The Relationship between Extractive Components and Density of Persian Ironwood

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The aim of this study was to assess the variation of extractives components of ironwood based on altitude above sea level (100, 500 and 700 meter) and the relationship between shared extractives compounds growing in three different altitudes (by GC-MS) and wood density. There were 6 extractives compounds at low altitude and 4 extractives compounds at intermediate and high altitudes. There were two shared extractive compounds of acetone extracts in three altitude classes, namely 1,2-benzendicarboxylic and 1-methyl-5,8-dimethoxy-1, 2,3,4-tetrahydro-1,4-iminonaphthalene. The highest contents of 1,2-benzendicarboxylic and 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene were found in high (700 m) and low altitudes (100m), respectively. A positive relationship between 1,2-benzendicarboxylic and wood density was found, whereas a negative relationship between 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene and wood density was observed.

Keywords: Altitude; Extractives compounds; Wood density

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INTRODUCTION

Parrotia persica (DC) CA Meyer (Persian ironwood) is one of the deciduous trees of Hyrcanian forests (Northern coast of the Caspian Sea in Iran), from the Hamamelidaceae family (Parsakhoo and Jalilvand 2009). *Parrotia persica* is usually a low-branched and multi stemmed small specimen tree (Parsakhoo and Jalilvand 2009; Kiaei *et al*. 2015).

The factors that cause the changes in the wood structure are the age and genetic properties of the tree as well as the environmental conditions (Doğu 2002). These factors affect the growth rate of the tree, composition, structure and wood different properties (Wilson and White 1986). Wood density (as an important wood properties) is a complex physical property, related to the anatomical structure, including cell wall thickness, vessel number and characteristics, as well as the wood chemical composition that responds to genetic, environmental and physiological influences (Wimmer *et al.* 2002, 2008). Site and environmental conditions affect density of wood and, therefore, its properties (Moya and Calvo-Alvarado 2012). In durable wood species, phenolic compounds, resin acids, terpenoids and tropolons have antifungal activity. Flavonoides, quinines, sesquiterpenoids, and stilbene have anti-termite activity, and their presence accounts for the natural durability of wood (Jorbandian and Farahani 2012). A deeper knowledge regarding the behaviour of these natural and eco-friendly components would help to evaluate its performance as preservants to enhance the wood durability.

A study of the relationship between altitude index and chemical properties (cellulose, lignin, ash, and extractives), mineral content and wood density was previously published by author and associates (Kiaei *et al.* 2015). Analysis of variance results (ANOVA) indicated that the effect of altitude, radial position, and their interaction on the wood density were significant. The highest and lowest values of wood density were found at intermediate (0.796 g cm^{-3}) and low altitudes (0.733 g cm^{-3}), respectively. The variation of wood density along radial position from pith to the bark decreased in the three altitudes. The mean of wood density was 0.769 g cm^{-3} for the three studied altitudes in north of Iran (Table 1). Also, the amount of extractives (Fig. 1) increased with increasing of altitude (Kiaei *et al.* 2015). In the following, the objectives of the present study were: (a) identification of extractives components (by gas chromatography mass spectroscopy) growing in three different altitudes (100, 500 and 700 m), (b) to determine shared extractive components growing in these altitudes, and (c) to investigate the relationship between shared extractives components and density for ironwood (*Parrotia persica*).

Table 1. Wood Density (g/cm^3) in Relation to Radial Position for Persian Ironwood Growing in Three Different Altitudes (Kiaei *et al.* 2015)

Altitude/position	Pith	Middle	bark	Average
100	0.810 (0.072)	0.706 (0.020)	0.683 (0.057)	0.733 (0.069)
500	0.806 (0.020)	0.796 (0.025)	0.786 (0.025)	0.796 (0.022)
700	0.823 (0.037)	0.790 (0.026)	0.720 (0.017)	0.777 (0.051)
Average	0.813 (0.042)	0.764 (0.048)	0.730 (0.047)	0.769 (0.056)

Legend: Standards errors are presented in brackets.

