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Organic geochemistry of fossil resins from the Czech Republic

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Abstract

Five fossil resins from various localities in the Czech Republic were investigated. To arrive at more detailed description of the resins, pyrolysis-gas chromatography/mass spectrometry with derivatisation using tetramethylammonium hydroxide, gas chromatography-mass spectrometry, and micropetrography were applied. The content of organic macerals, composition of biomarkers in the solvent extracts and in the pyrolysates have been determined and compared to amber samples. The analyses clearly indicate that all resins belong to the Class Ib type derived from regular labdane structures that lacked succinic acid. The presence of labdane type diterpenoids and the absence of plant triterpenoids in the resin point to a conifer (gymnosperm) source which contrasts with the angiosperm source of Sarawak amber from Malaysia. According to their chemical composition, all Czech resins can be assigned to the Cupressaceae family. There was an obvious difference between a Duxite sample (Miocene) and other resins that could be attributed to deposition inside wood, which did not allow degradation of the resin.

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Keywords: Fossil resin; amber; resinite; TMAH-Py-GC/MS

1. Introduction

The fossil resin is a term that refers to materials derived from a biological matter and incorporated into sediments. The ability of some resins to fossilize and to be preserved in the geological record is a fascinating aspect. High pressure, heat, bacterial processes, and strength of mineral crystallization caused oxygen deprivation and displacement of resinous substances into cracks in the fossilized wood matter and beyond it. Real fossilisation is actually polymerisation of terpenoid compounds that form the general polymeric structure. Because resin is a mixture of compounds, fossil resins are not completely consistent polymers. Moreover, some amount of terpenoids is nonpolymerisable, and they stay protected in fossilized polymer structure.

For this contribution, five fossil resin samples of Creataceous to Neogene age collected in the area of Czech Republic were chosen to observe differences among them. The purpose of this paper is to study chemical and maceral composition of the samples to correlate the resins from different geological locations by elemental and petrographic analysis, pyrolysis–gas chromatography/mass spectrometry using in situ sample derivatisation with

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tetramethylammonium hydroxide (TMAH-Py–GC/MS), and gas chromatography/mass spectrometry (GC/MS) of resins extracts. For comparison, two ambers were also analysed.

2. Experimental

2.1. Samples

Five samples of fossil resin from five localities in the Czech Republic were studied (Fig. 1). For comparison, two fossil resins of the consistent age, Baltic amber and Sarawak amber, were also analysed (Table 1).

Table 1. Overview of samples of fossil resins investigated.

Designation	*Locality*	*Lithology*	*Age*
Krizany	Křižany	uranium mine, sands	Cretaceous/Cenomanian
Straseci	Nové Strašecí	black clays	Cretaceous/Cenomanian
Valchovite	Valchov	coal clays	Cretaceous/Cenomanian
Studlov	Študlov	coal slate	Paleogene/Eocene
Duxite	Bílina	fossil wood in green clays	Neogene/Miocene
Baltic amber	Burg on Fehmarn (Denmark)	sands	Paleogene/Eocene
Sarawak amber	Merit Pila (Malaysia)	coal seam	Neogene/Miocene

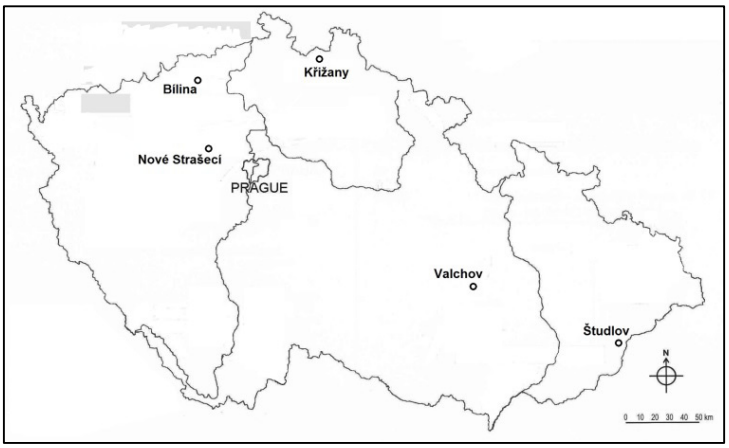


Fig. 1. Map of the Czech Republic with sampling locations of fossil resins.

