjunene, longifolene (=junipene), β-cedrene, α-calacorene, oxidohimachalene, isohimachalone, nerolidol, longiborneol, cadalene, limonene, and terpinolene were found as constituents of* Cedrus libani *oil for the first time.*

The genus *Cedrus* Link (Pinaceae) is represented in the world by four species:

1. *C. atlantica* Manetti (Syn. *C. libani* var. *atlantica* Hook) is distributed in the Atlas mountains of North Africa.
2. *C. brevifolia* (Hook) Henry (Syn. *C. libani* var. *brevifolia* Hook) grows only in Cyprus.
3. *C. deodara* (Roxb.) Loud. (Syn. *C. libani* var. *deodara* Hook and *C. deodara* Laws.) has a wide distribution in the Himalaya mountains.
4. *C. libani* A. Rich (Syn. *C. libanotica* Trew., *C. libani* Loud., *C. libanensis* Juss. and *Cedrorum libani* Hist.) grows in Turkey (Taurus mountains) and Lebanon. Four forms of *C. libani* have been recorded:
   - *C. libani* "argentea" Gord. (Silver-leaved)
   - *C. libani* "nana" Loud. (Dwarf form)
   - *C. libani* "nana pyramidata" Carr. (Dwarf and pyramidal)
   - *C. libani* "pendula" Knight et Pery (Pendulate)

Cedrus species are called "True Cedars," since *Juniperus* and *Thuja* species are also known as "Cedar" in the world trade. Therefore, confusion must be avoided by specifying the botanical source of Cedar [1].

Cedar is a showy forest tree with a wide trunk and thick branches. It can attain a height of 40 meters. In the world literature, *Cedrus libani* is known as "Lebanon Cedar." However, it has been suggested that it should be called "Taurus Cedar" since its main area of distribution is on the Taurus mountain range. In Lebanon it has only a very narrow distribution [2].

In Turkey, Cedar grows on the Taurus mountains in Southern Anatolia stretching from Köyceğiz in the west to Göksun and Kahraman Maraş with a south wing over the Amanus range in Hatay [3]. The continuation of this range leads to the Cedar distribution in Lebanon.

The best Cedar forests are situated in the Elmali, Bucak, Çiğlikara, Katrandağı, and Susuzdağ regions of Antalya province in Turkey. Cedar is an important forest crop with economic value. Cedar timber has been used as a building material for houses, palaces, temples, ports, ships, and castle arches for at least 5000 years. It is still used for making wire and mine polls, railway traverses, bridges, beehives, packaging materials, pencils, cupboards, chests, ships, interior and exterior building decorations, under-water constructions, and as raw material for paper pulp [3].

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TABLE 1. The Composition of the Essential Oils Obtained from *Cedrus libani* Root and Wood by Steam Distillation

Compound	A	B	C	D	E
α-Pinene	0.16	0.03	0.17	0.24	0.26
Limonene	tr	tr	tr	0.01	0.02
Terpinolene	tr	tr	tr	0.01	tr
Longipinene	0.10	0.02	0.11	0.08	0.07
α-Ylangene	tr	tr	0.02	0.02	tr
Camphor	0.02	tr	0.03	0.03	0.02
Sativene	tr	tr	0.01	0.01	tr
1-Methyl-4-acetylcyclohex-1-ene	0.28	0.16	0.29	0.07	0.08
α-Gurjunene	tr	tr	tr	tr	tr
Longifolene(=junipene)	0.52	0.10	0.62	0.41	0.37
α-Himachalene	11.7	2.57	12.82	11.52	10.25
(Z)-β-Farnesene	0.03	tr	0.08	0.05	0.04
γ-Himachalene	7.54	1.68	7.61	6.80	7.07
β-Cedrene*	0.90	0.29	1.80	2.27	1.10
β-Himachalene	34.23	9.24	38.17	34.34	27.46
8,9-Dehydroneoisolongifolene*	0.90	0.36	0.89	0.25	0.25
Cuparene	0.09	0.03	0.06	0.01	tr
α-ar-Himachalene	0.84	0.48	1.90	0.17	0.23
ar-Himachalene	0.25	0.11	0.34	0.14	0.17
β-ar-Himachalene	0.84	0.50	1.03	0.42	0.24
α-Calacorene	0.31	0.33	0.21	0.08	0.08
Libanone	0.28	0.68	0.21	0.07	0.21
Oxidohimachalene	0.51	0.40	0.57	0.15	0.18
(Z)-10,11-Dihydroatlantone	0.79	0.80	0.85	0.13	0.12
Nerolidol	0.20	0.16	0.13	0.16	0.14
Isohimachalone*	1.66	2.87	1.03	0.12	0.07
(E)-10,11-Digidroatlantone	3.24	3.19	3.65	0.02	0.13
Longiborneol	0.84	0.67	0.75	0.74	0.66
cis-β-Atlantone	0.99	3.21	1.09	2.50	2.28
Himachalol	1.11	0.45	1.17	8.84	9.70
trans β-Atlantone	1.34	4.04	1.35	2.44	2.28
Cadalin(=cadalene)	tr	tr	tr	tr	tr
cis-γ-Atlantone	0.92	2.75	1.05	0.37	0.34
trans-γ-Atlantone	0.90	2.73	0.98	0.50	0.45
Allohimachalol	1.50	3.78	1.80	2.26	2.19
cis-α-Atlantone	0.91	4.70	1.06	2.10	2.83
trans-α-Atlantone	3.91	32.23	7.77	14.78	23.72

