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CHEMICAL CHARACTERIZATION OF ORGANIC MATTER IN *GLYPTOSTROBUS EUROPAEUS* (BGT.) UNG. FROM THE NEOGENE SEDIMENTS AT LIPNICA MAŁA (ORAWA BASIN, POLAND)

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ABSTRACT. Fossilized remains of *Glyptostrobus europaeus* from the Neogene sediments at Lipnica Mała have been chemicaly analized, using the analytical pyrolysis method. The obtained results have shown a normal distribution of the C_{13} to C_{27} alkenes. The alkylphenols were the major lignin fraction. The proportion of polycyclic aromatic molecules, more characteristic for extremely coaly fossil materials was comparatively small. The results indicate that only a small transformation has been suffered by the cuticules and woody structure of *Glyptostrobus* during the taphonomic processes in the Orawa basin.

KEY WORDS: Biochemical composition, *Glyptostrobus*, Neogene, Poland

INTRODUCTION

The genus *Glyptostrobus* is one of the most widely distributed and most extensively described in the Northern Hemisphere, especially during the Miocene, where it acts as a biostratigraphic indicator. Remains of the species are readily available in sufficient quantities for chemical analysis, and have undergone relatively little transformation during the course of the taphonomic processes which have occured in the Lipnica Mała basin. The combination of these factors prompted us to undertake the present study.

CHARACTERISTICS OF THE LOCALITY AND MATERIAL

The remains studied were collected from the Neogene deposits in Lipnica Mała, in the north-western part of the Orawa-Nowy Targ basin, Poland. (Fig. 1)

The geological profile is composed of gray and brown clays and lignit layers interbedded with clays. The material was taken from the bottom part of the profile, from a 50 cm thick layer of lignits abundant in *Glyptostrobus europaeus* remains (Fig. 2).

The fossils belong to a reduced palaeoassociation, characteristic of a swampy forest, in which *Glystostrobus europeaeus* dominated amongst an association of marshy plants. The arctotertiary elements dominated, whereas the palaeotropical ones represented only 7% of the total (Lesiak 1994).

The Orawa layers from which the fossil remains were collected have been attributed to the Middle Miocene.

The studied remains consist of fossils in *sensu lato,* in which the epicuticular material is preserved with little chemical alteration in structure, whereas the remaining cell components have been degraded in the course of geological history. This type of fossilization is called mummification.

The samples subjected to chemical analysis were supplied by Prof. L. Stuchlik and the analysis was performed as part a series of Spanish-Polish cooperative Projects (1993–1996).

The analysed remains comprised small twigs covered by leaves, isolated leaves, as well as various microcones.

