Asian Journal of Chemistry; *Vol. 23, No. 6 (2011), 2782-2784*

ASIAN JOURNAL OF CHEMISTRY

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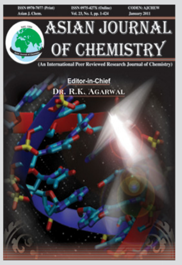

Chemical Composition of Essential Oils from Bark and Leaves of *Pinus brutia* Ten. from Turkey

EYUP BAGCI[1,*], SUKRU HAYTA[2] and GULDEN DOGAN[1]

[1]Plant Products and Biotechnology Research Laboratory, Department of Biology, Faculty of Science, Firat University, Elazig, Turkey
[2]Department of Biology, Faculty of Art & Science, Bitlis Eren University, Bitlis, Turkey

*Corresponding author: E-mail: eyupbagci@yahoo.com

(*Received*: 3 November 2010; *Accepted*: 28 February 2011) AJC-9663

The chemical composition of essential oils obtained by hydrodistillation of leaves and bark of *Pinus brutia* was investigated by GC and GC-MS. The essential oil content was 0.8 % (v/w), 0.7 % (v/w), respectively. In the leaf oil of *Pinus brutia*, β-pinene (29.5 %), germacrene D (17.9 %), α-pinene (14.4 %), β-caryophyllene (9.8 %) were the main constituents. In the bark oil *Pinus brutia*, α-pinene (14.9 %), β-caryophyllene (11.2 %), δ-3-carene (9.6 %), caryophyllene oxide (6.9 %) as the major constituents. A total of 95 compounds have been identified constituting 86.3 % bark, 94.1 % leaves in the essential oils.

Key Words: *Pinus brutia*, GC-MS, Essential oil, α-Pinene, Leaf, Bark.

INTRODUCTION

Pinus brutia Ten., *Pinus elderica* Medwed., *Pinus pyrenica* David., are some of the important forest trees of the Mediterranean region, reaches its greatest distribution in southern Turkey[1]. It grows fast in the early ages but under the conditions of understocked stand or open-grown trees the tree typically develops large spreading branches with diffuse crown. However, in suitable conditions, it grows exceptionally fast with straight trunk and narrow crown and it may reach to a height of 35 m. It is sensitive to continuous strong wind and in such a case it does not grow well[2].

In the Mediterranean region, pine forests comprise of 10 pine species and cover about 13 million hectares, which represents about 5 % of the total regional area and about 25 % of the total area forested. In the Mediterranean area, the most common species are *P. halepensis* and *P. brutia*, followed by *P. pinea*, scattered all over the region and *P. pinaster* on the western part. *P. sylvestris* is also widespread in the region, but is more abundant in the northern regions of Europe[3,4].

Pine oleoresin is an important forestry product, which is traditionally obtained by tapping the bark (bark chipping) of pine tree and collection of the resulting exudate. Oleoresins are complex mixtures of acidic and neutral diterpenes together with a more or less important fraction of volatile compounds (mono and sesquiterpenes). In the industry, the crude oleoresin is converted by steam distillation into gum turpentine (volatile compounds) and gum rosin (diterpenes), both gums in turn are processed into chemical industrial products such as food gums, adhesives, coatings, printing inks, disinfectants, cleaners, pharmaceuticals, fragrances and flavoring.

In study of seed oil fatty acid and tocochromanol studies of Turkish pines, *Pinus brutia* has low Δ^5-unsaturated fatty acid in seed oil and has found rich as more γ-tocopherol content in seed oil[5]. The medicinal and aromatic properties of the chemical compounds (*e.g.*, turpentine, resins and essential oil) of pine make it one of the most popular plants throughout all civilization. Pine is also still widely used in traditional therapeutic practice in world and has an economic importance[6]. The seed lipids and essential oils of some forest trees including *Pinus* species has more antimicrobial activity against some of the microorganism[7,8].

In this study, the essential oil composition of the leaves and bark of *P. brutia* collected from Turkey were analyzed by GC and GC/MS system, to evaluate the qualitative and quantitative differences in essential oil composition among the plant parts of *P. brutia*.

EXPERIMENTAL

Plant source: The materials (leaves and bark) belongs to the *Pinus brutia* was obtained from the specimen collected from Natural Habitats in Adana, Turkey. Voucher specimens are kept at the Firat University Herbarium (FUH).

Isolation of the essential oils: Air-dried aerial parts of the plant materials (100 g) were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h to yield.