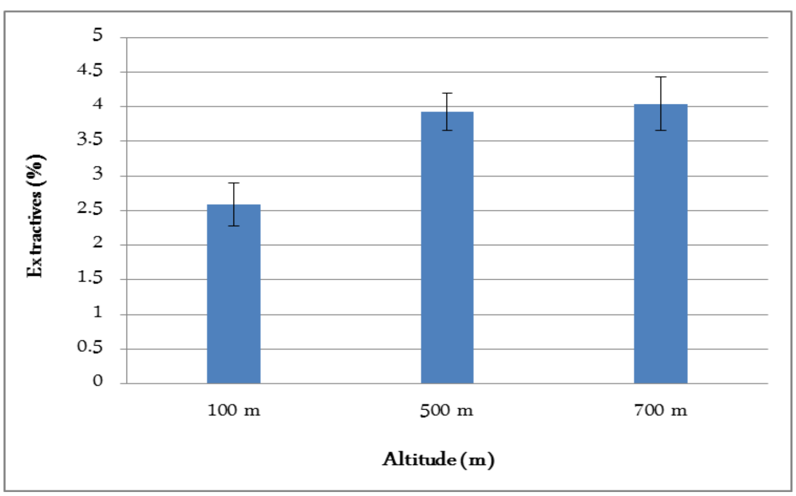

Fig. 1. The extractives values in three different altitudes for ironwood (Kiaei *et al.* 2015)

EXPERIMENTAL

Materials

In the present study, 9 normal Persian ironwood (*Parrotia persica*) trees were felled from three different altitudes, *i.e.*, 100 (low elevation), 500 (intermediate elevation), and 700 (high elevation) meters above sea level from northern natural forests (Noshahr region) in Iran. At all three sites, the trees were 35 to 40 years old.

Methods

All nine trees were randomly selected, taking into account stem straightness and the absence of evident decay. Traits of environmental and climate conditions of these sites and characteristics of trees are listed in Table 2. A cross-section with 15 cm in thickness was extracted from each tree at breast height. This cross-section was utilized for evaluation of wood properties. Afterwards, three samples were prepared along the radial position from pith to the bark (near to pith, middle between pith and bark, near to the bark). Wood density (according to ISO-3131) was determined in each position.

Table 2. The Characteristics of the Sites, and Climate of Persian Ironwood

Sites	Altitudes (m)	Annual temperature (°C)	Annual rainfall (mm)	Height (m)	Diameter (cm)
Noshahr region	100	13.5	1345	23.4	32
	500	11.5	1300	23.3	31.6
	700	8.5	1300	22.5	30.4

Extractive composition

To examine the chemical composition in terms of percent extractives and type, mature wood (samples, near to the bark), were selected. The specimens were 3 tree x 1 samples of mature wood x 3 altitude classes = 9 samples for chemical characterization. To identify the extractives compounds, ~ 1 mg of solid obtained extracts, mixed with 30 mL BSTFA [bis (trimethylsilyl) trifluoroacetamide], 1% TMCS (trimethylchlorosilane) reagent, and about 15 mL pyridine were mixed in a tube test. The samples were kept in a Bain Marie hot water bath at 70 ^{o}C for an hour, and then they were analyzed by GC-MS on an HP 6890 Gas Chromatograph (Agilent technology, USA), equipped with a split/split less injector and a 5973 Mass Selective Detector (MSD). The oven column was programmed as follows: Chromatography was done on a HP-5MS capillary column (SGE, 30 m, 0.25 mm), using 1mL/min of helium as carrier gas and a temperature program between 60 and 260 °C, with a temperature increase rate of 6 °C/min. To identifying the compounds, a GC diagram, representing the abundance and retention time of each compound was obtained. The calculation of quartz index and Adams table were premed as well.

Statistical analysis

The effect of altitude on the extractives composition was determined by GC/MS for Persian ironwood at the Noshahr region, in the north of Iran. Then, shared extractives compositions characterized in three different altitude classes were determined. Finally, the relationships between the shared extractives compounds and wood density were determined by Pearson matrix correlation.

