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Succinite, Baltic Amber: A Chemical Masterpiece of Nature

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Abstract: Succinite, Baltic amber, is one of the most appreciated fossil resins. Its beauty has fascinated people since prehistoric times. It is a substance, and also gemstone, whose uniqueness is due to its compelling, though still not fully understood, physicochemical nature. In this article, some facts about the physical and chemical properties of succinite in order to find an answer for questions about the unique properties of this resin, such as color, transparency, texture etc., are discussed. These properties are among the factors that determine the choice of Baltic amber as a gemstone. Commonly known properties of succinite, but also some less obvious features, have been linked to the organic and inorganic chemical composition and structural factors, including the sophisticated supramolecular structure masterfully created by nature. Changes of the properties of succinite used as a jewelry stone are discussed as a reflection of changes in its physicochemical nature. In this light, some methods that can be used to identify succinite (i. e., infrared spectroscopy and nuclear magnetic resonance spectroscopy) and their relevance to the classification of fossil resins are briefly discussed. This article highlights an important point: only by understanding the chemical and physical nature of the material we able to identify, modify and effectively use the goods that have been given to us by mother nature.

Keywords: Baltic amber; succinite; chemical composition; property

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INTRODUCTION

Resins can be found all over the world, but with different botanical sources and varied geological ages, they may in consequence, have different properties. This is a consequence of their internal structure and chemical composition. One of the most appreciated fossil resin is Baltic amber known for human beings since prehistoric times. Most of natural resins which are defined as "ambers" are called with their geographical names, e. g., Dominican, Mexican or Borneo amber. The term "Baltic amber"or for a long time just "amber" is reserved for a particular type of fossil resin with mineralogical name "succinite". The term "succinite" for description of Baltic amber was used for the first time by Breihaupt in 1820 (Breihaupt, 1820).

Nowadays, the natural beauty of succinite is more and more often affected by a variety of modifications resulting in easily observed change in physical properties such as color, transparency and texture. This is achieved by using various treatments such as high temperature, autoclaving (heat and pressure treatment) often in the presence of various

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作者简介:Ewa Wagner-Wysiecka (1972—), female, Ph. D., professor, main interests focus on synthetic and analytical supramolecular chemistry. E-mail:ewa.wagner-wysiecka@pg.edu.pl additives. Many other approaches that result in changing the amber properties are also used, but often remain a secret of the manufacturer. The process of pressing amber, which takes place under specific temperature conditions, has been known for a long time. Such material was once willingly used in technology, and today pressed amber is also used as jewelry material.

In this article, the author attempts to link the known facts about structure and chemical composition of an extraordinary fossil resin, succinite, the Baltic amber, and find the relationship between properties and structure/composition. In materials sciences, gemstones are just as materials. Having in mind the sophisticated properties of natural products, the author realizes that the above task is a challenge, but it might contribute to further creative discussion on the most beautiful and most precious among fossil resins——succinite.

SUCCINITE, THE BALTIC AMBER VS. OTHER FOSSIL RESINS

Natural resins can be classified in various ways. One of the criteria is their age and burial history, which results in maturation of the particular material, namely fossilization degree. According to this classification "modern or recent resins", "subfossil resins" and "ambers" are among the others highlighted. However, the nomenclature of natural resins is still debatable and out of the scope of this article. Nevertheless, it is worth to mention, this subject has been discussed in details by several authors (Anderson, 1996; Langenheim, 2003; Kimura et al., 2006; Vávra, 2009; Lambert et al., 2012; van der Werf et al., 2017) and recently by Solórzano-Kraemer et al. (2020).

One of the approaches in classification of natural resins was proposed byAnderson and co-workers described in a series of articles (*vide infra*). This attempt was achieved by taking into account the structural and chemical composition of natural resins. According to this classification, natural resins can be categorized into 5 main classes and subclasses depending on their (co)polymeric structure (Lambert et al., 2008; Poulin & Helwig, 2012, 2014, 2015, 2016; Anderson, 1994, 1995; Anderson & Bray, 2006 Anderson & Winans, 1991; Anderson et al., 1992; Vavra, 2009a; Pastorova et al., 1998). The classification system is shown in Fig. 1, Class Ⅰ, with four sub-classes Ⅰa to Ⅰd, covers resins based on labdanoid polymeric structure. Baltic amber is the only one in Class Ⅰa.

This classification system is often used when referring to known the chemical nature of resins. However, the method (i. e., GC-MS and its variations) on the basis of which the classification was developed is time-consuming and labor-intensive. Thus, in the author's opinion, it is hard to apply in everyday practice, when a fast and unambiguous assignment of a resin (especially of unknown identity) to a specific group is required. Here, the classification of resins (Lambert & Poinar, 2002) based on ^{13}C NMR spectra seems to be a bit more useful. The classification system proposed by Lambert et al. (2015) is consistent with proposed by Anderson

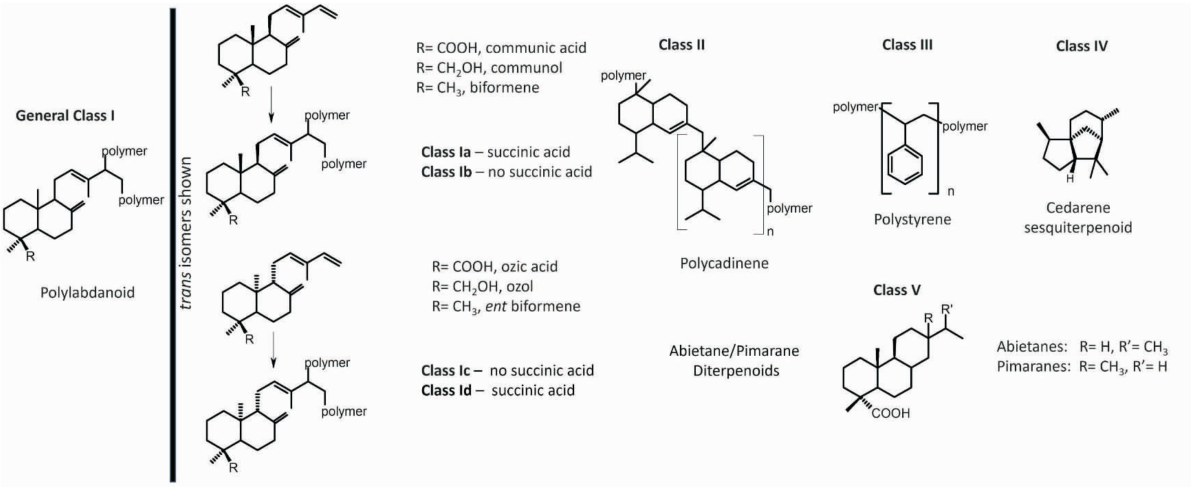


Fig. 1 Classification system for natural resins

(Anderson，1994，1995；Anderson & Bray，2006 Anderson & Winans，1991；Anderson et al.，1992). However，access to NMR equipment may be a limitation in the use of this method，because although NMR spectrometers are commonly used for structural studies in solution，still relatively few laboratories have the ability to record NMR spectra in the solid state. Some attempts have also been done to classify resins on the basis of their mid-infrared spectra (Kimura et al.，2006). It seems to be promising approach since mid-infrared spectrometers are widely used in analytical，including gemological practice. It is also fast and well proven method for the confirmation of the identity of substances and materials. Obviously both ^{13}C NMR and mid-infrared approaches need a reliable set of a reference data and can act as complementary analytical methods，together with Raman spectroscopy. However，saying this and having in mind that the review of the methods of studies of natural resins is out of scope of this article，it must be underlined，that in studies of the chemical character of natural resins，multidisciplinary approach is necessary. Obviously，the most of the current publications present interdisciplinary studies in resins examination. Here are some examples of combining different techniques：mid-infrared spectroscopy and Py/GC/MS (Park et al.，2016；Havelcová et al.，2016)，mid-infrared spectroscopy and time of flight-secondary ion mass spectrometry (ToF-SIMS) (Wolfe et al.，2016)，head space solid-phase (micro) extraction coupled with gas chromatography-mass spectrometry (Pastorelli，2011；van der Werf et al.，2014)，thermal desorption/gas chromatography/mass spectrometry (Vîrgolici et al.，2010)，mid-infrared spectroscopy and high performance liquid chromatography coupled with mass spectrometry (Truică et al. 2012).

