The Chemistry of Amber – Facts, Findings and Opinions

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(With 8 figures and 2 tables)

Abstract

Realizing the fact that many important modern studies related to chemistry of ambers have been published in journals and books not readily available to many earth scientists it seems worth to give a comprehensive overview about this topic including also the connections to mineralogy, palaeobotany, and related fields of study. Our intention has been to achieve a readable summary of the present state of knowledge rather than a compilation of too many details and data being probably rather confusing for the non-specialist. An extended list of references given should be understood as a suggestion for further reading and studies.

Keywords: Amber, resinite, organic minerals, chemistry, fossilization.

Zusammenfassung

In Anbetracht der Tatsache, dass viele wichtige moderne Untersuchungen zur Chemie des Bernsteins in Zeitschriften und Büchern publiziert wurden, die für viele Geowissenschafter schwer zugängig sind, erschien es nützlich, einen zusammenfassenden Überblick über dieses Thema inklusive seiner Querbezüge zur Mineralogie, Paläobotanik und anderen Forschungsbereichen zu bieten. Unsere Absicht war es, eine leserliche Zusammenschau des gegenwärtigen Wissensstandes zu bieten und nicht eine Anhäufung zu vieler Einzelheiten und Daten zu bringen, die für den Nicht-Spezialisten wahrscheinlich nur verwirrend wären. Eine ausführliche Literaturliste soll daher als eine Anregung zu weiterer Lektüre bzw. eigenen Studien verstanden werden.

Schlüsselwörter: Bernstein, Resinit, organische Mineralien, Chemie, Fossilisation.

Introduction

'Amber' as well as its German equivalent 'Bernstein' – and corresponding terms in many other languages – are used in a rather confusing way for fossil resins which may differ considerably not only in respect to their geological age, botanical affinities, and chemistry but also in respect to their properties. Amber may designate the mineral 'succinite' in the strict sense as introduced by BREITHAUPT in 1820 (fide BECK 1999) and still used by mineralogists nowadays, 'amber' has, however, been also used as a collective term for any fossil resin found in the Baltic area, amber has, moreover, been used as a term summarizing any fossil resin, whatever its geological age, its botanical or mineralogical affiliations may be (see also below).

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The following overview will focus not only on succinite, other 'ambers' will be included not only for sake of comparison but also to discuss their low-molecular-mass compounds ('LMM') as possible indicators for botanical affinities and as characteristics of various mineral species. A remarkable variety of mineral names have been applied – in a more or less official way – to different finds of 'ambers': gedanite, gedano-succinite, glessite, stantienite, beckerite, schraufite, rumanite, simetite, plaffeite,allingite, siegburgite, schlierseerite, walchowite, scheibeite, birmite/burmite, cedarite, ambrite – just to give a few examples. Revisions and characterizations of many of these single mineral species are still largely needed. One of the prerequisites in performing any such investigation is sometimes overlooked however: the availability of 'type material', i.e. the material which had been the basis for the first description, by which the new mineral name had been introduced into scientific literature. To follow such principles would be helpful and contribute essentially to clarify a number of questions. Nevertheless it is in many cases hopeless to locate the old 'type materials' in any accessible public collection. In many cases – to follow the terminology as used in biological taxonomy – one must be content to get something representing 'topotypes', i.e. material from same strata and from about the same area. Realizing that different organic minerals may occur at the same locality however one must be aware of the fact that many such studies of 'secondary finds' may have only a preliminary character.

Another item of great importance is the fact that only a limited number of ambers is available in considerable amounts making extensive chemical studies possible at all. Some fossil resins occur only in tiny amounts, being perhaps only sufficient for one infrared spectrum or for one sample for pyrolysis gas chromatography.

Summarizing all these circumstances one must be aware of the fact that inevitably results have to be summarized which are not always based on really reliable finds and that comparisons are also sometimes insufficient because only a limited number of methods could be applied. Any closer discussion of various methods, their possibilities, advantages and disadvantages had to be excluded from this publication for sake of shortness. For a summarizing overview representing a number of modern methods applied in amber chemistry see GOLLOCH & LÜHR (2000).

Fossil resins, amber, copal – a definition ?

To give a really satisfactory definition of any of these terms is far from being easy: each of them is at any case a typical collective term usually not precisely defined. 'Resin' has been used for numerous substances produced by plants in the form of saps or exudates. In a rather general way any sticky plant exudate has been called 'resin' regardless of its chemical characteristics. Sometimes this term has been applied to substances mainly insoluble in water and hardening after exposure to air (LANGENHEIM 2003: 23). Definitions for the term 'resin' as given by chemists are rather similar indeed (e.g. NEUMÜLLER 1979-1988): 'Collective term for a group of solid or semisolid organic substances, showing differences in respect to their chemistry but similarities in respect to a number of physical properties'.

The term 'amber' ('Bernstein') is also mostly regarded as a collective term including solidified resins of various origin, composition, colour, etc. Ambers are at any case the

result of fossilization, a process beginning with polymerisation yielding often a cross-linked copolymer subject to progressive changes influenced by age and burial history ('maturation'). Not all resins fossilize, some are not preserved at all, others represent sometimes a mixture of nonpolymerizable terpenoids however.

A number of terms have been in use for the early stages of fossilization of resins: beginning with 'modern or recent resins', 'ancient resins', and 'subfossil resins', yielding finally 'fossil resins', 'ambers' or 'resinites', the latter ones with a minimum age of 40.000 years (ANDERSON 1997). For ancient and subfossil resins the term 'copal' has been used by many authors. This term – derived from 'copalli' in Nahuatl language by the Spanish – referring originally to resins used by the Aztecs and Mayas (LANGENHEIM 2003: 392) has finally been used for all unfossilized resins worldwide (e.g. POINAR 1992 – and many others before him !). Following POINAR (1992) resins may preserve the qualities characterizing copal as long as 3 or 4 millions of years even. Any hope to define 'copal' and 'amber' on the basis of the geological age must remain problematical therefore.

The most useful criteria to judge whether some fossilized resin is copal or amber are obviously offered by physical characteristics like solubility, hardness and melting point (see POINAR 1992).

Some historical aspects

The first remark referring to a chemical constituent in succinite has been reported by the Arab physician and philosopher ʿAlī ibn Sīna (= AVICENNA, 980 (?) – 1037). He is quoted by SCHMID (1931) to have written: 'in succino odoratum camphorae vim inesse'. Relying on the odour only, it is very probable that he refers not to true camphor, bur rather to borneol (so-called 'Borneo camphor', see fig.1), the corresponding alcohol (BECK 1999). Among the early steps towards the development of modern organic chemistry some textbooks (e.g. NEUMÜLLER 1979 – 1988) refer to the isolation of succinic acid from amber in 1546 (sometimes also the years1544 or 1550 are mentioned; see KOPP, 1847) by AGRICOLA (1494 – 1555), the famous 'father of mineralogy'. Generally it is reported that he isolated succinic acid (fig. 1) by means of dry distillation of amber – such a procedure should, however, yield its anhydride only (ROTTLÄNDER 1983: 571). AGRICOLA himself believed to have isolated a salt ('flores succini') until Lémery recognized it as an acid in 1675 (BECK 1999). At any case this was obviously the only one organic acid (besides acetic acid) which had become available as early (16th/17th century).The very first attempts of a fractionation by extraction of succinite with ether and alcohol in 1828/29 were made by the famous Swedish chemist Johann Jakob Freiherr von BERZELIUS (1779 – 1848), being well-known to have established the basic principles of inorganic chemistry in 19th century.