2.2. Instrumentation

Micropetrography of fossil resins was studied on particulate polished sections using an Olympus BX51 microscope for reflected light according to [1-3]. The composition of liptinite macerals was checked in fluorescence mode according to [3] and [1].

The elemental organic composition was determined using a CHNS/O micro-analyzer. The samples were sonicated with dichloromethane and the extracts were analysed without derivatisation by GC/MS using a Trace Ultra - DSQ II instrument equipped with a capillary column with a fixed stationary phase TR-5MS. The GC oven was heated from 37 °C (3 min) to 100°C at a rate of 10°C/min and then to 300 °C (8 min) at a rate of 10 °C/min. 5-α(H)-androstane in isooctane was used as an internal calibration standard. The compounds were quantified using total ion chromatograms against peak area response of the androstane standard, and normalized to the weight of dry sample. Three replicate analyses were performed. The relative standard deviation for peak areas was between 2-7 %.

TMAH-Py-GC/MS analyses were performed using a CDS Pyroprobe 5150 pyrolysis unit connected to the GC/MS instrument described above. Samples of powdered resins together with 10 μL of 25% aqueous solution of TMAH for methylation trials were heated at 610 °C for 30 s. The Py-GC interface was kept at the maximum allowed temperature of 300 °C. The TR-5MS column was used and the temperature program of the columns was set from 35 to 300 °C at a rate of 5 °C/min. Identification of compounds was based on comparison of spectra with the National Institute of Standards and Technology mass spectral library or on data from literature [4].

3. Results

3.1. Micropetrographic analysis

The studied samples represent fossil resins of different age, shape, colour and micropetrographic characteristics (Table 2, Fig. 2). Clean fossil resins designated as Valchovite, Studlov, Duxite and Baltic amber are composed of resinite. Resinite prevails also in next three samples that include admixture of plant tissue remnants of the cellulose-lignin base. Fragments of lignite macerals were found in Sarawak amber (Fig. 3).

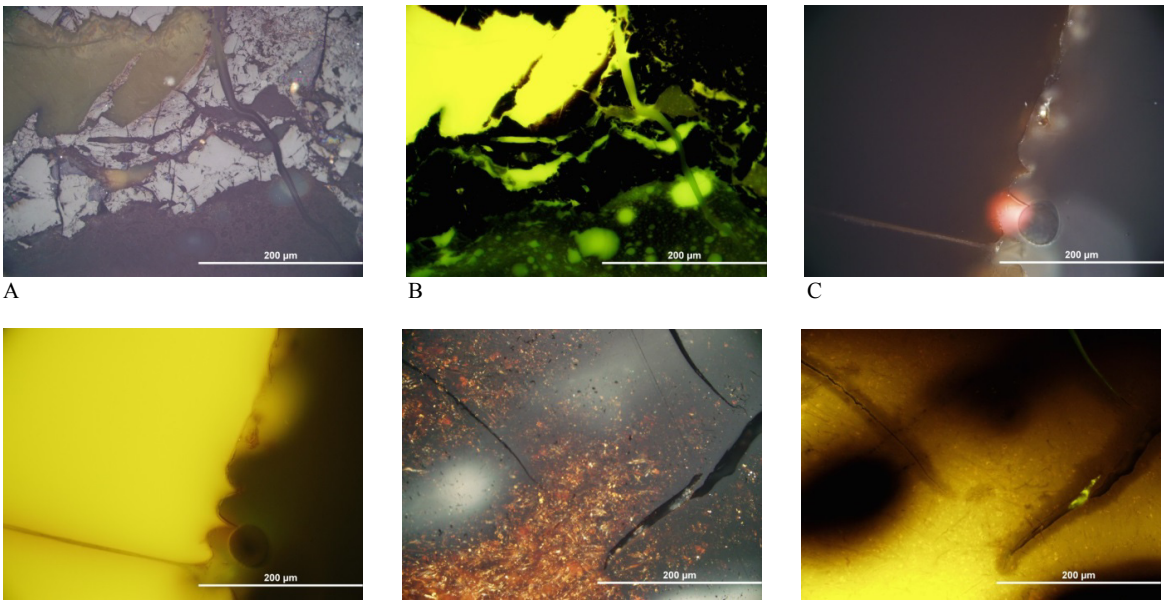
The carbon content ranged from 69.66 to 85.54 wt%. These high contents correspond with high solubility of the samples allowing their almost complete dissolution. The sample of Sarawak amber was also completely dissolved but the resulting extract was opalescent.

