

The comparison of structure and properties of fossil resins of the glessite type (from Germany, Europe) and of the dammar type (from Malaysia, Southeast Asia)

With 5 figures and 1 table

ANIELA MATUSZEWSKA

Kurzfassung

MATUSZEWSKA, A.: Vergleich von Struktur und Eigenschaften fossiler Harze vom Glessit-Typ (Deutschland, Europa) und vom Dammar-Typ (Malaysia, Südostasien)

Zu den fossilen Harzen Glessit (Sachsen-Anhalt) und Dammar (Malaysia, Borneo), die Gegenstand dieser Arbeit sind, gibt es bereits zahlreiche Veröffentlichungen. Diese Harze wurden in der Literatur jeweils einzeln beschrieben, oder sie wurden anhand einer Reihe ähnlicher Merkmale und Eigenschaften miteinander verglichen. Im Zuge der weiteren Forschungen werden die Daten ergänzt, Hypothesen verifiziert und die beobachteten Unterschiede und Ähnlichkeiten erläutert. Neuere Arbeiten stellen einige frühere Ergebnisse in Frage, insbesondere zum sachsen-anhaltinischen Harz, einschließlich seiner Phytogenese und chemischen Zusammensetzung. In einigen Arbeiten zu diesem Harz wurden gelegentlich ungewöhnliche „Glessit“-Proben erwähnt. Die Analyseergebnisse zeigen das Vorhandensein bestimmter Komponenten, die für die Harze von bedecktsamigen Gehölzen, von denen das Harz stammt, untypisch sind. Es wurde versucht, die Ursachen dieses Problems zu klären. Die chemische Zusammensetzung der getesteten Harze aus beiden Fundgebieten wird ebenfalls anhand der Ergebnisse der Elementaranalyse, der Infrarotspektroskopie und der Pyrolysetechnik (Gaschromatographie in Verbindung mit Massenspektrometrie) verglichen. Die Ergebnisse zeigen, dass es Ähnlichkeiten in der chemischen Zusammensetzung gibt, die hauptsächlich mit dem Gehalt an Verbindungen des Cadinentyps (zur Sesquiterpengruppe gehörig) und mit dem Vorhandensein einiger ähnlicher Triterpenoide zusammenhängen. Es wird darüber hinaus diskutiert, ob die bestehenden strukturellen Gemeinsamkeiten die Verwendung der Bezeichnung „Glessit“ sowohl für die Harze aus Sachsen-Anhalt als auch für malaysisches Harz bzw. allgemein Harz aus Südostasien durch einige Forscher rechtfertigen.

Schlüsselwörter: Glessit, Dammar, Infrarotspektroskopie, Gaschromatographie-Massenspektrometrie, Cadinen

Abstract

Fossil resins: glessite (Saxony-Anhalt, Germany) and dammar (Malaysia, Borneo), which are the subject of this work have already a rich bibliography. These resins were described separately in the literature, or they were compared due to a number of similar features and properties. Along with the progress

of the research process, data is expanded, hypotheses verified, and the observed differences and similarities are explained. Newer papers question some earlier findings, in particular concerning the resin from Saxony-Anhalt, including its phytochemistry and chemical composition. In some works describing this resin the mentions were made of occasional unusual “glessite” samples. The results of their analysis indicate the presence of certain components untypical for the resins of flowering trees, to which said resin belongs. An attempt was made to explain the causes of this problem. The chemical composition of the tested resins from both mentioned locations was also compared, using the results of elemental analysis, infrared spectroscopy and pyrolytic technique of gas chromatography coupled with mass spectrometry. Based on the obtained results it was found, that there are similarities in the chemical composition related mainly to content of compounds of the cadinene type (belonging to sesquiterpene group), and to presence of some similar triterpenoids. However, the simultaneously existing differences seem to be enough to not to confirm the hypothesis, set in some publications, about close relationship between plant families including parent trees for both types of resins. It was also questioned whether the existing structural similarities justify the inclusion by some researchers of the common name: *glessite* as well for theres in from Saxony-Anhalt as also for Malaysian resin (or more broadly – resin from Southeast Asia).

Keywords: glessite, dammar, ir, gc-ms, cadinenes

1 Introduction

Classification of fossil resins is a rather difficult task hence few classification systems have been developed so far (shortly described e.g. in a work MATUSZEWSKA 2010). Currently, the classification created by Anderson and colleagues is widely used (e.g. ANDERSON et al. 1992, ANDERSON & BOTTO 1993, ANDERSON & CRELLING 1995) based practically on chemotaxonomy. The variety of origin and composition of fossil resins, however, causes that this classification needs to be supplemented, what may be facilitated by further research using a modern equipment base. Although the resins discussed here [glessite (Saxony-Anhalt) and a fossil resin from Borneo] show a series of similar traits of chemical construction (as presence cadinenes from the group of sesquiterpenes or triterpenoid compounds), only the resin from Borneo is included in group II of the said classification. This resin can polymerize to the so-called polycadinene which was not found in the case of resin from Saxony-Anhalt. Since there is a difference in the construction of resins, which is fundamental for their classification, it would be worth considering, whether the use is justified of the common name *glessite*, for both discussed resins as it was presented in the series of works (e.g. YAMAMOTO et al. 2006, KOSMOWSKA-CERANOWICZ 2012, KOSMOWSKA-CERANOWICZ & VÁVRA 2015). One of the goals of this work was to comment on this problem. Another unresolved problem is the question whether the similarities in composition and certain properties of the resins under discussion justify the suggestions presented in some works, concerning of close affinity of the parent trees that were assigned to them (e.g. KOSMOWSKA-CERANOWICZ 1994, 1999b).