RESULTS

Extractives Composition

The major extractives compounds extracted from samples collected at three different altitudes are shown in Table 3. As it can be seen, six extractives compounds were detected at different concentrations at low altitude. Four extractives compounds of acetone extracts were obtained at intermediate and high altitudes.

Table 3. Ironwood Extractives in Acetone Solvent (Rt: Retention Time)

	Low altitude (100 m)		
Row	Compounds	Rt (min)	Area (%)
1	Ethylbenzene	5.591	0.27
2	Benzene, 1-3 dimethyl	6.659	1.63
3	Linalyl acetate	18.677	0.58
4	1-methyl-5,8-dimethoxy-1, 2, 3, 4-tetrahydro-1, 4-iminonaphthalene	28.937	0.92
5	1, 3, 4, 7, 7-pentamethyl-2-oxa-bicyclo (4, 4, 3) deca-3, 5-diene	29.060	0.19
6	1,2-Benzendicarboxylic acid	45.322	96.42
	Intermediate altitude (500 m)		
1	1-methyl-5,8-dimethoxy-1, 2, 3, 4-tetrahydro-1, 4-iminonaphthalene	28.930	0.27
2	Cheloviolene	29.060	0.05
3	8-amino-5-methoxy-1-tetralone	29.609	0.04
4	1,2-Benzendicarboxylic acid	45.257	99.6
	High altitude (700 m)		
1	Xylene	5.934	0.02
2	1-methyl-5,8-dimethoxy-1, 2, 3, 4-tetrahydro-1, 4-iminonaphthalene	28.937	0.74
3	(3E)-4- [trans-2, 4, 4, 5-tetramethyleyclohex -2-en-1-yl] but-3-en-2-one	29.060	0.17
4	1,2-Benzendicarboxylic acid	48.246	99

Shared extractives composition at three different altitudes				
Row	Shared extractives compositions	Altitude classes (m)		
		100	500	700
1	1-methyl-5,8-dimethoxy-1, 2, 3, 4-tetrahydro-1, 4-iminonaphthalene	0.92	0.27	0.74
2	1,2-Benzendicarboxylic acid	96.42	99.64	99

The main compounds at low altitude (100 m) were as follows: ethyl benzene (0.27%), benzene, 1-3 dimethyl (1.63%), linalyl acetate (0.58%), 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4- iminonaphthalene (0.92%), pentamethyl 1,3,4,7,7-pentamethyl-2-oxa-bicyclo (4,4,3) deca-3,5-diene (0.19%), and 1,2-benzendicarboxylic acid (96.42%). The main compounds found at intermediate altitude (500 m) were the following ones: 1-methyl-5, 8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene (0.27%), cheloviolene (0.05%), 8-amino-5-methoxy-1-tetralone (0.04%), and 1,2-benzendicarboxylic acid (99.64%). The main compounds found at high altitude (700 m) were: xylene (0.02), 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1, 4- iminonaphthalene (0.74%), (3E)-4-[trans-2, 4, 4, 5-tetramethyleyclohex-2-en-1-yl] but-3-en-2-one (0.17%), and 1,2-benzendicarboxylic acid (98.97%).

There were two shared extractives compounds of acetone extracts in the three altitude classes, namely 1,2-benzendicarboxylic and 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4- iminonaphthalene (Table 3). The highest and lowest values of 1-methyl-5, 8-dimethoxy-1, 2, 3, 4-tetrahydro-1, 4- iminonaphthalene were seen at low (0.92%) and intermediate (0.27%) altitudes. The value of 1,2-benzendicarboxylic at intermediate altitude (99.64%) was higher compared to other altitudes at Noshahr region. The lowest values of 1,2-benzendicarboxylic was found in low altitude (96.42%).