Table 2. Maceral composition and micropetrographic description of samples

Sample	*Colour*	*Maceral composition (vol. %)*	*Micropetrographic description*
Krizany	Opaque, dark brown	**Liptinite:** 96.5 % (82.7 % resinite-liptodetrinite-bituminite + 13.8 % altered liptinite) **Huminite:** 3.5 % (0.5 % textinite + 1.5 % ulminite + 1.5 % altered ulminite)	Liptinite of bright yellow fluorescence colour with a porous to fine-grainy structure. Occasional transitions from dark to lighter bands of degraded materials caused probably by thermal, or possibly also radiation alteration. The alteration can be seen in gellifed tissues - ulminite (R_r = 0.33%). Dispersed inorganic material cannot be excluded.
Straseci	Brown, partly transparent	**Liptinite:** 98.2 % (92.0 % resinite + 6.2 % altered resinite) **Huminite:** 1.8 % corpohuminite	Resinite of bright yellow fluorescence colour with numerous cracks and darker grooves at the grain edges probably caused by weathering. Formation of corpohuminite (R_r = 0.25%) rarely identified. Dispersed inorganic material cannot be excluded.
Valchovite	Butterscotch, opaque	**Liptinite:** 100 % resinite	Resinite of yellow to orange fluorescence colour with numerous bubbles and cracks of varying size. Grain edges weathered with brown to orange fluorescence rims. Easily melting material.
Studlov	Brown, partly transparent	**Liptinite:** 100 % resinite	Resinite with distinctive yellow fluorescence colour, sporadic cracks and particles at the grain boundaries. Easily melting material.
Duxite	Brown, partly transparent, resinous gloss	**Liptinite:** 100% resinite	Resinite with bright yellow fluorescence colour and occasional cracks. Dark gray colour in normal light, R_r<0.10%.
Baltic amber	Brown, partly transparent	**Liptinite:** 100% resinite	Optical properties similar to epoxy resin. Gray colour in normal light, Rr<0.10%. Green-yellow fluorescence colour in blue light.
Sarawak amber	Brown, partly transparent	**Liptinite:** 88.8.% (83.2% resinite +1.3% sporinite + 1.8 % suberinite, 0.3 % cutinite, 0.9 % exsudatinite + 1.3 % liptodetrinite) **Huminite:** 10.2 % (6.2 % ulminite + 3.1% densinite + 0.9 % corpohuminite) **Inertinite:** 1.0 % (0.4 % funginite + 0.3 %	Resinite with coal matter, with high content of solid bodies of resinite, distinctive bright yellow to green fluorescence colour. Various size of resinite bodies, the smallest in the form of dispersed droplets < 10 μm. The coal formed by ulminite (R_r = 0.43%) and densinite with other liptinite macerals, and rare funginite and makrinite.

A B C

Fig. 2. Photomicrographs of resinite occurrences: brown and partly transparent resin - Sarawak amber (A); brown opaque resin - Krizany (B); brown, partly transparent, resinous gloss - Duxite (C).



A B C

D E F

Fig. 3. Compact form of resinite (R_r = 0.17%) - Sarawak amber (A); yellow fluorescence colour and droplet resinite (R_r = 0.10%); yellow-green colour of fluorescence in mylonitized ulminite (R_r = 0.43%) with fissures filled by exsudatinite - Sarawak amber (B); resinite (R_r = 0.09%) - Studlov (C); yellow fluorescence colour - Studlov (D); fissures in unevenly altered resinite with R_r increased from 0.12% to 0.33% - Krizany (E); yellow fluorescence colour of unaltered resinite and brown to dark fluorescence colour of altered resinite – Krizany (F).

