

CHEMICAL COMPOSITION OF CENOMANIAN FOSSIL RESINS FROM MORAVIA

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Five samples of fossil resins from Moravia (Czechoslovakia) were subjected to extraction with pyridine and to pyrolysis. As shown by infrared spectrometry, gas chromatography, and mass spectra of the corresponding products, all the five samples probably exhibit a closely related chemical nature and a common plant origin. The samples were also compared with two foreign resins from Lower Cretaceous deposits and with the Eocene succinite.

The occurrence, fate, and composition of fossil resins has been paid attention by chemists for a long period of time. Thanks to the recent development of spectroscopic methods, a great progress has been recorded in investigations on the chemical composition of these resins including succinite¹⁻⁴. In this paper we wish to report on examinations of several samples of fossil resins from the freshwater Cenomanian deposits in Moravia. These samples have been compared with the Eocene Baltic succinite as well as with two samples of Lower Cretaceous resins of the Austrian and Lebanonian occurrences.

EXPERIMENTAL

Samples and their Origin

Walchovite. This resin was described in detail by Haidinger⁵ and named after the occurrence Valchov in Central Moravia. It forms microscopic grains to masses of about ten centimeters in diameter that are waxy yellow to yellowish brown, of conchoidal fracture, non-transparent to non-translucent, of the hardness 1.5–2.0, and of the specific gravity 1.035–1.069. Three various samples were analysed, namely, the sample W 388 from the occurrence near Hřebeč, the sample W 390 from Březina, and the sample W 391 from the occurrence near Valchov (inventory number 67, collection of the Moravian Museum in Brno, Czechoslovakia). For the elemental analyses see Table I.

Neudorfite (N 389; inventory number 2433, collection of the Moravian Museum). This resin was described in detail by Schroeckinger⁶ and named after its occurrence (Nová ves in Czech, Neudorf in German). It forms grains or masses up to the size of several centimeters in diameter

in the upper seam of the Cenomanian coal. Neudorfite is faintly yellow, of resinous lustre and conchoidal fracture; specific gravity, 1.045–1.060. The examined sample was not quite homogeneous since the faintly yellow almost transparent mass also contained deep brown non-transparent spots.

Muckite (M 397). This resin also occurs near Nová ves and was described in detail by Schroeckinger⁶. It occurs in lower seams of the Cenomanian coal. Its colour is greyish yellow or resembling honey. Muckite is both cloudy and translucent, with a glassy lustre similar to the colophony resin; specific gravity, 1.003; hardness, 1.0–2.0.

All the five above samples were deposited in meedstones and intermediary coal sediments of the Bohemo-Moravian Cretaceous Cenomanian near the city of Moravská Třebová.

Succinite (S). The sample was found on the beach of the peninsula Hel in the Baltic Sea. The weathered deep-coloured surface layer (S_{ox}) and the yellowish white non-translucent centre (S_{nat}) were examined separately in some cases. Succinite was used as an authentic sample for purposes of comparison.

Resin⁷ (A) from the Lower Cretaceous coal-bearing layers of sandstone of an Austrian occurrence (near Salzburg) and the amber^{8,9} (L) of a Lebanese occurrence were also used for comparison.

Extraction with Pyridine

In a test tube, pyridine (5 ml) was added to the weighed uncrushed sample and the mixture kept at room temperature for several hours. If required, the solvent was replaced by a fresh lot until colourless. The test conditions were as follows (designation of the sample, weight in g, extraction time in h, pyridine in ml, and % of the extract given): W 388, 0.41 g, 6 h, 5 ml, 46%; W 390, 0.44 g, 8 h, 5 ml, 30%; W 391, 0.43 g, 6 h, 10 ml, 25%; N 389, 0.46 g, 50 h, 10 ml, 20%; M 397, 0.40 g, 10 h, 5 ml, 30%; S, 0.50 g, 20 h, 5 ml, 30%. The insoluble residue was rinsed with pyridine and dried in an evacuated (15 Torr) desiccator over phosphoric acid for 24 h. For the elemental analyses see Table I. The pyridine extracts were combined, diluted with diethyl ether, and poured into dilute hydrochloric acid. The ethereal layer was separated, washed twice with water, dried, and the ether evaporated through a short column. For purposes of gas chromatography, the samples were esterified with ethereal diazomethane.