The temptation to tell a large part of the history of organic chemistry in connection with amber studies is great in fact. In the following only a very few important contributions on the way towards our present understanding of amber chemistry will be given however. The quantitative fractionation of succinite by application of extractions has been finally extended to a series of solvent extractions by the Swiss resin chemist Alexander Tschirch and his co-workers (e.g. TSCHIRCH & AWENG 1894). In this way they isolated
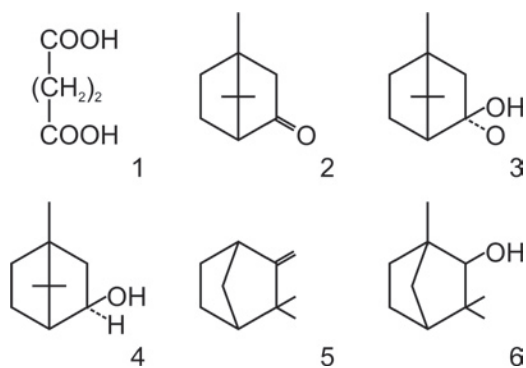
Fig.1: Some examples of 'LMM' compounds found in ambers: (1) succinic acid, (2) camphor, (3) borneol, (4) isoborneol, (5) camphene, (6) fenchol.

four fractions, which they believed to be pure compounds, two of them were regarded as resin acids – 'succino-abietic acid' and 'succino-silvic acid' respectively. On the basis of these investigations Leopold SCHMID at the University of Vienna developed a rather sophisticated scheme of fractionations, applying in addition extractions with petroleum ether, ammonium carbonate, sodium carbonate, and precipitation with methanol. In this way he and his co-workers yielded a separation into thirteen different fractions. In the last publication of this series of studies the authors realized that under their conditions of treating amber samples (for example: treating amber samples with boiling ethanol for months !) isomerizations and degradations had occurred (SCHMID & VOGL 1940). An important truly 'innovative' feature in the studies by Schmid and co-workers is the application of selenium dehydrogenation to most of their fractions, as developed already by DIELS et al. (1927) as a powerful tool of structure determination of compounds with cyclic structures. This reaction yields aromatic hydrocarbons which can be rather easily identified by standard methods of 'classical' analytical chemistry as being usually applied in these years. As pointed out by BECK (1999), they missed, however, the opportunity to draw the most important conclusion available on the basis of their results: all the insoluble fractions (about 70 % of the total succinite sample !) yielded dehydrogenation products being known to arise from resin acids with a bicyclic labdane skeleton (BECK 1999: fig. 5). For only one of the soluble fractions the carbon skeleton of abietic acid (the typical resin acid of the genus *Pinus*, fig. 2) could be found. Thus – obviously without realizing it ! – SCHMID and co-workers had been very close to identify the insoluble fraction of succinite (sometimes called 'succinin') as a product of the polymerisation of labdane units, a standpoint now generally accepted for this sort of ambers. This fact has become of great importance in the modern (chemical) classification of ambers: 'Resinites Class I' summarizing all fossil resins with a polylabdanoid structure (fig. 3).

As pointed out by BECK (1999: 41), all these results quoted above illustrate also the limits of classical chemical methods in the study of complex organic mixtures. It is also worth mentioning that Rottländer (pers. commun., 1985) repeated carefully the studies performed by Leopold Schmid and confirmed by his own investigations Schmid's results completely. Nevertheless Rottländer had also believed for a number of years at least in abietic acid as the building unit of succinite (ROTTLÄNDER 1969, 1970a, 1970b). His theory in respect to the structure of the 'polymer backbone' of succinite had some sort of fascination at its time however: on the basis of careful model experiments he sug-

gested a dimerization of abietic acid occurring during diagenesis, yielding a product (resulting after reaction of diabietic acid with water) representing a bifunctional molecule which was believed to undergo (self)-polycondensation. Succinite would – according to Rottländer's model – thus be a polyester. To confirm his theory Rottländer applied among others infrared spectroscopy. His studies deserve at any case great interest, first, because he suggested a modern structural model for the polymer fraction of succinite ('succinin') and second, because of his experimental approach towards a closer understanding of the processes transforming resin acids into amber.

He was by far not the very first to introduce infrared spectroscopy into the studies of ambers. The very first who published an infrared spectrum of succinite was probably Hummel (1958). Beginning with the sixties this method had been applied to numerous types of ambers by a rapidly increasing number of authors (e.g.: Beck et al. 1964, 1965, Sakvevich (1970) however. Such studies could be performed in a rather empirical manner, utilizing the spectra like 'fingerprints' of amber samples. The studies were performed usually for one of the following reasons:

(1) provenance of (archaeological) amber samples (e.g. Beck et al. 1964)
(2) establishment of botanical affinities (e.g. Langenheim 1969; Langenheim & Beck 1965, 1968)
(3) identification of single mineral species of ambers.

Besides the more common way of applying infrared spectroscopy like a 'fingerprinting'- method the application of pattern-recognition programs was shown to be a valuable extension of the possibilities offered by such spectroscopical studies (Beck et al. 1971). Nevertheless it must be stated that infrared spectroscopy is only 'one method among many others', but it offers also – in addition to some rather practical aspects like characterization of the total sample, small sample amount required, time-saving, rather fast method of characterization – in many cases the only one source of information. This is true especially for tiny or even unique samples in the case of archaeological finds and rare amber minerals.

A considerable increase of information about the chemistry of amber has finally been achieved by introducing gas liquid chromatography ('GLC') into amber chemistry. Especially its modern variety in combination with mass spectroscopy ('GLC/MS', usually performed by means of a 'mass sensitive detector' = MSD) yielded an incredible amount of data especially in respect to the compounds contained in various soluble fractions. In this connection studies by Gough & Mills (1972) have to be mentioned first. Their investigations included also the insoluble part of succinite, for which they pointed out a striking similarity with the polymer from kauri resin (from *Agathis australis*), proposing finally for the polymer part of amber a structure of a co-polymer of communic acid and communol (its corresponding alcohol) – 'though more extensively cross-linked and with the hydroxyl groups partly acylated with succinic acid'. They suggested an 'overall composition high in labdane units' – referring among others also to the results of selenium dehydrogenations as performed by Leopold Schmid and co-workers (see above).

A number of scientists respectively working groups engaged in chemical studies of amber have then successfully applied GLS/MS under various aspects. Only a few examples will be given here: Nicoletti (1975) identified a number of low molecular
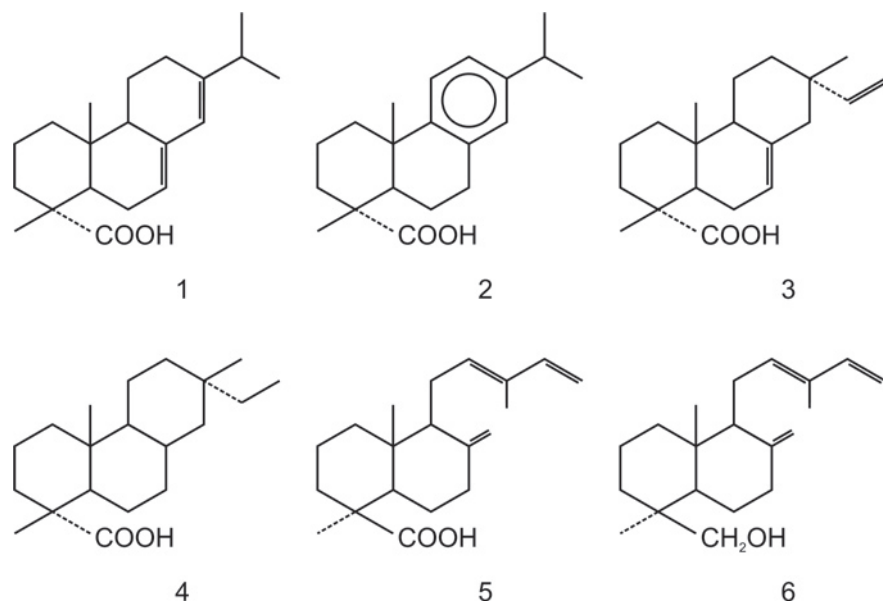
Fig. 2: Examples for diterpenoid resin acids and communol: (1) abietic acid, (2) dehydroabietic acid, (3) isopimaric acid, (4) sandaracopimaric acid, (5) communic acid, (6) communol.

mass constituents of succinite by their retention times, applying in an extension of his studies finally combined gas chromatography – mass spectroscopy. STREIBL et al (1976) studied the chemistry of fossil resins from the Cenomanian of Moravia (walchovite, neudorfite, and muckite) including – for sake of comparison – also succinite, material from the Lower Cretaceous of Salzburg, and amber of 'Lebanonian occurrence' in their investigations. Studies of succinite by means of GLC/MS have also been done by a working group at the 'Institute of Organic Chemistry and Technology' at the Technical University of Warsaw (e.g. URBANSKI et al. 1976) and by many others. Meanwhile a steadily increasing number of publications yielded by means of GLC/MS a very high number of compounds not only for succinite (e.g. CZECHOWSKI et al. 1996), but also for rumanite (STOUT et al. 2000), and various fossil resins from Bitterfeld (YAMAMOTO et al. 2006) – to give just a few outstanding examples.