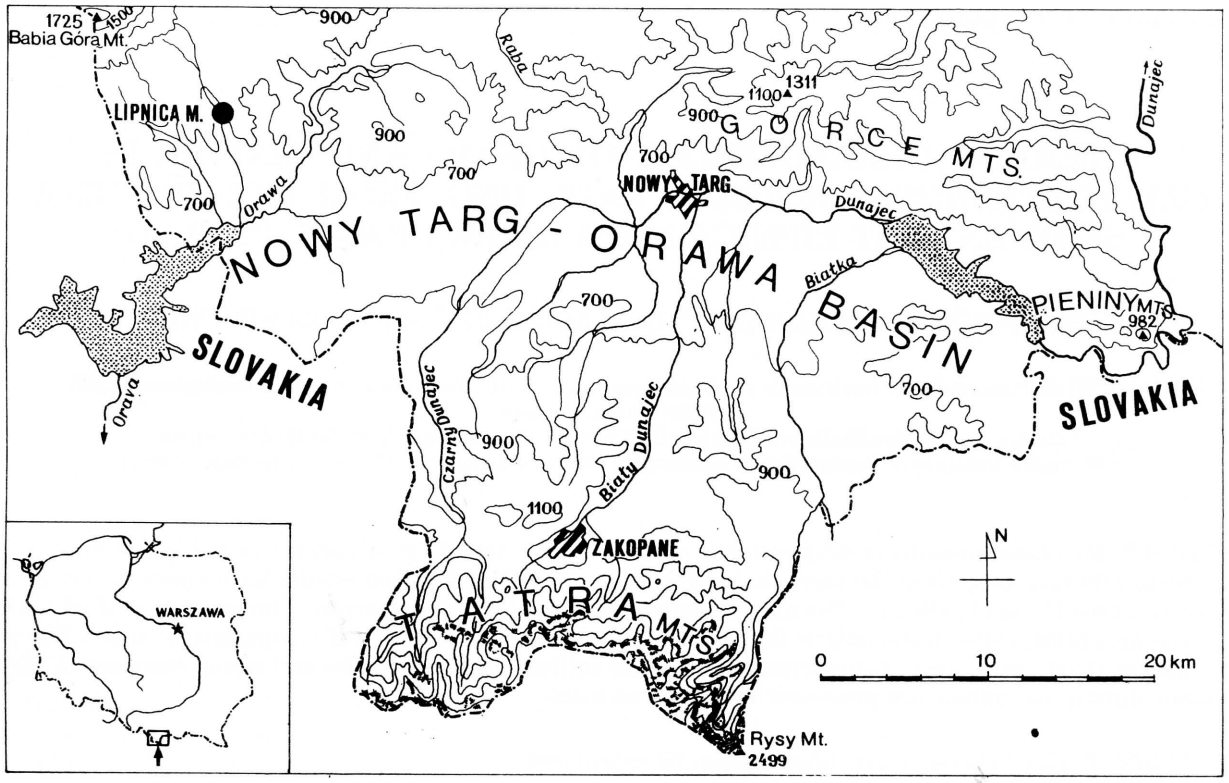

Fig. 1. Location of Lipnica Mała in north-western part of the Orawa – Nowy Targ Basin