Pyrolysis

The sample (80–100 mg each) was distilled under nitrogen in a small Hickman flask up to the bath temperature of 350°C. The distillate was transferred from the collar into a glass ampoule by means of 2–3 ml of methanol containing 4% of hydrogen chloride¹⁰. The ampoule was sealed, heated at 75°C for 6 h, the content neutralised with ammonia, and the ammonium chloride removed by centrifugation. The supernatant was analysed by gas chromatography.

Methods

Gas chromatography was performed in a Model 64 PYE series 104 Chromatograph with a dual system of columns and flame-ionisation detectors; 3% SE-30 on Gas Chrom Q and Porapak Q was used as packing. Mass spectra were recorded on a combined gas chromatograph (PYE)/mass spectrometer (A.E.I. MS 902) apparatus with the use of the Watson-Biemann separator at the ionic source temperature of 100°C (electron energy, 70 eV). Infrared spectra were taken on a Perkin-Elmer 621 apparatus in potassium bromide discs.

RESULTS AND DISCUSSION

The finds of fossil resins in Bohemia and Moravia have been known from 19th century. Walchovite was examined (fundamental chemical observations and analyses) by Schrötter¹¹ and Haidinger⁵. Neudorfite and muckite were studied in detail by Schroeckinger⁶. From the geological standpoint, the Cenomanian of the Bohemo-Moravian Cretaceous is of a fluvio-lacustrine origin. The layers of freshwater sedimentation repeat themselves cyclically. In the course of a calmer sedimentation, among the cycles, siltstones and mudstones with roots and coalified woods, coal mudstones, and sometimes, autochthonous seams of brown coal were deposited¹². The coal and mudstones frequently contain masses of fossil resins along with small beads of phosphorite and concretions of pyrite. As shown by palynological investigations of the Bohemian freshwater Cenomanian¹³, some genus of gymnospermae existing in the Tertiary period and in the present time (*e.g.*, *Pinaceae*, *Taxodiaceae*, *Araucariaceae*) and represented by numerous species, were accompanied by other genus (*e.g.* *Classopolis*) that died out during the Upper Cretaceous era or the Lowest Tertiary period. Palynological analyses of resin deposits have not been so far performed since neither pollen grains nor spores and cuticles could be found in mudstones or coal¹².

Detailed characteristics of the present samples were obtained by means of IR spectra. The chemical structure of fossil resins cannot be naturally determined from analysis of their spectra², but nevertheless, the comparison of spectra might lead to some interesting conclusions¹. Furthermore, after removal of monomers or decomposition products by extraction with a suitable solvent, the IR spectra of the remaining polymeric resin skeletons can be examined and compared². To the present knowledge, fossil resins are polymers of the polyester type to which low-molecular compounds are attached by a non-covalent bond. The Baltic amber (succinite) is assumed to be derived from the polymerised dimer of abietic acid^{2,14} or from communic acid⁴ which is of the labdane type.