3.2. Gas chromatographic analysis

Py–GC/MS is the most useful technique for detail analyses of fossil resin. Using TMAH upon heating, polar acids are converted to less polar methyl esters that are easily separated by GC. Classification of fossil resins has been based on their analysis using this method [5 and references therein].

The total ion pyrograms from the TMAH-Py–GC/MS analysis of the studied samples are shown in Fig. 3a). The identified peaks are listed in Table 3. Baltic amber and Sarawak amber, two fossil resins of consistent age, are included and their total ion pyrograms are in Fig. 3b). The pyrolysate contains mainly cycloalkanes, terpenoids, and alkyl benzenes. Series of unknown compounds interpreted as either sesqui- or diterpenoids based on their

fragmentation patterns and molecular weights were detected.

GC/MS analysis is another method used in characterisation of fossil resins. In the analysis of the total extracts of the studied fossil resins, mainly terpenes were identified (Fig. 4a). They are diagenetic products (biomarkers) of terpenoids which are common constituents of resins of higher plants. The amounts of the identified compounds are given in Table 4. Chromatograms of Baltic amber and Sarawak amber have also been included (Fig. 4b, Table 4).

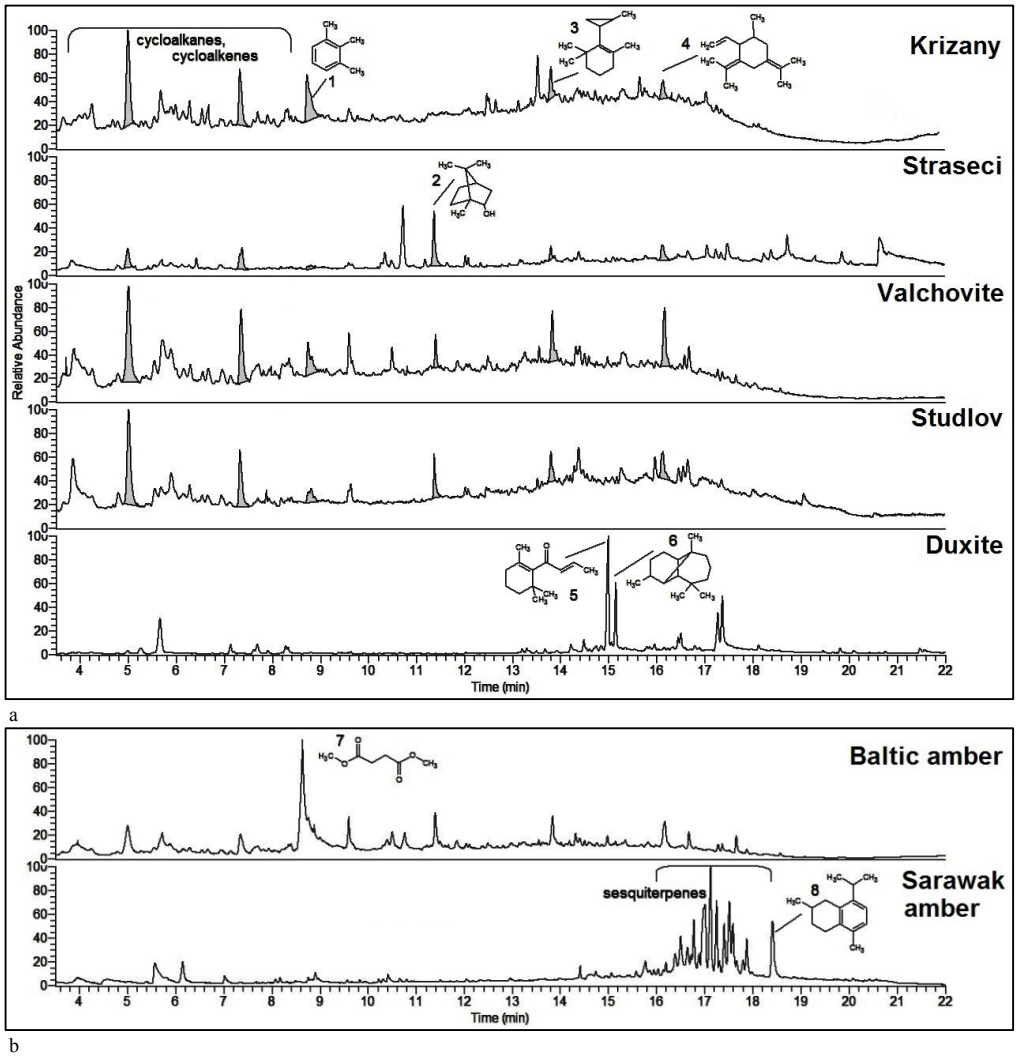
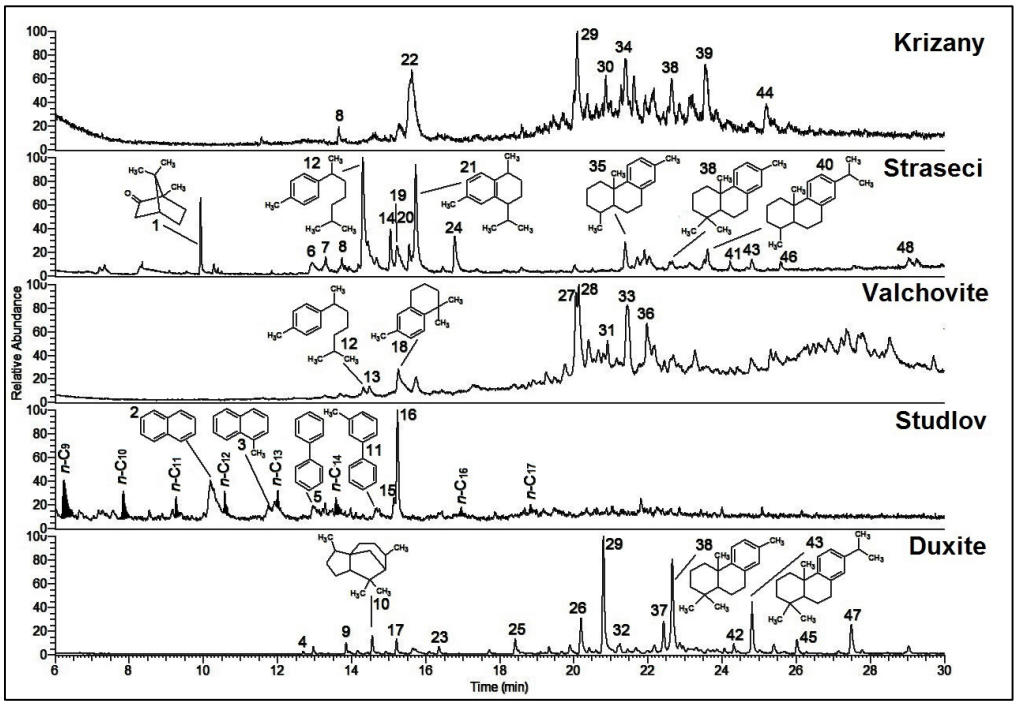