Gas chromatographic (GC) analysis: The essential oil was analyzed using HP 6890 GC equipped with and FID

TABLE-1
ESSENTIAL OIL CONSTITUENTS FROM THE BARK AND LEAVES OF *Pinus brutia* Ten

No.	Compounds	RRI	*Pinus brutia* (leaves)	*Pinus brutia* (bark)	No.	Compounds	RRI	*Pinus brutia* (leaves)	*Pinus brutia* (bark)
1	3-Hexen-1-ol	935	0.1	–	49	β-Farnesene	1414	–	0.1
2	α-Pinene	1021	**14.4**	**14.9**	50	α-Humulene	1418	1.4	2.5
3	Camphene	1034	0.3	0.5	51	Naphthalene	1432	0.3	–
4	Benzaldehyde	1043	0.1	–	52	Germacrene D	1434	**17.9**	0.1
5	Sabinene	1052	1.3	–	53	Butanoic acid	1441	1.4	–
6	β-Pinene	1055	**29.5**	5.7	54	Methyl isoeugenol	1442	0.3	0.1
7	β-Myrcene	1063	1.8	0.4	55	α-Muurolene	1446	0.2	0.1
8	α-Terpinene	1071	0.1	0.1	56	δ-Amorphene	1449	0.1	–
9	α-Phellandrene	1077	0.1	–	57	β-Bisabolene	1451	–	0.2
10	Δ^3-Carene	1078	0.1	**9.6**	58	γ-Cadinene	1455	0.2	–
11	Benzene, 1-methyl-2	1091	0.1	0.6	59	Δ-Cadinene	1458	0.6	0.1
12	Limonene	1094	1.3	2.9	60	Cadina,1,4-diene	1467	0.1	–
13	β-Phellandrene	1096	1.2	0.4	61	α-Cadinene	1469	0.1	–
14	*cis*-Ocimene	1099	0.2	–	62	α-Bisabolene	1472	0.5	–
15	1,3,6-Octatriene	1107	1.5	–	63	Valencene	1479	0.1	–
16	α-Terpinene	1116	0.1	0.3	64	Dodecanoic acid	1483	–	0.2
17	Benzene[2-methyl-1-propenyl]	1133	–	0.2	65	3-Hexen-1-ol, benzoate	1490	0.1	–
18	γ-Terpinolene	1136	0.1	1.0	66	Caryophyllene oxide	1498	0.6	**6.9**
19	*p*-Cymene	1140	0.1	0.7	67	Longiborneol	1510	–	0.9
20	Linalool L	1147	0.3	–	68	Humulene epoxide II	1513	–	1.1
21	D-Fenchyl alcohol	1162	0.1	0.4	69	*t*-Muurolol	1532	0.1	–
22	Nopinone	1175	0.1	–	70	α-Cadinol	1538	0.2	0.8
23	*trans*-Pinocarveol	1177	0.1	0.5	71	neo-Intermedeol	1540	0.3	–
24	*trans*-Verbenol	1180	0.1	–	72	γ-Gurjunene	1544	0.1	–
25	Camphor	1181	–	0.3	73	Tetradecanoic acid	1590	–	0.1
26	Exo methyl-camphenilol	1187	0.1	0.1	74	Benzyl benzoate	1596	–	0.5
27	Bicyclo[3.1.1]heptan-3-one	1191	0.1	0.1	75	Galaxolide 1 and 2	1631	–	0.2
28	Pinocarvone	1192	0.1	0.2	76	*n*-Hexadecanoic acid	1691	–	1.2
29	Borneol	1199	0.1	0.7	77	Pimaradiene	1697	0.1	–
30	4-Terpineol	1205	0.2	0.6	78	Ether,1-hexadecenyl methyl	1699	0.1	–
31	α-Terpineol	1214	1.1	6.7	79	Manolyl oxide	1715	0.1	–
32	*trans*-Carveol	1230	0.1	–	80	Heptadecanoic acid, methyl ester	1734	0.1	–
33	Nerol	1233	0.1	–	81	Abietadiene	1778	–	0.2
34	Thymol, methyl ether	1237	0.1	–	82	8,11-Octadecadienoic acid, methyl ester	1782	0.3	–
35	Linalyl acetate	1252	1.2	–	83	9-Octadecanoic acid, methyl ester	1787	0.1	–
36	Bicyclo[2.2.1]heptan-2-ol	1281	0.3	–	84	10-Octadecanoic acid, methyl ester	1790	0.1	–
37	Benzene, 1-methoxy-4	1283	–	0.6	85	Octadecanoic acid, methyl ester	1805	0.2	–
38	2,4-Decadienal	1311	–	0.7	86	9,12-Octadecanoic acid	1806	–	0.6
39	α-Longipinene	1339	–	0.5	87	Sandaracopimarinal	1838	0.1	–
40	Neryl acetate	1344	0.1	5.9	88	Abietal	1861	–	1.3
41	α-Ylangene	1354	0.1	–	89	Stilbene	1865	–	1.4
42	α-2,6-octadien-1-ol	1360	0.2	–	90	Eicasatetraenoic acid	1878	0.2	–
43	β-Bourbonene	1366	0.2	–	91	Abietal, dehydro	1882	–	0.5
44	β-Elemene	1370	0.4	–	92	Dehydroabietic acid	1916	0.1	0.5
45	Methyl eugenol	1377	0.2	–	93	Rosin acids	1943	–	0.6
46	Longifolene	1385	0.1	–	94	Phenanthrenecarboxylic acid	1959	0.1	0.3
47	β-Caryophyllene	1392	**9.8**	**11.2**	95	Docosahexaenoic acid	1967	0.1	–
48	β-Copaene	1400	0.1	–					
Total								**94.1**	**86.3**