SUCCINITE——IN GENERAL

Physical and chemical processes which took place in the excellent laboratory——Nature's laboratory，over millions of years，allow us today to enjoy the unique beauty of succinite. Formation of succinite were undoubtedly complex processes (e.g.，Clifford & Hatcher，1995；Anderson & Winans 1991；Ragazzi et al. 2003；Tappert et al.，2011；Seyfullah et al. 2015) (Fig. 2) involving chemical reactions such as polymerization，polycondensation，oxidation under various geochemical and different and often fluctuations depending on atmospheric conditions including humidity and temperature. Botta et. al (1982) suggested that in succinite formation，acid-catalyzed transformations of terpenes have occurred. A result of these transformations is a kingdom of the varieties of Baltic amber illustrated in Fig. 2.

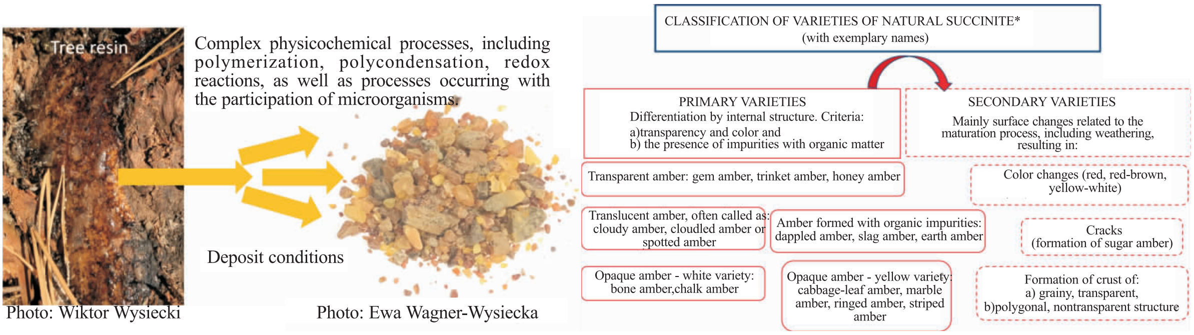


Fig. 2　Left：Schematic of fossilization of natural resins. Right：Classification of Baltic amber varieties
(Scheme developed on the basis of the content in：B. Kosmowska-Ceranowicz，2012)

The real interest in chemistry of amber，besides fascination with this material in prehistoric and ancient times，dates back to the end of the 19th and the beginning of 20th centuries. In this regard，an outstanding contributionwas done by Unverdorben (1827)，Berzelius (1828) or Berthelot (1860) works (in Urbański et al. 1984). In 1923，Tschirch et al. (1923) shown for the first time that Baltic amber is related to abietic acid. Identification of product of selenium dehydrogenation of a soluble fraction of amber as pimanthrene (1，7-dimethylphenanthrene) was a first evidence for the diterpenoid nature of succinite (Schmid & Erdös, 1933). This classical organic chemistry approach allowed also for isolation and identification of agathaline and retene (Rottländer, 1974).

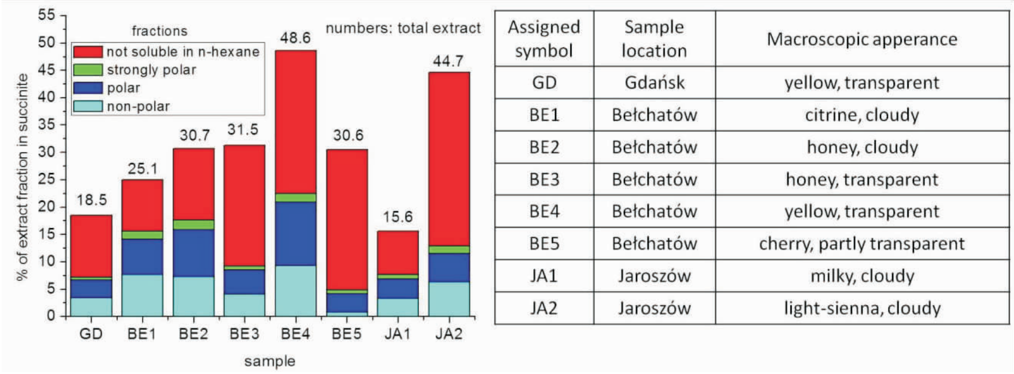
As it was pointed above, natural fossil resins are classified according to the structure of the macromolecular (hardly soluble) fraction (Fig. 1). In case of succinite, the polymer matrix is based on polylabdane skeleton, namely (co)polymers of communic acid and communol. In both subclasses Ia and Ib the basic polymer has the same structure, the difference is that in case of Class Ⅰa, diterpenoids are cross-linked with succinic acid, whereas in Class Ⅰb are not.

Succinite is a material of relatively low solubility, eventually partially soluble in some organic solvents (Table 1). The yield of the extracts is dependent both on the properties of solvent and the variety of succinite.

Data in Table 1 refers to solubility determined under various conditions (sometimes not defined temperature and time), but the differences of solubility of succinite in solvents of various nature (polar/non-polar, protic/aprotic) reflect the succinite molecular diversity. Solubility can be different also for the varieties of succinite. It is illustrated in Fig. 3 on the comparison of the fractions of chloroform: metanol (1∶1, v/v) extract obtained from succinite of various geographical origin in Poland (Czechowski et al., 1996).

Table 1　Solubility of Baltic amber [%] in popular organic solvents of various polarity

Source	Solvent	carbon disulfide	benzene	ethyl ether	chloroform	acetone	methanol	ethanol	potassium ethanolate
Gough & Mills, 1972		—	—	20 (cold solvent)	—	—	—	—	—
Helm, 1891, in Savkevich 1970, p. 93		24	9.8	18—23	20.6	—	13	20—25	—
Kucharska & Kwiatkowski, 1978		11.5	21	—	—	8—23	17—25	16—23	35
Klebs, 1896		20.07	—	—	—	8.42	—	20.8	35.5



Assigned symbol	Sample location	Macroscopic apperance
GD	Gdańsk	yellow, transparent
BE1	Bełchatów	citrine, cloudy
BE2	Bełchatów	honey, cloudy
BE3	Bełchatów	honey, transparent
BE4	Bełchatów	yellow, transparent
BE5	Bełchatów	cherry, partly transparent
JA1	Jaroszów	milky, cloudy
JA2	Jaroszów	light-sienna, cloudy

Fig. 3　Fractions of chloroform: methanol extract obtained from succinite of various deposits in Poland (left); characterization of succinite samples (right). (after: Czechowski et al., 1996)

The difference in solubility of succinite in ethanol was also reported by Kucharska and Kwiatkowski (1979). Transparent succinite was better soluble (23%) in organic solvent than translucent (18%). The lowest solubility was found for opaque variety (16%). Relatively low solubility of succinite was for a long time one of the limitations in its investigations.

