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Full Length Research Paper

Chemical analysis of essential oils from cone's rosin of Cilician fir (*Abies cilicica* subsp. *cilicica*)

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The essential oil from the resin of cones of *Abies cilicica* (Ant. Et Kotschy.) subsp. *cilicia* Carr. (*Abietaceae*) grown in Turkey was obtained by the hydro-distillation method and its chemical composition was analyzed by GC and GC-MS. The results showed that the essential oil contained about 92.78% monoterpenes, 2.7% oxygenated monoterpenes and 1.78% sesquiterpenes. Major components of the oil are as follows; α-pinene (68.19%), β-pinene (11.91%) and myrcene (8.62%).

Key words: Essential oil, *Abies cilicica*, Turkey, cone, resin, chemical, composition.

INTRODUCTION

Interest in the synergistic and balancing purpose of the plant's ingredients, which were previously considered inactive is growing. The growth of alternative medicines, now estimated at over $10 billion per year, is at least some evidence of their value (Janssen et al., 1987). The art of aromatherapy or the therapeutic use of essential oils, is among the fastest growing segments of the emerging alternative health care industry (Pattnaik et al., 1997; Dığrak et al., 1999; Dang et al., 2001). Essential oils can be used in a wide variety of ways for many different purposes from athlete's foot to enlightenment and almost every points between (Tylor, 1994; Kusmenoglu et al., 1995; Bagcı et al., 1999; Grassmann et al., 2000; Satil et al., 2003).

Cilician fir (*A. cilicica* (Ant. & Kotschy) subsp. *Cilicica*) is a member of the *Pinaceae* (*Abietaceae*) family. The genus *Abies* contains 10 species (Davis, 1967) and divisible into two subspecies: subsp. *cilicica* (buds not resinous; young shoots hairy) and subsp. *isaurica* (buds reinous; young shoots glabrous). *A. cilicia* subsp. *cilicica* is native to mediterranean region of Turkey (Davis, 1967). The height of trees of *A. cilicica* (Ant. and Kotschy) subsp. *cilicica* is up to 30 m. The bark of its young shoots is greyish-brown and hairy or globrous. It leaves are linear-oblong and emarginate, not clearly 2-ranked. Its buds are not resinous except for its female cones. The cone is subsessile, cylindrical and somewhat tapered above, up to 15 cm or more. The bracts are hidden within the scales. It can grow on slopes and lands with an altitude of 1200 - 2000 m and often as a dominant tree (Davis, 1967).

In fall, the cones of *A. cilicica* started to disintegrate and these cones together with their scales poured out *Abies* trees on ground. People collect the solidified resin on the scales of the cones. The resin has traditionally been used as antiseptic, anti-inflammatory, antipyretic, antibacterial and antiviral medicines and as chewing gum against some stomach disease (e.g., ulcer), lip-dryness and asthma, and for curing the wound in the form of ointment and plaster (Baytop, 1999). Some recent studies showed that essential oils of the root, stems (Kizil et al., 2002) and leaves (Bağcı and Dığrak, 1994; Bağcı and Dığrak, 1996) of nine *Abies* species had antibacterial and antifungal activities. On the other hand, in some region of Turkey, the resin of A. cilicica subsp. cilicica has been using as a stabilizator in food industry.

On the other hand, Bağcı et al. (1999) studied chemical composition of the essential oil composition of two subspecies of *A. cilicica* (Ant. et Kotschy) Carr. from Turkey. Hafızoğlu and Reunanen (1994) also studied the composition of oleoresins from bark and cones of *A. nordmanniana* and Picea *orientalis*.

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Table 1. Chemical composition of *Abies cilicica* subsp. *cilicica*.