The IR spectra of all eight original non-extracted samples were recorded and completed by spectra of modified samples obtained on removal of substances soluble in pyridine². The latter spectra are more significant and more suitable for purposes of comparison. The IR spectra of the original non-extracted samples (W 388, W 390, W 391, N 389, M 397, A, and L) are almost identical (except for the Baltic amber, S) similar to those of their fundamental polymeric skeletons (Fig. 1); the spectra lack bands due to the exocyclic double bond⁸ (particularly at 890 cm^{-1}) and exhibit a specific well developed doublet at 975 and 1025 cm^{-1} (C—O). In the sample W 391, this doublet is replaced by a shoulder; the sample A contains a weak band due to the terminal double bond (885 cm^{-1}), the carbonyl group band (1710 cm^{-1}) being weaker than with the remaining six samples. In accordance with observations of Beck and coworkers¹⁵, these seven spectra do not contain a frequency at $1150\text{--}1160\text{ cm}^{-1}$

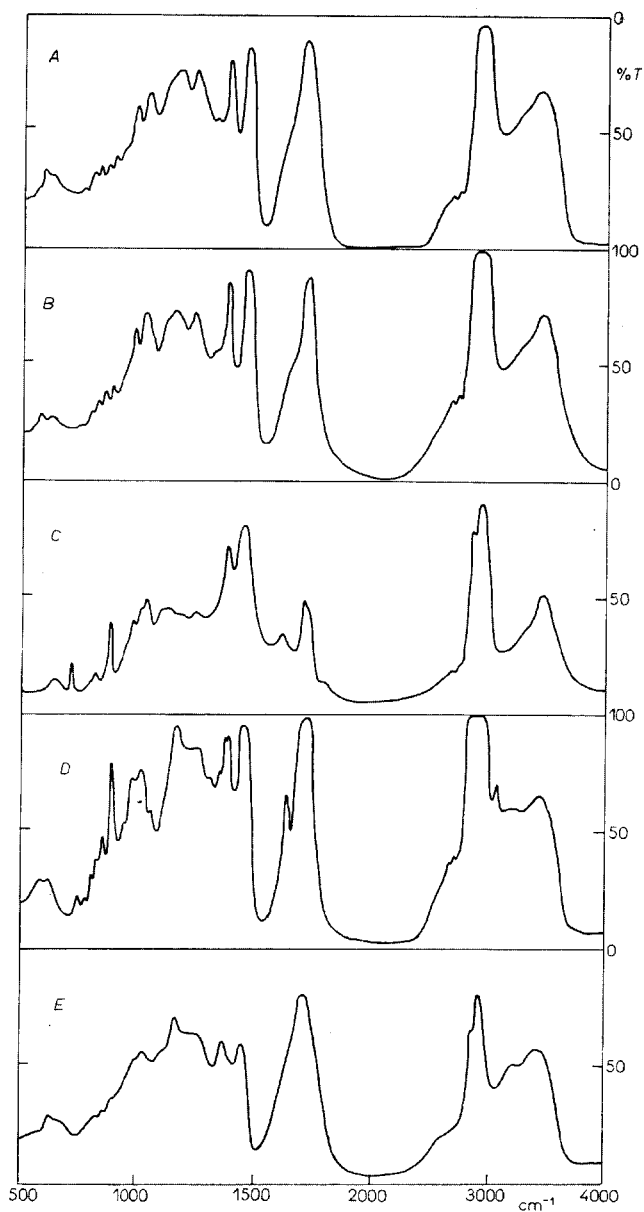


FIG. 1

IR Spectra: A, sample M 397; B, sample L; C, sample A; D, sample S_{nat} ; and E, sample S_{ox}

with a flat almost 80 cm^{-1} -wide shoulder ($1200\text{--}1280\text{ cm}^{-1}$); the latter system is typical only of ambers of the Baltic region (S). A similarly typical feature^{16,17} of the Baltic amber is the presence of an exocyclic double bond ($880, 1640, 3070\text{ cm}^{-1}$).