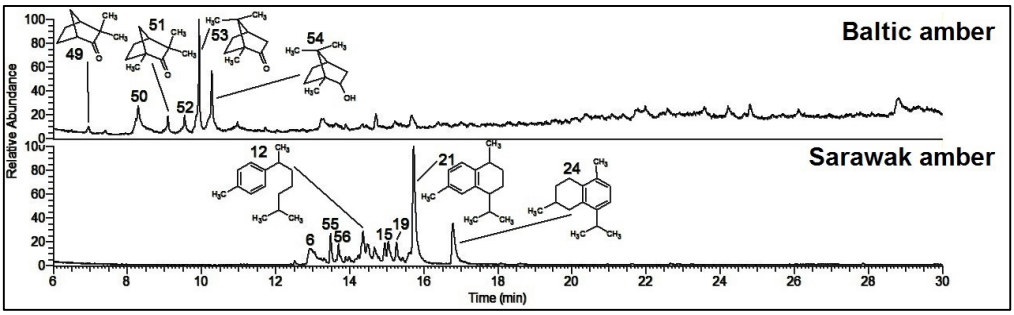
Fig. 4. Total ion pyrograms of (a) fossil resins collected in the Czech Republic; (b) ambers. Peaks of the compounds common for Krizany, Straseci, Valchovite, and Studlov samples are shown in gray: dimethylcyclohexene, tetramethylcyclopentene, trimethylbenzene (1), borneol (2), 1,3,3-trimethyl-2-(2-methylcyclopropyl)-1-cyclohexene (3), elemenene (4). The most intense compounds are drawn: β-damascone (5) and longipinane (6) in Duxite, succinic acid and methylester (7) in Baltic amber, cadinatriene (8) in Sarawak amber.

