GC/MS Analysis of Oil Extractives from Wood and Bark of *Pinus sylvestris*, *Abies alba*, *Picea abies*, and *Larix decidua*

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Wood and bark oil extractives components (OECs) of *Pinus sylvestris*, *Abies alba*, *Picea abies*, and *Larix decidua* grown in the Czech Republic were analyzed using gas chromatography/ mass spectrometry (GC/MS). The analysis showed the presence of monoterpene, sesquiterpene, diterpenoids, and resin acids. The highest percentages of OECs in the wood of *P. sylvestris* were α-fenchyl alcohol (26.04%), D-fenchyl alcohol (12.39%), and L-borneol (8.81%); the OECs in the bark included α-methyl-γ-butyrolactone (31.88%) and isodecyl octyl phthalate (15.85%). The most frequently occurring OEC in *A. alba* wood were 4-hydroxy-4-methyl-2-pentanone (73.36%), α-cedrol (10.08%), and 2,6-dimethyl-1,3,6-heptatriene (7.35%); the most OECs in the bark were di(2-ethylhexyl)phthalate (59.83%), methyl cyclopentane (16.63%), and 13-epimanool (6.31%). *P. abies* wood OECs included 4-hydroxy-4-methyl-2-pentanone (29.42%), α-cedrol (26.98%), ∆3-carene (6.08%), and terpinen-4-ol (5.42%); the most OECs in the bark were di(2-ethylhexyl)phthalate (30.91%), cyclohexane (12.89%), caryophyllene oxide (8.90%), and α-pinene (4.59%). OECs of *L. decidua* wood were α-terpineol (26.06%), isoborneol (14.12%), camphene (11.78%), D-fenchyl alcohol (10.39%), and larixol (4.85%); OECs in the bark were larixol (33.29%), phthalic acid mono-2-ethylhexyl ester (16.96%), 13-epimanool (15.40%), and cyclohexane (8.44%).

Keywords: Chemical composition; Oil extractives, Wood; Bark; Pinus sylvestris; Abies alba; Picea abies; Larix decidua

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INTRODUCTION

Softwoods from the family Pinaceae are widespread in the Mediterranean region, Caribbean area, Asia, Europe, North America, and Central America. Many important economic products such as paper, wood, building materials, and chemicals can be provided from softwoods (Kelly and Rohl 1989). Several works have been carried out in the past 20 years from different parts of the world to study the chemical composition of the essential oils of the family Pinaceae from the needles, branches, cones, seeds, and

bark, as well as their antimicrobial activities (Ekundayo 1988; Venskutonis *et al.* 2000; Macchioni *et al.* 2003; Tammela *et al.* 2003; Stevanoic *et al.* 2004; Dob *et al.* 2005; Sonibare and Olakunle 2008; Tumen *et al.* 2010; Abi-Ayad *et al.* 2011; Park and Lee 2011; Salem *et al.* 2014a,b). However, most of the studies concerning the chemical composition of softwood species have focused on North American and Central European species (Kubeczka and Schultze 1987; Sjödin *et al.* 1992; Hennig *et al.* 1994). The oils are used in perfumes, pharmaceuticals, and aromatherapy preparations. Commercial oils include European silver fir oil *(Abies alba* Mill.), Norwegian or Scotch pine needle oil (*Pinus sylvestris* L.), and others (Venskutonis *et al.* 2000).

It is known that conifers have well-developed resin ducts and high storage capacity for large amounts of oleoresin in response to wounding or damage to the plant (Gijzen *et al.* 1993). Also, the activity of monoterpene cyclase induced by damage found in needles of ponderosa pine was increased (Litvak and Monson 1998).

Monomeric terpenes in conifers are significant chemomarkers of environmental impact (Supuka and Berta 1998; Tiberi *et al.* 1999). Δ-3-carene, α-pinene, β-pinene, β-phellandrene, limonene, and myrcene are predominant volatiles for spruce, pine, and larch woods (Vuorela *et al.* 1989; Boscherini and Michelozz 1993; Manninen *et al.* 2002a; Wajs *et al.* 2006, 2007).