The 'polymer backbone' of ambers

High-molecular-mass compounds ('HMM')

For various fossil resins ('ambers') a considerable number of detailed investigations concerning the processes resulting in the formation of a high-molecular-mass forming the insoluble fraction of ambers have been published. The basic reactions are polymerisations of various types. To start a polymerisation process a monomer molecule (a 'small organic molecule') is needed, molecules which more or less easily react with each other yielding a product of comparatively high molecular mass – the polymer. Such reactions
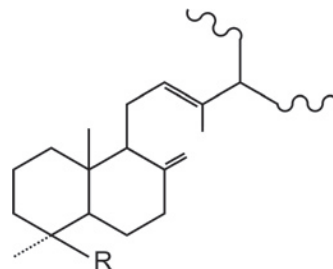
Fig. 3: Polymer of 'Class I Resinites': polymer of communic acid and/or communol (R = COOH or CH₂OH).

can be initiated by cations, anions or by radicals. In the case of the formation of amber-like substances traces of oxygen and/or enzymatic influences can be considered to start such reactions. In the case of succinite, communic acid (fig. 2.5) respectively communol (fig. 2.6), its corresponding alcohol, are the monomers involved. In the case of an other subclass of 'Class I Resinites' ozic acid and zanzibaric acid are the monomers. A number of Recent plant taxa are producing resins based on these compounds: genera of Araucar-iaceae (*Agathis)*, Leguminosae (*Hymenaea*, *Copaifera*), and Cupressaceae.

Polymers of labdatriene carboxylic acids ('Class I Resinites')

In describing the various types of polymers respectively copolymers forming the insolu-ble fraction of ambers it seems useful to follow the scheme indicated by the chemical classification of fossil resins as introduced by ANDERSON et al. (1992). This system has been modified respectively additional classes introduced ('Class V') in the following years (ANDERSON & BOTTO 1993; ANDERSON 1994). In 'Class I' fossil resins are sum-marized based on polymers of laddatriene carboxylic acids. They include by far the most common ones, among others all 'succinites' (Class Ia) as well as New Zealand and Victorian Brown Coal Resinites (Class Ib), and the fossil *Hymenaea*-resins from Mexico and the Dominican Republic as well.

The polymer fraction of the 'classical succinite (i.e. the so-called 'succinin') is derived from polymers of communic acid, partially copolymerised with communol (fig. 3). Characteristic is the occurrence of succinic acid, its function being probably the estab-lishment of cross-linking by means of esterification ('Class Ia Resinites').

Class Ib Resinites contain polymers of communic acid too, succinic acid, however, be-ing absent (Examples: fossil resins from New Zealand and Victoria).

Class Ic Resinites contain polymers of ozic acids and/or zanzibaric acids (CUNNINGHAM et al. 1983, MILLS & WHITE 1987). Examples for this type of fossil resins are not only the ambers from Mexico and the Dominican Republic, but also some (East) African Resinites. For Mexican amber genera of the Leguminosae (especially *Hymenaea*) have been identified as the botanical source already rather early (LANGENHEIM 1966, LAN-GENHEIM & BECK 1968), for amber from the Dominican Republic even a special species of this genus (*Hymenaea protera*) with African affinities has been described as resin-producing tree (POINAR 1991).

Initial polymerisation occurs in all these cases primarily across a terminal olefinic group being characteristic for all the monomers mentioned above located in the side chain.

One has to realize that not only copolymerisation between two monomers occurs to a varying degree, as mentioned above, but also different amounts of other materials (e.g. communol) can contribute to the polymer structure on hardening of the fossil resin. Whatever the details may be, the dominant monomer has always a labdatriene structure. Like other organic materials, also fossil resins undergo different stages of maturation, i.e. numerous chemical changes during different processes of diagenesis. These facts are not only of interest to the organic geochemist as examples for the diagenesis of terpene compounds in general but have to be considered carefully also in connection with the identification and classification of various types of ambers. A publication showing rumanite to be thermally altered succinite has been mentioned above in other connections already (STOUT et al. 2000). An apparent effect of diagenesis ('maturation') on the structure of Class I resinites is the loss of exomethylene groups by means of isomerization. This structure can be easily detected by means of spectroscopical methods (infrared spectroscopy and/or ^{13}C-NMR).

Of special interest in respect to the qualities of ambers, representing examples of natural copolymers, is also the occurrence of low-molecular-mass compounds (e.g. triterpenes), extractable in solvents, and acting as natural plasticizers.

Polymers of cadinene ('Class II Resinites')

'Ambers' with a polymer structure represented by polycadinene (fig. 4) are much less common than 'succinite' and related types of amber as described above. Corresponding modern examples are commercially available under the term 'damar' and are produced by trees belonging to the Dipterocarpaceae. For material of this type PACLT (1953: 343) had introduced the name 'Paradamarite'. Characterization and extensive studies of these resinites have been published by VAN AARSSEN and co-authors (AARSSEN 1992; AARSSEN, & LEEUW 1991a, 1991b, 1992; AARSSEN et al. 1990, 1992, 1994). By these studies the main structures of these resins have been established. A few authors have noted different forms within Class II resinites however; for any details see ANDERSON et al. (1992) and the references given therein.

Fossil resins with polycadinene structure as well as their modern counterparts can easily be distinguished from the polymers of labdatriene carboxylic acids ('Class I resinites like 'succinite') by means of pyrolysis gas chromatography combined with mass spectroscopy or by infrared and NMR data.

Polymers of styrene ('Class III Resinites')

The first representative of this group of 'ambers' has been described already in 1875 by LASAULX: by distillation of larger amounts of this material KLINGER & PITSCHKI (1884) obtained styrene and cinnamic acid (fig. 5) – a fact confirming the unique chemical character of this 'organic mineral'. Fragments and casts of leaves belonging to *Liquidambar europaeum* having been found near Siegburg, this representative of Hammamelidaceae was already then suggested as the botanical source of this material (WEBER 1884, mentioned in PASTOROVA et al. 1998). A modern chemical investigation of siegburgite from Bitterfeld (PASTOROVA et al. 1998) has established 3-phenylpropanylcinnamate to be an additional building block of this copolymer and furthermore confirmed the botanical origin of siegburgite from Hammamelidaceae by detecting a
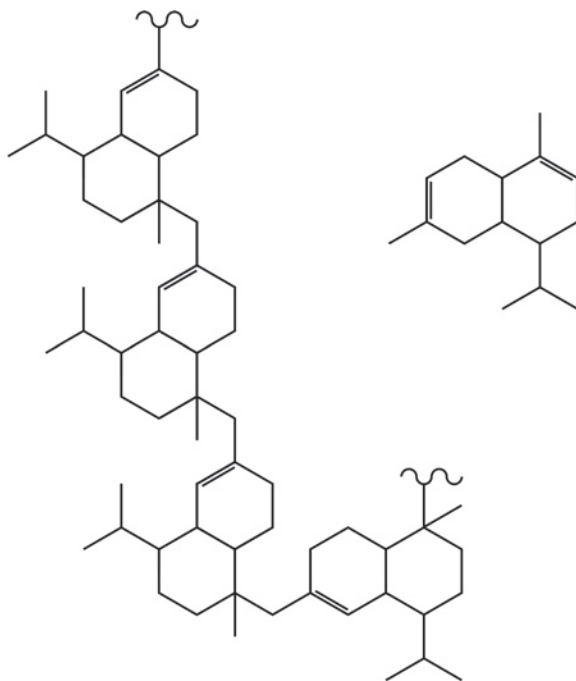
Fig. 4: Cadinene and polycadinene – the polymer of 'Class II Resinites'

