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ESSENTIAL OIL COMPOSITION AND PLANT-INSECT RELATIONS IN SCOTS PINE (*PINUS SYLVESTRIS* L.)

Review: **Janina Kamińska, Ph. D., D. Sc.**

A review of methods of isolation, chemical composition and biological activity of essential oil of different organs of Scots pine (Pinus sylvestris) was presented. The data on relation between herbivorous insects and plant were also reviewed.

1. Botanic characterization of Scots pine

Pines are coniferous trees of the genus *Pinus*, family Pinaceae. There are about 115 species of pine which are divided into three subgenera, based on cone, seed and leaf characters: *Strobus* (white or soft pines), *Ducampopinus* (lacebark and bristlecone pines) and *Pinus* (yellow or hard pines). Pines are commercially among the most important of species used for timber and wood pulp in temperate and tropical regions of the world. This is due to their fast growing softwoods that can be planted in relatively dense stands, and because their acidic decaying needles inhibit the growth of other competing plants [1].

Pinus sylvestris L., also known as the Scots pine, belongs to the subgenus *Pinus*. The threes normally grow up to 25 m in height and in exceptional cases up till 40 m. They have a thick bark which is scaly dark grey-brown on the lower trunk, and thin flaky orange on the upper trunk and branches. The mature trees are distinctive due to their long, bare and straight trunk topped by a rounded or flat-topped mass of foliage. The needles are blue-green, 3-5 cm long and occur in fascicles of two. The cones are pointed ovoid in shape and 3-7 cm long [2].

P. sylvestris is the most popular of three original *Pinus* species in Poland and the only one in Great Britain. It can be found in most of Northern and Eastern Europe ranging all the way to Siberia. Sinclair *et al.* by analyzing mitochondrial DNA, found that *P. sylvestris* of Europe can be divided into at least three evolutionary units (Spain, north central Europe and Scandinavia) each of which had a different origin after glaciations. *P. sylvestris* has also been widely planted in New Zealand and in the colder regions of North America and is listed as an invasive species in some areas there [3].

2. Biological activity of pine oil

Pine oils are essential oils mainly obtained by the hydrodistillation of needles, twigs and cones from a variety of pine species, e.g. *P. sylvestri*s, *P. mugo*, *P. palustris*. Essential oil of *P. sylvestris* needle is a colorless or pale yellow mobile liquid with strong, dry-balsamic, turpentine-like aroma. It is nontoxic for live organisms and nonirritating in low concentrations. It is known that Scots pine oil possess wide therapeutic effect, e.g.: antibacterial, antifungal, antiviral, antiseptic (pulmonary, urinary, hepatic), antineuralgic, cholagogue, choleretic, diuretic, expectorant, hypertensive. It is used in illnesses of respiratory system like cough or catarrh and applied in medical baths, compresses and massages (warm effect). Its insecticidal and deodorant properties are also known [4;5].

3. Methods of isolation and analysis of essential oil from *P. sylvestris*

The composition of volatiles can give information for chemosystematic investigation and may provide valuable information on the ability of plants to resist external stress factors. Essential oil composition also provides the basis for quality control in industry [6]. The composition of each oil depends strongly, among other variables, on the method of isolation. Although the main method of essential oil preparation is conventional hydrodistillation, several other methods to get and analyze the pine needle oil were applied: simultaneous distillation-extraction (SDE), supercritical fluid extraction (SFE) [7;8], headspace (HS) [9] and solid-phase microextraction (SPME) [10].

Orav *et al.* [7;8] compared two methods: SDE and SFE with CO_2, for isolation of volatiles from Estonian *P. sylvestris* needles. Widely used, especially in laboratory, SDE method have some disadvantages such as the decomposition of thermolabile compounds, hydrolysis of water sensitive compounds and solvent contamination. Moreover, compounds with low vapor pressure cannot be completely isolated by this technique. SFE method was shown to be an attractive alternative to the conventional extraction and steam-distillation for a wide variety of analytes. SFE is less laborious and less time-consuming than other extraction techniques. To some extent the solvent strength can be controlled by the pressure, temperature and modifiers [7]. The yield for essential oil obtained by SDE was 1% [8], for SFE product 25%, and for SFE with modifier 51% [7]. SFE at used conditions did not exceed SDE in extraction of monoterpenes but was far better in extraction of oxygenated mono- and sesquiterpenoids and diterpenoids.

It is known that the most volatile compounds can be lost during the hydrodistillation of the plant material. Vourela *et al.* [9] analyzed the composition of the volatiles of *P. sylvestris* needles by conventional hydrodistillation-gas chromatography (HD-GC) and headspace-GC (HS-GC). They indeed confirmed that small amounts of terpene compounds was selectively lost during hydrodistillation. HS-GC is therefore a more suitable quantitative method for low boiling compounds in the analysis of aromatic plants than HD-GC technique. This is in some agreement with Pohjola *et al.* [11] who wrote that the terpene patterns of pine needle volatiles obtained by HS-GC and GC of essential oil did not differ much.

Santos *et al.* [10] applied headspace-solid phase microextraction (HS-SPME) for the isolation of volatiles from four pine species that were subsequently analysed by GC on both achiral and chiral columns in order to differentiate *Pinus* species. They concluded that HS-SPME, a relatively new method [12], is a simple, quick, sensitive and versatile method of sample preparation, suitable for routine analysis of monoterpenes in tree tissues.

Xiao-geng *et al.* [13] compared five methods of pine needle oil separation, namely: enzymatic, microwave-assisted, steam-distillation, microwave-assisted enzymatic (MAEZ), and microwave-assisted ionic liquid enzymatic methods. The results showed that essential oil yield from MAEZ method was 0.49%-0.53% and was 12% higher than of single enzymolysis.

Gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC-MS) are preferably used today for monitoring the composition and quality of essential oils. Despite the universality of these methods, in order to obtain reliable results in analysis of complex mixtures, there occurs need to use at least two columns with different polarity. Reliable results can be also obtained by high resolution NMR (nuclear magnetic resonance) spectroscopy. According to Skakowskii *et al.* [14] the major components of the pine needle oil can be analyzed using the proton spectra obtained on routine NMR spectrometers with low operating frequency for hydrogen nuclei. But detailed analysis is not possible due to the overlap of lines from many compounds. The situation is simplified when we use spectrometers with high operating frequency. Since the range of chemical shifts for ^{13}C nuclei is significantly greater than the range of chemical shifts for ^{1}H nuclei, applying ^{13}C-NMR we can obtain good results for quantitative analysis of the studied mixtures using spectrometers with low operating frequencies.