Wood, including the bark, of *Pinus sylvestris* was characterized with 3-carene myrcene and *β*-phellandrene, as well as *α*-pinene and *β*-pinene content (Sjödin *et al.* 1992). P-cymene was detected in the volatile fraction from twigs of *P. sylvestris* (Mumm *et al.* 2003). Some semi-volatiles, such as diterpenoids, fatty acids, higher alkanes, and other compounds are also reported in the wood oils of Norway spruce, Scots pine, and European larch, such as *cis*-abienol and thunbergol (Ucar *et al.* 2003). Bicyclic diterpene alcohols are also found in twigs and bark of Norway spruce (Staccidi *et al.* 1999) and derivatives of diterpene acids constituted of wood volatiles (Lorbeer and Zelman 1988), pine and larch (Wajs *et al.* 2006), lipophilic non-volatile compounds of spruce rosin (Norin and Winell 1972; Back and Allen 2000; Wajs *et al.* 2006), and in *P. sylvestris* sapwood and heartwood like C16:0, C18:0, C18:1, and C18:2 (Saranpää and Nyberg 1987; Piispanen and Saranpää 2002). It was reported that monoterpenes can be detected from root extract of Scots pine by n-hexane, and the most abundant of them are α-pinene, 3-carene, and β-pinene (Ludley *et al.* 2009). n-Hexane extraction also revealed a certain amount of resin components in branch wood of Scots pine (Nuopponen *et al.* 2004).

As a part of an extensive phytochemical analysis of some softwood species growing in the Czech Republic, the oil extractives by n-hexane solvent from wood and bark of *Pinus sylvestris*, *Abies alba*, *Picea abies*, and *Larix decidua* were analyzed by gas chromatography/ mass spectrometry (GC/MS).

EXPERIMENTAL

Materials

Preparation of wood and bark samples

Four species of the Pinaceae family, Scots pine (*Pinus sylvestris* L.), European silver fir (*Abies alba* Mill.), Norway spruce (*Picea abies* (L.) H. Karst.), and European larch (*Larix decidua* Mill. subsp. *decidua*), were felled in August 2014. Stemwood samples were stored in airtight plastic bags in a freezer (-24 °C) at the Department of Wood Processing, Faculty of Forestry and Wood Sciences, Czech University of Life

Sciences Prague, Czech Republic until needed. The samples were sent to the Laboratory of Wood Technology (Forestry and Wood Technology Department, Faculty of Agriculture (EL–Shatby), Alexandria University, Egypt). Fresh wood and bark samples were prepared in small pieces. Wood small pieces were sawdust and wood shavings mixtures with a particle size of 0.3 to 0.4 mm. Bark samples were with a particle size of 0.1-0.2 mm.

Methods

Oils extraction

Small pieces (200 g) from each type of wood and bark of the four studied species were extracted by soaking in 150 mL of n-hexane for two weeks and the extracts were filtrated and the residue was processed similarly with the same amount of solvent for the same period in a dark place at laboratory conditions. The obtained oils were dried over anhydrous Na_2SO_4, and the yield was measured with respect to the fresh weight of the sample. The oil extractives were kept dry in sealed Eppendorf tubes with aluminum sheets and stored at 4 °C in a refrigerator prior to chemical analysis (Salem *et al.* 2013).

Gas chromatography–mass spectrometry (GC-MS) analysis

The chemical composition of the oil extractives was performed using a Trace GC Ultra-ISQ mass spectrometer (Thermo Scientific, USA; carried out at the Atomic and Molecular Physics Unit, Experimental Nuclear Physics Department, Nuclear Research Centre, Egyptian Atomic Energy Authority, Inshas, Cairo, Egypt) with a direct capillary column TG–5MS (30 m x 0.25 mm x 0.25 µm film thickness). Helium was used as the carrier gas (flow rate of 1 mL/min), and the oven temperature program was: 45 to 165 °C (4 °C/min) and 165 to 280 °C (15 °C/min) with post run (off) at 280 °C. Samples (1 µL) were injected at 250 °C, with split/split-less injector (50:1 split ratio) in the splitless mode flow with 10 mL/min. The solvent delay was 2 min and diluted samples of 1 µL were injected automatically using Auto-sampler AS3000 coupled with GC in the split mode. EI mass spectra were collected at 70 eV ionization voltages over the range of *m/z* 40 to 550 in full scan mode. The ion source and transfer line temperatures were set at 200 and 250 °C, respectively.

The components were identified by comparison of their retention times and mass spectra with those of Wiley 09, mainlib, replib, and NIST 11 mass spectral database (Adams 2001).