number of biomarkers ('chemofossils') characteristic also for modern Gum Storax from *Liquidambar orientalis*. In this connection it may also be mentioned that one species of the genus *Liquidambar* is called 'amber tree' with its common name. Pastorova et al. (1998) compared siegburgite also with a fossil resin from North America (Squankum, New Jersey), having a polystyrene matrix comparabale to that of siegburgite. In respect to this material from New Jersey it must be mentioned that botanical affinities of 'New Jersey amber' with the Hammamelidaceae had been established already by Langenheim (1969) for fossil resins from Harrisonville and Pemberton (both: New Jersey). Detailed studies of these ambers have been published by Grimaldi et al. (1989), summarizing not only the chemistry but also occurrence and palaeontology. Shedrinsky et al. (1991) studied in their comparative investigation of ambers and copals by means of pyrolysis gas chromatography among others also one sample, which had been collected in 19th century about 130 miles west of Miles City (Montana, USA). The pyrogram yielded by these author indicates that this sample was almost identical with modern polystyrene (Shedrinsky et al. 1991: fig. 13). This is an important confirmation that 'Montana Amber' is indistinguishable from New Jersey material, as stated already by Langenheim & Beck (1968).

In connection with the discussion of the botanical source for these resin materials it is also worth mentioning that in the course of the search for biomarkers in a fossil resin from the Eocene of Stolzenbach (near Kassel, Germany) the occurrence of cinnamic acid and dihydrocinnamic acid (fig. 5) could be confirmed (Vávra, in Gregor 2005). Also in this case a possible connection to Hammamelidaceae has been discussed.
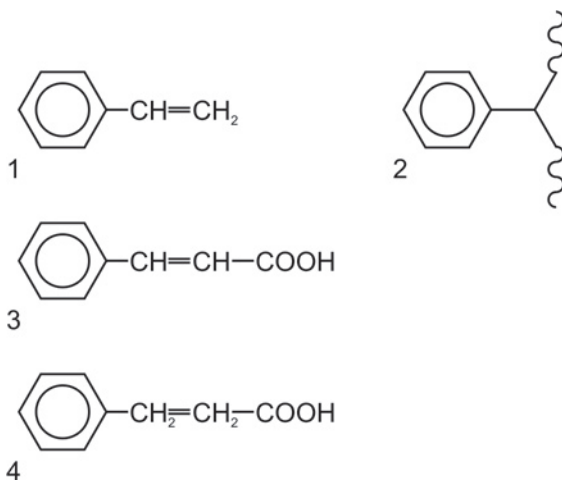
Fig. 5: Chemistry of 'Class III Resinites':
(1) styrene, (2) polystyrene, (3) cinnamic
acid, (4) dihydrocinnamic acid.

Polylabdanoids in 'Class I Resinites' ('Oligomeres')

Only a few modern investigations have been dealing with substances isolated by extraction techniques and having molecular masses exceeding those of any non-polymeric occluded terpenoids. Studies of such substances have been done for a few samples of fossil resins from Australia and New Zealand, the ages of which range from Eocene to Miocene (CLIFFORD et al. 1999) and for polylabdanoid resins of Holocene age (CLIFFORD et al. 1997). The structural characteristics confirmed by ^{13}C and ^{1}H NMR spectroscopy and pyrolysis gas chromatography combined with mass spectroscopy were similar to those described for polylabdanoids in native resinites. Detailed structures for such a 'polylabdanoid' trimer including also possible reactions of maturation are given by CLIFFORD et al. (1997). These studies show something like 'snapshots' of the very first steps of amber formation. The maturation processes occurring during diagenesis of polylabdanoid structures could also be confirmed for such 'oligomeres': (1) Depletion of exomethylene and total olefinic carbon functionalities, (2) rearrangement of double bounds, and (3) defunctionalization of ring systems.

Characterization of polymer structure of ambers

Within the last few decades a lot of detailed information concerning the chemical structure of the polymer fraction of ambers has been achieved as summarized above. Nevertheless some physical and physico-chemical methods have been applied by various authors yielding informations about the 'genuine' structure of the samples studied without any chemical treatment like extractions etc. preceding their studies. One standard method to be mentioned here is infrared spectroscopy. Though it has rather limited possibilities in respect to the elucidation of structures of macromolecules in general, it will nevertheless remain a standard method for 'fingerprinting' of amber samples. It has its merits also for the identification of 'succinite' ('baltic shoulder' etc.) and in connection with a number of studies concerning possible botanical affinities of fossil resins (e.g. BECK et al. 1964; LANGENHEIM 1969; LANGENHEIM & BECK 1965, 1968). Another

method able to characterize also the whole sample without any preceding treatment like extraction or derivatization is pyrolysis gas chromatography, which can also be applied successfully for a very effective characterization and for sample comparisons (e.g. Heck 1999). This method becomes even far more informative by means of combination with mass spectroscopy, as mentioned already for a number of examples given above.

An important step forwards towards a better understanding of carbon functionalities in ambers has been achieved by applying methods developed to obtain high-resolution NMR spectra of solids. Lambert & Frye (1982) were among the pioneers applying NMR by using the techniques of magic angle spinning and cross polarization ('CPMAS NMR') to powdered material of various amber samples. By means of this special technique of ^{13}C-NMR they confirmed that ester linkages, acidic groups as well as exomethylene groups do occur in Baltic amber from Samland. They , moreover, confirmed differences to other amber minerals, like Romanian amber (schraufite), simetite (Sicilian amber) and walchowite from Czech Republic (Moravia). This method has been applied also to various samples of Cretaceous amber confirming for them a common, however geographically dispersed botanical source (Lambert et al. 1996).

By a set of different physical methods (e.g. measuring of the internal friction in amber samples) Weller & Wert (1984) investigated the structure of the polymer fraction of fossil resins adding additional information towards a better understanding of the amorphous qualities of such cross-linked large molecules.

Valuable data representing a semiquantitative analysis of amber structures can also be achieved by infrared spectroscopical studies of the residues remaining after extracting amber samples, as shown by Matuszewska & Karwowski (1999).

Non-polymeric ambers ('Class IV Resinites')

Before giving a few examples for low-molecular-mass compounds detected in soluble fractions of fossil resins and before discussing some 'organic minerals' related to terpenes and terpenoids, a few remarks referring to the so-called 'Class IV Resinites' (sensu Anderson et al. 1992) shall be given. This Class of resinites has been introduced to summarize amber-like materials being sesquiterpenoid in their basic structure, especially based on the carbon skeleton of cedrane. Apparently they are not polymeric substances at all. Examples given are among others the 'Moravian resinites' (Streibl et al. 1976). For this last type of fossil resins the statement by Anderson et al. (1992: 839) that 'further investigation is …required' is still largely true, even nowadays. This is valid not only – as stated in the passage quoted – for the botanical origin of these substances but very often in a more general sense too.

Resins enriched in triterpenoid compounds

As suggested already by Otto et al. (2001) for fossil resins rich in triterpenoids a separate class of fossil resins should be established. This standpoint has been emphasized also by Yamamoto et al. (2006: 34). This class would then include a number of fossil resins of angiosperm origin like glessite, Highgate copalite, guayaquilite (a resin of unknown geological age from Ecuador, e.g. Langenheim & Beck 1968), rosthornite (from the paleogene of Carinthia, Austria) and a few others too. For closer details see below.