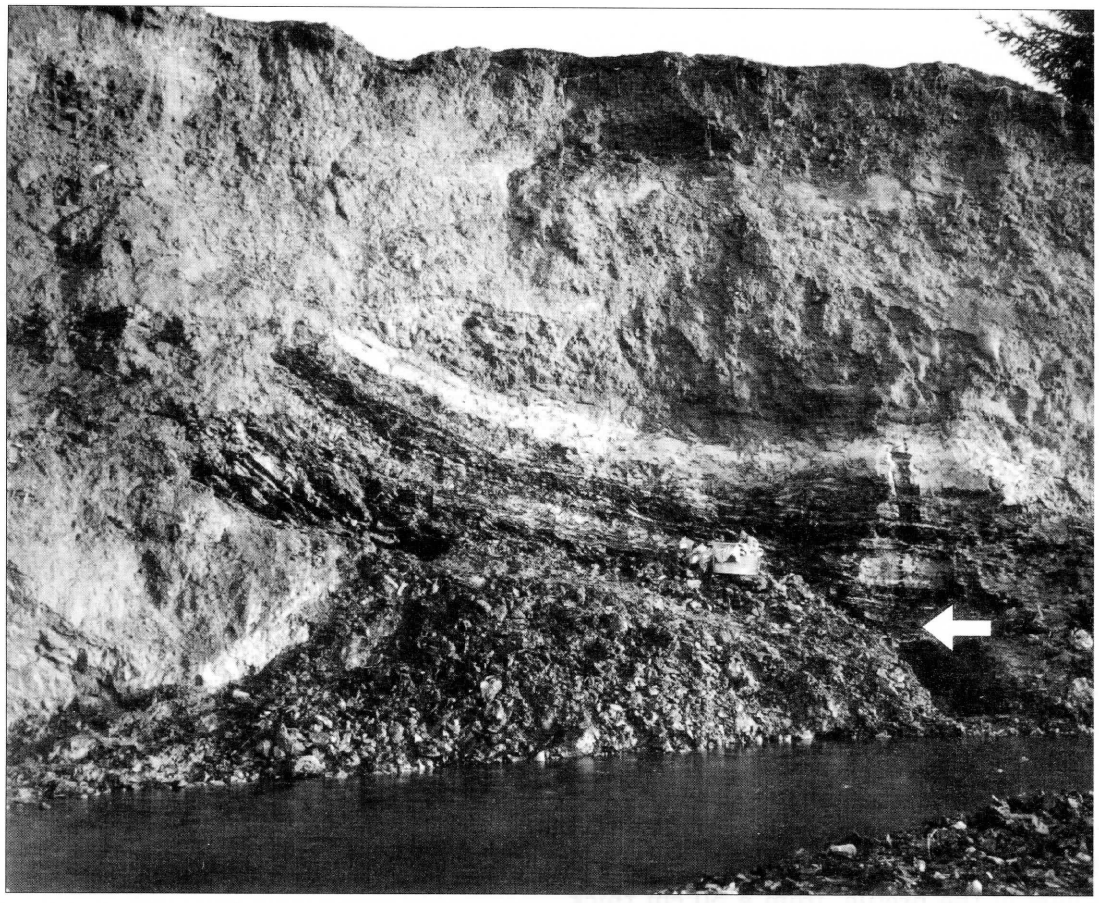

Fig. 2. Outcrop of the Miocene profile in Lipnica Mała with the layer from which the material has been collected (Photo L. Stuchlik)

BOTANICAL FEATURES OF *GLYPTOSTROBUS EUROPEAEUS* (BGT.) UNG.

Current distribution and stratigraphic distribution of the genus *Gyptostrobus*

Nowadays, the genus *Glyptostrobus* is confined to South-eastern China and Vietnam (Fig. 3), and is represented by *G. pensilis* (Staunton) K. Koch.

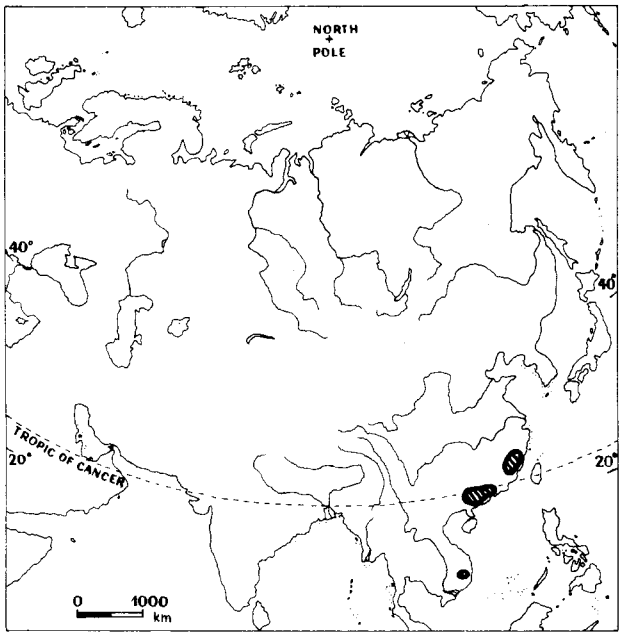

Fig. 3. Geographical distribution of extant *Glyptostrobus pensilis* (Staunton) K. Koch

Glyptostrobus europaeus exists exclusively as a fossil and is widely distributed in the Northern hemisphere. This species was present throughout the period of the Upper Cretaceous to the end of the Pliocene (Alvarez Ramis et al. 1992, Depape 1922, Givulescu 1971, Greguss 1967, Laurent & Marty 1923, Knobloch 1969, 1992, Łańcucka-Środoniowa 1966, 1979, Matthews & Ovenden 1990, Srinivasan & Friis 1989 and Wolfe 1977).

Characteristics of *Glyptostrobus europaeus* (Bgt.) Ung.

This plant is a member of the Taxodiaceae family, and shows a series of anatomical and morphological features in its leaves and twigs common to other genera in this family. Its pollen is of the "*Inaperturopollenites*" type, the arrangement of the areolated pits is very similar to that exhibited by the genera *Chamaecyparis* and *Sequoia,* and it contains resin that, in the fossil gymnosperms may be present in granular or pulverulent form. (Almendros et al. 1982, Alvarez Ramis et al. 1984, 1992, Alvin & Boulter 1974, Greguss 1967, Łańcucka-Środoniowa 1966, 1979, Lyons et al. 1984, Zalewska 1959).