Another else important task with regard to the resins under investigation was to list the literature data on hypotheses and evidences related to the determination of their phytochemistry. In the case of fossil resins, the attribution of phytochemistry is often a very difficult issue. This is undoubtedly due to the complex history of fossil resins, among others: geological (wandering continental discs, environmental conditions of expulsion and deposition of resins, diagenesis, catagenesis, volcanism), geographic (climate, migration of resin to the secondary place of deposition), as well as biological (plant evolution, decay of plant debris).

In the case of resins discussed here less doubt exists, however, about phytogenesis of the resin from Southeast Asia, because, as researches show, contemporary tropical forest in this area is not changed much in relation to paleo-forests also in terms of the composition of the resins produced there. The resins from this area are described by general name *dammar*. LANGENHEIM (2003) explains that there exist much of confusions with the use of this name. However, the cited author uses mainly the term *dammar* to the resins from trees belonging to the popular in this Asiatic region the genus *Shorea* and genus *Hopea*, both from the same family Dipterocarpaceae.

In a case of the resin from Saxony-Anhalt, because of many of factors mentioned earlier, a sufficiently complete and accurate characterization is much more difficult.

It is not easily to explain the above mentioned doubts if they exist yet despite many tests carried out and the results presented in the literature of subject. The aim of this study was among others, to summarize the literature data and the results of own research to formulate the causes of doubts in the comparative interpretation of the investigation results of the resins under discussion, an attempt to explain them and suggest the directions for further researches.

1.1 Characteristics of glessite - an accessory fossil resin from Saxony-Anhalt

The name of this fossil resin comes from the word *glessum* mentioned by the Roman historian Tacitus (55–120) to refer to the Baltic amber. Glessite was first found on the Baltic coast and in Sambia Peninsula (Russia) as an accessory fossil resin deposited together with succinite. Glessite was described for the first time in 1881 by a Gdańsk pharmacist, an amber researcher Otto Helm (1826–1902, HELM 1881). He has estimated the specific gravity of this resin in the range of 1,015–1,027 g/cm³ and the Mohs hardness as about 2 (KOSMOWSKA-CERANOWICZ 1999b, *loc.cit.*).

1.1.1 Deposits of the glessite fossil resin

Apart from a few other small European finds of resins with a similar composition [as Samland (Russia), the Goitsche and Golpa open pits, the Oberlausitz (Germany) and the North Sea shore] (LANGENHEIM & BECK 1968, KOSMOWSKA-CERANOWICZ et al. 1993), the largest accumulations of glessite in Europe, are around the city of Bitterfeld (Middle Germany, Saxony-Anhalt) where glessite is one of the accessory resins accompanying succinite in the interbedding of brown coal deposits, e.g. in the mine Goitsche. Amber was exploited there together with brown coal in the period from 1975 to 1993 year (KRUMBIEGEL 1995) with the annual output coming up to 50 tons of amber per year (KRUMBIEGEL & KRUMBIEGEL 2006b). The fossil resin is there in Palaeogene deposits classified as Upper Oligocene–Lower Miocene (Bitterfeld layers). Bitterfeld amber is a result of an increase in the release of resin, caused probably by the alteration of the environmental conditions (temperature, humidity, salinity of the ground). These processes took place during the marine ingression phase of the epicontinental north-western European sea (KRUMBIEGEL & KRUMBIEGEL 2006a). In the Bitterfeld region, glessite has been discovered by FUHRMANN & BORS DORF (1986).

1.1.2 The age of glessite

The Miocene age was at first assigned for the so called Bitterfeld amber from the Cottbus Formation near the town of Bitterfeld in Saxony-Anhalt (BARTHEL & HETZER 1982). Later geochronological investigations have indicated the age of these sediments as the Late Oligocene (Chattian; 23,0–28,1 Ma) (KNUTH et al. 2002). However, the newer results of paleontomological research of different authors, presented by WOLFE et al. (2016) suggest that succinite from the Bitterfeld region like this from the Baltic region, is of Eocene age. Eocene succinite could migrated later to the Miocene layers, together with other resins co-occurring with succinite, glessite including.