Low-molecular-mass ('LMM') compounds in ambers

Extensive studies of low-molecular-mass compounds occurring in soluble fractions of ambers and related 'organic minerals' have become possible not until with the application of combined gas liquid chromatography and mass spectroscopy in studies of fossil resins. Such studies can be performed to achieve at least three different goals:

(1) Extensive 'finger-printing' of samples to have an additional, and very powerful tool for comparison of different samples of fossil resins

(2) Search for any possible 'biomarkers' (= 'chemofossils') being hopefully characteristic for some group or perhaps even genus of source plants – studies of botanical affinities.

(3) Investigation of diagenesis of various chemical structures – low-molecular-mass compounds are usually easier to be studied in this respect than any polymer structures.

Studies of Recent resins are of great interest not only in respect to the solution of any chemotaxonomical problem but also for an understanding of plant/insect relationships. For such studies performed for single species of the genus *Pinus* the distribution patterns of monoterpenes have been found to be of rather limited value only. In contrast to these facts sesquiterpene hydrocarbons showed significant differences even among morphologically closely related species. Also tricyclic diterpenes of the abietane and pimarane type have been found to be useful for chemotaxonomical purposes (STURM et al., 1983). About the chemistry of terpenoids in conifers there exists of course an extensive literature being reviewed from time to time in comprehensive articles (e.g. SAN FELICIANO & LOPEZ 1991).

So far just a few introducing remarks concerning the chemistry of Recent resin materials, just to show that the search for 'biomarkers' in amber samples is far from being hopeless. Differences of chemistry of resins originating from different parts of the same species of plants, differences also due to seasonal and/or geographical variations may have influences. All these 'chemotaxonomical possibilities' can finally be studied only after various diagenetic changes which are frequently only partly understood. Thus the search for 'biomarkers' will always retain some character of 'gambling'.

Succinic Acid

The fact that succinic acid (fig. 1.1) can be isolated from a number of ambers (now summarized as 'Resinites Class Ia' in modern systematics of ambers as introduced by ANDERSON et al. 1992), is known already since the days of AGRICOLA (1546, see also above). The fact that dry distillation of amber ('succinite') yields the anhydride of this acid and not the acid itself has been emphasized by ROTTLÄNDER (1983: 571). The question how this acid occurs in amber has resulted in a number of partly contradictory statements and discussions. ROTTLÄNDER (e.g. 1983) tried to show that succinite did not contain free succinic acid or its anhydride either. He supposed the existence of some structure yielding succinic acid by means of alkaline saponification respectively the anhydride as a result of dry distillation. Recent studies (YAMAMOTO et al. 2006) have shown – at least for succinite from Bitterfeld – that free succinic acid as well as six different esters could be identified in solvent extracts. Even the possibility that ester formation may occur by

cross-linking between two different polymer chains with their communol units has been discussed (Anderson et al. 1992 and the references given therein).

An interesting hypothesis how succinic acid may have come into existence in resins has been proposed by Szykuła et al. (1990). These authors have studied neutral fractions of amber and detected among many other compounds also a typical plant sterol (β-sitosterol). Quite a number of microorganisms (representatives of the genera *Nocardia*, *Pseudomonas*, *Mycobacterium*, *Corynebacterium*, *Arthrobacter*, and *Rodococcus*) are able to use plant sterols as a source for carbon compounds. One of the final products of these degradations is succinic acid (Kieslich 1985). Combining these two facts Szykuła et al. (1990) suggested that phytosterols and possibly also other components of wood may be the source materials for succinic acid.

An additional interesting aspect about the occurrence of succinic acid in the 'classical' succinite has been the fact that it has been used not only for discriminating between amber respectively 'amber-like' fossil resins on one side and other fossil resins (characterized by the absence of succinic acid) on the other side, but , moreover, for a geographical attribution of archaeological materials: fossil resins identified as 'succinite' have then been automatically attributed to the Baltic area. These problems (including also some physico-chemical methods) have been discussed in detail by Savkevich (1981): realizing the fact that succinite occurs in a considerable number of countries and places (Black Sea, north-east of the Carpathians to Baltic countries, Denmark, North Sea, Sweden, Great Britain), such geographical attributions will nearly always remain only speculations. The first investigations dealing with such problems had been published by Helm (1885), who studied amber finds from Schliemann's excavations at Mycenae (Greece).

Realizing how important succinic acid determinations have been for many amber studies it is no great surprise, that mineralogists have even suggested a mineral name for this acid: 'succinellite' (Hey 1950: 276). As far as I can see, this name has not been accepted by the scientific community however.

Camphor and related substances

As an example for the occurrence of terpenes in amber being probably genuine and even more or less also characteristic for succinite camphor and related substances (fig.1, 2 – 5) may be mentioned here. Even here exists a connection to the ancient history of amber studies: as mentioned already above ʿAlī ibn Sīna (= Avicenna) realized already about thousand years ago that amber had 'a smell of camphor'. Indeed there have been quite a number of compounds belonging to this group of compounds detected in amber samples. The corresponding saturated hydrocarbon ('camphane'), the unsaturated compound with the same carbon skeleton – camphene (fig. 1.5), and the two corresponding alcohols: borneol (fig. 1.3) and isoborneol (e.g. Czechowski et al. 1996). These two alcohols have been even detected in the form of their esters: fenchylbornyl succinate, fenchylisobornyl succinate, dibornylsuccinate, bornylisobornylsuccinate, and diisobornyl succinate (Yamamoto et al. 2006).

An isomer of borneol – fenchol (fig. 1.6) – and related substances are also well-known from succinite samples: fenchane, fenchone, and difenchyl succinate.

The significance of the occurrence of camphor and related substances in succinite can be an object of speculation only. Together with many other low-molecular-mass compounds they will possibly act as plasticizer.

Aromatic compounds in fossil resins

To present a summarizing review about these substances would distinctly exceed the scope of this publication. Therefore only a few basic concepts and facts can be mentioned here, pointing out among others also the important connection existing towards the chemistry of crude oils. Realizing that remains of plants and animals buried in aquatic environments to be the main sources for petroleum one has to be aware of the fact, that aquatic organisms are poor in lignin and protein – two major sources for aromatic compounds in diagenesis. The question then arises, how to account for something like 5 % (or even more) of aromatics in crude oils ? After various discussions in this direction BROOKS (1948) suggested terpenes to be converted to aromatics under the relatively mild conditions generally postulated for the formation of petroleum. SKRIGAN (1951) studied turpentine isolated from resinous matter from pine stumps in a peat bog (age: about 1000 years) and found that disproportionation of pinene had resulted in the formation of p-menthane and cymene (fig. 6.1) after such a comparatively short time already. A rather simple model substance – limonene – had been used for further studies about aromatisation of terpenes, sulphur respectively clays having been used as catalysts (e.g. WEITKAMPF 1959; FRENKEL & HELLER-KALLAI 1977). In respect to the question, how coals formed from such amber-producing trees and could become the source rocks for oil see the discussion in POINAR et al. (2004) and the references given therein. In this publication *Agathis levantensis* is proposed not only as the source for coal but also, at least in part, for the oil in the Khafji and adjoining Safaniya oilfields.

Realizing how manifold the starting materials may be, realizing , moreover, that aromatisation occurs in many steps, following different reactions schemes, the great variability of aromatic compounds described and identified until now in various fossil resins is no surprise at all. Thus – to give one example at least – naphthalenes, phenanthrenes (fig. 6. 2 – 4) and anthracenes have been thoroughly studied by means of luminescence analysis, the identified compounds being also confirmed by results of combined gas liquid chromatography – mass spectroscopy (MATUSZEWSKA & CZAJA, 2002). Among the naphthalenes described two isomers of dimethyl-naphthalene and among the phenanthrenes 1-methyl-7-isopropyl-phenanthrene (better known as 'retene', fig. 6.4) must be mentioned as common substances in extracts of various fossil resins.