Burzo *et al.* [15] demonstrated that identification of the volatile components from *P. sylvestris* can be carried out through GC-FTIR, a complementary method to the GC-MS, which allowed a qualitative analysis by comparing obtained spectra with that in library.

4. Constituents of *Pinus sylvestris* essential oil of different origin

The composition of the essential oils of different pine species was the subject of many investigations. Chemically, pine oils, among them *P. sylvestris* oil, consist mainly of 50-90% monoterpene hydrocarbons, other components are sesquiterpene hydrocarbons as well as oxygenated mono- and sesquiterpenes. *P. sylvestris* trees can be divided in two groups: low car-3-ene chemotype and high car-3-ene chemotype, according to low and high concentration of this compound in needles and trunk xylem [16].

Góra and Lis [4] as well as Lawrence and Reynolds [17] reviewed the first researches of Scots pine essential oil and compared the amounts of main components in pine oil from: Austria, Russia (Caucasus and Siberia), France and Portugal. The more recent papers described essential oils of pine trees from different parts of Europe: Estonia [8], Slovakia [18], Lithuania [19, 20], Greece [21] and France [17]. All these investigation were conducted using GC and GC-MS. A summary of the results can be seen in Table 1.

Table 1

Constituents of *P. sylvestris* needle essential oil of different origin

Compound	**RU$_1$** [4]	**RU$_2$** [4]	**EE** [8]	**LT$_1$** [19]	**LT$_2$** [21]	**SK** [18]	**GR** [20]	**PT** [4]	**FR$_1$** [17]	**FR$_2$** [17]	**D** [22]
	%										
Tricyclene	tr		0.7	0.2-1.2	0.3-1.4		0.2		0.8	0.7	1.0
α-Thujene			0.2	0.1-0.7							
α-Pinene	**20.3**	**28.0-31.0**	**28.1**	**18.5-33.0**	**19.8-35.0**	**20.7-69.1**	**19.4**	**20.3**	**22.2**	**41.1**	**42.1**
Camphene	**9.4**	**6.0-8.5**	**3.4**	**1.5-5.3**	**0.8-2.2**	0.1-1.7	**2.3**	**7.1**	**3.2**	**3.3**	**4.1**
Sabinene			1.0	0.3-0.7	**0.2-1.4**			0.9	0.5	0.3	0.7
β-Pinene	**2.0**	**8.3-10.3**	**2.1**	**0.6-2.1**		**0.17-11.6**	**17.3**	**4.7**	**3.8**	**18.4**	**1.9**
Myrcene		**2.1-3.8**	**2.1**	**1.3-2.3**	**0.8-1.1**	**t-1.0**	**14.0**				**2.2**
α-Phellandrene			0.2			**0.1-31.4**	0.1		**3.1**	**3.6**	
Car-3-ene	**20.4**	**9.5-11.3**	**23.7**	**9.1-24.6**	**22.7-33.7**			**1.8**	**43.4**	tr	**20.6**
α-Terpinene	3.2		0.2	t-0.1				3.0	tr	tr	0.1
p-Cymene	tr		0.1	0-0.2	0.2-0.5	0-0.4			0.3	0.2	0.1
β-Phellandrene	**4.0**	**8.6-10.9**	1.0		0.7-1.4		**29.1**		0.7	0.9	0.3
Limonene	3.1		0.8	0.6-1.2		0-0.1		3.6	0.9	2.6	5.2
1,8-Cineole											
(Z)-β-Ocimene				0-t	t-0.5			2.3	1.1	1.3	0.8
(E)-β-Ocimene			1.5	0.3-1.8	0.4-2.0						
γ-Terpinene	0.2	0.2-0.4	0.3	0.1-0.3	0.3-0.9	0-0.1		0.3	1.1	0.1	0.3
Terpinolene	tr		2.6	1.0-2.4	0.6-2.9		0.2	2.3	4.1		1.7
Myrtenol							0.3				
γ-Carveol							0.2				

Table 1 *continued*

Compound	**RU$_1$** [4]	**RU$_2$** [4]	**EE** [8]	**LT$_1$** [19]	**LT$_2$** [21]	**SK** [18]	**GR** [20]	**PT** [4]	**FR$_1$** [17]	**FR$_2$** [17]	**D** [22]
	%										
p-Mentha-1,5-dien-8-ol				0-0.2	t-0.2						
Borneol		**0.1-0.3**	**0.3**		**0.4-1.1**			**0.3**	**1.8**^{1}	**5.8**^{1}	
p-Cymen-8-ol				0-t	t-0.4						
Terpinen-4-ol			0.4	t-0.1	0.6-2.4			1.9	1.1	0.8	
β-Guaiene									1.0	0.4	
β-Farnesene									0.1	0.4	
m-Cymen-8-ol					0-0.3						
Decan-2-one					0-0.3						
α-Terpineol	1.9		0.1	0-0.1	0.3-1.2	**0-6.7**		0.4			tr
γ-Patchoulene									0.2	0.9	
β-Citronellol			tr			0-0.15					
Thymol metyl ether					0-0.7						
Linalyl acetate							0.1				
Bornyl acetate	**1.7**	**2.9-4.2**	**1.8**	**0.5-2.6**	**1.0-3.4**	**2.5-8.8**	**1.3**	0.6	0.3	0.1	0.1
Undecan-2-one				0.1-1.1	0-0.8						
Terpinen-4-yl acetate				0.2-0.4							
Deca-(2E, 4 E)-dienal					0-0.3						
α-Terpinyl acetate			0.6	t-0.2	t-1.4		1.0				
δ-Elemene					0.4-0.2				0.4	0.2	
Neryl acetate			tr								
α-Cubebene					t-0.5						0.2
Geranyl acetate			tr								
α-Ylangene									0.1	0.1	
α-Copaene			0.1	0.2-0.6	0.2-0.6		0.3		0.1	0.3	
Junipene							0.3				
β-Bourbonene			0.1	0.1-0.2	0.1-0.5						
β-Cubebene					0.2-0.4		0.2				