1.1.3 Botanical origin of glessite

Determination of phyto genesis of glessite was first realized by the use of infrared spectroscopy (IR) when the similarity was noticed of IR spectrum of glessite with that of the extant resin from *Bursera bipinnata* of the Burseraceae angiosperm family (LANGENHEIM 1969). It was because the author cited has suggested that the plants which could produce glessite derive probably from the Burseraceae family (LANGENHEIM 1969). FRONDEL (1967) has shown, in turn, the similar patterns of the X-ray diffraction curves for glessite and for the resin of *B. bipinnata*. The presence of Burseraceae family trees in the period of the glessite-precursor resin production in Bitterfeld region is in accordance with the paleoecological data indicating possible there the temperate and subtropical to tropical climates (YAMAMOTO et al. 2006).

When the presence has been stated of α - and β -amyrins (penta-cyclotriterpenoids) (Fig. 1b) in the glessite from Goitsche mine, the opinions were presented, that glessite can be attributed to elemi type of resin from trees of the *Canarium* genus (Burseraceae family) of characteristic abundant resin expulsion (e.g. KOSMOWSKA-CERANOWICZ et al. 1993). It should be also mentioned that resins called elemi are produced as well by other members of the family Burseraceae, as particularly *Dacryodes*, *Protium* and sometimes *Bursera* (LANGENHEIM 2003).

The later investigations by YAMAMOTO et al. (2006) indicated that the presence in glessite of triterpenoid compounds of the allobetulane class can suggest the possible botanical origin of glessites from the *Betula* genus trees of the Betulaceae family. It should be underlined that birches (Betulaceae) produce more resins when growing in tropical climates than the same species in temperate regions (FUKSMAN et al. 1979).

1.1.4 The general data of the chemical composition and properties of glessite

Chemical composition of glessite (like other resins from deciduous trees) characterizes the presence of volatile fraction (monoterpenes and sesquiterpenes) as well as nonvolatile fraction (containing mainly five-ring triterpenoids), and also an insoluble high molecular weight network surrounding low molecular weight components (e.g. OTTO & SIMONEIT 2001).

Particularly important for the biological function of the released resin and for the possibility of its subsequent use there is a sesquiterpenoid group of compounds. In a case of glessite there are characteristic bicyclic compounds of the cadinene type with various degree of unsaturation, up to five double bonds. Carbon skeleton of their precursor-cadinane is presented on a Fig. 1a. A series of these sesquiterpenoids has important biological functions: antibacterial or antifungal.

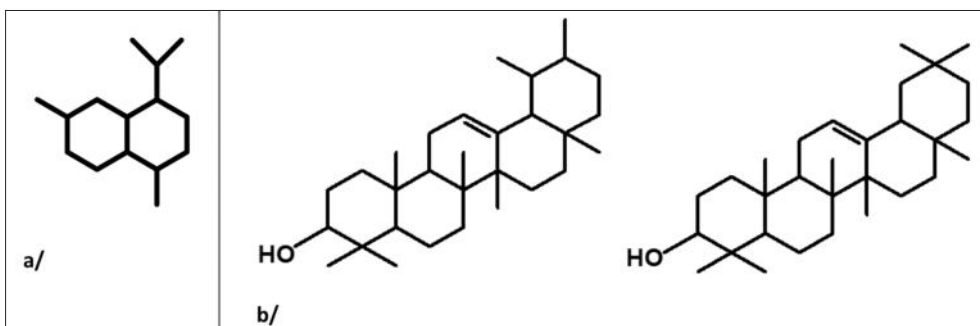


Fig. 1: Chosen chemical structures characteristic for analyzed resins: a/ structure of cadinane- precursor of cadinenes; b/ structures of α -amyrine and β -amyrine.

The triterpenoid group of compounds is dominated by derivatives of the oleanane, ursane, lupane and allobetulane classes indicating the angiosperm origin of glessite. The high molecular fraction of glessite is a secondary fraction made upon influence of light and oxygen after expulsion of resin by a parent tree.

1.1.5 Characteristics of the fossil resins of the dammar type from Southeast Asia

Resin from the Asia tropics is frequently called dammar (MILLS & WERNER 1955; VAN AARSSSEN et al. 1990, LANGENHEIM 2003). However, in Malaysia, local people have commonly used name dammar for resin in general but particularly for that from trees belonging to the families Dipterocarpaceae and Burseraceae (GIANNO 1990). LANGENHEIM (2003), known specialist in the domain of amber botany, underlying that primary source of dammar are members of the family Dipterocarpaceae (angiosperm trees growing abundantly in Southeast Asia), uses the name *dammar* mainly for resins derived from *Shorea* but also *Hopea*, typical dipterocarps of the Asia tropics. For Borneo resin HILLMER et al. (1992) have indicated more precisely the *Shorea robusta* as a parent tree. In presented work the name *dammar* is used in accordance with these ideas.

In the tropical rainforests of the Southeast Asia the considerable amounts of the dammar resin exists, however, especially large on the Borneo island, where the world's largest deposit of fossil resin was found (e.g. KOSMOWSKA-CERANOWICZ 1994). The most-known place of the significant accumulation of the dammar resin is the Merit Pila brown coal mine (Sarawak, Borneo). This type of resin was also found e.g. in coal deposits on Sumatra (KOSMOWSKA-CERANOWICZ et al. 2017).