Relationship among Various Wood Properties

The relationship between shared extractives compounds (1,2-benzendicarboxylic and 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene) and wood density were determined by Pearson matrix correlation (Table 4). They were found to be positive. Significant relations between 1, 2-benzendicarboxylic ($r = 0.839$) and wood density were obtained. 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene ($r = 0.940$) had a significantly negative correlation with the density of ironwood (Table 4).

Table 4. The Relationship between Shared Extractives Components and Density in Rronwood (n=9)

Relationships between wood properties	r	Sig
WD and 1, 2-Benzendicarboxylic	+0.839**	0.005
WD and1-methyl-5, 8-dimethoxy-1, 2, 3, 4-tetrahydro-1, 4-iminonaphthalene	-0.940**	0.001

DISCUSSION

The amount of obtained extractives increased with the altitude. This observation could be explained by the site conditions. This result was previously reported by Doğu (2002) and Kiaei *et al.* (2012). Extractives components had a negative effect on pulping and bleaching operations (Tajik *et al.* 2015).

1-2-Benzendicarboxylic (Fig. 2) acid is one of the active compounds in *Stellera chamaejasme* L. plants that have antifungal properties (Zhu 2012). This component ($C_8H_6O_4$, classed as an organic acid) is one of important extractives components, which was found in some Iranian wood species such as eucalyptus wood (Tajik *et al.* 2014), elm wood (Kiaei and Tajik, 2013), Sweet Locust wood, False Acacia wood (Vaysi 2014), and *Morus alba* wood (Sadeghifar *et al.* 2011).

Ethyl benzene is an organic compound with the formula $C_6H_5CH_2CH_3$. It is a highly flammable, colorless liquid with an odor similar to that of gasoline. This monocyclic aromatic hydrocarbon is important in the petroextractives industry as an intermediate in the production of styrene, the precursor to polystyrene, a common plastic material. In 2012, more than 99% of ethylbenzene produced was consumed in the production of styrene. Ethylbenzene is also used to make other extractives s, in fuel, and as a solvent in inks, rubber adhesives, varnishes, and paints. Ethylbenzene exposure can be determined by testing for the breakdown products in urine (Rabus and Widdel 1995).

1-3 dimethyl benzene is an aromatic hydrocarbon. The major extractives use of benzene,1-3 dimethyl (*meta*-xylene) is in the manufacture of isophthalic acid, which is most often used as a copolymerizing monomer to alter the properties of polyethylene terephthalate (PET), making PET more suitable for the manufacture of soft drinks bottles. To convert m-xylene on an industrial scale to isophthalic acid, the two methyl groups are bothcatalytically oxidized to carboxyl groups.

Shared extractives components for Persian ironwood growing in three different altitudes were 1,2-benzendicarboxylic and 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1, 4-iminonaphthalene. A positive correlation between 1,2-benzendicarboxylic and wood density was observed. 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene had negative correlation with wood density.

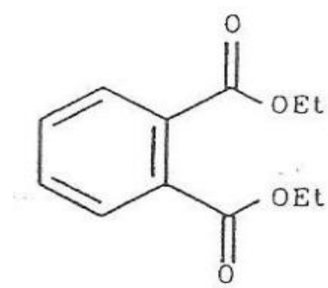

Fig. 2. Formula of the 1, 2-Benzendicarboxylic

CONCLUSIONS

The extractives compositions of ironwood at three altitudes were studied in Noshahr region, the northern Iranian forest. The main extractives components of Persian ironwood growing in three different altitudes were 1,2-benzendicarboxylic and 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene. 1,2-Benzendicarboxylic was found to be an abundant extractives component for ironwood at the three different studied altitudes (over 96%). 1,2-Benzendicarboxylic was correlated with the increasing of wood density. An inverse relationship between 1-methyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-iminonaphthalene and wood density was observed for persian ironwood. Overall, the1, 2-Benzendicarboxylic had an important role on the ironwood durability.

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Article submitted: April 29, 2016; Peer review completed: May 29, 2016; Revised version received and accepted: June 16, 2016; Published: **June 25, 2016.**