In the case of the succinite sample (S), the spectra of both the weathered surface layer (S_{ox}) and the intact centre (S_{nat}) were measured. The S_{ox} spectrum exhibited only a very weak band of the terminal double bond (890 cm^{-1}) and a somewhat more intensive peak of the carbonyl group (1710 cm^{-1}). On the other hand, S_{nat} exhibits well developed bands of the exomethylene double bond ($890, 1640, 3070\text{ cm}^{-1}$). It may be thus inferred on the basis of this observation on the Baltic amber that the terminal double bond belongs to the polymeric fundamental skeleton and that the weathering process results in destructive oxidation of this double bond with the formation of a carbonyl function^{1,16,17}. Some differences in the shape and intensity of spectral bands in the above mentioned region ($1160\text{--}1280\text{ cm}^{-1}$) were detected

TABLE I
Elemental Analyses of Fossil Resins
+ traces

Sample	% C	% H	% N	% S	% O	% ash
W 388	79.94	10.70	1.15	0.77	—	0.24
W 390	79.75	10.60	0.97	0.41	—	0.01
W 391	79.52	10.37	1.00	1.17	—	0.03
N 389 ^a	81.34	10.63	1.10	2.45	—	0.30
N 389 ^b	77.42	10.22	0.88	3.19	—	0.36
M 397	75.57	9.93	1.05	0.62	—	0.02
S_{ox}	75.13	9.76	0.71	0.76	—	0.10
S_{nat}	78.66	10.33	0.62	0.83	—	0.10
Walchovite ⁴	80.30	10.68	—	—	9.02	—
Walchovite ⁴	80.20	10.74	—	—	9.08	—
Walchovite ⁴	80.70	10.62	—	—	8.68	—
Neudorfite ⁵	78.04	10.14	0.40	+	11.60	1.5—4.3
Muckite ⁵	79.22	9.57	—	—	11.21	—
Residues after extraction						
W 388/2	78.03	9.96	2.08	1.13	—	—
W 390/2	78.39	10.07	2.33	0.83	—	—
W 391/2	77.43	10.04	2.37	+	—	—
N 399/2	78.36	9.97	1.82	3.07	—	—
M 397/2	76.74	9.68	2.53	1.04	—	—

^a Light portion of the sample; ^b dark portion.

on comparison of the IR spectra of the native Baltic amber with those of the extracted sample. Thus, the flat shoulder of the non-extracted amber sample was replaced by two bands at 1214 and 1250 cm^{-1} (minimum at 1230 cm^{-1}) in the spectrum of the extracted sample. It may be concluded that the extraction of the native amber was accompanied by removal of substance with an acetate functional group; virtually, the IR spectrum of the pyridine extract of sample S exhibited quite distinct bands at 1250 cm^{-1} (C—O—) and 1724 cm^{-1} (C=O) confirming unequivocally existence of the acetate group.

The pyridine extraction of sample N 389 (see also Table I) was much slower than of the other samples (including sample S) in spite of the double volume of pyridine; moreover, the insoluble residue was darkest from all extracted samples and the extract content was lowest. The anomalous course of the extraction is obviously in connection with a somewhat different result of the elemental analysis (a higher content of sulfur) and with the non-homogeneity of the resin.

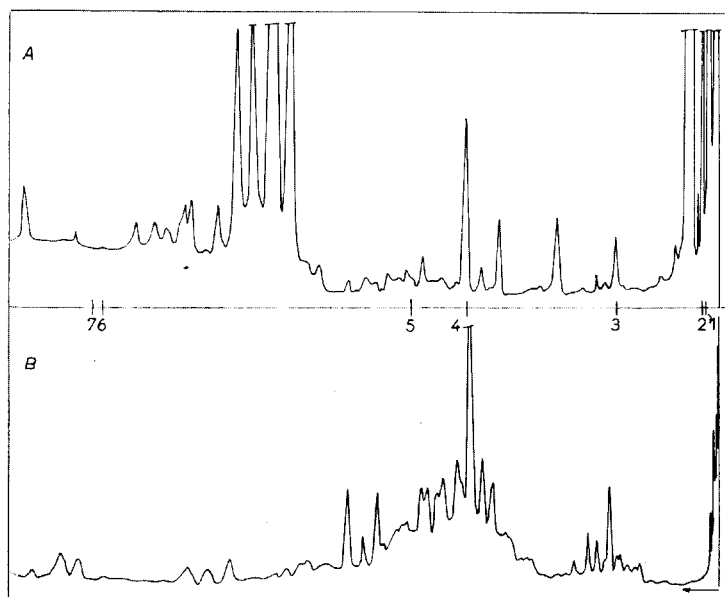


FIG. 2
Chromatograms of Extractable Substances; A, the Baltic succinite (S); B, the Moravian Neudorfite (N 389)