Tabel 1 *continued*

Compound	**RU$_1$** [4]	**RU$_2$** [4]	**EE** [8]	**LT$_1$** [19]	**LT$_2$** [21]	**SK** [18]	**GR** [20]	**PT** [4]	**FR$_1$** [17]	**FR$_2$** [17]	**D** [22]
	%										
β-Elemene			0.3	0.8-2.7	0.7-2.3						
Longifolene	3.5	0.5-1.2	0.1					1.1	t		
β-Caryophyllene	**1.7**	**3.3-3.8**	**2.9**	**2.6-4.9**	**2.6-7.0**		**1.3**	**1.1**	**3.8**	**3.1**	**1.0**
β-Copaene			0.1		0.1-0.8						
Aromadendrene				0.1-0.4	0.1-1.2						
α-Humulene	1.8		0.5	0.6-1.5	0.8-1.8	0-0.1	0.6	0.7	0.6	1.1	tr
α-Guaiene			0.1								
α-Cadinene		0.3-0.6		0.2-0.4	0.2-0.5				0.1	0.3	
cis-Muurola-4(14),5-diene				0-0.1	0.1-0.4						
allo-Aromadendrene				0.1-0.4							
γ-Gurjunene				0-0.3							
β-Gurjunene				0.1-1.0	t-0.5						
γ-Muurolene		**0.5-0.9**	**2.0**	**0.5-1.5**	**0.8-7.3**				**0.9**	**0.8**	
ε-Muurolene			0.3								
β-Guaiene											
Germacrene D				**1.4-6.0**	**0.8-6.9**			0.4			**1.5**
β-Selinene				0.5-1.3	0.5-1.4						
Calamenene			0.2						0.2	0.4	
epi-Cubebol				**2.1-6.2**							
Bicyclogermacrene					**0.2-2.0**						
α-Muurolene	2.6	7.8-11.6	2.8	0-1.3	1.5-5.0		0.4		0.3	0.1	
α-Farnesene			0.8								
β-Bisabolene	0.2										
γ-Cadinene	**5.4**		**1.2**	**3.0-5.5**	**1.2-9.3**				0.5	0.8	**4.8**
δ-Cadinene	**9.5**		**4.8**	**4.7-11.6**	**2.9-9.0**		0.5		1.2	**4.0**	
Cadina-1,4-diene				0.1-0.3							

Tabel 1 *continued*

Compound	RU$_1$ [4]	RU$_2$ [4]	EE [8]	LT$_1$ [19]	LT$_2$ [21]	SK [18]	GR [20]	PT [4]	FR$_1$ [17]	FR$_2$ [17]	D [22]
					%						
β-Elemene			0.3	0.8-2.7	0.7-2.3						
Longifolene	3.5	0.5-1.2	0.1					1.1	t		
β-Caryophyllene	**1.7**	**3.3-3.8**	**2.9**	**2.6-4.9**	**2.6-7.0**		**1.3**	**1.1**	**3.8**	**3.1**	**1.0**
β-Copaene			0.1		0.1-0.8						
Aromadendrene				0.1-0.4	0.1-1.2						
α-Humulene	1.8		0.5	0.6-1.5	0.8-1.8	0-0.1	0.6	0.7	0.6	1.1	tr
α-Guaiene			0.1								
α-Cadinene		0.3-0.6		0.2-0.4	0.2-0.5				0.1	0.3	
cis-Muurola-4(14),5-diene				0-0.1	0.1-0.4						
allo-Aromadendrene				0.1-0.4							
γ-Gurjunene				0-0.3							
β-Gurjunene				0.1-1.0	t-0.5						
γ-Muurolene		**0.5-0.9**	**2.0**	**0.5-1.5**	**0.8-7.3**				**0.9**	**0.8**	
ε-Muurolene			0.3								
β-Guaiene											
Germacrene D				**1.4-6.0**	**0.8-6.9**			0.4			**1.5**
β-Selinene				0.5-1.3	0.5-1.4						
Calamenene			0.2						0.2	0.4	
epi-Cubebol				**2.1-6.2**							
Bicyclogermacrene					**0.2-2.0**						
α-Muurolene	2.6	7.8-11.6	2.8	0-1.3	1.5-5.0		0.4		0.3	0.1	
α-Farnesene			0.8								
β-Bisabolene	0.2										
γ-Cadinene	**5.4**		**1.2**	**3.0-5.5**	**1.2-9.3**				0.5	0.8	**4.8**
δ-Cadinene	**9.5**		**4.8**	**4.7-11.6**	**2.9-9.0**		0.5		1.2	**4.0**	
Cadina-1,4-diene				0.1-0.3							

Table 1 *continued*

Compound	**RU$_1$** [4]	**RU$_2$** [4]	**EE** [8]	**LT$_1$** [19]	**LT$_2$** [21]	**SK** [18]	**GR** [20]	**PT** [4]	**FR$_1$** [17]	**FR$_2$** [17]	**D** [22]
	%										
Germacra-1(10)E, 5E-dien-4-ol											1.9
Nerolidol								**8.0**			
trans-Cadina-1(2),4-diene					0.1-0.7						
α-Calacorene					tr-0.4						
β-Calacorene					0-0.2						
Germacrene B			0.2								
Globulol				0.1-0.3							
Caryophyllene oxide			**4.9**		**0.6-1.7**						
Hex-3(Z)-enyl benzoate				0-0.4	0-0.2						
Spathulenol				**2.6-13.2**	**0.5-5.2**						
Germacrene D-4-ol					**0.5-5.2**						
Gleenol					0-0.4						
β-Oplopenone				0-0.5	0-0.1						
1,10-diepi-Cubenol				0.1-0.3	0.4-1.1						
T-Cadinol			**0.7**		**4.3-6.7**				**0.3**	**0.9**	**0,6**
T-Muurolol			**1.0**						**0.3**	**0.9**	**0.6**
α-Muurolol				0-0.7							
α-Cadinol			**2.7**	**1.9-7.7**	**4.9-7.8**				**0.4**	**1.6**	**1.3**
α-Bisabolol				0.1-0.2		0-0.2					
Benzyl benzoate				0-0.2							
Abietadiene					0-0.3						
Manoyl oxide					0-0.4						

RU$_1$ – Caucasus; RU$_2$ – Siberia; EE – Estonia; LT$_1$; LT$_2$ – Lithuania; SK – Slovakia; GR – Greece; FR$_1$; FR$_2$ – France (two chemotypes); D – Germany;

tr – trace quantity (<0.05%); ^{1} – borneol + α-terpineol

Orav *et al.* [8] examined the composition of the needle oil of *P. sylvestris* from different places in Estonia. The oil was obtained by simultaneous hydrodistillation-extraction (SDE) micromethod for 30 min., with hexane as a solvent and n-tetradecane as internal standard. About 50 constituents were identified, among them 16 monoterpenes, 17 sesquiterpenes, 15 oxygenated terpenes (mainly 1,8-cineole, bornyl acetate, borneol, camphor, camphene hydrate, α-terpineol). There were high concentration (20% in total) of common sesquiterpenes like γ- and α-muurolene, α- and δ-cadinene, and β-caryophyllene. The authors observed only slight qualitative and quantitative variations of the monoterpenoic and sesquiterpenoic compounds among 13 samples of the oil and gave only the mean results. They concluded that *P. sylvestris* trees of Estonia belong to a high car-3-ene chemotype.