CHEMICAL ANALYSIS

Methods

Analytical pyrolysis (500°C) was carried out in a CDS Pyroprobe 190 unit with a Pt-coil heater. The samples (2 mg) were pyrolyzed in a quartz tube under He atmosphere at a rate of 20°C ms^{-1}, and the volatile products were condensed in a cold trap submerged in liquid N_2. The condensed products were dissolved in methylene chloride and analyzed in a Hewlett-Packard 5988A GC/MS system. with a SE-30 cross-linked capillary column (20 m, 0.1 mm i.d.) (Walton 1990)

Results

The pyrolysis products from *Glyptostrobus* rests are presented on table 1 and the chromatographic separation of them is illustrated on the Fig. 4, on which the structures of the major compounds are indicated on the peaks.

The C_{13} to C_{27} alkenes showed a normal distribution with a maximum at C_{20}, and no preference for the even-C number alkanes (even-to-odd ratio= 0.81). The alkane series showed no even-to-odd preference (ratio= 1.09) and reached a maximum in C_{23}.

A very short series of fatty acids (C_{12}-C_{20}) with strong even-to-odd C number preference (ratio= 4.04) suggests a small diagenetic alteration of protective aliphatic biopolyesters such as cutins or suberins, which are composed of building blocks with a similar range of chain-length (Kolattukudy 1980).

Alkylphenols were the major pyrolysis products of the *Glyptostrobus* sample, which suggests a major lignin fraction (Martin et al. 1979). The presence of methoxyphenols suggests a high degree of suitable preservation, as indicated by the intact aryl methoxyl substitutions in addition, up to C_3 alkyl substituents. Some of these alkylphenols had unsaturated-side chains which as methoxyl-containing ketones are also typical molecular tracers for the structure of lignin (Fengel & Wegener