CHEMICAL NATURE OF SUCCINITE

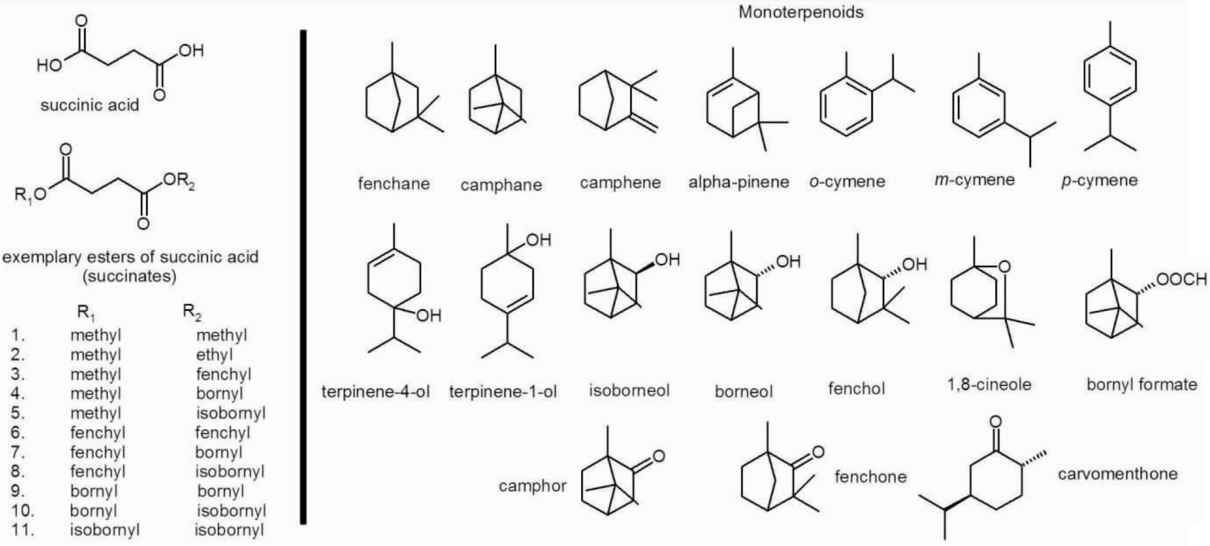
Organic Components

One of the most important characteristics of

Baltic amber is the presence of succinic acid. Its quantity as 3％－8％（w/w）was confirmed for the first time by Otto Helm，an apothecary in Gdańsk（Danzig）in dry distillation or alkaline hydrolysis（Helm，1877；Lambert，1988）. The largest amounts of succinic acid were found in a weathered layer（crust）. Other resins do not contain this substance or contain it in diverse amounts（e. g.，fossil resins of class Id found in deposits in Canada）（Poulin & Helwig，2012）. The most of succinic acid in Baltic amber is present as ester derivatives，succinates（Fig. 4）（Czechowski et al.，1996；Yamamoto et al.，2006；Wagner-Wysiecka & Ragazzi，2011）or is cross-linked with polymers of communic acid and communol. The presence of free succinic acid was investigated in water/methanol soluble fraction of succinite using mass spectrometry（ESI in positive and negative modes）（Tonidandel et al.，2009）. It was found that in this soluble part of Baltic amber the content of free succinic acid can reach 0.04％－0.005％. Even succinite is amorphous；some crystalline phases were detected in its structure. The presence of free succinic acid in crystalline form was confirmed in a white variety of succinite by Kosmowska-Ceranowicz（2008）.

Succinic acid is known to be biologically active agent（e. g. incardiovascular therapy，Wang et al.，2020）and this is probably one of the reasons for the special interest in Baltic amber in ancient，folk and nowadays medicine. For example，Steadman and co-workers have been investigated Baltic amber teethers recently（Nissen et al. 2019）. They confirmed the presence of succinic acid in their material，but they found out that this substance could not feasibly be released from material to be penetrated through the skin.

Soluble fraction of succinite，however not indicative for its total structure，gives some information about its chemical nature. One of the first work on identification of terpenes in succinite was published in 1980（Mosini et al.，1980）. Mosini and co-workers have compared the composition of the volatile fraction of pine resins（before and after aging）and Baltic amber. From the comparison it was concluded that the nature of terpenes found in succinite argues against a pine origin of this fossil resin. Mills et al. investigated both soluble and insoluble fractions of succinite（Gough & Mills，1972；Mills & White，1984/1985）. The main group of identified compounds constitutes of methyl esters of abietane and isopimarane acids. Methyl esters of agathic and dihydroagathic acids were also identified，however in less amounts. In summary，the structure of monoterpenes（cf. Fig. 4），diterpenes（cf. Fig. 5）and compounds of the skeleton of abietic，pimaric，agathic acids was confirmed in soluble fraction. Hydrocarbon and car-



	R1	R2
1.	methyl	methyl
2.	methyl	ethyl
3.	methyl	fenchyl
4.	methyl	bornyl
5.	methyl	isobornyl
6.	fenchyl	fenchyl
7.	fenchyl	bornyl
8.	fenchyl	isobornyl
9.	bornyl	bornyl
10.	bornyl	isobornyl
11.	isobornyl	isobornyl

Fig. 4　Succinic acid and its exemplary esters（left）；chemical structures of monoterpenoids isolated from soluble fraction of succinite（Gough & Mills，1972；Mosini et al.，1980；Mills & White，（1984/1985）；Czechowski et al.，1996；Yamamoto et al.，2006；Wagner-Wysiecka & Ragazzi，2011）.

boxylic derivatives of the abietane and pimarane skeletons together with minor hydrocarbon series of 13，14-dialkylnorpodocarpatriens are the main diterpenoids identified in Baltic amber（Mills & White，（1984/1985）；Czechowski et al.，1996；Yamamoto et al.，2006）. Diterpene resin acids were also identified by ToF-SiMS as a useful tool to investigate succinite organic composition（Sodhi et al. ，2013，2014）.

Interestingly，it was found that monoterpenes found in succinite correspond to those which were identified in fossil kauri.

Besides succinates also bornyl，isobornyl and fenchyl esters of pimaric，isopimaric，abietic and dehydroabietic acids were also detected in Baltic amber. Exemplary monoterpenyl pimarates are shown in Fig. 5.

Sesquiterpenoids are represented by isomeric derivatives of cadinene，ledol，palustrol. To this group belong also compounds such as dihydro-*ar*-cumene，monoaromatic drimanes and calamenene（Czechowski et al.，1996；Mills & White，（1984/1985）；Yamamoto et al.，2006）（Fig. 6）.

Triterpenoids have not been detected in succinite（Mills & White，（1984/1985）；Czechows-

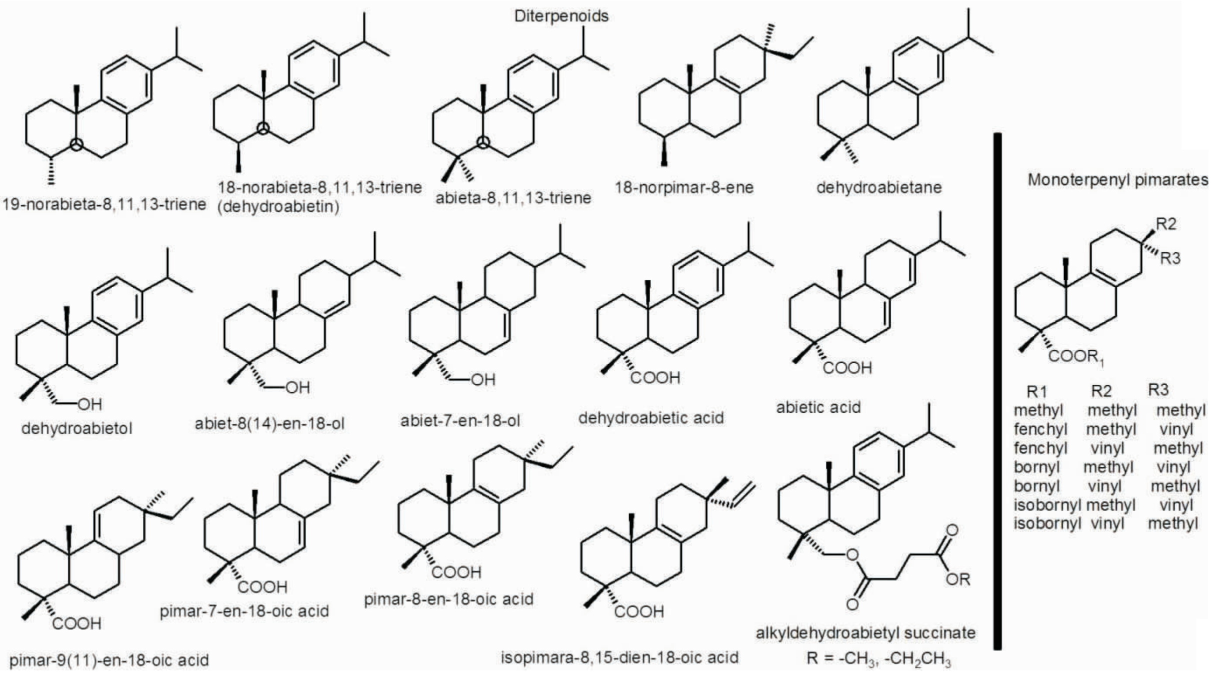


Fig. 5　Diterpenoids（left）and monoterpenyl pimarates（right）identified in succinite（Mills & White，（1984/1985）；Czechowski et al.，1996；Yamamoto et al.，2006）.