Oil of *P. sylvestris* was produced from plant material collected from different locations in Lithuania with the yield of approximately 1%. More than 70 constituents were identified in the oil. α-Pinene (18.5-33.0%) and car-3-ene (9.1-24.6%) were dominating constituents with the only one exception when germacrene-4-ol content was 13.2%. The important bornyl acetate content varied from 0.5% to 3.0%. The main sesquiterpenes were: β-caryophyllene, germacrene D, bicyclogermacrene, γ- and δ-cadinene, garmacrene D-4-ol, cubenol (2.0-5.1%) and α-cadinol (1.9-7.7%) [19].

Essential oil from *P. sylvestris* current-year and one-year-old needles collected in Lithuania in the impact zone of a nitrogen fertilizer factory was isolated by hydrodistillation (2 hours). The yield varied (0.25-0.5%) in both current-year and one-year-old samples. The oil from different samples contained: 58.4-72.4% of monoterpene hydrocarbons (high car-3-ene chemotype), 3.2-5.9% of oxygenated monoterpenes, 14.5-25.7% of sesquiterpene hydrocarbons, 4.7-12.0% of oxygenated sesquiterpenes and 0.4-4.7% of diterpenoids [20].

The oil from twigs of 50-100-year-old trees of *P. sylvestris* from a natural stand growing in Greece was isolated by hydrodistillation (3 hours). Twenty one compounds were identified that accounted for 89% of the total oil composition, the main were β-phellandrene (29.1%), α- (19.4%) and β-pinene (17.3%); no car-3-ene was detected in this oil [21].

Kubeczka and Schultze [22] stated that *P. sylvestris* oil from Botanical Garden of the University of Würzburg belonged to high car-3-ene chemotype (20.6%). The other main volatiles were: α-pinene (42.1%), camphene (4.1%) adn myrcene (2.2%).

Both chemotypes of *P. sylvestris* trees were found in French Massif Central. Chalchat *et al.* examined the composition of essential oil produced from twigs and needles of *P. sylvestris* and identified 38 components. In high car-3-ene chemotype (43.4%), α-pinene was the second main component (22.2%). The main constituents in low car-3-ene chemotype were: α-pinene (41.1%) and β-pinene (18.4%) [23].

The composition of the needle oil obtained from three *P. sylvestris* trees in Finland showed that one tree belonged to a low car-3-ene and two other trees to a high car-3-ene chemotype (Table 2) [24].

Table 2

Constituents of *Pinus sylvestris* needle oil of three trees in Finland [24]

Compound	1	2	3
	%		
α-Pinene	**38.4-57.6**	**22.1-35.0**	**29.5-55.0**
Camphene	**3.7-6.8**	**2.9-4.6**	**2.5-3.9**
β-Pinene+Sabinene	2.5-3.8	1.7-2.4	1.5-2.6
Car-3-ene+Myrcene	**1.5-2.7**	**14.5-20.0**	**15.0-25.8**
α-Terpinene	0-0.2	0.1-0.5	0.2-0.4
Limonene	2.0-4.7	0.4-0.8	0.6-1.1
β-Phellandrene	0-0.4	0.5-0.7	0.5-1.5
1,8-Cineole	0.2-0.4	0.3-0.9	0-0.4
γ-Terpinene	0.3-0.5	0.1-0.5	1.1-1.8
Terpinolene	0.5-0.8	1.0-2.1	1.5-2.8
β-Caryophyllene	1.4-3.3	2.0-3.8	0.8-1.9
Bornyl acetate	1.4-4.2	2.5-4.9	3.1-7.3
Borneol	2.1-5.6	5.1-7.8	1.5-4.6
γ-Cadinene	0.7-1.8	2.3-3.4	0.8-2.0
δ-Cadinene	**5.3-14.9**	**6.7-13.5**	**4.0-11.1**

Thoss *et al.* [25] investigated intraspecific and phenological variability of monoterpenes of Scots pine seedlings (3- and 8-week-old, 1427 samples), saplings (3-12 year-old, 2 populations) and mature trees (one population, 574 trees). Authors stated that 18% of mature trees belonged to low car-3-ene chemotype (they named it "no-car-3-ene chemotype") and that diferences in oil composition depended on chemotype. Needles of the low car-3-ene chemotype had higher absolute concentration of α-pinene, β-pinene, camphene and total monoterpenes than of the high car-3-ene chemotype. Authors found correlation between tree age and concentration of different monoterpenes, especially car-3-ene. There was consistent trend of higher relative concentration of car-3-ene in growing needles for the high car-3-ene chemotype and higher total monoterpene concentration in the low car-3-ene chemotype for mature needles.

A very unusual composition of *P. sylvestris* essential oil was given for the sample from Royal Botanical Garden in Edinburg that main component was mannoyl oxide (30.2%); 19 sesquiterpenes were also found among which the major were: caryophyllene oxide (12.7%) and spathulenol (4.3%) [26].

Marculescu and Gleizres [27] characterized constituents in *P. sylvestris* needle oil from Romania and identified 10 monoterpene hydrocarbons, 4 oxygenated monoterpenes, 11 sesquieterpene hydrocarbons and 1 sesquiterpene alcohol.

The content of six main components of pine needle samples grown in five different areas of Belarus was analysed by ^{13}C- and ^{1}H-NMR. The samples were taken in natural pine forests from 20-40-year-old trees in autumn and winter (the period of maximum essential oil) and the volatile compounds were separated by hydrodistillation. The major components of the oil were: α-pinene, that content varied in a broad range (14-35%) and car-3-ene (8-13%). The content of the other compounds: camphene, β-pinene, myrcene, limonene, α-terpineol and bornyl acetate was significantly lower (1%-4%) [14].

Apart from essential oil obtained from needles and twigs of *P. sylvestris*, pines as well as other coniferous trees of Pinaceae family, are a source of huge amounts of oleoresin. By the distillation of oleoresin turpentine (also called spirit of turpentine, oil of turpentine) is obtained. Oil of turpentine can be also the by-product during the production of wood-based panels. This oil is rich in sesquiterpene fraction. According to Kula *et al.* [28] main constituents identified in the sesquiterpene fraction were: α-muurolene (22%), longifolene (17.5%), γ-muurolene (6%) and δ-cadinene (5%).

According to investigation of Dormont *et al.* [29], α-pinene was reported to be dominant component of volatiles emitted and collected using headspace from needles (45,7%) and cones (43,5%) of *P. sylvestris* from France. However, only traces of car-3-ene were detected.