*: tentative identification.

A: Antalya-*C. libani* wood, first 4 hour.

B: Antalya-*C. libani* wood, last 4 hour.

C: Antalya-*C. libani* wood, total.

D: Tarsus-*C. libani* wood, total.

E: Tarsus-*C. libani* root, total.

A tar obtained by dry-distillation of its stem and branches is internally used for respiratory and urinary diseases and externally as an antiseptic for skin diseases in folk medicine in Turkey. It is also known to be effective on mange in sheep, goats, buffalo, and camels [1, 4, 5].

The essential oil of true cedarwood is used in perfumery and toiletries due to its pleasant and persistent fragrance. It is also used as a medium in microscopy.

Recent studies have shown that sesquiterpene alcohols in the cedarwood oil have antispasmodic activity and that cedarwood oil has antibacterial and antifungal properties [6].

Most chemical studies on true cedarwood have been carried out on *Cedrus atlantica* and *C. deodara*. Only a few studies have been realized on *C. libani* and almost none on *C. brevifolia* [1].

In this study, wood of *C. libani* from Antalya, and wood and root of *C. libani* from Tarsus (Içel) were used. They were chipped and subjected to hydro and steam distillations separately. Water-distillation was carried out using a laboratory-scale glass Clevenger-type apparatus with 100 g of chipped or ground material in distilled water for 11 hours. The oil yields were recorded as 4.02% (Antalya-wood), 4.39% (Tarsus-root), 4.44% (Tarsus-wood) on dry weight basis. Steam distillation was carried out using two different size (30 L and 200 L capacity) stainless-steel distillation pilot plants. 4.5 kg and 14-23 kg chipped materials, respectively, were subjected to steam distillation for 8-10 hours, with a steam rate of 0.6 to 2.5 kg-steam per kg material.