Dammar is used dependently on chemical composition. When nonvolatile fraction dominates, higher viscosity is favorable for application of resins as varnishes. In the case of volatiles domination the use is preferred as medicament or fuel. The presence of triterpenoids (in the bicadinane forms) and primary sesquiterpene hydrocarbons in both fresh dipterocarp and fossil resins strongly support the role of dipterocarp resin in petroleum formation in numerous parts of Southeast Asia: Sumatra, New Guinea, Java, China, Malay Basin, India, Bangladesh, Myanmar, Philippines, areas in which Dipterocarpaceae are dominant today and grew during a time of oil formation (STOUT 1995). The dipterocarp oleoresins in which triterpenoid components were dominated by volatile sesquiterpenes, were used by the Malays for illumination. As a biological destination of dammar components, the antibacterial, anti-fungal and antiinsect activity should be underlined (LANGENHEIM 2003).

1.1.6 Some geological data for Malaysian fossil resin

Fossil resins in Malaysia are Early Miocene in age (23 Ma; some are younger). The deposits of fossil resin in Borneo have been discovered in 1991 year by German paleontologist G. Hillmer (HILLMER et al. 1992). The resin deposited among coal layers is extracted together with brown coal. It was calculated that together with coal mining in the Merit Pila mine (Borneo) 2–5 thousand tons of resin can be obtained annually (KOSMOWSKA-CERANOWICZ 1994). Expulsion of the large amounts of resin from plants could be provoked by intense volcanism documented by numerous intrusions in this area (SZENDERA 2008).

1.1.7 Phyto genesis of main fossil resin from the Southeast Asia

The plant source of fossil and extant resins dominant in Southeast Asia are, as was mentioned earlier, members of the angiosperm family Dipterocarpaceae, the most important, producing resin in tropical rainforests of Southeast Asia. As ones of the most leading dipterocarp types of trees producing dammar resin are the genera *Shorea* and *Hopea* (BRACKMAN et al. 1984), typical for tropical part of Asia but grow as well for example in the tropical part of Africa. The richness of forest complexes in this part of Asia can complicate, however, the resin classification. As one example an extant tree is taken into account: so called *black dammar* in India is a burseraceous resin from *Canarium strictum* or other species of *Canarium*, but not from Dipterocarpaceae family (LANGENHEIM 2003).

1.1.8 Chemical composition of main fossil resins from the Southeast Asia

Fossil resins of the dammar type are composed of both – a low molecular fraction and a macromolecular phase (VAN AARSEN et al. 1990). The low molecular fraction contains a large number of sesqui- and triterpenoids, primarily of the cadinane, oleanane and dammarane skeletal types. These compounds are characteristic for angiosperms (SIMONEIT 1977).

The compounds from the cadinane precursor are present in dammar in the unsaturated forms – cadinenes, like in glessite. However, only for dammar the formation of polymerized structures is described in the literature, from bicadinenes by tricadinenes etc. up to polycadinenes. The capacity to polymerization process was a cause to place the dammar resin in the class II of actual fossil resin classification mentioned earlier.

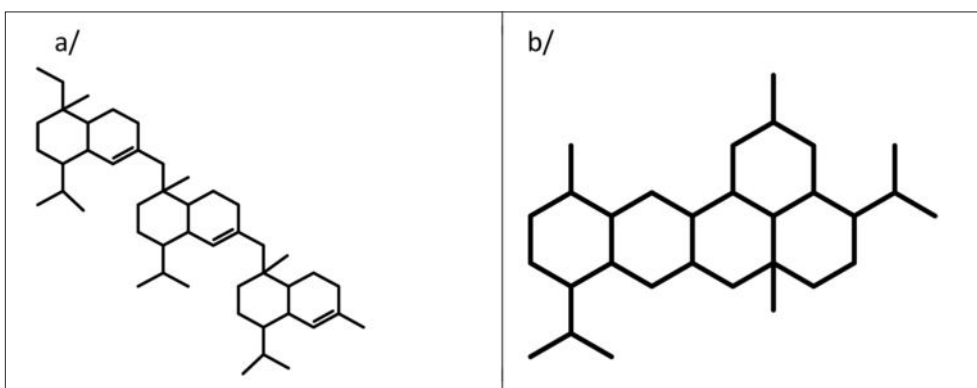


Fig. 2: Theoretical model of polycadinene macromolecule of dammar (a) and structure of bicadinane (b), presented by VAN AARSEN et al. (1990).

VAN AARSSSEN et al. (1990) have suggested a theoretical model of polycadinene (Fig. 2a), questioned, however, by ANDERSON & MUNTEAN (2000), as not adequate to real structure. These authors underline, however, that this model rationalizes the observed formation of bicadinanes and individual cadinenes as a result of thermolysis of the macromolecular phase. The probable structure of bicadinane (Fig. 2b) is suitable with structures of compounds identified in source rock extracts and crude oils exploited in the region under discussion. The dammar resin has probable a contribution to formation of this crude oil.