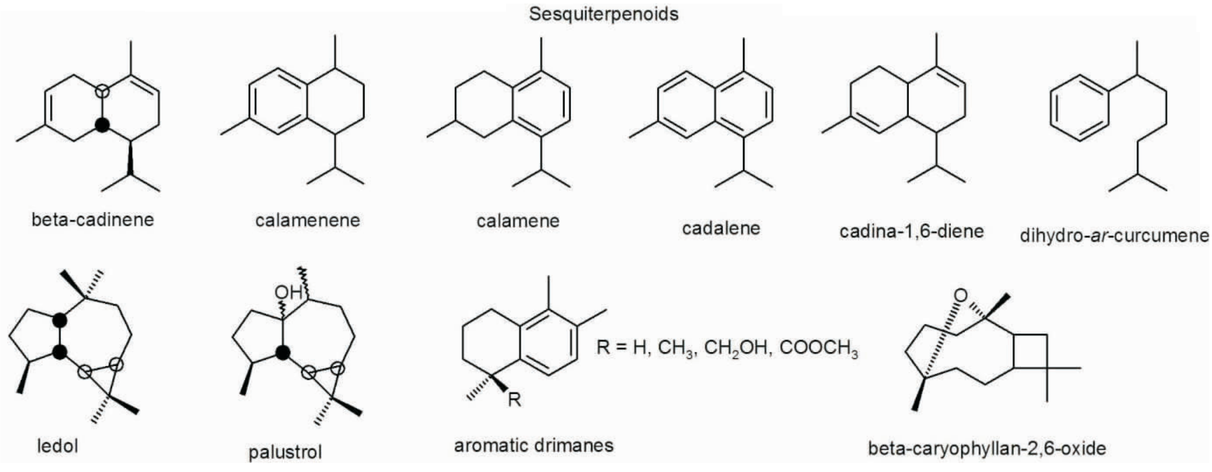


Fig. 6　Sesquiterpenoids identified in succinite（Czechowski et al.，1996；Mills & White，（1984/1985）；Yamamoto et al.，2006）

ki et al.，1996；Yamamoto et al.，2006；Wagner-Wysiecka & Ragazzi，2011). It is one of the characteristic features of succinite when comparing its chemical composition with other fossil resins e.g.，glessite (Yamamoto et al.，2006).

The above results well correlate with data sets obtained in more or less routine studies of succinite. Below，only two examples of spectroscopic methods which enable investigation of succinite in a solid state are recalled. Mid-infrared spectroscopy was the first and still is the basic instrumental tool used successfully in the identification of fossil resins of various geographical and botanical origin. It is also one of the main methods used in gemmology during classification of Baltic amber gemstones in natural，modified or pressed form. A plenty of space was devoted to infrared characterization of succinite and other natural resins with mid-infrared spectroscopy，thus here only the model mid-infrared spectrum of succinite is presented to show the correlation between the chemical composition discussed above and infrared spectral pattern of succinite (Fig. 7，left). For details see exemplary references (Beck，1964，1986；Schwochau et al.，1963；Savkevich & Szaks，1964；Matuszewska et. al. 2001；Kosmowska-Ceranowicz et al.，2012，Kosmowska-Ceranowicz，2015；Wagner-Wysiecka，2018；Wimmer & Wagner-Wysiecka，2019；Manasterski，2022) and Table 2.

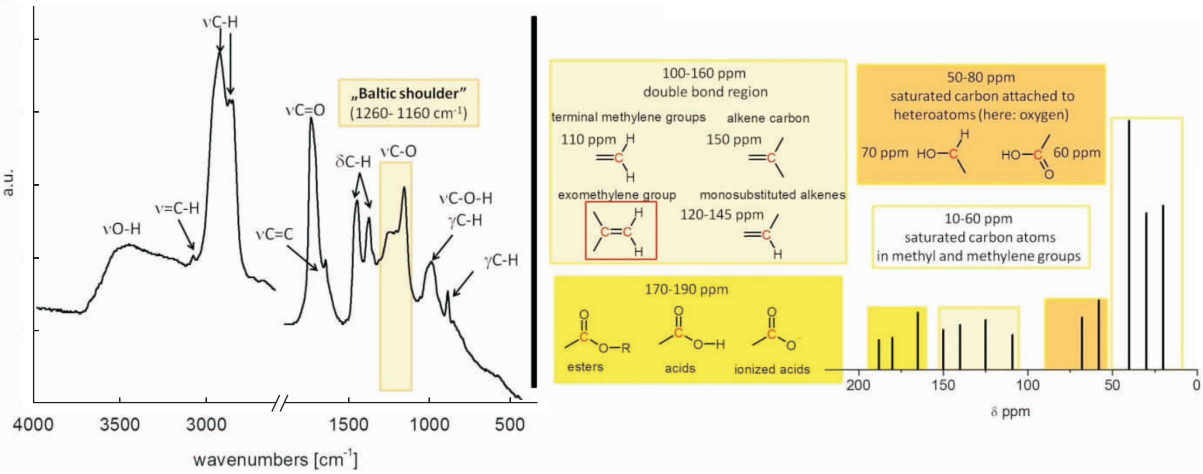


Fig. 7　Simplified and schematic presentation of the main bands in mid-infrared (left) and peaks in ^{13}C NMR solid state (right) spectra of succinite. For real spectra please see references.

Table 2　Chemical functionalities in natural succinite seen in mid-infrared spectra：the main bands and their proposed assignment.

Approximate position of band [cm^{-1}] and proposed assignment	Character of functional group
2 930 s，2 870 s－m，2 850 s－m：νC－H in methyl (－CH_3) and methylene (－CH_2－)， 1 455 m：δ_{as} －CH_3，δ_{sym} －CH_2－， 1 375 m：δ_{sym} －CH_3	Saturated C－H moieties
3 080 w：ν=C－H， 1 642 m－w(v)：alkenyl νC=C， 980* m(v)：vinyl $\gamma RHC{=}CH_2$， 888 m(v)：vinylidene $\gamma R_2C{=}CH_2$，	Unsaturated，alkenyl moieties
1 736 s：νC=O in esters 1 725－1 695*,** s：νC=O in acids Baltic shoulder：～1 260－1 160* m：νC－O in esters and carboxylic acids，νC－OH in 3 °alcohols	Oxygen containing functional groups such as esters of aliphatic acids，carboxylic acids，alcohols
3 500 m (b)：νO－H 1 020* m：νC－OH in 1 ° and 2 ° alcohols (often doublet like signal (1 020 and 980 cm^{-1})	Moieties bearing hydroxyl groups：alcohols，carboxylic acids

Relative intensity：s - strong，m - medium，w - weak，b - broad，v - various intensity. Vibrations：ν- stretching，δ- deformational in plane，γ- deformational off the plane，as-asymmetric，sym-symmetric；* region of overlapping of different functional groups，** band observed in some varieties.