TABLE 2. The Components Detected in *C. libani* Oil and Extract

Compound	Antalya-wood oil		Fethiye-wood oil	Wood-extract[10]
	steam-dist.	water-dist.[Δ]	water-dist.[9]	
α-Pinene	0.17	0.10	–	–
Limonene	tr	0.05	–	–
Terpinolene	tr	0.03	–	–
α-Thujone	–	–	0.02	–
Longipinene	0.11	0.07	–	–
α-Ylangene	0.02	tr	–	–
α-Copaene	–	–	0.02	–
Camphor	0.03	0.02	–	–
Sativene	0.01	tr	–	–
1-Methyl-4-acetylcyclohex-1-ene	0.29	0.68	0.23	–
α-Gurjunene	tr	tr	–	–
Junipene	0.62	0.42	0.31	–
α-Bergamotene	–	–	0.13	–
β-Ylangene	–	–	–	+
α-Himachalene	12.82	8.51	4.87	+
(Z)-β-Farnesene	0.08	0.05	0.07	–
γ-Himachalene	7.61	6.02	4.44	–
β-Cedrene*	1.80	0.67	–	–
β-Himachalene	38.17	23.94	8.08	–
8,9-Dehydroneoisolongifolene*	0.89	0.96	–	–
Cuparene	0.06	0.06	–	–
Binbogen	–	–	–	–
α-ar-Himachalene	2.90	1.22	1.56	–
ar-Himachalene	0.34	0.34	–	–
β-ar-Himachalene	1.03	1.26	1.49	–
α-Calacorene	0.21	0.22	–	–
Libanone	0.21	0.58	0.48	–
Oxidohimachalene	0.57	1.22	–	–
6,7-Epoxihimachalene	–	–	7.52	–
(Z)-10,11-Dihydroatlantone	0.85	2.10	–	–
Nerolidol	0.13	2.32	–	–
Isohimachalone*	1.03	0.21	–	–
(E)-10,11-Dihydroatlantone	3.65	7.81	–	–
Longiborneol	0.75	1.36	–	–
(Z)-β-Atlantone	1.09	1.64	–	–
Himachalol	1.17	1.36	19.70	–
(E)-β-Atlantone	1.35	2.29	–	–
Cadalin	tr	tr	–	–
cis-γ-Atlantone	1.05	1.96	0.31	–
cis-Atlantone	–	–	–	–
trans-γ-Atlantone	0.95	1.76	0.28	–
trans-Atlantone	–	–	–	–
Allohimachalene	–	–	2.49	–
Allohimachalol	1.80	2.74	–	–
cis-α-Atlantone	1.06	1.20	1.89	–
trans-α-Atlantone	7.77	9.54	19.69	–
Amanosone	–	–	0.19	–
Berit	–	–	–	–
Dehidrolibanone	–	–	–	–
Maruson	–	–	–	–
7-Epihimachalol	–	–	–	–
Goksunone	–	–	–	–
Andirolactone	–	–	–	–
trans-Atlantone-6-ol	–	–	–	–

Δ: present study.

9: Tumen et al. 1993.

10: Avcibasi, 1977.

*: tentative identification.

tr: trace (<0.01%).

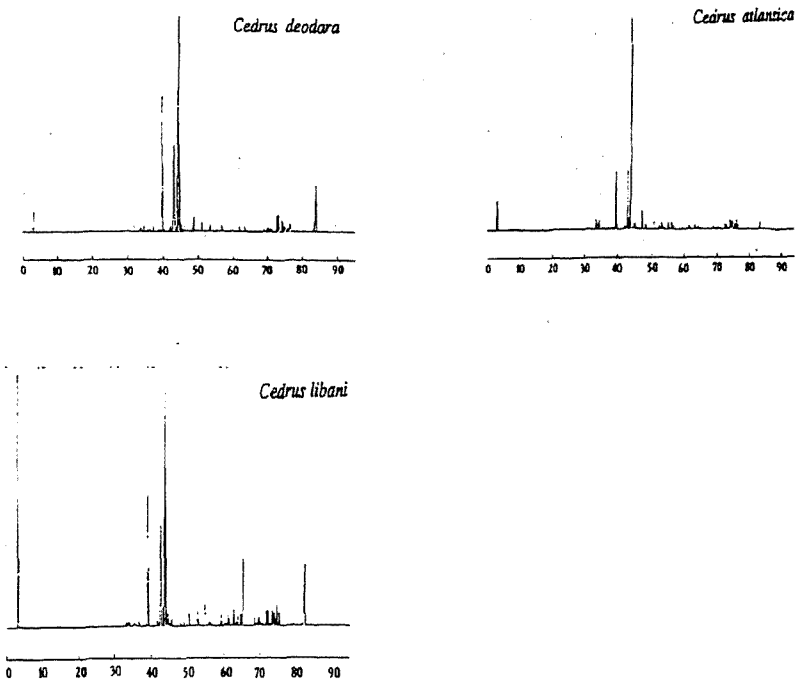

Fig. 1

For the Antalya-wood material, distillation was continued for 8 hours and the oil obtained in the first and last four hours were kept separately. The yield of oil was 6.91% on dry weight basis. Tarsus-wood and root materials were separately worked up by steam distillation for 10 hours each and fractions were collected at 0.5 h intervals. The oil yields were recorded as 5.97% for roots and 5.27% for wood on dry weight basis. All these fractions were analyzed by GC and GC/MS.

Total oils of Antalya-wood and Tarsus-wood and root materials contained β-himachalene (27.5-38.2%), *trans*-α-atlantone (7.8-23.7%), α-himachalene (10.3-12.8%), and himachalol (1.2-9.7%) as major components.