3% SE-30 on GAS CHROM Q (100–120 mesh), $100\text{--}250^\circ\text{C}$ (2°C per min). Retention values of reference terpenic hydrocarbons: 1, 2 C_{10} ; 3 C_{15} ; 4 C_{19} (pristane); 5 C_{20} ; 6, 7 C_{30} .

The pyridine extracts of five samples under investigation and of the Baltic amber sample extract were also examined by gas chromatography after the previous esterification of the constituents with diazomethane (ref.⁴). Neither formic acid nor succinic acid have been detected in any of the five extracts. Two further conclusions can be drawn from comparison of records taken under the same conditions with a linear rise of the temperature (100–250°C). The chromatogram character of substances extracted from sample S differs from the other five extract chromatograms but is very similar to the chromatogram of the ethereal extract of another Baltic amber sample recorded by Gouch and Mills⁴. All extracts (including that of sample S) especially contain isoprenoids of a terpenic character as confirmed on comparison of retention times with authentic samples (Fig. 2) and by means of a typical fragmentation (mass spectra). Each of records always contains a group of chromatographic waves, the retention times of which correspond to monoterpenes, sesquiterpenes, diterpenes (including pristane), and, in some cases, to triterpenes. A detailed description of results obtained in analysis of extracts by gas chromatography and mass spectrometry will be reported elsewhere.

The samples of resins were also subjected to pyrolysis up to 350°C, the condensate esterified with methanol and hydrogen chloride¹⁰ in a sealed ampoule, and the product analysed by gas chromatography under various conditions. The five samples of Moravian resins exhibited qualitatively almost identical chromatograms in contrast to the chromatogram of sample S. Moreover, the pyrolysate of sample S was shown to contain a considerable amount of succinic acid (in the form of the dimethyl ester) which was identified by gas chromatography with the use of an authentic specimen and by mass spectrometry. Furthermore, the analysis of mass spectra of the particular chromatographic waves of the pyrolysate S indicated the presence of isoborneol, several ketones (C₅—C₉) and sesquiterpenic compounds. The pyrolysate of sample N 389 contained an aromatic substance (M⁺ 184), sesquiterpenic hydrocarbons, alcohols, and other oxygen-containing derivatives.

As indicated by IR spectral analyses, comparison of extracts, and analysis of pyrolytical products, all the five samples from Moravian deposits hitherto classified as particular organic minerals, exhibit a very similar or identical chemical composition suggesting coniferae of the same family as the common source of these resins. The Cenomanian resins are owing to their composition very closely related to the Lebanonian (L) and Austrian (A) resins from the Lower Cretaceous deposits the mutual similarity of which has been described by Rottländer⁸. It is also assumed by this author⁸ that samples L and A originate from the genus *Araucariaceae*. In view of the relatively same age of samples A and L and our samples from Moravia, the present results could confirm the earlier idea of Paclt¹⁸ that the Moravian samples originate from *Araucariaceae*, e.g., from *Damarophyllum* (cf. also ref.^{1,3}). However, all the above samples differ from the sample of succinite in IR spectra as well as in behaviour when subjected to pyrolysis. It should be taken into consideration that the plant origin

of resins can be elucidated by a detailed investigation on the chemical composition of fundamental polymers and extractable substances along with comparison with the present types of resins. Thorough investigations in this direction are in progress, particularly examination of skeleton types of diterpenoids (labdane-pimarane-abietane) similarly to those occurring in the Baltic succinite (Gouch and Mills⁴).

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