	Component	RT	*RI*[a]	%
1	Monoterpene C10.H16 [b]	5,280	921	0.52
2	Tricyclene	5.383	924	0.04
3	*α*-Thujene	5.533	928	0.03
4	*α*-Pinene	5.833	937	68.19
5	Camphene	6.317	950	0.53
6	Thuja-2,4(10)-diene	6.517	955	0.12
7	Sabinene	7.317	974	0.14
8	*β*-Pinene	7.450	977	11.91
9	Monoterpene C10.H18 [c]	7.967	988	0.04
10	Myrcene	8.133	991	8.62
11	Δ^3-Carene	8.967	1.009	1.27
12	*α*-Terpinene	9.283	1.016	0.01
13	p-1-Menthene+m-Cymene	9.550	1.021	0.02
14	p-Cymene	9.667	1.024	0.08
15	Limonene	9.900	1.028	1.88
16	1,8-Cineole	10.000	1.030	0.08
17	*(Z)*-β-Ocimene	10.517	1.041	0.01
18	*(E)*- β-Ocimene	11,064	1050	0.01
19	*γ*-Terpinene	11.550	1.059	0.02
20	Terpinolene+ *p*-Cymenene	13.233	1.086	0.15
21	*α*-Pinene oxide	13.670	1.093	0.01
22	Linalool	14.033	1.098	0.40
23	Perillene	14.067	1.099	0.01
24	2,2,6-Trimethyl-3-oxo-6-vinyl tetrahydropyrane	14.333	1.103	0.12
25	*α*-Campholenal	15.417	1.123	0.12
26	(*E*)-Pinocarveol	16.150	1.135	0.25
27	(*Z*)-Verbenol+Camphor	16.383	1.139	0.12
28	(*E*)-Verbenol	16.600	1.143	0.40
29	Mentadien-8-ol isomer [d]	16.833	1.146	0.04
30	(*E*)-Pinocamphone	17.467	1.156	0.04
31	Pinocarvone	17.600	1.158	0.04
32	Borneol	17.883	1.162	0.05
33	p-Mentha-1,5-dien-8-ol	18.083	1.165	0.02
34	(*Z*)-Pinocamphone	18.333	1.169	0.02
35	Terpinen-4-ol	18.700	1.174	0.03
36	p-Cymen-8-ol	19.233	1.182	0.02
37	*α*-Terpineol	19.600	1.187	0.02
38	Myrtenal	19.750	1.189	0.14
39	Myrtenol	19.950	1.192	0.11
40	Verbenone	20.583	1.200	0.14
41	(*E*)-Carveol	21.483	1.216	0.01
42	Cumin aldehyde, isomer [e]	21.550	1.217	0.02
43	Nerol	22.250	1.228	0.16
44	Carvone	22.983	1.240	0.02
45	Bornyl acetate	25.883	1.282	0.03
46	*δ*-Elemene	29.317	1.335	0.08
47	*α*-Cubebene	30.083	1.347	0.07
48	*α*-Ylangene	31.400	1.367	0,01
49	*α*-Copaene	31.683	1.371	0.04

Table 1. Contd.

50	*β*-Bourbonene	32.200	1.379	0.42
51	*β*-Cubebene	32.483	1.383	0.01
52	*β*-Elemene	32.800	1.387	0.09
53	Tetradecan	33.717	1.400	0.02
54	*β*-Caryophyllene	34.317	1.411	0.16
55	Cedrene isomer ?	34.350	1.411	[h]
56	*β*-Gurjunene ?	34.983	1.422	0.06
57	(*E*)-*α*-Bergamotene	35.633	1.433	0.02
58	Sesquiterpene C15.H24 [f]	36.017	1.439	0.17
59	*α*-Humulene	36.467	1.446	0.04
60	Muurola-4(14),5-diene	37.267	1.459	0.04
61	*γ*-Muurolene	38.033	1.471	0.04
62	Germacrene D	38.233	1.474	0.30
63	*β*-Selinene	38.483	1.478	0.05
64	δ-Selinene ?	38.933	1.485	0.04
65	*α*-Selinene	39.067	1.487	0.05
66	*α*-Muurolene	39.550	1.494	0.04
67	*γ*-Cadinene	40.283	1.506	0.07
68	*δ*-Cadinene	40.967	1.518	0.12
69	*α*-Cadinene	41.733	1.531	0.01
70	Sesquiterpene C15.H24[g]	42,317	1542	1.01
71	*α*-Cadinol	48,560	1657	0.02
72	Abieta-8,11,13-triene	68.883	2.040	0.02
73	Abieta-7,13-diene	70.033	2.064	0.04

[a] Identification was based on comparison of mass spectra and retention Indices (RI) on a SE54 column with authentic reference compounds or data described by Adams.
[b] m/e 93,41,67,69,77,108,121 (similar to bornylene)
[c] m/e 69,41,95,123,138 (a dimethyloctadien isomer)
[d] m/e 59,79,91,94,43
[e] m/e 105,77,133,91,148
[f] m/e 105,91,119,161,133,204
[g] m/e 93,41,79,80,119,121,67,109,204
[h] m/e 91,105,161,120,133, not separated from *β*-Caryophyllene
? means tentative identification.

However, to our knowledge no studies were found on the essential oils from the gum of cones of *A. cilicica* subsp. *cilicica*. Therefore, the aim of this study was to investi-gate the chemical composition of the essential oil from the resin of *A. cilicica* subsp. *cilicica* growing in Turkey.