There was identifed about 20 volatile compounds in the essential oil from Scots pine roots grown *in vitro*. Among the identified constituents, α-pinene (36%) and car-3-ene (36%) were dominant. Other constituents with relatively high levels (β-pinene, longifolene, sabinene, terpinolene, limonene, β-phellandrene) were amounting together to 20% [30;31].

As can be seen in Table 1., diversity in the composition of *P. sylvestris* essential oil from different areas of Europe was observed. High car-3-ene chemotype is more popular than low car-3-ene one. In different oil samples from 6 to 70 constituents were identified amounting to more than 100 altogether. The most common group of volatile compounds in Scots pine oil, with the one exception, are monoterpene hydrocarbons, the two main being: α-pinene (20-42%, 69% in one sample) and car-3-ene (0-43%). The content of other important monoterpenes varied greatly: β-pinene (0.2-18%), β-phellandrene (0-29%), camphene (0.1-10%), myrcene (0-14%), limonene (0-5%) and terpinolene (0-4%). Considerable amount of α-phellandrene (trace-31%) in pine oil in Slovakia seems to be questionable and may be misidentification. Only in Estonia and Greece small amounts of this compound were found (0.2% and 0.1%, respectively). Other monoterpene hydrocarbons occurred in lower concentration like: sabinene, myrcene, α- and γ- terpinene, tricyclene and p-cymene.

The second important and the most numerous group of volatile compounds in pine oil are sesquiterpene hydrocarbons. Among them the compounds with cadinane skeleton occurred the most frequently and in the highest amounts:

δ-cadinene (up to 12%), γ-cadinene (up to 9%), α-muurolene (up to 12%) and γ-muurolene (up to 7%). In pine oil samples in Estonia germacrene D (up to 7%) belonged to the main components. Common sesquiterpene hydrocarbons are β-caryophyllene and α-humulene. Other compounds from this group appeared rarely.

Most common compounds of the group of oxygenated monoterpenes were: bornyl acetate (0.5-9%), borneol (0.5-6%), α-terpineol (0.05-7%) and terpinen-4-ol (0.4-3%); and of oxygenated sesquiterpenes: α- and T-cadinol as well as α-and T-muurolol. Some components occurred sporadically in considerable content, e.g. nerolidol in Potugal (8%), spathulenol in Lithuania (0.5-13%).

5. Enantiomers of chiral monoterpene hydrocarbons

A prerequisite for studies of insect-conifer relationship is a knowledge of the contents and variations of attractants within and among the trees. Monoterpene hydrocarbons play an important role in the complex interactions between forest insects and their conifer hosts. From biosynthetic point of view, a few enantiomers of a chiral monoterpene must be considered as two separate constituents and they often exhibit differences in biological activity [32].

Sjödin *et al.* [16;32] investigated the composition of enantiomers of seven major monoterepene hydrocarbons in eight different tissues of four Scots pine trees. Material was extracted with hexane and analyzed by two-dimensional gas chromatography (2D-GC). Large differences in the relative amounts as well as in enantiomer ratios were found both within and between individuals. Variation of monoterpene enantiomers among tissues indicates the importance of a careful specification of the tissues when analyzing host-insect relations. The extremely large relative amounts of (+)-car-3-ene and (–)-limonene were found in the samples of one-year-old phloem and bark of branches and in the shoots of some of the trees and were not found in the xylem of trunk or root or in needles of the same tree. Only the (+)-enantiomer of car-3-ene was find. The (–)-enantiomers of β-pinene, sabinene and β-phellandrene dominated over corresponding (+)-enantiomers in all investigated samples [16]. Clear positive correlation was observed between (+)-α-pinene and (+)-camphene in four tissues. Good positive correlations were found between (–)-α-pinene and (–)-camphene in two types of xylem, beetwen (+)-α-pinene and (+)-β-pinene in resin, and between tricyclene and (–)-camphene in resins and needles [32]. This was in agreement with Hiltunen and Laasko [33] who found close linkages between (–)-α-pinene, tricyclene and (–)-camphene in (–)-series), and between (+)-α-pinene and (+)-β-pinene in the (+)-series. Groupings of the monoterpene enantiomers by multivariate analysis reflected well the known biogenetic linkages.

Wibe *et al.* [34] determined enantiomeric composition of seven monoterpene hydrocarbons in headspace volatiles of *P. sylvestris* seedlings. For six monoterpenes: α-pinene, camphene, β-pinene, sabine, limonene, and β-phellandrene, both enantiomers were present, whereas only (+) enantiomer of car-3-ene was found (Table 3).

Ochocka *et al.* [35] examined the concentration of four monoterpene hydrocarbon enantiomers found in *P. sylvestris* obtained from four different geographical regions. These results are interesting because they showed that the proportion of α-pinene enantiomers appears to be dependent on the origin of the oil (Table 3).

Table 3

Enantiomeric composition of monoterpene hydrocarbons in *Pinus sylvestris* from different regions

Compound	**Poland** [35]	**Austria** [35]	**Italy** [35]	**Korea** [35]	**Norway** [34]	**Portugal** [10]
	%					
(1R,5S)-(+)-α-pinene	**61.5**	**17.0**	**8.0**	**12.6**	**29.0**	**11.9**
(1S,5S)-(–)-α-pinene	**19.2**	**56.4**	**51.1**	**25.1**	**17.6**	**10.5**
(4R)-(+)-camphenene	0.5	1.3	0.9	0.1	0.5	
(4S)-(–)-camphenene	5.6	-	0.1	0.5	0.8	
(1R.5R)-(+)-β-pinene	0.1	0.4	1.1	0.4	0.4	0.3
(1S,5S)-(–)-β-pinene	**5.6**	**10.9**	**29.6**	**7.7**	2.2	0.2
(4R)-(+)-limonene	**5.1**	**2.8**	**1.2**	**20.4**	0.3	
(4S)-(–)-limonene	**0.1**	**8.0**	**2.9**	**10.2**	0.8	
(+)-car-3-ene					**45.8**	**11.4**
(–)-car-3-ene					0	
(+)-sabinene					<0.05	
(–)-sabinene					1.5	
(+)-β-phellandrene					<0.05	
(–)-β-phellandrene					0.8	
(+)-limonene						3.5
(–)-limonene						0.3

According to the presented results great intraspecific variation in composition of enantiomers of chiral monoterpene in *P. sylvestris* was observed with the one exception of car-3-ene that occurred only in (+)-form.

6. Variability of composition of *Pinus sylvestris* essential oil according to environmental condition

Several studies have been conducted to analyze if there were any difference in essential oil composition between pine needles grown in polluted and nonpolluted areas.