Table 3. Compounds identified in pyrograms of fossil resins and ambers.

	Krizany	Straseci	Valchovite	Studlov	Duxite	Baltic amber	Sarawak amber
dimethylcyclopentene		x		x			
dimethylcyclohexenes	x	x	x	x		x	
dimethylcyclohexadiene			x	x		x	x
tetramethylcyclopentene	x	x	x	x		x	x
1-isopropenyl-2,3-dimethylcyclopentane					x		x
1-methyl-3-(2-methyl-1-propenyl)cyclopentane					x		
1-acetyl-2-methyl-1-cyclopentene							x
dimethylbenzene			x				
succinic acid, dimethyl ester						x	
tetramethylcyclohexane					x		
trimethylbenzene	x	x	x	x			
trimethylheptatriene				x	x		
2-isopropyl-1,3-dimethyl-1-cyclopentene					x		
isobornyl methyl ether			x			x	
cadinane isomer	x		x	x			
fenchol		x				x	
2,4-dimethyl-3-methylenecyclopentanecarboxylic acid methyl ester						x	
camphor		x				x	
borneol		x	x	x			
cyclocitral			x			x	
1,3,3-trimethyl-2-(2-methylcyclopropyl)-1-cyclohexene	x	x	x	x		x	
sesquiterpene (204)							x
sesquiterpene (206)							x
sesquiterpene (206)							x
sesquiterpene (206)							x
sesquiterpene (206)							x
cadinatriene		x					
eudesmadiene		x					x
sesquiterpene (206)							x
sesquiterpene (206)							x
cadinatriene(202)							x
eudesmadiene		x					x
sesquiterpene (204)							x
calacorene = 3,4-dihydrocadalene (200)							x
cadinatriene							x
cadinatriene (202)							x
elemenene	x	x	x	x			
diisopropylmethylbenzene				x	x		
tetramethyloctahydro-1-naphtenylacetate					x		
pentamethylcyclohexanpropanol					x		
trimethyltetralin = ionene					x		
β-damascone					x		
longipinane					x		
α-cedrane					x		
aromadendrene					x		
sesquiterpene (206)					x		
sesquiterpene (204)					x		
sesquiterpene (218)					x		
methyl-β-ionone					x		
C18 diterpene (248)					x		



a



b

Fig. 5. Total ion chromatograms of (a) fossil resins collected in the Czech Republic; (b) ambers. The filled peaks are n-alkanes. The numbers refer to Table 3.

Table 4. Concentration of biomarkers identified in the resins. The numbers in brackets are molecular weights of the compounds.

No.	Name	Concentration (mg/g)						
		Krizany	Straseci	Valchovite	Studlov	Duxite	Baltic amber	Sarawak amber
1	camphor		0.25					
2	naphthalene				0.12			
3	methylnaphthalene				0.04			
4	nordrimane					0.45		
5	biphenyl				0.03			
6	dimethyltetraline		0.27					4.53