Solid state ^{13}C NMR spectra registered for series of succinite samples present some main features which are the reflection of the chemical composition of this material (Lambert et al., 1988, 2012, 2015; Lambert & Frye 1982; Lambert & Poinar 2002; Martínez-Richa et al., 2000; Barone at al.,2016). The most characteristic regions in solid state ^{13}C NMR spectrum of succinite are shown schematically in Fig. 7 (right). For real spectra please see exemplary references (Lambert et al., 1988, 2012, 2015; Lambert & Frye 1982; Lambert & Poinar 2002; Martínez-Richa et al., 2000; Barone at al., 2016).

The first is resonance at ca. δ 170 ppm corresponding to carbon in carbonyl functionalities in carboxylic acids. It can be ascribed to the presence of succinic acid. The second is the spectral region between δ 100 and 160 ppm characteristic for resonances from carbon-carbon double bonds (olefinic $-C=C-$). Namely: peaks from $-C-HC=CH-C-$ are observed in the range δ 120—145 ppm, at ca. δ 110 ppm signals come from unsubstituted alkene carbon atoms $-C=CH_2-$, whereas signals coming from carbon atoms in disubstituted alkenes $>C=C-$ are seen as signals at ca. δ 150 ppm. Peaks at δ 110 and 150 ppm point out the presence of exomethylene or terminal group $>C=CH_2-$. The third part of spectral characteristic of succinite covers region between δ 10—60 ppm, where signals of carbon atoms are of the highest relative intensity. The characteristic signal region for saturated carbon atoms in methyl and unbranched methylene groups is observed at ca. δ 20 ppm. Methylene groups with adjacent branching resonate at 30 ppm. Dominant peak in ^{13}C NMR spectrum of succinite is localized at δ 40 ppm and corresponds to carbon atoms in methine and methylene groups with more adjacent branching. Signals observed in the region δ 10—60 ppm correspond to the carbon atoms in terpenoid hydrocarbons. Electron-withdrawing groups, namely oxygen functionalities in alcohols and esters shift carbon atom signal towards higher ppm values (δ 60—100 ppm). Carbon atoms next to hydroxyl groups $HO-CH_2-$ resonate near δ 70 ppm, and ca. δ 60 ppm signals coming from ester carbon atoms $-(C=O)OCH_2-$ are observed.

Direct mass spectrometry, namely laser desorption ionization (LDI-MS) can be also used for the direct measurements of solid samples of natural resins, including Baltic amber (Tonidandel et al., 2008).

Inorganic Components

In fossil resin investigation, the main efforts are focused on organic chemistry with almost forgotten contribution of inorganic components. In fact, as it can be expected, the mineral composition of succinite and other fossil resins is minor part of the total structure of these materials, but in author's opinion, in general view structure-properties can't be omitted. It must be taken into account that the presence of the inorganic components might be an effect of their accumulation at various stages of geological deposition and evolution of the material within millions of years (e.g., in the soil under formation process or/and under redeposition in marine and other environments). On the other hand microelements such as iron, copper, zinc and other are essential for all living organisms, also for plants. Their compounds are soluble both in cellular and extracellular fluids or can be present as insoluble components of tissues. Thus, it cannot be excluded that microelements were taken by plants together with nutrients analogously as it is nowadays.

Some reports on mineral composition have been published. Savkevich (1981) using emission atomic spectrometry identified and determined certain metallic elements. Among them were copper, iron, manganese, calcium, aluminum and magnesium. These and also silicon, boron, titanium and chromium were found in succinite at levels $10^{-3}\%-10^{-4}\%$ (Koziorowska, 1984). The content of inorganic components was different depending on the degree of the weathering of succinite. The highest content of inorganic components was reported for copper and iron.

Analysis of the composition of inclusion droplets in succinite also confirmed the presence of inorganic matter (Buchberger et al., 1997). In droplets, the presence of different amounts of ammonium>sodium>potassium>magnesium>calcium cations was detected. The high content of sodium is not unexpected taking into account wide abundance of this element in nature. Among determined anionic species were inorganic and organic anions such as acetates and succinates. The quantitative contribution of anions can be put in order：succinates＞nitrates＞bromides＞acetates＞chlorides＞sulfates. The composition of the droplets was compared to the composition of the natural water such as splash water from marine，brackish，lacustrine and rain water. From this comparison it can be concluded that the presence of ammonium and succinate ions is a typical in contrast to other determined ionic species. The origin of these two ions and also acetates was suggested to be resulting from the proteinous material present in muddy splash water. The other possibility is that，this ions comes from proteinous matter from the sap of the amber producing trees. It seems to be reasonable explanation when recalling the Krebs's cycle（the tricarboxylic acid cycle），where one of the product is succinate. On the other hand，the presence of ammonia and acetates can be an effect of the amino acids transformations under specific conditions. Depending on these conditions one might assume that，for example，Stickland reaction took place. It is a process that involves the coupled oxidation and reduction of amino acids to organic acids（Barker，1981）. One of the product is ammonia. For example，when glycine serves as an oxidizing agent in the Stickland reaction，it is reduced to acetate and ammonia in a complex enzymatic reaction. Acetates and ammonia are also products of lysine or ornithine transformation by anaerobic bacteria. Aspartate is transformed by anaerobic bacteria to succinate and ammonia via the fumarate reductase system. Ammonia formation is also a result of the thermal degradation of amino acids（Maillard reaction）- deamination of amino acids（Sohn & Ho，1995）. However，in case of succinite，this process seems hardly to be possible as it occurs under high temperatures. But hypothetically the reaction analogous to Maillard reaction cannot be excluded，especially that we still in fact do not know sufficiently enough about the chemical environment of the world in times when succinite was formed.

Besides the carbon，hydrogen and oxygen，which can be determined by elemental analysis also sulfur is an element which is detected in succinite. The percentage of this element is different for succinite of different varieties and geological location. Its content can vary in range 0.30％－4.89％（Kosmowska-Ceranowicz et al.，1996）and is higher for succinite from Neogene sediments of the Carpathian Foredeep（3％－5％）than for succinite from other deposits（0.3％－0.5％）. The presence of sulfur is explained by some authors as a component which comes from water containing hydrogen sulfide，which is penetrating the succinite. Sulfur in succinite occurs in a bound form. Namely，it can be detected as pyrite（FeS_2）（Garty et al.，1982；Flamini et al.，1975），also in a form of marcasite（Kowalewska & Szwedo，2009）. Among other salts calcium sulfate and carbonate and also sodium chloride as halite were detected as inorganic inclusions in the Baltic amber（Flamini et al.，1975）.

The content of sulfur compounds，precisely iron sulfur connections-can give some light and allow to formulate additional hypotheses about the environment of Baltic amber formation and support the presence（or involvement?）of bacterial organisms. It is visualized in Fig. 8 by diagrammatic representation of pyrite formation（Berner，1984）.

Inclusions and the presence of the mineral matter in succinite could be also an effect of their absorption by resin flowing along tree at the early stage of formation. It could be also a result of the incorporation into fluid resin by means of atmospheric agents or by insect paws. Highly probable is also permeation from mineralized solutions into cracks and pore space of fossilized resins.

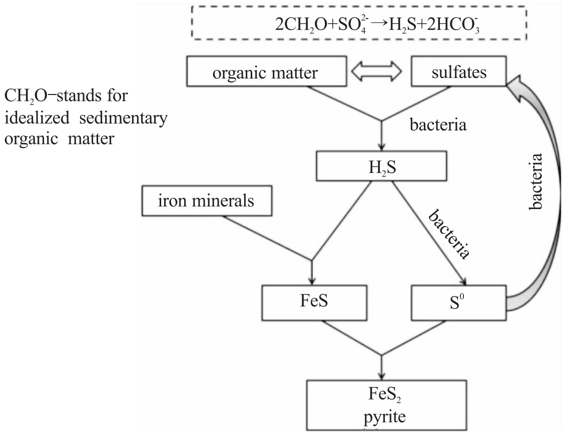


Fig. 8 Diagrammatic representation of the overall process of sedimentary pyrite formation（after Berner in：Berner，1984）.