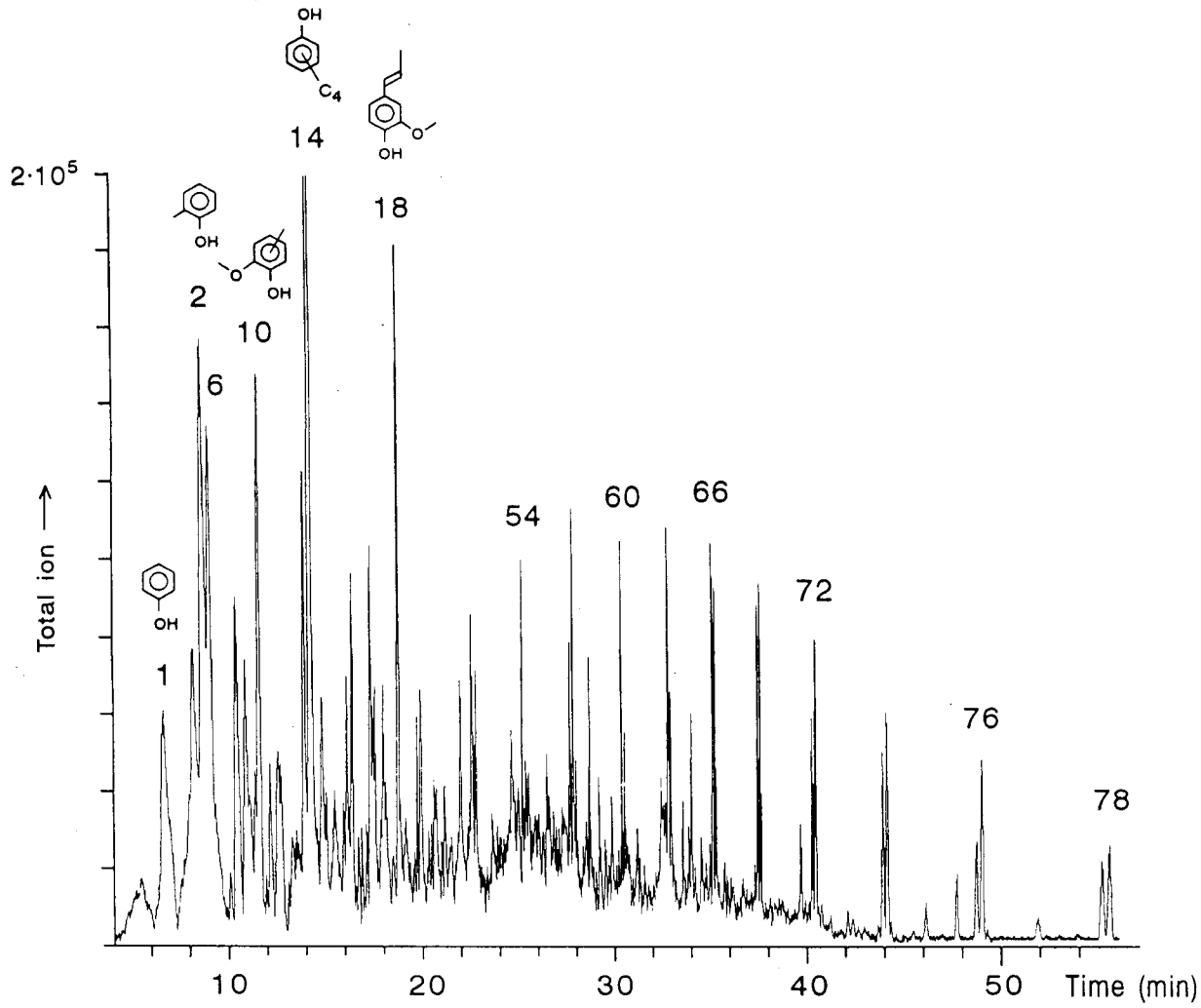

Fig. 4. Chromatographic separation of pyrolysis products from *Glypotostrobus europeaeus* (Bgt.) Ung. Peak labels refer to Table 1. Structures of the major compounds are indicated on the peaks

1984). The C_0 to C_3 catechols were the only diphenols found in the series.

The proportion of polycyclic aromatic molecules, more characteristic for extremely coaly fossil materials (Walton 1990), was comparatively small. The pyrogram showed a small series of naphthalenes (maximum at C_2), as well as an overlapping series of C_{14} tricyclic aromatic hydrocarbons (anthracenes + phenanthrenes) (maximum at C_1) and pyrenes.

The low amounts of heterocyclic molecules (dibenzofurans/xanthenes) and benzofurans have also been reported amongst lignin pyrolysis products (Martin et al. 1979). The tetralins (C_1 to C_2) and fluorenes (C_1 to C_3) which amounted to less than 2% of the total products are characteristic for soil humic substances and fossil macromolecules, and are rarely obtained from unaltered lignins.

No traces of the typical carbohydrate-derived pyrolysis products were found after monitoring the diagnostic ions (Ralph & Hatfield 1991).

DISCUSSION

The results indicate that only a small transformation has been suffered by the cuticles and woody structures of *Glyptostrobus* during the taphonomic processes in the Orawa basin, as would have been expected from the type of preservation (mummification) undergone by the samples.

The low degree of transformation detected suggests that most of the products obtained by the chemical analyses would correspond to essential chemical constituents of *Glyptostrobus*.

The results obtained by pyrolysis-gas chromatography-mass spectrometry indicate that