2 Experimental

2.1 Short characteristics of analyzed samples

The brown colored fossil resin sample from Bitterfeld region (Saxony-Anhalt, Germany) was received to analysis from collection of Earth Museum, Polish Academy of Science in Warsaw. Glessite was deposited between brown coal layers in coal mine Goitsche, being an accessory resin accompanying the main resin – succinite. The age of coal layers containing various resins was described as Upper Oligocene–Lower Miocene but the resin itself derives probably from the older, Eocene layers. Later the resins migrated to secondary, younger, sedimentation deposit. The phyto genesis of glessite is still under discussion but the broadly accepted opinion is that of Burseraceae family trees (*Bursera bipinnata*) as a source of this resin. However, there is also a new hypothesis concerning trees from the genus *Betula* (Betulaceae) as parent ones for glessite (see chapter 1.1.3).

The brown-yellow colored was a sample of fossil resin from Borneo island (Malaysia, Sarawak state). Analyzed sample derives from coal mine Merit Pila (Borneo). Like glessite the dammar resin was placed between brown coal layers. The age of the resin is Early Miocene. HILLMER et al. (1992) have indicated the *Shorea robusta* as a parent tree for Borneo resin.

2.2 Methods of analysis

For comparison of the structure and properties of both analyzed fossil resins a series of investigations has been performed: elemental analysis, infrared spectroscopy (IR) and pyrolytic gas chromatography-mass spectrometry (Py-GC-MS).

2.2.1 Elemental analysis of samples

In the Table 1 the data are presented of main elements' contents in both analyzed samples in comparison with literature data for resins of the same type.

General differences between glessite and Borneo resins are here, respectively: in average – lower oxygen contents, higher sulfur contents and higher amounts of carbon and hydrogen, in the case of glessite. It can be explained by the fact of various phyto genesis of both resins and different age – after newer suggestions glessite is older than resin from Borneo (WOLFE et al. 2016). This reason could explain also a higher degree of coalification of glessite (higher C^{daf} and lower O^{daf} contents, in average). There is also other, additional, possible cause of increase of carbon contents in sedimentary organic matter – a volcanism. However, in the case of glessite, the literature data indicate well only earlier volcanism (Carboniferous-Permian) in the region adjacent to the glessite occurrence in the Bitterfeld [the „Hallescher Vulkanit-Komplex“; KRUMBIEGEL & KOSMOWSKA-CERANOWICZ (1992)].

Tab. 1: The contents of main elements in both analyzed samples, compared with literature data for resins of the same type.

fossil resin	C ^{daf} [%]	H ^{daf} [%]	O ^{daf} [%]	S ^{daf} [%]
from Borneo (coal mine Merit Pila) [KOSMOWSKA-CERANOWICZ 1999b]	77,55– 84,76	9,48– 12,68	11,10–4,17	-
HELM 1881	79,36	9,48	10,72	0,44
from Borneo (coal mine Merit Pila) [MATUSZEWSKA 2010]	82,35	12,31	5,23	0,0
glessite (coal mine Goitsche, Germany) [KOSMOWSKA- CERANOWICZ 1999b <i>loc. cit.</i>]	82,99 81,80	11,19 11,39	5,82 7,61	(the most frequently <0,3, max.: 1,87) -
glessite (coal mine Goitsche, Germany) [MATUSZEWSKA 2010]	83,88	12,42	3,14	0,56

In turn, in the case of Borneo island, the literature data (SZENDERA 2008) can confirm the likely influence of volcanism on the structure of resin organic matter. As an other evidence can be here a broad range of the carbon contents for Borneo resins, indicating a considerable diversification of environmental conditions in paleo-forests).

2.2.2 Infrared analysis (IR)

For both tested resins the IR spectra have been registered by transmission technique, using Fourier transform infrared spectrophotometer Bio-Rad FTS-600 (Fig. 3). The bands are observed of vibrations of saturated hydrocarbon fragments of the structure (aliphatic, alicyclic: 2956, 2869, 1463, 1384 cm⁻¹), unsaturated ones (1644, 887 cm⁻¹) and of functional oxygen groups (3429, 1735, 1693, 1243, 1164, 1047 cm⁻¹). The spectra indicate very similar shapes for both samples under discussion. However, there are some differences e.g. relatively higher intensity of bands of oxygen groups for resin from Borneo, what can confirm that this resin is younger (lower maturation degree). Adiverse phylogenesis can be here other important reason of observed differences. Both spectra have pronounced bands from vibrations of double bonds C=C (at 1644 cm⁻¹), deriving from a numerous unsaturated structures existing as well in molecular as also in macromolecular parts of the structure of resins.