RESULTS AND DISCUSSION

Oils Concentrations

Table 1 presents the concentration of oil extractives present in the wood and bark of *P. sylvestris*, *A. alba*, *P. abies*, and *L. decidua*. Among the studied species, the highest content of oil extractives was found in *L. decidua* bark (4.76 mL/100 g fresh sample) followed by *A. alba* bark (4.12 mL/100 g fresh sample), *L. decidua* wood (3.67 mL/100 g fresh sample), and *P. sylvestris* wood and bark (3.15 and 2.75 mL/100 g fresh sample, respectively). The lowest content was presented in *P. abies* wood (0.90 mL/100 g fresh sample) and 1.13 mL/100 g fresh sample was found in *A. alba* wood.

Table 1. Yield of Oil Extractives from Wood and Bark of the Studied Softwood Species

Tree species	Tree Part	Oil (ml/100 g fresh sample)
Pinus sylvestris	wood	3.15
	bark	2.75
Abies alba	wood	1.13
	bark	4.12
Picea abies	wood	0.90
	bark	2.60
Larix decidua	wood	3.67
	bark	4.76

From the literature and the present study, the variation could be related to some physiological aspects, such as the amount of live cells in the xylem of fertilized trees, the growth rate, tree vigor, and the carbon/nutrient balance hypothesis and/or geographic and environmental locations (Kramer and Kozlowski 1979; Bryant *et al.* 1983; Stockfors and Linder 1998).

Wood and Bark Oil Extractives of *Pinus sylvestris*

Table 2 presents the chemical constituents of the oil from wood and bark of *P. sylvestris*. The oil from wood of *P. sylvestris* was found to comprise 34 compounds, of which 88.07% were identified compounds. The major constituents of oil extractives from *P. sylvestris* wood were α-fenchyl alcohol (26.04%), D-fenchyl alcohol (12.39%), L-borneol (8.81%), 2,4-dimethoxybenzo[h]quinazoline (6.88%), α-pinene (6.01%), abietic acid (4.75%), α-pimaric acid (4.00%), camphene (2.55%), palustric acid (2.33%), docosane (2.20%), isoborneol (1.73%), dl-limonene (1.51%), and naringenin (1.34%). Ten compounds were reported in bark oil extractives of *P. sylvestris*, and the major oil compounds were α-methyl-γ-butyrolactone (31.88%), isodecyl octyl phthalate (15.85%), 3-methylhexane (7.23%), heptyl formate (5.51%), heptane (5.34%), α-phellandrene (4.86%), and benzene, methyl- (3.25%).

The resin acid content of *P. sylvestris* was comprised of monoterpenes and phenolics, which were found at low concentrations in the sapwood (Saranpää and Nyberg 1987). Monoterpenes, acetaldehyde, and ethanol, as different compositions of wood volatiles, have been found in healthy and top-cut samples of *P. sylvestris* (Sjödin *et al.* 1992). Resin acids including abietic, dehydroabietic, neoabietic, palustric, and levopimaric are the major components in the oleoresin of *P. sylvestris* (Manninen *et al.* 2002b; Semiz *et al.* 2007). 3-Carene and limonene were found in phloem and bark of branches of some *P. sylvestris* specimens **(**Sjödin *et al.* 1992, 1996). The identified oils from bark samples were included terpenes (α-pinene, Δ-3-carene, and p-cymene), oxygenated terpenes (α-terpineol and verbenone), sesquiterpenes (α-longipinene, longifolene, E-β-farnesene, γ-cadinene, and pentadecane), and diterpenes (manoyl oxide and pimaral) (Szmigielski *et al.* 2012). Longifolene, γ-cadinene and E-β-farnesene were detected in bark and twig emissions of *P. sylvestris* (Mumm *et al.* 2003).

α-Pinene, camphene, β-pinene, sabinene, limonene, and *β*-phellandrene were found in different tissues of four studied *P. sylvestris* trees (Sjödin *et al.* 1996). α-Pinene, sabinene, *β*-pinene, and limonene were detected in the essential oil of twigs (Zafra and García-Peregrín 1976), while in the present study sabinene was found in wood at low concentration (0.24%). The essential oils of *P. sylvestris* twigs from French Massif

Central were reported to consist mainly of α-pinene, Δ3-carene, terpinolene, α-terpineol, and borneo1 (Chalchat *et al.* 1985).