SOME RELATIONSHIPS：STRUCTURE/CHEMICAL COMPOSITION——PROPERTIES

Succinite as Supramolecular Structure

All mentioned（but probably also all of these which are not mentioned because of not being investigated enough）organic and inorganic components are responsible for unique properties of succinite. Amorphous nature of Baltic amber is well known.

Microscopic techniques are used for gemstones for determining the factors important from gemological point（jewelry and decorative stones）of view such as the shape，size and the distribution of the air bubbles（micrometer-sized voids），to trace microfractures，which are among the others responsible for transparency and color. Besides optical microscopy also more advanced optical methods are used to investigate the nature of materials，including gemstones，such as electron scanning microscopy（Stockton & Manson，1981）. Scanning electron microscopy allowed to determine the particle size distribution in succinite. The minimal size was estimated at 450 nm（Gold，1999）. Moreover，microscopic investigations of several samples of succinite of various provenance shown supramolecular structure composed of tens to first few hundreds of nanometers in size of diversified shapes（Golubev et al.，2011）. Perfectly isolated globules as well as poorly shaped particles were found in succinite depending on its variety. Interestingly such structures were not observed in gedanite which is often found as accessory succinite resin. Surface analysis of the succinite with atomic force microscopy（AFM）revealed the presence of the complex structure with humps and hollows with directional orientation of bubbles and microfractures. Globular elements of diverse size and shapes are dominating. The size of the found drop-like and ellipsoidal formations range from 50 to 140 nm with longitudinal and transversal sizes of 110 and 70 nm. Globule-like particles were found to form aggregates of various degree of molecular organization. Well organized areas are formed by inorganic mineral components in a form of fringes up to 10 nm length. AFM imaging proved the chemical and structural homogeneity of succinite and together with the amorphous nature of the material supports that succinite can，indeed，be regarded as a polymeric network（Barletta & Wandelt，2011）.

Supramolecular structure of the fossil resins can be an explanation of their properties such as viscosity and fragility. The globular structure is ascribed to viscosity，like in case of succinite and rumanite（the last is considered as thermally alerted succinite）. Polymers both with a loose packing structure and with supramolecular assemblies are more flexible and can elastically distort due to the mobility of the structural elements. Materials with close packing of macromolecules have decreased ability to deformation，increased fragility，and approaching to the characteristic of glasses（Rostiashvili et al.，1987 in Golublev，2012）. Thermal properties of a succinite material which undergoes thermal transformation at relatively high temperature can also reflect its supramolecular nature（Golubev，2012）. Thermal properties of succinite are well known property used in gem processing（including pressing）. At higher temperature intermolecular interactions change. Then self-organized structure is destroyed and leads to liquid-like behavior. The phase transition solid-liquid is to some degree reversible for succinite in defined range of temperatures. It is characteristic feature of supramolecular polymers（de Greef，2008），thus succinite to large degree can be considered as one of them，together with other naturally occurring polymers of this type，like proteins for example. It is worth to mention here，that the first supramolecular polymers were obtained intentionally by Lehn J. M.（Fouquey et al.，1990）Nobel Prize awarded scientist-together with Pedersen Ch. and Cram D. for their achievements in supramolecular chemistry.

Supramolecular polymer is three-dimensional network of cross-linked macromolecules connected by non-covalent bonds. In polymeric network low molecular weight organic compounds which does not polymerize are trapped physically. It means that it is the assembly of continuous noncovalent bonds of unit molecules（Brunsveld et al.，2001；De Greef et al.，2009）. One of the crucial interactions in supramolecular systems（both natural and artificial）influencing their properties are hydrogen bonds. In case of succinite the multiple hydrogen bonded network is relatively easily to form, because of the presence of oxygen bearing structures such as carboxylic acid and esters. Acids can play as donor of hydrogen bonding, whereas carbonyl groups can be regarded as its acceptors. Alcohols which presence was confirmed in succinite can be also engaged in the formation of the hydrogen bonded network of succinite. Besides hydrogen bonds also other non-covalent interactions can play role in the unique structure of succinite. The presence of polar oxygen functionalities make it possible ionic interactions to occur: such as ion-ion, ion-dipol, dipol-dipol. If we have in mind the presence of inorganic components, these interactions can be treated as more than possible. Obviously in such complex chemical environment as in succinite, non-covalent interactions of other type such as cation-π, anion-π, van der Waals interactions are possible. The interactions which result in supramolecular structure of succinite (Fig. 9) are a sum of the all possible non-covalent interactions that realized complementarity, degree of preorganization, additivity and cooperativity factors.

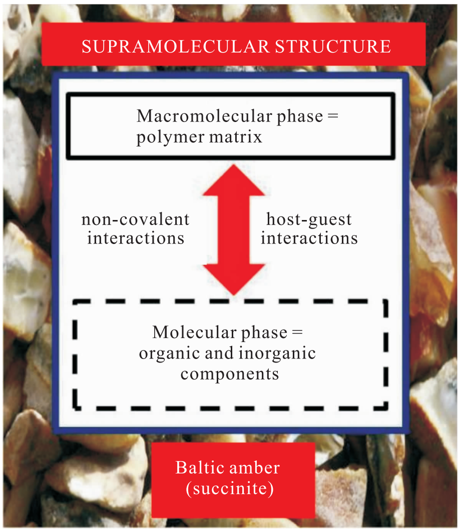


Fig. 9 Diagrammatic presentation of the supramolecular structure of succinite.

Color and Transparency

Succinite, the Baltic amber admires both "ordinary" people as well as artists and scientist of various professions. Its extraordinary beauty attracts attention and provokes asking questions, what is its cause, why it is as it is. However, these are questions which, in the light of the not fully understood physicochemical structure of amber, cannot always be unequivocally answered. And, in turn, this secret of millions of years that succinite hides makes it an even more unusual material.

Perhaps categorizing amber just as a material does not fully harmonize with the social perception of amber, but only such a perspective, material, allows us to seek answers to bothering questions about the beauty of amber.

Material dependencies are important not only from the cognitive point of view, but also have a practical aspect, e. g. in gemology. Here, the issues of identifying the material as well as determining its processing from the moment of extraction to the moment when it becomes a gemstone are extremely important. The knowledge about the structure of natural amber and its changes taking place under the conditions of material modification gives the possibility to choose appropriate for the particular case research and identification techniques.

Below some issues that are often addressed on various more or less specialized forums (not only scientific) regarding the properties of succinite are given. The following considerations-attempts to explain-are in well-established statements, sometimes hypotheses, which should be treated as a field for a broader debate about what we know and what we still do not know about Baltic amber.

One of the most frequently question is why succinite occurs in so many varieties differing in color and its shades and degree of transparency (cf. Fig. 10 and Fig. 11).

To answer this question the theory of color in few words must be recall. Color is the observable result of the interaction of electromagnetic radiation with matter. The final effect which we observe as a color can be an effect of various phenomena. In general, there are fifteen specific causes of color arising from various physical and chemical mechanisms (cf. Nassau, 1983). When considering the passing of light through the semi-transparent material some part of the radiation can be transmitted. Part of the light can be reflected. If the surface is smooth then the specular (mirror-like) reflection occurs. If the surface has some roughness-the diffuse reflection is observed. The diffused reflected light reveals the color of the object more strongly than specular reflected light. When a surface is extremely

Fig. 10 Examples of primary varieties of natural succinite: (a) transparent; (b) translucent; (c) opaque-yellow; (d) opaque-white; (e) succinite with organic impurities. Photos by Małgorzata Siudak-courtesy, International Amber Association.