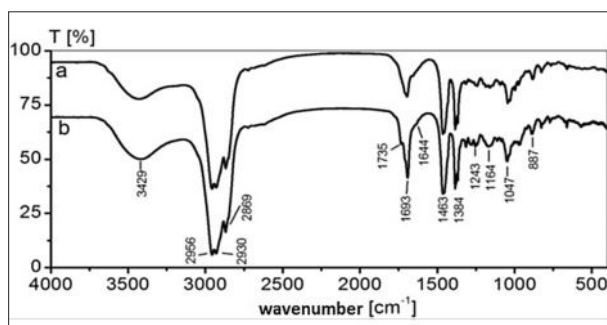


Fig. 3: Resemblance of the infrared spectra of glessite [Saxony-Anhalt, Germany (a)] and dammar resin [Malaysia, Borneo (b)], reflecting some structural similarity of both resins.

2.2.3 Analysis of thermal decomposition products of analyzed resins

As it was mentioned earlier, tested groups of resins are composed of a low molecular phase – soluble in organic solvents and of insoluble high molecular fraction. The last one shows a complicated construction with the character of the irregular polymer. This construction can be analyzed only after thermal decomposition – depolymerization, on a basis of fragments of resin macromolecules formed during pyrolysis. In this work for this purpose a method of Py-GC-MS – pyrolytic gas chromatography coupled with mass spectrometry – was used. The analysis was performed, using gas chromatograph (Hewlett-Packard) with a capillary column (60 mm × 0,22 mm × 0,52 μm), coupled with mass spectrometry (HP) and pyrolyser (PyeUnicam, type 79 5050). Curie-point pyrolysis was realized at temperatures: 480 °C and 610 °C. On the Fig. 4, as an example a fragment of the mass chromatogram is shown of the glessite sample pyrolysed at the temperature: 480 °C. The identification of a series of sesquiterpenoids is presented.

The comparison of the results of analysis obtained for glessite and dammar, including also the literature data, indicates a significant similarity of chemical composition of glessite and dammar, especially in the sesquiterpene group of the cadinene type structure. Both analyzed resins differ, however, in qualitative and quantitative distribution of components. In the case of the second important component of the tested resins – the triterpenoid group, the differences in composition are even more clearly marked. The third main fraction of analyzed resins is macromolecular, insoluble part difficult to direct analysis. Thanks to pyrolysis the products obtained of partial destruction can inform about macromolecular structure. The products of pyrolysis of resin macromolecules enriched also a composition of molecular fractions mainly

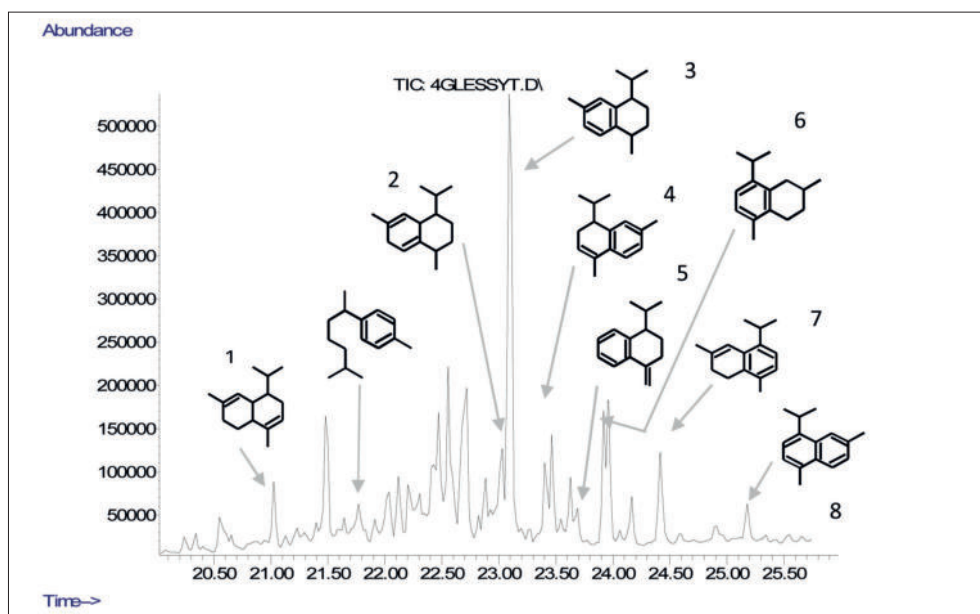


Fig. 4: Mass chromatogram (TIC) of the glessite pyrolysate products obtained at 480° C with the use of pyrolytical technique (Py-GC-MS). Identified compounds: 1/ α -muurolene; 2/ dihydrocurcumene; 3/ 1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene; 4/ calamenene; 5/ α -calacorene; 6/ isopropyl-6-methyl-1-methylene-1,2,3,4-tetrahydronaphthalene; 7/ cadina-1(10)6,8-triene; 8/ α -corocalene; 9/ cadalene.

these of sesquiterpenoids and triterpenoids. It proves that compounds of this type construct the considerable fragments of resin macromolecules. This construction has been formed during contact of exudated resin with oxygen from air, and as a result of sun light action. The products of pyrolysis have not probably the primary structure in a whole because of thermal transformations. During pyrolysis the structure of products could undergo e.g. the disproportionation processes by change of saturation or unsaturation and also – aromatization degree. It is process similar to natural slow processes of diagenesis and faster catagenetic processes induced by drastic changes of environmental conditions (e.g. thermal, as fires or volcanism). On the Fig. 5 some sesquiterpenoid structures are presented derived from cadinane precursor. In a simplified manner the possible transformations described earlier are there shown, from lower degree of unsaturation up to totally aromatized cadalene.