Shpak *et al.* [36] investigated the composition of essential oil from *P. sylvestris* needles that were exposed to pollution. Samples were taken from industrial zones, radioactively contaminated areas and from ecologically clean areas. As can be seen from Table 4, the composition of Scots pine oil changed by contamination. The total contribution of monoterpenoides decreased substantially as contamination by industrial and radioactive elements increases. The content of α-pinene, car-3-ene, camphene, myrcene, β-pinene, limonene and terpinolene dominated in the monoterpene fraction in all samples and underwent a complicated change depending on the contamination level of the area. As the contamination increased, the contents of α-pinene, camphene, and limonene increased whereas those of car-3-ene, β-pinene, and terpinolene decreased.

This is in some agreement with Berta *et al.* [18] who evaluated the effects of urban conditions on the composition of terpenes in needles of *P. sylvestris* in comparison with a relatively clean environment of the Arboretum Mlynany (AM). Content of terpenoids was higher from the relatively clean site (AM), however they do not specified whether this is the specific case for monoterpenes, which made the results from the two authors hard to compare. The accumulation of α-pinene, citral, myrcene and camphene decreased in the urban environment compared to the relative clean one. On the other hand, production of some other terpenes increased, and namely: β-pinene, p-cymene, α-bisabolol, eugenol, carvone and terpineol. Proportions of α- and β-pinene, citral, bornyl acetate, terpineol and camphene also changed.

Other results were obtained by Judzentiene *et al.* [20] who characterized the changes of secondary metabolites (content and chemical composition of needle essential oil) of young Scots pines growing along an ammonia gradient in the impact zone of emissions from the nitrogen fertilizers factory in Lithuania. Under the effect of industrial pollution higher amounts of shorter chain terpenes and lower amounts of longer chain terpenes were produced. This dependence was more strongly expressed in the oils of the current-year than one-year old needles. Changes in oil yield were not significant in relation to distance from the factory.

Lamotkin *et al.* [37] showed that it is very valid to observe changes in composition in pine needle oil from pine needles because the results can be used as an indicator of ecological situation in consider area. The composition of essential oil and the contents of toxic elements in pine needles mostly depends on degree of needle pollution.

Waliszewska *et al.* [38] showed the composition of terpenes in *P. sylvestris* oil from 5 areas with different degrees of air pollution in Poland. The contents of volatile compounds in pine needles ranged from 0.29 to 1.08%. GC analysis revealed the presence of α-pinene, camphene, limonene, borneol, car-3-ene, cedrene and other sesquiterpenes; location differences in their levels are discussed. The needle contents of Cu, Zn, Cd, and Pb were also detected.

Table 4

Variability of composition of *Pinus sylvestris* essential oil according to environmental condition

Compound	**Belarus** [37]			**Slovakia** [18]		**Lithuania** [21]	
	Rad. [1]	**Ind.** [2]	**Clean** [3]	**Clean** [4]	**City** [5]	**Current year**	**One-year old**
Tricyclene	2.2	1.3	1.0			0.3-1.4[6]	tr-0.8[6]
α-Pinene	**61.6**	**65.1**	**28.8**	**23.0**	**17.7**	**19.8-35.0**	**18.0-28.0**
Camphene	**7.1**	**4.6**	**3.4**	1.1	0.2	**0.8-2.2**	**1.5-4.7**
Fenchene	0.1	0.1	0.1				
Sabinene	0.5	0.2	1.3			0.2-1.4	1.3-2.7
β-Pinene	4.1	4.1	8.1	0.2	9.1		
Myrcene	2.5	5.6	2.7	0.7	0.2	0.8-1.1	0.9-3.3
Car-3-ene	**16.6**	**6.4**	**45.0**	**-**	**-**	**22.7-33.7**	**19.9-25.9**
β-Phellandrene	0.1	0.2	0.1	**20.7**	**7.6**	**0.7-1.4**	**0.9-2.7**
Limonene	**2.7**	**5.6**	**3.0**				
α-Terpinene	0.1	0.1	0.2				
γ-Terpinene	0.2	4.3	1.2			0.3-0.9	0.5-1.3
p-Cymene	0.2	0.1	0.1	0.25	-	0.2-0.5	tr-0.3
Terpinolene	1.6	1.0	4.2			0.6-2.9	0.5-2.7
β-Caryophyllene						**2.6-7.0**	**2.7-6.5**
Bornyl acetate				**5.6**	**6.7**	**1.0-3.4**	**0.5-2.4**
Borneol						0.4-1.1	0.3-1.2
γ-Cadinene						**1.2-9.3**	**1.7-11.1**
δ-Cadinene						**2.9-9.0**	**1.3-10.6**
Monoterpenes	**45.6**	**44.8**	**59.9**			**58.4-72.4**	**45.0-60.8**
Sesquiterpenes	**48.3**	**52.6**	**38.0**			**14.5-25.7**	**18.5-33.1**
Total O-containing compounds	2.5	2.6	2.0			15.2-20.1	10.8-24.8

[1] radioactively contaminated woods
[2] industrial zone
[3] ecologically clean area
[4] arboretum
[5] town of Nitra
[6] +α-Thujene

Manninen *et al.* [39] investigated the composition of terpenoids in the stemwood of pine seedlings exposed to ozone at different nitrogen availability. They concluded that neither elevated level of ozone nor nitrogen availability had the effect on the concentration of carbon-based secondary compounds, e.g. terpenes and resin acids (Table 5).

According to Werner *et al.* [31] there is correlation between environmental conditions and terpenoid level and composition of *P. sylvestris* seedling roots cultivated on two substrates: polluted and unpolluted. Pine seedlings grown on both substrates accumulated essentially the same major volatiles but some quantitative differences were observed. Among identified compounds, α-pinene and car-3-ene were dominant. Their amounts in pine root SFE extract from unpolluted substrate were 48% and 36%, whereas from polluted substrate 34% and 29%, respectively.

According to investigations of Fuksman [40] reaction of *P. sylvestris* to different stress factor (low temperatures, man-caused pollution, effect of fungi) showed changes of content and composition of secondary metabolites (phenols, resins, essential oils) in wood tissue. Components of needle essential oil reacted to stress the most quickly – their synthesis removed to formation of volatile substances, especially α-pinene. It is an optimal indicator of early diagnostics of pine stand state. Changes which appeared in secondary metabolite in *P. sylvestris* needles under an influence of studied stress factors, may be considered as non-specific reaction to stress.