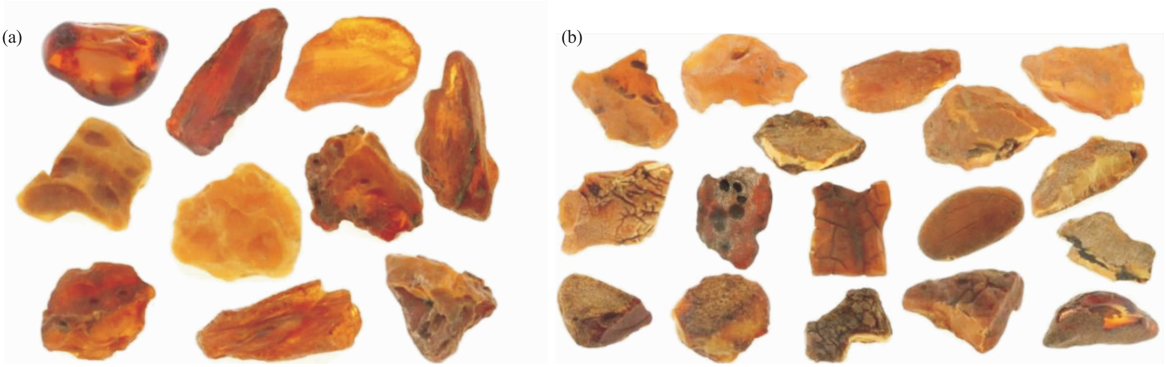


Fig. 11 Examples of secondary varieties of natural succinite: (a) color changes and cracks; (b) with various types of crust. Photos by Małgorzata Siudak-courtesy, International Amber Association.

rough then the light is almost completely scattered at air-particle interfaces. No penetration occurs and as result no color is observed. A good example from everyday life is white color of paper resulting from the light scattering at fibers and fillers composing it or the white foam observed upon a glass of the colored liquids such as for example beer or cola-type drinks. The presence of any component which is able to fill the free spaces in material causes the loss of the air-particle interferences. Objects appear colored also because the part of the light can be absorbed. Some of the absorbed light can be reemitted at lower energy-then fluorescence can be observed. Fluorescence can also add to the color. Another phenomena is light deflection, when it enters or leaves a transparent material. The deflection of light depends on the difference in refractive index between two media. If there is no difference then material can seem to be invisible (e.g. glass ball immersed in a liquid of the respective refractive index). The deflection of light is also dependent on the angle of incidence.

Succinite can be found in different varieties such as completely transparent light yellow pieces, different shades of yellow to dark yellow. Completely opaque varieties are also well known. Among the richness of colors red-brown varieties are also common. Taking into account the complex structure of succinite and the above simplified deliberations about light/matter interactions it seems to be obvious that all of them can contribute to the color of succinite in different degree. The different tones of various colors of succinite are result of the physical phenomena such as：light scattering，refraction，deflection，absorption. The cause of color often cannot be deduced directly from knowing only the chemical composition. These effects are changing within the time for succinite as organic material undergoes continuous transformations upon interaction with the surrounding environment（air as oxidant，the presence of the moisture，exposition to ultraviolet and visible light，etc.）.

The degree of transparency/opacity of succinite was the subject of the early chemical investigations done by O. Helm（Helm，1877）. Relatively rare is a variety characterizing with a bluish or green(-ish) shade. The nature of this fascinating color was the subject of debates. One of the theories is that，that for this characteristic appearance-observed in opaque，milky varieties-inclusions of inorganic matter such as marcasite are responsible. Sometimes it is connected with the residual presence of the blue-greenish in color glauconite. Sometimes also greenish shade of succinite is observed. The above colors are the most probably pseudochromatic. It can be an effect of the scattering of light of the given energy by particles of the defined size. Depending on the wavelength of the electromagnetic radiation and the size of the particles diverse colors of succinite can be observed，analogously to well-known effect of the light scattering resulting in a blue sky or red sun sets. Then the observed white color of succinite in chalky or bone varieties is an effect of the light scattering on the particles of the larger sizes. Other phenomena as it was mentioned earlier such as light reflection contribute to the variety of the colors of succinite.

The transparency of succinite is connected with its physical structure and depends on the number and type，size and regularity of fractures and included matter. According to literature reports the transparency is dependent，among the others，on the number of small bubbles in the matrix. The bubbles can be combined via open pore system or not. It was postulated that in the cloudy amber the bubbles are closed and not connected through the pores（Czechowski et al.，1996）. Transparent succinite does not contain any included matter or the inclusions are randomly spread in the structure. The transparency/opacity depends on the amount and the size of the particles. The more and the smaller particles（gas bubbles packed tightly）the more light is scattered from the surface without penetrating the material.

In succinite the presence of gaseous matter is connected with processes of its formation and the transformations of more or less foamy fresh resin. Succinite varies in degree of the transparency depending on the gas bubbles organization in the internal structure. Katinas（1971 in Matuszewska 2010，p. 29）reported that transparency of succinite depends on the number and size of gas bubbles. Transparent material-no clusters- there are single gas bubbles，in translucent opacity is caused by gas clusters. For opaque yellow varieties（range of shades from yellow to beige）up to 600－2 500/ mm^2 gas bubbles of the diameter 0.002 5－0.05 mm are observed. The white color of succinite is an effect of the light interactions with material in which the presence of gaseous matter is found as high as up to 900 000/mm^2 with bubble diameter 0.000 8－0.001 mm. Similar in trend relationship between transparency/opacity of amber was found by Wang & Wang（2016）.

The fascinating cloudy amber is probably an effect associated with the process of traveling of a fresh resin on a moist surface（e. g. tree bark）. The more air and moisture is retained during resin solidification，the higher the density of the resin and the rate of phase transformation. The degree of the transparency can be also connected with the presence of inorganic compounds and amount of water. The presence of last might affect solubility of organic compounds entrapped in polymer matrix which result in change in transparency（Wagner-Wysiecka，2018）. The influence of water as a component influencing the structure and finally the physical appearance of succinite can be well proved when comparing the opacity and color of succinite after the hydrothermal treatment of transparent material（Wang et al.，2019）.

As it was shown in relatively simple experiments，namely thin layer chromatography for analyzing the composition of ethanol soluble fraction of succinite the composition of the different varieties of succinite can vary depending on the degree of the transparency and specific gravity (Lebez, 1968; Kucharska & Kwiatkowski, 1979; Matuszewska, 2000; Matuszewska & John, 2004). All extracts obtained from succinite are colored liquids: dark yellow/brownish. Having in mind the organic chemistry of the colored compounds and looking at the structures of the components of the molecular phase of succinite (Fig. 4— Fig. 6) it is clearly seen that the presence of the certain compounds can affect the observed color of this material. The essential chromophore unit (defined as electron withdrawing groups) in succinite seems to be the carbonyl group (>C=O), whereas auxochromes are hydroxyl moieties. The presence of last in the skeleton of the chromogenic molecule shifts absorption maximum bathochromically. Jointly with the systems of the conjugated double bonds the above structural features might contribute to the colored nature of succinite. For example, abietic acid is brown and some of the terepenes are yellow in color. The ethanol extract of succinite shows bands at 380, 400 nm and 420 nm (deflection) in excitation spectrum (Vogler, 2018) which corresponds to yellow color of solution. The evidence for the role of the carbonyl group as chromophore component finds confirmation in infrared spectra of succinite. The band at 1 700—1 740 cm^{-1} is attributed to stretching vibrations of carbonyl group in esters and acids. The increase of the relative intensity of this band is well observable for thermally modified succinite of changed color (cf. Fig. 12). Similar trend was observed for the blood amber from Myanmar (Dong, 2021).