2.2.4 General summary of the results of own research

Infrared spectra (Fig. 3), and derivatograms obtained during thermal experiments realized earlier (CEBULAK et al. 2003), indicated considerable similarity in the structure and properties of analyzed resins. The methods used have given, however, the averaged information about chemical composition of the tested substances. The more precise analyses of tested resins was realized using Py-GC-MS method by identification of particular components being products of simple distillation and products of pyrolysis as it was described earlier. Comparison of these products indicated some similarities and differences in qualitative and quantitative distribution of various groups and of particular compounds.

The composition of sesquiterpenoid group in pyrolysate of glessite (Fig. 4) is similar to obtained for glessite resin by other authors (e.g. YAMAMOTO 2006), including characteristic domination of calamenene peak in both compared results. This compound is probably the most thermally stable among other ones from this group. The pyrolytic own experiments indicate, moreover, the increase of the variety and relative amounts of sesquiterpenoids at higher temperature of pyrolysis (here at 610 °C). It was observed in the case of both tested samples and has shown that macromolecular fractions of both analyzed resins contain a considerable amount of sesquiterpenoids as incorporated fragments of a crosslinked structure. Borneo resin has given more products of pyrolysis. It is in accordance with earlier presented characteristic about lower degree of maturation of this resin and also with probable input of this type of resin to regional crude oil (as mentioned earlier after STOUT 1995). The differences observed between chemical composition of both compared resins (glessite and dammar), even if not fundamental, but suggests among others the possible difference between metabolism processes of the parent trees of both compared resins. It may be a result of different phytogenesis and also – of various environmental conditions during expulsion, then diagenetic and catagenetic processes. The analytical methods used here did not allow study the macromolecular structure as a whole. In the future, it would be advisable to learn more about the construction of insoluble fraction of glessite and dammar by more detailed studies of the similarities and differences in their structure, and to supplement the existing classification of resins.

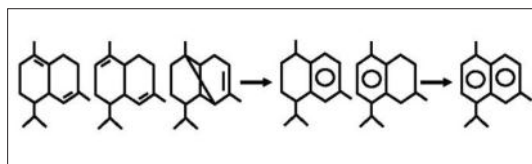


Fig. 5: Selected structures of the unsaturated derivatives of cadinane. In various diagenetic and catagenetic conditions their transformation can have place up to totally aromatic structure of cadalene.

Actual state of knowledge, after already relatively rich literature describing the chemistry of glessite, does not explain of the construction details of the glessite macromolecule. On the contrary, for dammar the polycadinane polymer is suggested as formed probably by linking of unsaturated cadinenes, at first to bicadinenes and then up to polycadinane type of polymolecular structure. Theoretically judging, such compounds could be formed also in the case of glessite during processes of diagenesis and catagenesis. It is, however, probable that during maturation of glessite the precursor components (cadinenes including) form other type of macromolecule. In the case of glessite the macromolecule seems to have a construction of lower regularity than dammar but simultaneously of denser network. The confirmation should be here high micro-hardness of glessite (309 MPa) (MATUSZEWSKA 2010). The practical significance of such macromolecular structure is well ability of glessite to mechanical treatment (KRUMBIEGEL & KOSMOWSKA-CERANOWICZ 1992). In the same time the surface of resin lump from Borneo during mechanical treatment shows a thermal susceptibility and it is because such process should be performed in coldness (KOSMOWSKA-CERANOWICZ 2012).

3 The analytical and substantive problems during researches of resins under discussion

3.1 The common name glessite?

The ascription of the name *glessite* (used primary for European resin accompanying succinite) also for the dominating resin from Southeast Asia, was caused by similarity of the infrared spectra of these resins (KOSMOWSKA-CERANOWICZ 1999a). Other authors have used this term for both kinds of resins under discussion, taking into account the series of similarities in the results of analyses made using gas-chromatography coupled with mass spectrometry (YAMAMOTO et al. 2006). However, these resins derive from trees of various families: Burseraceae and Dipterocarpaceae, respectively, differential clearly by substantial botanical features (LANGENHEIM 2003). The resins expelled from trees belonging to these families, contain a series of similar compounds, including sesquiterpenoids from cadinene group. However, the differentiated distribution of these and other groups of compounds in a case of resins from both mentioned plant families, may confirm a dissimilarity of these families what manifests one self among others by the differences of metabolism processes. It should be, however, mentioned simultaneously, that there is also probable some relationship between resin composition and environmental conditions, which influence the process of metabolism of trees too. These exterior conditions, climate including, influence undoubtedly expulsion process (e.g. by extortion of growth of amounts of volatile compounds facilitating resin exudation) and further transformations of resins during diagenesis or catagenesis. The climatic conditions during formation of the precursors of glessite and dammar resins, was distinctly different. Europe during the Tertiary period encompassed a subtropical and a temperate zone in which the presence of Dipterocarpaceae family trees has not been noted (HILLMER et al. 1992). In turn, the resin from Borneo (Southeast Asia) was produced in a tropical climate just by trees belonging to this family.