detector and an HP-5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 μm) capillary column was used. The column and analysis conditions were the same as in GC-MS. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

Gas chromatography/mass spectrometry (GC-MS) analysis: The oils were analyzed by GC-MS, using a Hewlett Packard system. HP-Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Res. Lab. (BUBAL) in Firat University. HP-5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 μm) was used with helium as the carrier gas. Injector temperature was 250 ºC, split flow was 1 mL/min. The GC oven temperature was kept at 70 ºC for 2 min and programmed to 150 ºC at a rate of 10 ºC/min and then kept constant at 15 ºC for 15 min to 240 ºC at a rate of 5 ºC/min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries (WILEY, NIST). The identified constituents of the essential oils are listed in Table-1.

RESULTS AND DISCUSSION

In the essential oils of *Pinus brutia* leaves and barks, 75 and 51 components were identified, constituting 94.1 and 86.3 %, respectively. The isolated essential oil was obtained by hydrodistillation of the leaf and bark in yields of 0.8 and 0.7 % (w/w). The results of their GC and GC-MS analyses are given in Table-1, where the compounds are listed according to their order of elution. The major components of the leaf were found β-pinene 29.5 %, germacrene D 17.9 %, α-pinene 14.4 %, β-caryophyllene 9.8 %. The main components from bark were α-pinene 14.9 %, β-caryophyllene 11.2 %, δ-3-carene 9.6 %, caryophyllene oxide 6.9 %. The leaves and bark essential oils for *Pinus brutia* was characterised by a high percentage of sesquiterpene and monoterpene hydrocarbons. α-Pinene (14.4 %, 14.9 %) and β-caryophyllene (9.8 %, 11.2 %) were the main components of the oils obtained from the leaves and barks of *Pinus brutia*, respectively, while β-pinene 29.5 % was also important in the leaves oil.

The major constituents of the essential oil of gum turpentines of *Pinus brutia* were α-pinene (68 %), β-pinene (16 %) and Δ^3-carene (*ca.* 12 %)[9]. Although, α-pinene was the major component of the oils for the leaves and barks of *Pinus brutia*, β-pinene was also important in the leaves oil. Besides, Δ^3-carene was only major component of the oil for barks of *Pinus brutia* in this analyses results (Table-1).

α-Pinene (17.8 %), β-pinene (25.5 %), δ-3-carene (16.2 %) and β-caryophyllene (12.1 %) were the main components of the oils obtained from the twig oil of *Pinus brutia* from Greece[10]. The composition of the essential oils isolated from the needles of *Pinus brutia* grown in Morocco were investigated by GC and GC/MS. The most abundant compound in *Pinus brutia* oil was also β-pinene (33.6 %) as a major component[11]. Similarly, in present analyses results showed that β-pinene was the major component of the essential oils from barks of *Pinus brutia*. The study of the variation in composition of the essential oils produced from different ratios of needles to terminal twigs of *Pinus brutia* Ten., pure needle oil was found to be much richer in oxygenated compounds than that of pure twig oil with a corresponding reduction in amounts of monoterpene hydrocarbons[12]. There is a large difference between *Pinus brutia* bark and leaves oil. It is of interest to note that a survey of the two types of oil revealed that they showed a wide variation in the number of identified compounds, their contents and chemical composition.

This difference was reflected also in biological activities. This paper describes the qualitative and quantitative chemical composition of the essential oil obtained from leaves and bark from native plant of *Pinus brutia* collected in Turkey in order to establish whether a difference exists between the oils and if so to quantify it.

Conclusion

β-Pinene was found as major compound in leaves and of *Pinus brutia* higher than bark of the plants. In addition, α-pinene was determined as predominant compound in bark of *Pinus brutia*. These findings have also ecological and economic significance for utilization of the species in the pharmaceutical, cosmetic and chemical industries.

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