7	sesquiterpene (204)		0.13					
8	sesquiterpene (204)	0.14	0.11					
9	sesquiterpene (206)					1.02		
10	α-cedrane					1.64		
11	methylbiphenyl				0.02			
12	dihydro-ar-curcumene		1.36	1.07				3.50
13	4-butyl-indan-1-ol			1.15				
14	sesquiterpene (202)		0.30					
15	sesquiterpene (206)				0.01			2.05
16	sesquiterpene (204)				0.10			
17	sesquiterpene (220)					1.66		
18	trimethyltetralin			2.03				
19	eudesmadiene		0.35					1.22
20	cuparene		0.16					
21	calamenene		1.37					21.54
22	sesquiterpene (204)	0.08						
23	C16 bicyclic sesquiterpene (222)					1.83		
24	5,6,7,8-tetrahydrocadalene		0.51					1.62
25	C18 diterpene (246)					4.99		
26	C20 tricyclic terpane (276)					14.63		
27	tetramethyltetralin			1.68				
28	C18-bicyclic diterpane			9.68				
29	C18 diterpene (248)	0.75				16.21		
30	C18 diterpene (248)	0.29						
31	C18-bicyclic diterpane							
32	C20 diterpane (276)					3.03		
33	C19-tricyclic terpane			6.26				
34	C19 triterpene	0.24						
35	15,16,17-trisnorabieta-8,11,13-triene		0.38					
36	C18-bicyclic diterpane			4.23				
37	8b(H)-labdane					14.80		
38	16,17-bisnordehydroabietane	0.23	0.14			24.50		
39	diterpene (224)	0.59						
40	18-norabieta-8,11,13-triene		0.24					
41	19-norabieta-8,11,13-triene		0.10					
42	abietane					1.08		
43	dehydroabietane		0.10			1.00		
44	dimethylphenanthrene	0.30						
45	simonellite					3.35		
46	10,18-bisnorabieta-5,7,9(10),11,13-pentaene		0.12					
47	retene					0.83		
48	L ferruginol		0.14					
49	camphene (2,2-Dimethyl-3-methylene-bicyclo[2.2.1]heptane)						1.15	
50	o-cymene (1-Methyl-4-(1-methylethyl)benzene)						3.28	
51	fenchone (1,3,3-Trimethylbicyclo[2.2.1]heptan-2-one)						0.49	
52	fenchol (1,3,3-Trimethylbicyclo[2.2.1]heptan-2-ol)						0.64	
53	camphor (1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one)						3.26	
54	borneol (1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ol)						1.98	
55	sesquiterpene (204)							2.75
56	sesquiterpene (204)							1.70
	n-C_9				0.03			
	n-C_{10}				0.02			
	n-C_{11}				0.02			
	n-C_{12}				0.02			
	n-C_{13}				0.02			
	n-C_{14}				0.02			
	n-C_{15}				0.04			
	n-C_{16}				0.02			
	n-C_{17}				0.02			

4. Discussion

Polymerisation is the main process in resin fossilisation. Individual tree species produce different types of resins, however, not all types of resins can fossilize. The starting resin must be resistant to decay. Fresh resin sealed and preserved in rocks changes its structure over time, formation of a complex compound of higher molecular weight and conversion of volatile and reactive components into stable compounds occur. This leads to curing of the resin, like the synthetic resins do, however, this process is much slower and, of course, depends not only on time, but also on a complex of geological conditions including composition of the original resin. Resin can fossilize as either precipitated product of tree bark, or nonexcluded, inside the tree. In anaerobic environments, the resin is concentrated during formation of peat swamp and its concentration could still increase mainly in formation of coal. Despite chemical alteration during diagenesis, the biomarkers still have the characteristic basic skeletal structures of their precursors in natural resins, and can thus be used as chemosystematic markers [6].