Pentacyclic ringsystem of triterpenoid compounds yield as a result of various single steps of aromatisation during diagenesis a rich variety of substances during coalification (e.g. HAYATSU et al. 1987; STOUT 1992). Even polymer structures of fossil resins have been found to be possible precursors of aromatic hydrocarbons in fossil fuels (AARSSEN & LEEUW 1992).

Resin acids

The possibly earliest study of amber chemistry describing the isolation of resin acids has been performed by TSCHIRCH & AWENG (1894), who reported the isolation of 'succino-abietic' and 'succino-silvic acid'. Studies of this kind have then been intensified in the
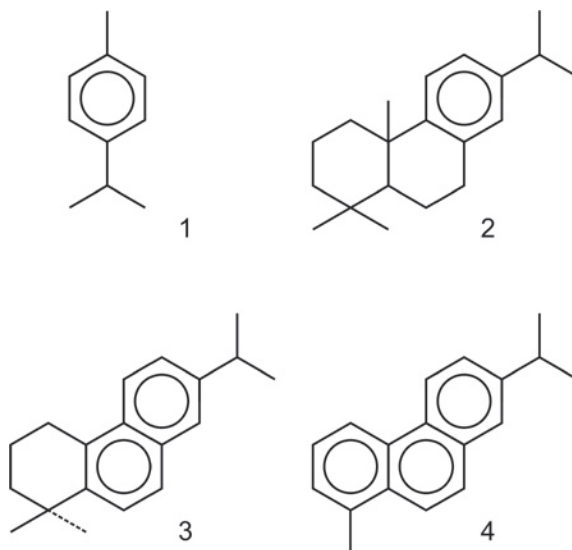
Fig. 6: Aromatic hydrocarbons in ambers: (1) p-cymene, (2) dehydroabietane, (3) simonellite, (4) retene.

first half of 20th century especially by Leopold SCHMID at the University of Vienna resulting in a series of publications about amber studies by means of applying the methods of 'classical' analytical chemistry. The last paper has been published in 1940 (SCHMID & VOGL 1940).

After introducing gas liquid chromatography and combined gas chromatography into amber chemistry by GOUGH & MILLS (1972) the knowledge referring to resin acids in amber samples increased rapidly. After applying methylation with diazomethane to a soluble fraction of amber in cold ether, these authors could identify a number of various resin acids as corresponding methyl esters: isopimaric acid (fig. 2.3), dihydroisopimaric acid, sandaracopimaric acid (fig. 2.4), abietic acid (fig. 2.1), dehydroabietic acid (fig. 2.2), agathic acid, and dihydroagathic acid. Such studies have been continued by a number of authors in the following years (e.g. MILLS et al. 1984/85 and others). The results yielded have been of great interest in connection with details of the polymerisation processes leading to the formation of 'HMM' compounds starting with labdatriene carboxylic acids and resulting in the formation of 'Class I Resinites' (see above).

The distribution patterns of resin acids in soluble fractions of amber samples have also been used in the course of discussions about possible botanical affinities as some sort of finger-printing in comparing fossil resins among each other.

Amyrines in ambers

FRONDEL (1967, 1969) has obviously been the very first author detecting a special type of pentacyclic triterpenes – the amyrines (fig. 7) – in various amber samples. By means of thin-layer chromatography (FRONDEL 1969) she identified amyrines not only in Highgate copalite from the London Blue Clay, but also in glessite from the Baltic area, and in guayaquilite. Through comparative studies with modern Burseraceae resins she was finally convinced that amyrines were a reliable indicator to identify the botanical
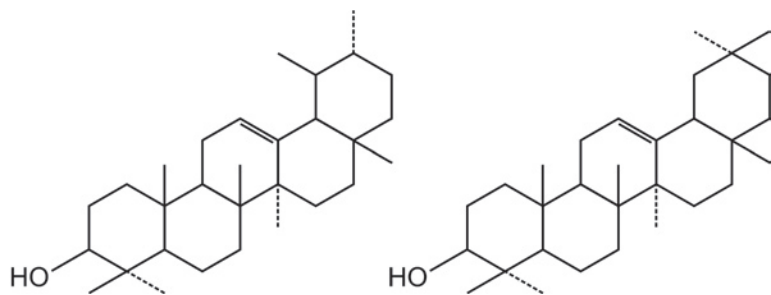
Fig.7: Amyrines – examples for penta- cyclic triterpenes in angiosperm resins: α-amyrine (left) and β-amyrine (right).

origin of these various ambers: she regarded these ambers as fossil 'elemi' resins. The amyrines have also been shown to occur in glessite from Bitterfeld by means of com- bined gas liquid chromatography-mass spectroscopy (KOSMOWSKA-CERANOWICZ et al. 1993). This material has recently been restudied, the resulting publication being an ex- cellent example showing what a lot of additional information and data can be achieved by means of the application of more advanced methods and technologies (YAMAMOTO et al. 2006). Instead of two amyrines, as many as 12 different triterpenoids could be identified, one of them being allobetul-2-ene, which is according to SIMONEIT (2002) a specific biomarker of *Betula* (birch-tree).

Amyrines have also been detected in a fossil resin ('rosthornite') from the Eocene of Carinthia (Austria). In the Eocene Basin of the 'Krappfeld' (NNE Klagenfurt) existed at the Sonnberg near Guttaring a small coal mine operated between 1773 and 1933. From this locality HÖFER (1871) had reported the discovery of a fossil resin, which had recently been discussed in some detail by VÁVRA (2005: 268-269).

As a consequence of such studies and a number of related investigations a discussion re- sulted concerning the botanical origin of these various ambers. Triterpenes are regarded since more than 20 years to indicate angiosperm origin of fossil resins (BRACKMAN et al. 1984 and the references given therein). Therefore the identification of pentacyclic triterpenes (e.g. amyrines) in ambers can be regarded as a reliable indicator for an angiosperm origin of the material studied. Unfortunately, however, such substances are rather common in many groups of plants (VÁVRA 2005; YAMAMOTO et al. 2006). If one restricts such considerations to resin-producing plants however, the number of families can be largely reduced: one of the most attractive 'candidates' remaining are the Burseraceae. Modern representatives (16 – 20 genera, about 600 species of bushes and trees) occur in tropical America and NE-Africa. *Commiphora* and *Boswellia* are even of commercial interest as the sources for myrrh and frankincense. Elemi-resins in the strict sense are formed especially by species belonging to the genus *Canarium* (e.g. *Canarium luzonicum* producing the so-called 'Manila-elemi'). Such products are still of some interest for special purposes in chemical industry (lacquers, ointments, etc.).

For glessite from Bitterfeld – one of the more uncommon species of organic minerals, summarized in German language usually as 'akzessorische Harze' – an origin from birch-trees has now been established by means of a special biomarker (allobetul-2-ene, see above), the details being extensively discussed by YAMAMOTO et al. (2006: 34 – 36). Other angiosperm resins which have yielded amyrines too, may still be open to discus- sion. In this connection it is perhaps also worth mentioning that some endocarps of the

genus *Canarium* have been found in the paleogene of Czech Republic (GREGOR & GOTH 1979). Finally a short historical remark: already HELM (1881) in describing glessite as a new species of amber minerals, referred to a similarity between this material and modern 'Gummiharzen' (= gum resins) like myrrh and has in this respect been very close to identify it as an angiosperm resin already at his time.

How unreliable designations respectively identifications in old collections may be is convincingly illustrated through the publication by ANDERSON & BOTTO (1993), who investigated a sample of glessite from Prussia, in which no triterpenoids could be detected. To generalize on the basis of such a result that glessite has gymnosperm origin can not be accepted however. Everybody studying amber samples makes similar experiences: the author of this paper for example once analyzed 'walchowite' from Moravia, which turned out to be succinite, a sample of possible glessite from the North Sea area turned out to be no glessite at all – the list of such misleading identifactions may be long.