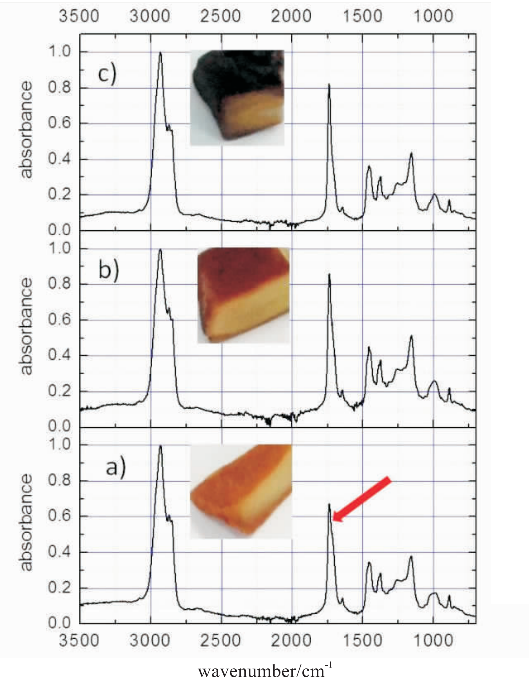


Fig. 12 The comparison of the normalized FTIR spectra (ATR) of (a) natural, (b) and (c) thermally modified succinite. Arrow points the stretching vibrations of carbonyl group (Wagner-Wysiecka, unpublished results).

The color and degree of transparency of succinite gemstones are well known from ages to be possible to change by temperature treatment. It is observed by naked eye as the change of the physical appearance like the color change and the occurrence of more or less significant (dependent on the conditions) cracks (well seen after cooling). The processes which occur under thermal treatment (or autoclaving of succinite, but in fact, also other resinous materials) are complicated and complex. The most expected and obvious consequence of the action of the elevated temperature must be release of the volatile components of succinite. The loss of the low molecular mass fraction within time during weathering/maturation processes was confirmed by MALDI-TOF-MS studies (Zhang & Shen, 2022). It is also an evidence that not all components of succinite constitute the polymer network. How does this treatment affect the structure? Experiments where succinite was cut into jagged pieces and then was subjected to heating have shown the change of edges to rounded ones (Gold et al., 1999). It can point out that the volatile components entrapped in succinite matter affect the surface tension. The cracks often observed in modified Baltic amber are evident for the thermal transformations. When the material is glassed then stress forces cause the appearance of the mentioned cracks. In this point it is worth to pay attention on the term "melting". Baltic amber and other fossil resins are amorphous thus the "softening temperature" or "glass transition temperature" should be used instead of "melting point" or "melting temperature". For succinite the range of temperature of transformations is different depending on its variety. However, it can be said that softening temperature range is between 125—200 ℃ (Matuszewska, 2010). At higher temperature, namely 330—380 ℃ the transition to liquid state is observed and the decomposition of material can occur at 370—380 ℃. The above thermal properties, as mentioned in earlier part of this article, are used in processing of succinite, when pieces or even dust of material is subjected to temperature treatment under the conditions of softening to obtain pressed amber.

Under thermal treatment besides evolving of the volatile organic compounds and water, acting as solvents at the formation stage of succinite, also other processes occur. One of them can be reactions leading to the increase of the saturation degree i. e. reactions with involvement of double bonds (polymerization and/or polycondensation). This is well seen in infrared spectra of treated succinite as lowering or even complete disappearing of the bands at 3 080, 1 645 and 888 cm^{-1} (Wagner-Wysiecka, 2018; Wang et al., 2017). Analogous processes occur also in Nature without thermal activation of succinite. The rate of such natural transformations is much lower and is difficult to compare in detail with laboratory conditions, since the presence of moisture, oxygen and electromagnetic radiation affect not only the rate, but also the course of the succinite transformations. Usually for matured succinite deeper colors are observed (cf. Fig. 11). White-yellow or yellow pieces can turn into orange-like, beige, brown and even dark cherry which appears black at first glance. These color changes can be connected for example with oxidation processes, also activated by UV radiation and probably catalyzed by inorganic components, such as transformations of hydroxyl groups in alcohols to carbonyl compounds or aromatization. During weathering one of the processes is also ester hydrolysis and the removal of some of the components which are soluble in contact with the surrounding environment, e. g. water soluble compounds. It is quite well confirmed by the analysis of the infrared spectra pattern of "fresh" and weathered succinite (Czechowski et al., 1996; Wagner-Wysiecka, 2018).

Besides color, the above transformations affect also other physical properties, like hardness or refractive index. The last usually increases upon thermal treatment (Wang et al., 2017). The thermal treatment under defined conditions also increases the transparency of the material.

Fluorescence

The well-known property of the succinite (but also other resins) is fluorescence (photoluminescence) observed under ultraviolet light illumination for both bulk material and solvent extracts (Czechowski et al., 1996; Wang et al., 2017; Zhang, et al., 2020; Matuszewska & Czaja, 2002; Mysiura et al., 2017; Vogler, 2018). The color of fluorescence varies depending on the variety of succinite and it could be: yellowish-white, yellow or bluish. The photoluminescence when succinite is illuminated with UV light is shown in Fig. 13.

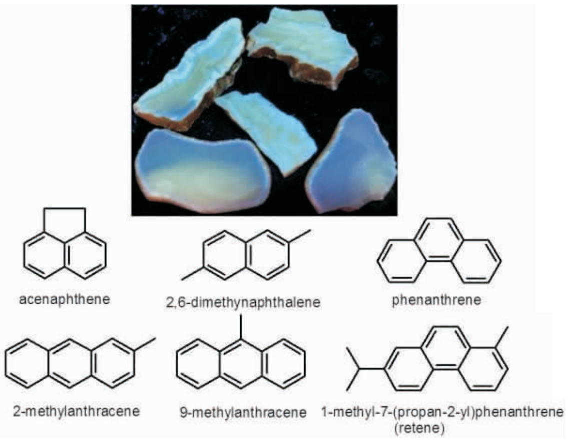


Fig. 13　Top: long-wave fluorescence (254 nm) of succinite (photo: E. Wagner-Wysiecka). Bottom: examples of luminophores identified in succinite.

The observable fluorescence of fossil resins is connected with their chemical composition. It is an effect of the presence of organic compounds (luminophores) of easily excited π electrons in a system of double bonds and aromatic derivatives, including also these with oxygen functionalities. Examples of organic compounds identified in extract of succinite which are responsible for its fluorescence are shown in Fig. 13. Interestingly the intensity of fluorescence decreases or is completely quenched for treated succinite (Wang et al., 2017; Park & Lim, 2012). The explanation might be the loss of the low molecular compounds upon treatment. On the other hand photoluminescence is known to high sensitivity. Thus the intensity of fluorescence can be affected by several structural factors, including intermolecular forces, such as hydrogen bond, π-interactions. As it was stated above the supramolecular structure of succinite is affected by the external conditions, thus interactions upon treatment can be different that in untreated material. They can include the loss of the planarity of the particular systems. The chemical environment upon treatment may also change the affinity towards formation of excimers or exciplexes.

CONCLUSIONS

The interdisciplinary analyses of the succinite have revealed its sophisticated nature. The complexity of the structure is a consequence of biogeochemical transformation during diagenesis and also of the secondary processes occurring when succinite was deposited in environment of various natural conditions including temperature, access of humidity, oxygen and UV-Vis light. Succinite still continuously undergoes transformations thus we can constantly observe their unique changes. In the jewelry industry, attempts are made to imitate these natural processes by material modifications under various temperature conditions (as well as pressure and temperature conditions) in the presence/absence of additives, e.g. noble gases, water etc.

All of the visually observed features of succinite (both natural gemstones and those that have been modified) are a result of the sophisticated physical and chemical transformations of the organic-inorganic matter. Understanding of these is a key in differentiating between natural resins and those which are reworked in various increasingly sophisticated modification methods of gemstones processing due to expectations of the market and also caused by the deficiencies of the raw material of the demanded properties.

An indirect proof of the complex structure of succinite is the necessity to use many analytical methods for its analysis. However, a lot work has been done to understand the nature of succinite so far, still many questions regarding the relationship between structure and properties remain unanswered. Succinite, which we have in our hands today, both as a natural and as a treated material, is therefore an example of a masterpiece of nature, which, according to the author's knowledge, has not yet found a worthy imitator among synthetic materials.

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