Pyrograms of the studied resins slightly differ, however, it is possible to find several common compounds for Straseci, Valchovite, and Studlov: borneol, cycloalkanes, and cadalene isomers. The monoterpenoid borneol has been described from several ambers and occurs in modern conifers (e.g. [6-7]). Cadalenes of the cadinane group are common constituents of higher plants, and thus non-specific markers. The resin Krizany is close to the resins Straseci, Valchovite and Studlov except for borneol, which was not found in the former resin. Chromatograms of these resin extracts differ significantly among themselves. In Krizany and Valchovite extracts, diterpene compounds prevail, whereas sesquiterpene compounds prevail in Straseci and Studlov extracts. The occurrence and distributions of terpenoids in the fossil resins provide evidence of their higher plant precursors. Calamenene (21), dihydro-*ar*-curcumene (12), and other unknown compounds interpreted as either sesqui- or diterpenoids based on their fragmentation patterns and molecular weights were the most abundant compounds detected in the extracts. Calamenene (21) and 5,6,7,8-tetrahydrocadalene (24), derivatives of cadalene, are among the most abundant sesquiterpenoids in the geosphere, which have been reported to be widely distributed in angiosperm and gymnosperm plant families (Cupressaceae) [8]. Dihydro-*ar*-curcumene (12) is an aromatic sesquiterpenoid derived probably from bisabolane type precursors [6]. The precursors of cadalene and bisabolane derivatives are widely distributed among higher plants and are not source-specific [9]. However, the absence of plant triterpenoids and specific diterpenoids (such as ozic acid) in the studied resin eliminates the angiosperm plant family as a possible source. Presented sesqui- and diterpenoids suggest that the resins come most likely from the family Cupressaceae: ferruginol, e.g., has been used to classify a resin as being Cupressaceous. Fossil resins can be distinguished from the recent resin, copal, and right amber stages. The more resin components are polymerized, the closer it is to the features of true amber as hardness and insolubility in solvents. This logically means that the more the resin is polymerized the lower is yield of extractable compounds that can be analyzed in extracts. However, some amount of terpenoids always remains nonpolymerisable, and they stay protected.

No succinic acid was detected in the Czech resins, contrary to the Baltic amber. The botanical source of the Baltic amber could not be determined unambiguously, but there are mixed signals suggesting either Araucarian or Pinaceous trees. Krizany, Straseci, and Valchovite are of the same age (Cenomanian) and their consistent fingerprints point to their identical or very similar plant source. The Cenomanian was one of the warmest periods of the Phanerozoic and corresponds to one of the most important transgressive episodes of the geological record. The Cenomanian floras have been known for their diversity [10], exhibiting high diversification of angiosperms together with numerous gymnosperms. The results point clearly to the conifer source trees. The Studlov resin is of Eocene age but its fingerprint is close to the Cenomanian samples, suggesting a similar plant source.

In contrast, the Duxite sample is quite different, and the difference can be seen from TMAH-Py-GC/MS and GC/MS as well. Gymnosperm wood is common in the Tertiary of northwestern Bohemia, the sampling region of Duxite, and represents the major part of all fossil wood found there. According to our previous results [11] and other published data, the fossil wood found there might belong to Glyptostrobus and Quasisequoia plants, representatives of the coniferous family Cupressaceae. Mainly the presence of α-cedrane points to Cupressaceae species. The composition of Duxite corresponds to the results already published for this resin [12]. The presence of 8β(H)-labdane as the most abundant sesquiterpene in the extract directly confirms a polylabdanoid structure of this resin. The pyrogram is dominated by a damascone peak, longipinane, aromadendrane, and other sesquiterpenes were also identified compounds.

The terpenoid signatures support a relationship of all studied Czech fossil resins to the Cupressaceae family. Following the classification by [5], the analyses clearly indicate that all studied resins belong to Class Ib type derived from regular labdane structures that lacked succinic acid. It is known that there is a chemical difference in resins from tree and from soil, which indicates a diagenetic change after the resin burial [13]. Degradation of resins is indicated by the presence of an unresolved complex mixture (UCM) in chromatograms and pyrograms. The UCM hump appears when the compounds cannot be resolved and identified by GC. Duxite has no UCM, neither in pyrogram nor in chromatogram, suggesting no significant degradation of the material. This could be due to younger age of this resin compared to other resins studied, but it can be also due to different storage of this material. Actually, Duxite is the only one of the fossil resins studied that was found inside of a fossil tree, where it was sealed and mothballed. This could be the reason why its fingerprint has been well preserved, contrary to the other fossil resins being as well members of the Cupressaceae family.

Sarawak amber (Neogene/Miocene) has completely different fingerprints that diverge from all the samples studied. The major sesquiterpenes in the fossilised resin extracts are cadalene-based compounds widely distributed among higher plants, such as calamenene, dihydro-*ar*-curcumene, and 5,6,7,8-tetrahydrocadalene. The most intense compounds in the pyrogram are in sequence of sesquiterpenes with molecular weight 206 that are isomers of cadinane derivate. It is known that this amber was produced by angiosperm trees of the Dipterocarpaceae genus, which still grow in the sampling area and produce copious amounts of resin.

Acknowledgements

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