Table 2. Chemical Composition of the Oil Extractives from *Pinus sylvestris* Wood and Bark

Wood oil					
t_r (min)	Compound	Area (%)	t_r (min)	Compound	Area (%)
2.51	α-Pinene	6.01	5.81	α-Fenchyl alcohol	26.04
2.67	Camphene	2.55	6.02	3-Caren-10-al	0.37
3.21	Sabinene	0.24	6.26	Eucarvone	1.03
3.33	p-Cymene	0.40	6.34	Fenchyl acetate	0.26
3.39	dl-Limonene	1.51	7.65	Bornyl acetate	0.17
3.47	1,8-Cineole	0.24	8.94	Tetradecane	0.29
3.95	Pinol	0.24	9.77	Geranyl isovalerate	0.08
4.15	P,α-Dimethylstyrene	0.31	12.01	9-Hexyl-heptadecane	0.15
4.24	Fenchone	0.30	12.44	Cembrene	0.09
4.60	D-Fenchyl alcohol	8.81	14.26	Hexadecane	0.18
4.73	2,4,6-Octatrien-1-ol, 3,7-dimethyl-(E,E)-	0.12	16.46	Docosane	2.20
5.06	Isopinocarveol	0.87	17.63	2,4-Dimethoxybenzo[h]quinazoline	6.88
5.17	Camphor	0.46	21.87	Androst-5-en-4-one	0.11
5.25	Trans-sabinene hydrate	0.49	24.31	Palustric acid	2.33
5.36	Borneol	1.73	25.34	Abietic acid	4.75
5.49	Borneol	12.39	26.63	α-Pimaric acid	4.00
5.64	1-(3,3-dimethylbutenyl)-2-formyl-1-cyclohexene	1.13	30.11	Naringenin	1.34

Bark oil					
t_r (min)	Compound	Area (%)	t_r (min)	Compound	Area (%)
2.62	2,2-Dimethoxy-propane	2.70	3.40	Heptane	5.34
2.76	α-Methyl-γ-butyrolactone	31.88	5.13	Benzene, methyl-	3.25
2.93	3-Methylhexane	7.23	11.00	α-Phellandrene	4.86
3.11	*cis*-1,3-Dimethylcyclopentane	1.76	13.52	Decane	2.61
3.22	Heptyl formate	5.51	43.62	Isodecyl octyl phthalate	15.85

Note: t_r is the retention time.

P-cymene, found at low concentration (0.40%) in wood oil, was reported in gum turpentine of Russian *P. sylvestris* (Bardyshev 1955). Chemical compounds such as limonene, benzene, α-pinene, 3-methylhexane, heptane, β-pinene, and caryophyllene were identified in bark volatile oil from *P. armandii* (Chen *et al.* 2007). Pentadecanoic acid was found in pine heartwood (Wajs *et al.* 2007). Thuja-2,4(10)-diene, benzaldehyde, verbenene, p-cymene, nonanal, p-mentha-1,3,8-triene, mcymen-8-ol, methyl chavicol, decanal, 3,4-dimethoxytoluene, and *trans*-verbenyl acetate were identified in wood of *P. sylvestris* (Wajs *et al.* 2007).

Wood and Bark Oil Extractives of *Abies alba*

Table 3 shows the chemical constituents of wood and bark oil extractives from *A. alba*. Five compounds, representing 97%, were identified in wood oil extractives of *A. alba* namely, 4-hydroxy-4-methyl-2-pentanone (73.36%), α-cedrol (10.08%), 2,6-dimethyl-1,3,6-heptatriene (7.35%), 4-terpinenol (3.25%), and α-phellandrene (2.96%). Nine compounds represented 99.98% and were identified in bark oil of *A. alba*. The major compounds were di(2-ethylhexyl)phthalate (59.83%), methyl cyclopentane (16.63%), 13-epimanool (6.31%), methyl cyclohexane (3.73%), and 3-methylhexane (3.29%).