Discrimination of fossil resins by means of 'LMM' compounds in soluble fractions

A convincing example how to use detailed studies of low-molecular-mass compounds in soluble fractions of various ambers yielding valuable data for a clear distinction of different mineral species has been published by YAMAMOTO et al. (2006). In soluble fractions of samples from glessite, succinite, goitschite, and stantienite 120 different compounds have been detected and identified by means of their mass spectra. In the following table a few data from this publication are summarized to mention at least one example in a rather simplified manner. The differences between the angiosperm resin ('glessite') and the gymnosperm resin ('succinite') are evident.

Botanical origin of succinites:

Though there exists general agreement that succinites are derived from conifers, the identification of a single taxon as 'the amber tree' is still a rather delicate matter. Whereas in the early stages of establishing some sort of chemotaxonomy for fossil resins infrared spectroscopy has been the leading method for some time (e.g. LANGENHEIM

Tab. 1: Comparison of glessite and succinite (soluble extracts) based on a rough summary of data from YAMAMOTO et al. (2006).

Compounds	Glessite	Succinite
Succinic acid	none	+
Fenchol, Isoborneol, Borneol	none	+
Sesquiterpenoids	+	+
Diterpenoids	none	+
Triterpenoids	+	none
Triterpanes (hopanes)	none	none
Succinates	none	+
Monoterpanyl diterpenoates	none	+
Esters of various fatty acids	none	none
Total all compounds (mg g^{-1})	58.4 – 59.6	14.6 – 23.2

& Beck 1965, 1968), during the last years comparative studies of biomarkers detected in soluble fractions of ambers have become more and more important (Yamamoto et al. 2006: 38–39). A few suggestions concerning the botanical source of (Baltic) succinites are summarized in table 2.

Trying to summarize data from the literature one can perhaps say in a rather general way that the Baltic amber has obviously been produced by an extinct conifer taxon which has been characterized by chemical criteria reminiscent of Araucariaceae. Modern *Agathis* represents an excellent example for such an 'amber tree' producing considerable quantities of resins easily undergoing polymerisation reactions and having therefore good chances to survive in the fossil record.

Also for the succinites from Bitterfeld area ('Saxonian amber', see Krumbiegel 1995) a number of different botanical affinities have been discussed: besides Araucariaceae and Pinaceae also Taxodiaceae, Geinitziaceae and Cupressaceae have been suggested as possible sources for this fossil resin. Most recent studies of this kind give the genera *Picea* or *Pinus* as the most likely sources for Bitterfeld succinites and also for the goitschite (Yamamoto et al. 2006).

Some aspects of the chemistry of Cretaceous ambers

Mesozoic ambers are usually of great scientific interest for palaeontologists, especially if they yield inclusions: whereas faunas from Cenozoic resins show generally a rather 'modern' appearance, Mesozoic amber inclusions offer first-hand information about earlier and important steps in the evolution of many groups of insects. Co-evolution of flowering plants and insects, early evolution of social forms among ants and bees, various cases of parasitism – these are just a few topics showing that the study of Mesozoic inclusions is a matter of general biological interest. Realizing the fact that ambers from Triassic or Jurassic strata are usually very rare and available only in small amounts, it is not surprising that studies of Mesozoic ambers are largely identical with investigations of Cretaceous resins. A modern overview of (fossiliferous) Cretaceous ambers has been given by Poinar (1992: 50-63).

The 'traditional' infrared spectroscopy is often not sufficient for a detailed characterization of such old ambers however. The spectra achieved show usually no significant absorption bands to be useful for sake of comparison or for the identification of possi-

Tab. 2: Some examples of suggestions for botanical affinities concerning the (Baltic) succinite.

Botanical affinity suggested	Author(s)
Pinaceae: *Pinus succinifera*	Schubert (1961)
Pinaceae: *Pinus*	Langenheim (1969)
Araucariaceae: *Agathis*	Gough & Mills (1972)
Pinaceae	Mosini & Samperi (1985)
Pinaceae: *Cedrus*	Katinas (1987)
Araucariaceae: *Agathis*	Beck (1993)

ble plant sources. Other methods or combinations of various methods have contributed nevertheless to identify possible plant sources. As an example for such studies a few details will be given concerning data about Middle East ambers, results having been summarized by POINAR & MILKI (2001). For Lebanese amber carbon 13 nuclear magnetic resonance spectroscopy has been used to match spectra with those of resins from recent trees. By means of this 'finger-printing' method amber from Lebanon has been confirmed to have been produced by members of the genus *Agathis* (Araucariaceae), trees existing only in the Australasian region (southern hemisphere) today (LAMBERT et al. 1996). Araucariaceae have been determined also as the plant source of Lower Cretaceous amber from Jordan (BANDEL & VÁVRA 1981). Summarizing data from literature POINAR & MILKI (2001) have listed a remarkable number of occurrences of *Agathis* ('kauri pine') in the northern hemisphere, based on results of various chemical studies. In addition these authors give also a detailed characterization of the Cretaceous kauri forest.

These examples show how chemical studies of ambers can contribute to problems of palaeobotany and plant geography in general.

Terpenes as minerals: origin and interpretation

In the following passages informations about various organic minerals will be summarized, substances which could be classified as 'Class IV Resinites' according to the classification introduced by ANDERSON et al. (1992) – a group including non-polymeric substances related, however, to terpenes and terpenoids. I will focus on a few examples which have been restudied within the last years (e.g. VÁVRA 2004). Quite a number of them can be easily summarized under the title:

'Phyllocladane-Group'

Phyllocladanes (fig. 8) are hydrocarbons reported to occur in lignites from Australia, Austria (VÁVRA 1998), China, Czech Republic, Germany, Hungary, Italy, Nigeria and Russia (BOUŠKA et al. 1998 and the literature given therein). They can be found not only in extracts of lignites but do occur also as well-defined organic minerals, hartite being the best-studied among them.

Hartite

This organic mineral has been already described by HAIDINGER (1841) from lignite (Karpatian age, Middle Miocene) mined until 1949 at Oberhart near Gloggnitz (Lower Austria). From this mine even a few more organic minerals have been described, some of them having been products isolated by extraction procedures only ('alphaharz' and 'betaharz' described by SCHRÖTTER 1843). Hartite itself had been recognized as a crystallized hydrocarbon already in 1856 (ROLLE 1856). Nevertheless it has been erroneously regarded as a fossil resin rather often (e.g. DAMMER & TIETZE 1928; EXEL 1993). It is occurring sometimes even in idiomorphic crystals, as described by MACHATSCHKI (1924). Its structure as a tetracyclic diterpane had been finally established by BRIGGS (1937). A number of other organic minerals have been shown to be identical with hartite and must therefore be regarded as junior synonyms: bombiccite, branchite, hofmannite,
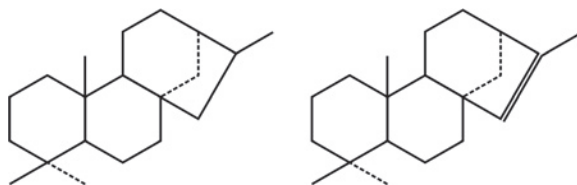
Fig. 8: Two examples for the phyllocla-
dane carbon skeleton: α-phyllocladane
(left) and isophyllocladene (right).

iosene (=josene). Hartite has been thoroughly restudied by Bouška et al. (1998) on the basis of material from the open-cast coal mine of Bílina (Bohemia, Czech Republic).