MATERIALS AND METHODS

Plant and chemicals

In this study, resin from the cones (female) of cilician fir [*Abies cilicica* (Ant. and Kotschy.) Carr. subsp. *cilicia* (Abietaceae)] was collected on October 27, 2002 from a Turkish state forest established in Baskonus district, South-east mediterranean part of Turkey, having an altitude of 1.100 m. Voucher specimens were deposited in the Herbarium of Faculty of Forestry, Kahramanmaras Sutcu Imam University.

Preparation of essential oil

The essential oil of the gum (50 g) of Cilician fir was obtained by hydro-distillation method by using a Clevenger-type apparatus for 3 h. The white-colored essential oil was dried over anhydrous sodium sulphate (Na_2SO_4) and stored at -18°C.

Chemical analysis

Identification of the essential oil (11.5 mg) diluted in diethyl ether (Et_2O) (1 ml) was analyzed on a Finnigan-MAT 8200 mass spectrometer coupled with a Hewlett-Packard GC-5890II series GC by using A SE-54 fused silica capillary column (30 m x 0.25 mm i.d.; 0.25 µm film thickness). Helium (He), having a flow rate of 1.15 ml/min, was used as carrier gas. The GC oven temperature was kept at 60°C for 5 min and programmed to 260°C at a rate of 2°C /min and then kept at 260°C. The injector temperature was 250°C. The amount of injection was 1 µl. The carrier gas was delivered at a constant pressure of 5 kg/cm^2. MS spectra were taken at EI ion source of 70 eV. Split ratio was 1:5.

Retention indices for all the components were determined according to Van Den Dool method (Dool and Kratz, 1963) using n-alkanes as standard. Identification of the components was based on comparison of their mass spectra with those of internal (computer) library, NIST libraries and those described by Adams (Adams, 1995).

Quantification of the essential oil was conducted by gas chromatography with flame ionization detector (GC-FID) on a Hewlett-Packard GC-5890II series GC. 1 µl oil was injected into the same column under the same GC conditions as described for GC-MS study. However, split ratio was 1:14.

Determination of refractive Index

The refractive index (nD) of the essential oil was measured at 20°C by means of Abbe refraktometer A3 und A1 (A.Krus GmbH).

RESULTS AND DISCUSSION

The yield, density (d) and refractive index (nD) of the oil were determined as 3.47%, 0.88 g/cm^3 and 1.467 - 1.472, respectively, by conventional methods.

Table 1 represents the chemical composition of the essential oil of the resin from the cones of *A. cilicica* subsp. *cilicica*. As is shown in this table, 79 compounds, representing 97.32% of the essential oil of the resin from the cones of *A. cilicica* subsp. *cilicica*, were determined. The results showed that the essential oil contains 92.78% monoterpenes, 2.0% oxygenated monoterpenes and 1.78% sesquiterpene.

Specifically, α-pinene (68.19%), β-pinene (11.91%) and myrcene (8.62%) are the major components of the oil (Table 1). Hafızoğlu and Reunanen (1994) reported that the composition of oleoresins from bark and cones of *A. nordmanniana* was of following dominant constituents such as of α-pinene (21.9 and 17.2%) and abietic acid of resin acids (11.4 and 19.8%). They also found that bark and cones from *Picea orientalis* comprised, mainly, of abietic acid of resin acids (29.1 and 40.1%), Δ^3-carene (14.1%) and β-pinene (7.3%) (Hafızoğlu and Reunanen, 1994).

Furthermore, it was reported that the oil from the young shoots of *A. cilicica* subsp. *cilicica* grown in the southern part of Turkey contained Δ^3-carene (14.2%), caryophyllene oxide (8.6%) and β-caryophyllene (7.8%) as the major constituents. Moreover, the main components of oil from the young shoots of *A. cilicica* subsp. *Isaurica* were determined to be β-pinene (29%), α-pinene (10%), eremophilene (9.3%) and β-caryophyllene (8.8%) (Bağcı et al., 1999).

The other minor components are aslo shown in the same table. It is important to notify that myrcene content in the oil is higher than that of other essential oil from the rosin of genus *Pinus* (Zinkel, 1989). However, it is found that the main chemical constituents of the essential oil from the cones of *A. cilicica* subsp. c*ilicica* are similar to that of the rosin from genus *Pinus* in view of α-pinene and β-pinene contents. It was also reported that α-pinene (67% of the total), β-pinene, limonene and β-phellandrene were dominant in the cone volatiles of Swiss stone pine (Dormont et al., 1997).

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