It was observed in the Antalya-wood oil that himachalenes (β-, α-, and γ-, 34.2%, 11.7%, and 7.5%, resp.) were predominant components of the first 4-hour fraction, while atlantones (*trans*-α-, *cis*-α-, *trans*-β-, *cis*-β-, *cis*-γ- and *trans*-γ-, 32.2%, 4.7%, 4.1%, 3.2%, 2.8%, and 2.7%, resp.) and allohimachalol (3.8%) were predominant components of the last 4-hour fraction (Table 1).

Himachalenes are sesquiterpene hydrocarbons and atlantones are oxygenated sesquiterpenes. Experiments have shown that prolonged distillation time is required to distill the oxygenated sesquiterpenes, although 90% of the oil is obtained in the first four hours. The prolongation of distillation by two hours from 8 to 10 hours has resulted in an additional ca.1% yield of oil rich in trans-α-atlantone.

In order to prove their identity, eight compounds representing 67-76% of the oils were isolated and analyzed by spectral techniques. Apart from the already known constituents of the oil of *Cedrus libani*, e.g., α-himachalene, β-himachalene, himachalol, allohimachalol, *trans*-α-atlantone and cis-α-atlantone the following two compounds: (*Z*)-10,11-dihydroatlantone and (*E*)-10,11-dihydroatlantone were characterized for the first time in the oil of *C. libani*. The latter was previously isolated from *C. atlantica* oil [7] and the heartwood extract of *Ginkgo biloba* [8]. The former was isolated and characterized from the heartwood extract of *Ginkgo biloba* [8].

Furthermore, the occurrence of the following minor constituents is reported for the first time in the wood and root oils of *C. libani*: cadalin, camphor, β-cedrene, 8,9-dehydroneoisolongifolene,* longifolene, longipinene, nerolidol, sativene, α-ylangene.

In the only previous GC/MS study of the Turkish *Cedrus libani* oil, we reported the occurrence of himachalol (19.7-30.1%) and trans-α-atlantone (19.7-28.0%) as major constituents in the wood oil [9]. Avcibaşi had previously isolated 27 sesquiterpenes from the heartwood extract of *C. libani* [10-12]. The compounds characterized by him are listed in Table 2.

*It has recently been reported that the isomer of this compound 8,9-dihydroisolongifolene was identified in the oil of *Cedrus atlantica* wood oil [13].

Figure 1 gives a comparative view of the capillary gas chromatogrammes of the steam distilled oils of *C. deodara*, *C. atlantica*, and *C. libani*. It is apparent that there is a remarkable qualitative and somewhat quantitative resemblance, the difference being mainly in the case of minor components. This is supportive of the theory that there is only one species of *Cedrus* as *Cedrus libani* and the other species are only its geographically distant varieties.

EXPERIMENTAL

Antalya-wood material was supplied by the Foresty Department of Antalya Region and Tarsus-wood and root materials were supplied by the Eastern Mediterranean Forestry Research Directorate in Tarsus, Içel, Turkey in 1993. They were chipped and subjected to water distillation using a Clevenger apparatus and to steam distillation using stainless steel pilot plants.

The oils were analyzed by GC and GC/MS. The GC analysis was carried out using a Shimadzu GC-9A with CR4A integrator. Thermon 600T fused silica capillary column (50 m × 0.25 mm i.d.) was used. Carrier gas was nitrogen. Oven temperature was kept at 70°C for 10 min programmed to 180°C at a rate of 2°C/min, then kept at 180°C for 30 min. Injector and detector (FID) temperatures were 250°C. The GC/MS analysis was carried out with quadrupole Shimadzu GC/MS QP2000A system. Thermon 600T FSC column was used with helium as carrier gas. The temperature programming conditions were the same as GC. Mass spectra were taken at 70 eV. Scanning speed was 2 scans/sec from *m/z* 10 to 400. Identification of the separated constituents was carried out by library search using LSS-30 Library Search Software from the "NBS/NIH/EPA Library" and the private "TBAM Library of Essential Oil Constituents."

IR spectra were taken on a Shimadzu IR-435 as a thin layer. FT-NMR spectra were recorded on a Jeol JNM-EX90A at 90 MHz (^1H) and 22.4 MHz (^{13}C) in $CDCl_3$ with TMS as internal standard.

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