Table 1. Pyrolysis products from *Glyptostrobus europaeus* rests at Orawa basin

No.	MW	Compound	Relative amount[a)]
1	94	Phenol	*
2	108	Methyl phenols [cresols]	*
3	110	1,2-Dihydroxybenzene [catechol, benzenediol]	.
4	122	C_2-Alkyl phenols [dimethyl phenols + ethylphenol]	*
5	124	Methyl benzenediols [methyl catechols]	.
6	124	3-Methoxyphenol [guaiacol]	*
7	128	Naphthalene	+
8	136	C_3-Alkyl phenols	*
9	138	C_2-Benzenediols [C_2-catechols]	.
10	138	3-Methoxy-4-methylphenol [4-methylguaiacol]	*
11	142	Methyl naphthalenes	.
12	146	Methyl(1,2,3,4-tetrahydronaphthalenes) [Methyl tetralins]	.
13	146	Dimethyl benzofuran	+
14	150	C_4-Alkyl phenols	*
15	152	3-Methoxy-4-ethylphenol	*
16	156	C_2-Alkyl naphthalenes	*
17	160	C_2-Alkyl(1,2,3,4-tetrahydronaphthalenes) [C_2-tetralins]	.
18	164	3-Methoxy-4-propenylphenol	+
19	166	Fluorene	.
20	166	Ethanone, hydroxy-methoxyphenyl	+
21	166	3-Methoxy-4-propylphenol	+
22	168	Dibenzofuran	+
23	170	C_3-Alkylnaphthalenes	.
24	178	Phenanthrene	.
25	178	Anthracene	+
26	180	Methyl fluorenes	+
27	180	Propanone, hydroxy-methoxyphenyl	+
28	182	Xanthene	.
29	182	Methyl dibenzofuran	.
30	184	C_4-Alkyl naphthalenes	.
31	192	Methyl (C_{14} tricyclic aromatic hydrocarbons)	.
32	194	C_2-Alkylfluorenes	.
33	196	C_2-Alkyldibenzofurans	.
34	196	Tetradecene (C_{14} alkene)	.
35	196	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone [acetosyringone]	.
36	198	Tetradecane (C_{14} alkane)	.
37	202	Pyrene	.
38	202	Fluoranthene	.
39	206	C_2-Alkyl (C_{14} tricyclic aromatic hydrocarbons)	.
40	210	C_3-Alkyldibenzofurans	.
41	210	Pentadecene (C_{15} alkene)	.
42	212	Pentadecane (C_{15} alkane)	.
43	214	Dodecanoic acid (C_{12} fatty acid, lauric)	.
44	216	Methyl pyrenes	+
45	220	C_3-Alkyl (C_{14} tricyclic aromatic hydrocarbons)	+
46	224	Hexadecene (C_{16} alkene)	+
47	226	Hexadecane (C_{16} alkane)	+
48	228	Tridecanoic acid (C_{13} fatty acid)	.
49	230	C_2-alkyl pyrenes	+
50	234	C_4-Alkyl (C_{14} tricyclic aromatic hydrocarbons)	+
51	238	Heptadecene (C_{17} alkene)	+
52	240	Heptadecane (C_{17} alkane)	+

Table 1. Continued

No.	MW	Compound	Relative amount[a)]
53	242	Tetradecanoic acid (C_{14} fatty acid, myristic)	.
54	252	Octadecene (C_{18} alkene	+
55	254	Octadecane (C_{18} alkane	+
56	256	Pentadecanoic acid (C_{15} fatty acid)	.
57	266	Nonadecene (C_{19} alkene)	+
58	268	Nonadecane (C_{19} alkane)	+
59	270	Hexadecanoic acid (C_{16} fatty acid, palmitic)	.
60	280	Eicosene (C_{20} alkene)	+
61	282	Eicosane (C_{20} alkane)	+
62	284	Heptadecanoic acid (C_{17} fatty acid, margaric)	.
63	294	Heneicosene (C_{21} alkene)	+
64	296	Heneicosane (C_{21} alkane)	+
65	298	Octadecanoic acid (C_{18} fatty acid, stearic)	.
66	308	Docosene (C_{22} alkene)	+
67	310	Docosane (C_{22} alkane)	+
68	312	Nonadecanoic acid (C_{19} fatty acid)	.
69	322	Tricosene (C_{23} alkene)	+
70	324	Tricosane (C_{23} alkane)	+
71	326	Eicosanoic acid (C_{20} fatty acid, arachidic)	.
72	336	Tetracosene (C_{24} alkene)	+
73	338	Tetracosane (C_{24} alkane)	+
74	350	Pentacosene (C_{25} alkene)	+
75	352	Pentacosane (C_{25} alkane)	+
76	364	Hexacosene (C_{26} alkene)	+
77	366	Hexacosane (C_{26} alkane)	+
78	378	Heptacosene (C_{27} alkene)	+
79	380	Heptacosane (C_{27} alkane)	+

[a)] *: major compund (> 2% total chromatographic area (%), +: <2>0.1 %; ·: <0.1 %

the *Glyptostrobus* remains contain a mixture of guaiacyl-type lignin and polyalkyl biopolymers, the latter being responsible for the major series of saturated and unsaturated hydrocarbons.

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