Table 3. Composition of Oil Extractives from *Abies alba* Wood and Bark

Wood			Bark		
t_r (min)	Compound	Area (%)	t_r (min)	Compound	Area (%)
7.48	4-Hydroxy-4-methyl-2-pentanone	73.36	2.75	Methyl cyclopentane	16.63
11.00	2,6-Dimethyl-1,3,6-Heptatriene	7.35	2.93	3-Methylhexane	3.29
12.55	α-Phellandrene	2.96	3.40	3-Hexanone	2.79
20.51	4-Terpinenol	3.25	3.97	Methyl cyclohexane	3.73
34.76	α-Cedrol	10.08	4.91	2,2-dimethoxybutane	2.80
			5.13	Benzene, methyl-	1.76
			11.00	(E)-β-ocimene	2.84
			39.91	13-Epimanool	6.31
			43.61	di(2-ethylhexyl)phthalate	59.83

Wood and Bark oil extractives of *Picea abies*

Table 4 shows the chemical constituents of wood and bark oils from *P. abies*. Sixteen compounds represented 95.28% and were identified in wood oil extractives of *P. abies*; the major compounds were 4-hydroxy-4-methyl-2-pentanone (29.42%), α-cedrol (26.98%), Δ3-carene (6.08%), terpinen-4-ol (5.42%), α-humulene (3.79%), isopulegol acetate (3.76%), and thujopsene (2.85). Twenty-three compounds identified in bark oil extractives of *P. abies* represented 91.95% of the oil and the major constituents were di(2-ethylhexyl)phthalate (30.91%), cyclohexane (12.89%), caryophyllene oxide (8.90%), α-pinene (4.59%), geranyl-linalool (3.66%), thunbergol (3.52%), 3-methylhexane (2.85%), and dehydroabietic acid (2.67%).

Wood oil of *P. abies* presented small amount of sabinene (2.46%) which was reported by Sjödin *et al.* (1992). Previously, Wajs *et al.* (2007) reported that sapwood of spruce comprised of α-fenchene and p-mentha-1,3,8-triene, while p-cymene, α-fenchol, α-campholene aldehyde, camphene hydrate, pinocamphone, and borneol were found only in heartwood. α-pinene, 3-carene, sabinene, germacrene D, and thunbergol were found in *P. abies* (Zhao *et al.* 2011).

Moreover, α-longifolene, isocaryophyllene, and δ-cadinene were the main compounds found in oleoresin of spruce (Martin *et al.* 2002; Isidorov *et al.* 2003; Wajs *et al.* 2006). The components of α-pinene, myrcene, β-caryophyllene, β-pinene, and γ-eudesmol were found in *P. abies* (Lee *et al.* 2015). Diterpene compounds; isomers of cembrene, palustradiene, abietatriene, and pimaral, earlier identified in spruce wood (Wajs *et al.* 2006), were found, in this study, also in pine and larch stemwood (Wajs *et al.* 2007). Pentadecanoic and octadecanoic acid, and isopropyl hexadecanoate occurred in heartwood and *cis*-abienol occurred in sapwood (Wajs *et al.* 2007). The condensate that

was collected during the industrial kiln drying processes contained terpenoids, ketones, alcohols, and traces of aldehydes like terpinen-4-ol, hexanal, 2-pentanone, delta-3-carene, and tridecane (Rathke and Stratev 2013).

Table 4. Chemical Composition of the Oil Extractives from *Picea abies* Wood and Bark

Wood oil					
t_r (min)	Compound	Area (%)	t_r (min)	Compound	Area (%)
4.89	Hexanal	2.14	26.62	Isopulegol acetate	3.76
7.45	4-Hydroxy-4-methyl-2-pentanone	29.42	29.21	Junipene	1.28
10.98	Δ3-Carene	6.08	29.62	Thujopsene	2.85
12.54	Sabinene	2.46	30.31	α-Humulene	3.79
13.50	2-Methyl- decane	1.34	34.32	Caryophyllene oxide	1.49
17.42	Tetradecane	1.95	34.51	Palustrol	2.07
20.52	Terpinen-4-ol	5.42	34.76	α-Cedrol	26.98
21.20	Dodecane	2.04	43.62	di(2-ethylhexyl)phthalate	2.21