Table 5

Composition of terpenes in *Pinus sylvestris* wood in different nitrogen and ozone availability [39]

Compound	**Ambient ozone**			**Elevated ozone**		
	LN	**control**	**HN**	**LN**	**control**	**HN**
α-Pinene	**37.1**	**40.7**	**31.3**	**33.7**	**40.7**	**39.7**
Camphene	0.5	0.5	0.4	0.4	0.5	0.5
Sabinene	1.6	1.5	2.0	2.0	1.5	1.5
β-Pinene	**4.5**	**3.7**	**3.3**	**2.9**	**4.0**	**3.0**
Myrcene	**3.4**	**3.9**	**3.2**	**3.0**	**3.5**	**3.2**
Car-3-ene	**34.8**	**29.7**	**41.0**	**44.0**	**30.3**	**29.6**
Limonene + β-Phellandrene	**13.2**	**15.4**	**13.0**	**7.8**	**14.6**	**17.8**
Terpinolene	**4.1**	**3.8**	**5.2**	**5.3**	**3.8**	**3.7**
Bornyl acetate	0.1	0.2	0.1	0.2	0.2	0.3
α-Copaene	0.1	0.1	0.1	0.0	0.0	0.0
Longifolene	0.4	0.4	0.2	0.4	0.6	0.4
β-Caryophyllene	0.1	0.0	0.1	0.1	0.1	0.1
α-Humulene	trace	trace	trace	trace	trace	trace
Total terpenes (mg/g)	1.29	1.34	1.06	1.24	1.02	1.19

LN – low nitrogen availability
HN –high nitrogen availability
Control –optimum nitrogen availability

7. Antifungal and antibacterial activity of pine volatiles

In conifers, biosynthesis and infiltration of tissues with resins are involved in the defence system in response to wounding and fungal infections. In reaction to injury pines accumulate 40% more oleoresin that contains resin acids (60-70%) as well as volatile and non-volatile terpenoids. Monoterpenes are toxic to wood-inhabiting and wood-decomposing fungi whereas the resin acids display low toxicity and function mainly as mechanical barriers [30;31]. Mycorrhizal fungi play important role in protecting plants against root pathogens. Stimulation of the host root to syntheses of volatile antimicrobial substances is one of the suggested mechanism of protection. In their research, Napierała-Filipiak *et al.* [30] and Werner *et al.* [31] evaluated the qualitative and quantitative changes in content and composition of terpenes in roots of *P. sylvestris* seedlings after inoculation of mycorrhizal fungi. They confirmed that inoculation of pine seedlings with six strains of fungi resulted in higher biosynthesis of volatiles, and mainly of α-pinene and car-3-ene [30]. They found also that the effect depended on the potting substrate. On the unpolluted substrate, inoculation of plants with the fungi resulted in a similar amount of volatiles, while on the polluted substrate the mycorrhizal roots showed significantly lower content of terpenoids (32-33%) than nonmycorrhizal roots (56%). The mycorrhizal fungi showed different effects on the concentrations of several terpenoids on both substrates. Of the minor constituents, the amounts of the β-pinene, myrcene, terpinolene and γ-muurolene were drastically reduced on polluted soils. On the contrary, contents of other compounds, especially sesquiterpenes increased [31].

Motiejūnaitė and Pečiulytė [41] investigated biological activity of *P. sylvestris* needle oil toward microorganisms which possess allergenic and toxic properties and are known risk factors for occupational respiratory diseases. The MIC (minimum inhibitory concentration) values were as follows: 13 strains of fungi (e.g. *Aspergilus spp*., *Chaetomium spp*., *Penicillium spp*., *Rhizopus stolonifer*) 1.0-2.5%, 2 yeast-like fungi 1.0-1.2%, yeast 0,5-0.75% and 2 bacteria 0.75-1.2%. Among 52 essential oils investigated for their antibacterial (9 strains) and anticandidal activity, *P. sylvestris* oil belonged to the group of moderately active with MIC of 2% or >2% [42]. On he contrary, antifungal activity of pine oil against 8 strains was very poor (MIC > 5000 μg/mL) [43].

8. Herbivorous insects: the cause of major defoliation in pine

Conifer forests can suffer extensive defoliation after attacks from herbivorous insects. Therefore many investigations regarding the interaction between the insects and conifers have been performed. It has been determined that monoterpenes have an important role in the interaction process. In conifers the monoterpenes acts as toxins to fungal pathogens and as feeding and oviposition deterrents to a variety of herbivores [44].

Some of the most important insect herbivores, with regards to defoliation of pine trees, are *Lymantria monacha* (nun moth), *Lymantria dispar* (gypsy moth) and *Diprion pini* (saw fly). As mentioned in the introduction, *P. sylvestris* is common in many parts of Europe, ranging from Great Britain all the way to eastern Siberia. Especially in Poland *P. sylvestris* is widespread and the damage caused by these insect herbivores can have extensive environmental as well as economic consequences. The *L. monacha* is the worst defoliating insect pest of *P. sylvestris*, one caterpillar can damage about 300 pine needles during its development. A spruce tree normally does not survive if more then 50% of its needles defoliate, however *P. sylvestris* is more resistant [45].

To investigate the potential risk of *L. monacha* spreading, Keena and Withers [46] compared the survival and development of *L. monacha* larvae during their first 14 days on 26 north American and 8 introduced Eurasians host plants. Establishment of *L. monacha* in North America would be catastrophic because of the large number of economically important tree species on which it can survive and develop, and the ability of the mated females to fly and colonize new areas. Based on host suitability ratings seven conifer species, here amongst *P. sylvestris*, and six broadleaf species were tested suitable for *L. monacha* survival and development.

According to Wibe *et al.* [34], the monterpene configuration were of importance for the attraction of different insects. The pine weevil, *Hylobius abietis*, is highly attracted to volatiles produced by seedling of *P. sylvestris*. The authors suggest that the enantiomers may be used by *H. abietis* to detect host and nonhost plant species. In spite of individual variations, each plant species contained consistently more of one enantiomer than of the other, e.g. *P. sylvestris* contained more (–) than (+)-α-pinene. The different enantiomers either stimulated or inhibited neurons, thereby making the insect able to recognize different plants, and in this way choose a suitable hostplant [34].

In another investigation Wibe *et al.* [47] investigated plant volatiles activating single receptor neurons in the pine weevil (*Hylobius abietis*). Naturally produced plant volatiles, eliciting responses of single olfactory receptor neurons in the pine weevil, were identified. The receptor neurons were classified in 30 types, according to the compound which elicited the strongest response in each neuron, 20 of which compounds were identified. Most potent for 14 types of neurons were monoterpenes, including bicyclic (e.g. α-pinene, camphor and myrtenal) for 8 types, monocyclic (limonene, carvone, α-terpinene) for 3 types and acyclic (e.g. myrcene and linalool) for 3 types. Other compounds eliciting strong response of a neuron were five sesquiterpenes, including α-copaene and a farnesene-isomer, and an anethole type which has no biosynthetic relationship with terpenes. The results suggested that this structure-activity relationship was significant for encoding plant odour information in the pine weevil.