Ixolyte (also: 'ixolythe' and 'ixolithe')

This extremely rare organic mineral has been described by Haidinger (1842) – in fact he mentioned already in an earlier publication (Haidinger 1841) that a mineral at Oberhart (near Gloggnitz, Lower Austria) has been found, in fissures of bituminous wood. He had observed a smell reminiscent of hartite and mentioned its dark, hyacinth-red colour. From the fact that this substance – after melting at 76° – does not become completely liquid until 100° but remains viscous and sticky he derived the scientific name which he then proposed for this new mineral: the ancient Greek words for 'bird-lime' or 'glue' (ιξος) and for 'I dissolve', here: 'I melt' (λυω) thus resulted in the proposal for a new mineral name – 'ixolyte'. From the fact that thick layers of this mineral – up to half an inch – enclosed bubble-shaped cavities he concluded that this substance had once been liquid or molten. Ixolyte has been mentioned only from a very few other localities in Austria: Meixner (1957) tentatively reported it from St. Stefan im Lavanttal (Carinthia), Taucher & Hollerer (2001) also from Styria.

By restudying authentic material from the type area (deposited at the Museum of Natural History, Vienna, Inv.No. 1844.II.54 = NHMW 1844/0002/0054) interesting analytical results have been yielded: a solution of the sample in methanol yielded a gas chromatogram with three major peaks. The main peak was identified by its mass spectrum as phyllocladane, the two others as norpimarane and sandaracopimarane (Vávra 2004; Vávra 2005: fig. 6). On the basis of these results ixolyte must be regarded now as a mixture of hydrocarbons, phyllocladane being its main constituent.

Jaulingite

Zepharovich (1855) described from a small coal mine, which existed in the 19th century in an area called 'Jauling' (S St. Veit, Triesting Valley, 5 km SE Berndorf, Lower Austria) a new mineral under the name 'jaulingite'. This hyacinth-red material had been found on some damaged fossil tree-trunks of Miocene age. This material has in the following decades been reported to occur at various other places in Austria too: Oberdorf near Voitsberg, Voitsberg, Köflach, Lankowitz, Piber (Styria). Further data are to be found in Taucher & Hollerer (2001).

Restudy of type material from the type area kept in the collections of the Museum of Natural History, Vienna (Inv. No. 1855.XXVI.1 = NHMW 1855/0026/0001) has shown that this organic mineral contains as its main constituent phyllocladane too (more than 82 area % in a solution of methanol; see Vávra 2004: figs 2, 3). Further studies have

shown that material kept under the determination 'jaulingite' in old collections is rather heterogenous however (VÁVRA 2004). Careful revisions are needed for all such samples in future.

Koeflachite (resp. köflachite)

DOELTER (1878) had described an organic mineral from a coal mining area in Styria (district of Voitsberg-Köflach) for which he introduced the new mineral name 'koeflachite'. In the course of a revision (VÁVRA 1993) material from Styria determined as 'koeflachite' turned out to be a mixture of various hydrocarbons: dehydroabietane (fig. 6.2), eudesmane, norpimarane, retene (fig. 6.4), sandaracopimarane, simonellite (fig. 6.3), and phyllocladane (fig. 8). Three of them (dehydroabietane, simonellite, and retene) can be regarded as products of the diagenesis of phyllocladane (see ALEXANDER et al. 1987). Phyllocladane being the main constituent also in this case, realizing , moreover, that three hydrocarbons – as just mentioned – possibly came into existence by diagenetical changes of phyllocladane – it seems justified to include also 'koeflachite' in our so-called 'phyllocladane-group'.

In respect to this revision it must be stated, however, that in this case no authentic material belonging to DOELTER's studies has been available. His finds could not be relocated in any of the collections at our disposal. Realizing, moreover, some obvious differences between his descriptions and the material we could use for the investigations mentioned above, some uncertainty remains, to be clarified hopefully in the course of future studies.

Possible (palaeo-)botanical affinities indicated by phyllocladanes

Compounds with the typical carbon skeleton of phyllocladane are not uncommon in quite a number of different genera of trees. The corresponding unsaturated hydrocarbon is known to be the main constituent in the essential oils of some species of the genus *Phyllocladus* (Coniferopsida) as well as in the genus *Dacrydium* (Podocarpaceae). Kaurene (= podocarprene), an isomeric hydrocarbon, has been found in various species of the genus *Podocarpus*. Phyllocladene has been reported to occur in *Sciadopitys* (Taxodiaceae). Isophyllocladene respectively a corresponding alcohol (phyllocladanol) has been found – among others – to occur in the genus *Cryptomeria* (Coniferopsida).

During diagenesis phyllocladanole yields the corresponding unsaturated hydrocarbons (β-elimination), which by means of hydrogenation finally results in the formation of phyllocladane itself. How readily such processes of diagenesis may occur has been recently shown by means of studies of a trunk of *Cryptomeria japonica* (age: 3500 – 3800 years only !) preserved in volcanic ash, which contained not only α-phyllocladane but even simonellite (NARITA & YATAGAI 2006).

Realizing the fact that compounds with a phyllocladane type carbon skeleton are rather widespread among different species of Podocarpaceae, Araucariaceae, Cupressaceae, and Taxodiaceae it is obviously not very promising to start any considerations about possible botanical affinities of hartite and related organic minerals. As pointed out for example already by OTTO et al. (1997) the use of phyllocladane-type 'biomarkers' will remain always rather difficult. On the basis of palaeobiogeography of plants, however,

quite a number of genera can be cancelled from the list of possible botanical sources at least for phyllocladanes found in Middle Europe. For the Austrian Miocene two genera: *Sciadopitys* (Recent occurrence: Southern Japan) and *Cryptomeria* remain as possible candidates for the formation of phyllocladane. Both are well-known from the fossil record of lignites (ZETTER, 1988; respectively: ZETTER, personal communication). The fact that remains of *Sciadopitys* are very common indeed in some cases is well illustrated by the fact, that a special variety of lignite derives a local German name from the bulks of grass-like needles of this tree occurring in these coal seams: 'Graskohle'. It may therefore be acceptable to regard *Sciadopitys* and/or *Cryptomeria* as possible botanical sources for hartite and related organic minerals at least for Central Europe.

Duxite from Bohemia

As last example for an 'organic mineral' with obvious terpene affinities, duxite from Bohemia, will now be briefly mentioned. It may serve in this connection as an example of a mineral representing a mixture of hydrocarbons with no evident relationship to the phyllocladane-group. Obviously local accumulations of hydrocarbons in lignitic coal seams are very common: depending on the various botanical sources they show different chemical patterns. Terpenes are obviously the source for such 'minerals' – there may be either no material among them which can readily undergo polymerisation, or they may be no starter for such processes (anaerobic conditions).

Duxite has been first described by DOELTER (1874) from a Miocene coal seam (former Emeran Mine) at Duchcov (German name: Dux; Bohemia, Czech Republic): a blackish brown substance with resinous lustre, conchoidal fracture to be found in lentile-like layers, 2 – 8 cm thick. A modern revision (VÁVRA et al. 1997) based on material from the Bílina open-cast mine, situated near the type area, has shown a number of various hydrocarbons to occur in this material: drimane, labdane, simonellite, retene, a C_{16}-bicyclic sesquiterpane, and a C_{18}- tricyclic diterpane could be identified by means of their mass spectra. ZELENKA (1982) had regarded duxite as a mixture of waxes and resins however – this obviously contradictory results will require further studies. Of great importance in this connection would be once again the availability of real 'type material' referring to DOELTER's first description. Otherwise there will always remain the risk that things are revised or compared with each other which are not authentic at all. The question hydrocarbon vs. resin has also been discussed by KRUMBIEGEL (2002).

Conclusions

The main goal of this publication has been to offer for non-specialists interested in amber an overlook of the present state of knowledge of the chemistry of fossil resins ('ambers') and some related organic minerals. Such studies are not only required to establish reliable possibilities for the identification of different species of organic minerals, but play , moreover, an essential part in discussions about botanical affinities of various ambers and will – hopefully – in future also achieve better and more reliable possibilities for geographical attributions of archaeological amber finds. An additional item being of great practical importance in amber chemistry – the identification of fakes and imitations – has been excluded from this paper.

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