Bark oil					
t_r (min)	Compound	Area (%)	t_r (min)	Compound	Area (%)
2.21	Methyl-cyclopentane	3.97	39.46	Geranyl-linalool	3.66
2.73	Cyclohexane	12.89	39.66	Manoyl oxide	0.68
2.90	3-Methylhexane	2.85	39.90	Thunbergol	3.52
3.09	3,3-Dimethylglutaric anhydride	0.78	40.34	Phenanthrene, 9-dodecyltetradecahydro-	1.57
3.19	Isopropylcyclobutane	1.96	40.44	Caryophyllene oxide	8.90
3.37	Heptanal	2.22	41.23	2-[5-(2,2-Dimethyl-6-met hylene-cyclohexyl)-3-meth yl-pent-2-enyl]-[1,4]benzo quinone	1.30
4.89	2,2'-Dimethoxy-3-hydroxy -1,1'-binaphthalene	1.33	41.52	1-Phenanthrenecarboxaldehyde, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-	1.08
5.10	1,6-anhydro-2,4-dideoxy-3 -O-benzyl-α-threo-hexopyranose	1.66	42.01	Methyl Dehydroabietate	1.25
10.98	α-Pinene (E)-β-Ocimene	4.59	42.22	Larixol acetate	0.82
13.51	Decane	1.04	42.61	Methyl sandaracopimarate	1.07
17.43	Undecane	1.23	42.92	Dehydroabietic acid	2.67
			43.61	di(2-ethylhexyl)phthalate	30.91

Wood and Bark Oil Extractives of *Larix decidua*

Table 5 shows the chemical constituents of wood and bark oils from *L. decidua*. Twenty four compounds that represented 98.16% were identified in wood oil extractives from *L. decidua*; the major compounds were α-terpineol (26.06%), isoborneol (14.12%), camphene (11.78%), D-fenchyl alcohol (10.39%), larixol (4.85%), decane, 3,3,4-trimethyl- (3.10%), d-limonene (3.03%), 13-epimanool (2.77%), undecane (2.67%), and isocarvestrene (2.66%). Twelve compounds that represented 93.29% were identified in bark oil extractives from *L. decidua*; the major constituents were larixol (33.29%),

phthalic acid mono-2-ethylhexyl ester (16.96%), 13-epimanool (15.40%), cyclohexane (8.44%), methyl-cyclopentane (4.18%), and 2,2-dimethoxybutane (4.24%).

Table 5. Composition of Oil Extractives from *Larix decidua* Wood and Bark

Wood oil					
t_r (min)	Compound	Area (%)	t_r (min)	Compound	Area (%)
3.96	Cyclohexane, methyl-	0.71	19.46	Camphene hydrate	1.07
5.12	1,5-Heptadien-3-yne	0.81	19.78	endo-Borneol	1.85
7.47	4-Hydroxy-4-methyl-2-pentanone	1.15	20.13	Isoborneol	14.12
11.01	Camphene	11.78	20.52	4-Terpinenol	1.14
11.60	Limonene	3.03	20.75	4-methoxybenzoic acid 2,5-dioxo-1-pyrrolidinyl ester	1.30
13.52	1,4-Dioxaspiro[4.5]decane	2.07	21.05	α-Terpineol	26.06
14.01	α-Thujene	1.12	21.21	Decane, 3,3,4-trimethyl-	3.10
14.73	Isocarvestrene	2.66	21.72	Verbenone	1.31
17.09	1H-Indene, 2,3-dihydro-1-methyl-	1.08	34.76	α-Cedrol	1.13
17.43	Undecane	2.67	39.90	13-Epimanool	2.77
18.09	Fenchyl alcohol	10.39	41.25	Podocarp-7-en-3-one, 13α-methyl-13-vinyl-	0.87
19.29	Benzofuran, octahydro-6-methyl-3-methylene	1.12	42.22	Larixol	4.85
Bark oil					
2.23	Methyl-Cyclopentane	4.18	3.97	Methyl-cyclohexane,	2.22
2.62	Propane, 2,2-dimethoxy-	1.05	4.91	2,2-dimethoxybutane	4.24
2.75	Cyclohexane	8.44	11.00	β-ocimene	2.45
2.93	1-Heptene, 4-methyl-	1.78	39.90	13-Epimanool	15.40
3.22	trans-1,2-Dimethylcyclopentane	1.57	42.22	Larixol	33.29
3.40	Heptane	1.71	43.61	Phthalic acid mono-2-ethylhexyl ester	16.96

α-Fenchol, camphene hydrate, and α-terpineol occurred in the heartwood of larch (Wajs *et al.* 2007). Also, some new aldehydes, *i.e.*, hexanal, heptanal, benzaldehyde, (E)-2-octenal, nonanal, decanal, and two decadienals, were identified together with Z-(β)-ocimene, methyl thymol, *trans*-sabinol, and methyl chavicol (Macchioni *et al.* 2003; Ucar *et al.* 2003; Wajs *et al.* 2007).