To investigate why herbivores are attracted trough pines Mumm *et al.* [48] investigated the headspace volatiles of *P. sylvestris* induced by egg deposition of the saw fly (*D. pini*). To detect the volatiles that attract the egg parasitoid, the attractive odor blend of systemically oviposition-induced pine was compared to the non attractive odor released by artificially damaged pine twigs mimicking the slitting conducted by a *D. pini* female prior to oviposition. The analysis revealed that only the amounts of (E)-β-farnesene were significantly higher in the volatile blend of the oviposition induced twigs. Volatiles from pine twigs treated with jasmonic acid also attract the egg parasitoid. Further investigations would provide a better understanding of the attraction, and thereby possibly give means to protection of trees in forestry [48].

Litvak and Monson [44] investigated whether the monoterpene synthesis was induced by herbivore attack in four different conifer species and also investigated the spatial pattern of constitutive monoterpene production within ponderosa pine needles. The results indicated that the tiger moth larvae, the herbivore used in this study, consistently consumed only half or two thirds of a pine needle before switching to an undamaged needle. These results were believed to be caused by the higher concentration and diversity of monoterpenes found in the bottom part of the needles. The findings are supported by previous studies. The authors, however, did not exclude other explanations to this observation such as distribution of water or nitrogen availability. They also concluded that tissue damage actively triggered monoterpene cycles synthesis in all species except Engelmann spruce [48].

Mumm and Hilker [49] described the chemical defense mechanism of conifers against different defoliating insects, with particular focus on pines. They concluded that the most important defense mechanism is the production of phenolic compounds and oleoresin.

Wanner *et al.* [50] investigated the possible side effects of two insecticides on non-target soil arthropods which play an important role in food and energy turnover of forest eco-systems. The study mainly focused on ground beetles because they are sensitive bioindicators. The results showed that both insecticides tested effectively suppressed an increase of the nun moth and that epigamic non-target macroarthopod communities did not suffer any severe short term damage.

Tomicus piniperada is endemic species able of colonizing weakened, stressed or recently killed trees. The larvae excavated galleries in the phloem of trunks and freshly cut logs, while adults must feed on shoots to complete sexual maturation. Host selection was achieved by detection of the monoterpenes (released by the trees), which act like kairomones [10].

According to Santos *et al.* [10], variations in the relative compounds of the bouquet of essential oil are responsible for the outcome of different biological processes, such as mate finding, egg-laying site recognition and host selection. The volatiles present in phloem samples of four pine species, *P. halepensis, P. sylvestris, P. pinaster* and *P. pinea*, were identified and characterized with the aim of finding possible host-plant attractants for native pests, such as the bark beetle *T. piniperda*. They found 10 monoterpenes in *P. sylvestris* (α-pinene, camphene, sabinene, β-pinene, myrcene, car-3-ene, α-terpinene, p-cymene and limonene) that were reported to play a role in the process of the host tree selection by conifers phytophagous insects. It can be concluded that it is possible to discriminate pine species based on the monoterpenes emissions of phloem samples.

Almquist *et al.* [51] carried out studies which aim was to investigate the host selection capacity of the pine shoot beetle, *Tomicus piniperda*, in the shoot-feeding phase and analyzed the chiral host volatiles in five *Pinus* species originating from France (*P. sylvestris, P. halepensis, P. nigra laricio, P. pinaster maritime, P. pinaster mesogeensis*). Dominating monoterpenes were (–)-α-pinene, (+)-α-pinene, (–)-β-pinene and (+)-3-carene. The amounts of the enantiomers varied considerably within and among the species. On the basis of the composition of essential oil pine species were divided into two groups. *P. halepensis* and *P. sylvestris* were grouped according to the amounts of (+)-α-pinene and (–)-β-pinene. *P. nigra laricio* was the species most attacked and *P. halepensis* the one least attacked by *T. piniperda*.

Sjödin (1996) *et al.* [32] reported that the attraction of *Tomicus piniperada* to α-pinene and reduction of the attraction of *Hylobius abietis* to limonene is independent on enantiomeric composition of these monoterpenes. And here it can be found an agreement with Almquist [51].

Poland *et al.* [52] evaluated blends of semiochemical disruptants, which included nonhost volatiles and verbenone, for their ability to disrupt attraction of *T. piniperada*, shoot beetle to traps containing attractant α-pinene. A single blend of nonhost volatile blend of nonhost volatiles alone (comprised of hexan-1-ol, (Z)-hex-3-en-1-ol, (E)-hex-2-en-1-ol, octan-3-ol, and oct-1-en-3-ol) or nonhost volatile blend combined with verbenone, significantly reduced attraction of *T. piniperada* to attractant-baited traps by 68-77%.

*Dioryctria zimmermani (*Zimmerman pine moth) is a pest of Scots pine that resistance varies widely among European geographic varieties. Sadof and Grant [53] evaluated monoterpene composition of *P. sylvestris* varieties resistant and susceptible to this pest. They stated that the susceptibility of trees to *D. zimmermani* wounds was not correlated with monoterpene proportion and enantiomer ratio. Two resistant varieties emitted relatively high levels of the limonene.

Byers *et al.* [54] carried out investigations on repellent effect to bark beetle (*Pityogenes bidentatus*) by nonhost plants like moutain ash, oak, alder buckthorn, blueberry, raspberry and grass. *P. bidentatus* searches in mixed conifer and deciduous forests of nothern Europe for suitable branches of its host, *P. sylvestris*. Volatiles from leaves or bark of each of these investigated plants significantly reduced the attraction of the beetles to their pheromone. Odors collected from these nonhosts contained monoterpenes (α- and β-pinene, camphene, car-3-ene, β-ocimene), sesquiterpenes ((–)-trans-β-caryophellene and β-cubebene) and “green-leaf” alcohols (hexanol isomers, e.g. (Z)-hex-3-en-1-ol, (E)- hex-2-en-1-ol, hexan-1-ol), several of which reduced the attraction to pheromone in the field and elicited electroantennographic responses.

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SKŁAD OLEJKU ETERYCZNEGO SOSNY POSPOLITEJ (*PINUS SYLVESTRIS* L.) ORAZ RELACJE ROŚLINA-OWAD

Streszczenie

Przedstawiono przegląd literatury dotyczącej metod izolowania, składu chemicznego oraz właściwości biologicznych olejku eterycznego z różnych organów sosny pospolitej (*Pinus sylvestris*). Omówiono interakcje między rośliną a jej szkodnikami – roślinożernymi owadami.

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