Diterpenoids found in the wood were found in bark oil extractives of *P. abies* (geranyl-linalool), and bark oil of *A. alba* (13-epimanool) (Sjöström 1993); these can be used as rosin or sizing agents. Resin acids are main parts of the composition in pine wood oleoresin and rosins which consist mainly of pimaric, sandaracopimaric, isopimaric, abietic, levopimaric, palustric, neoabietic, and dehydroabietic acids (Sjöström 1993).

Spruce, pine, and larch wood contained non-terpenoids such as aldehyde compounds like hexanal, heptanal, 2-octenal, nonanal, decanal, isomers of decadienal, and aromatic derivatives such as 3,4-dimethoxytoluene (Lindmark-Henriksson 2003; Wajs *et al.* 2007).

Also, in the present study phthalate and related phthalic acid esters were previously found in some natural extracts, *i.e.*, 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl)ester was found in the n-hexane extract of stem bark of *Mangifera indica* (Singh *et al.* 2015), 1, 2-benzenedicarboxylic acid, bis (2-ethylhexyl) ester from the twigs

of *Thevetia peruviana* (Save *et al.* 2015) and this compound was identified using NMR spectroscopy techniques, 1H, 2D, HMQC, HMBC, LCMS, FTIR, and HRMS, and the HPLC, and butyl-2-methylpropyl phthalate, hexadecane acid, diheptyl phthalate, bis (2-ethyl-hexyl) phthalate, benzenedicarboxylic acid decyl-hexyl ester, and benzene-dicarboxylic acid isodecyl-octyl ester were found in *Euphorbia* honey (Tóth-Soma *et al.* 1993).

CONCLUSIONS

1. The major constituents of oil extractives from *P. sylvestris* wood were α-fenchyl alcohol (26.04%), fenchyl alcohol (12.39%), L-borneol (8.81%), 2,4-dimethoxybenzo[h]quinazoline (6.88%), α-pinene (6.01%), abietic acid (4.75%), and α-pimaric acid (4.00%).
2. The major bark oil extractives of *P. sylvestris* were α-methyl-γ-butyrolactone (31.88%), isodecyl octyl phthalate (15.85%), 3-methylhexane (7.23%), heptyl formate (5.51%), heptane (5.34%), and α-phellandrene (4.86%).
3. The major wood oil extractives of *A. alba* were 4-hydroxy-4-methyl-2-pentanone (73.36%), α-cedrol (10.08%), 2,6-dimethyl-1,3,6-heptatriene (7.35%), 4-terpinenol (3.25%), and α-phellandrene (2.96%).
4. The major compounds of bark oil of *A. alba* were di(2-ethylhexyl)phthalate (59.83%), methyl cyclopentane (16.63%), 13-epimanool (6.31%), methyl cyclohexane (3.73%), and 3-methylhexane (3.29%).
5. The major compounds of wood oil extractives of *P. abies* were 4-hydroxy-4-methyl-2-pentanone (29.42%), α-cedrol (26.98%), Δ3-carene (6.08%), terpinen-4-ol (5.42%), α-humulene (3.79%), isopulegol acetate (3.76%), and thujopsene (2.85).
6. The major constituents of bark oil extractives of *P. abies* were di(2-ethylhexyl)phthalate (30.91%), cyclohexane (12.89%), caryophyllene oxide (8.90%), α-pinene (4.59%), geranyllinalool (3.66%), and thunbergol (3.52%).
7. Wood oil extractives from *L. decidua* showed the major compounds of α-terpineol (26.06%), isoborneol (14.12%), camphene (11.78%), D-fenchyl alcohol (10.39%), larixol (4.85%), and decane,3,3,4-trimethyl- (3.10%).
8. Bark oil extractives from *L. decidua* contained the major constituents larixol (33.29%), phthalic acid mono-2-ethylhexyl ester (16.96%), 13-epimanool (15.40%), cyclohexane (8.44%), methyl-cyclopentane (4.18%), and 2,2-dimethoxybutane (4.24%).

ACKNOWLEDGMENTS

The authors extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding this research group, No. (RG 1435-011).

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Article submitted: July 19, 2015; Peer review completed: September 12, 2015; Revised version received and accepted: September 13, 2015; Published: September 30, 2015.
DOI: 10.15376/biores.10.4.7725-7737