In general, however, the differences observed between the qualitative and quantitative composition of the resins under investigations seem to be one of the evidences of dissimilarity, which excludes close genetic relatedness of the families Burseraceae and Dipterocarpaceae, which was suggested on a basis of similarity of infrared spectra of respective resins

(KOSMOWSKA-CERANOWICZ 1994). This conclusion could be also a confirmation of the thesis posed in this work, that adaptation of the name *glessite* (at first used for European resin) also for Asiatic resin, is inadequate. This last resin has already his own name: *dammar* as it was explained earlier (LANGENHEIM 2003). The additional confirmation of a considerable peculiarity of both resin types under discussion there is a fact, that it was only dammar, but not glessite, included to the actual classification of fossil resins. Despite a significant similarity of composition, the use of common name *glessite* in the case of resins from trees belonging to the families Burseraceae and Dipterocarpaceae seems to be, therefore, inadequate in the light of current knowledge about the nature of both types of resins under discussion.

3.2 Pollutions of resin samples and mistakes in the selection of samples for analysis

The natural environment of resins can record the informations of their features by adsorption of diagenetic products, at first in soil or lignites and finally on the surface or in pores of other, accompanying resins, causing their contamination and disturbing the results of their analyses. The problem of classification of resins can be therefore complicated because of influence of many environmental factors in various localizations of the resin depositions.

After the literature data diterpenes are generally characteristic for the gymnosperm trees (e.g. OTTO & WILDE 2001) and triterpenes for angiosperms (OTTO & SIMONEIT 2001). In the context of the matter of this work, the surprising informations have been presented in some scientific publications about identification of diterpenoids together with triterpenoids in samples of resins described initially as deriving from the Burseraceae (angiosperms) (ANDERSEON & BOTTO 1993, BECERRA et al. 2001). Co-occurrence of di- and triterpenoids indicates of incorrectly defined phyto genesis or contamination of samples in a sediment. It could be also another unknown type of plants having more complicated metabolism, producing very differentiated composition of resins but LANGENHEIM (1995) has stated that the resins not exist containing both di- and triterpenoid fractions. In the first case the redefinition should be made of the plant source of the resin. It is now well known, that there are trees there, exuding mainly the resin containing components attributed typically to conifers (diterpenoids), but at the same time contain considerable amount sesquiterpenoids, e.g. cadalenes, more typical for the resin of deciduous trees (KARBER et al. 1977). In the case of contamination, the polluting component will have rather a lower concentration. It is known that the soil, or for example, co-occurring brown coal, are good adsorbents which can keep the compounds secreted from the resins into sediment. These compounds, in turn, can move to a porous surface of other resins in the neighborhood. The author of this work also came into contact with a sample acquired as glessite but beyond a small amount of calamenene and traces of other similar compounds, the sample turned out to have a resin composition of conifers rich in abietans and pimarans.

There can be also other reason of doubtful results of analysis, as unauthorized samples from unreliable source. It could be a cause that even among some museum collections one can find sometimes the improperly described samples.

3.3 Is the presence and content of amyrine a chemotaxonomic feature only for glessite?

It is interesting a considerable similarity of resin composition from Southeast Asia as well fossil as extant. However, the conditions of expulsion and sedimentation of resins could cause a transformation of some resin components from one to other form, for example during diagenesis or as a result of thermal processes induced by volcanism or fires. All these phenomena can be a reason of differences in the composition of various characteristic groups present in the resins from trees of the same family. These differences can be even more considerable in a case of various families. In the triterpenoid group, for example, the lack of α - and β -amyrine was indicated for dammar from Lower Miocene deposits in the coal mine Merit Pila in Sarawak (KOSMOWSKA-CERANOWICZ 1999b). In turn, the presence of this group of compounds in Bitterfeld glessite resin (from Burseraceae family) was described as a typical one for glessite (VÁVRA 1990). The results of analyses of several dammar samples have shown, however, the presence of amyryns also in this type of resins (BISSET et al. 1971, VAN AARSEN et al. 1990). It is because amyryns can not to be the chemotaxonomy indices for glessites. It seems, however, that the additional investigations should be performed to estimate e.g. relative proportions between various triterpenoids, amyryn including, as classification parameters for both resin groups under discussion.

4 Conclusions

1. As a result of pyrolysis of resins: glessite and dammar, made as part of the own research, the products were obtained, containing among others the characteristic compounds of the cadinene group. A richer composition of dammar pyrolysates relative to these of glessite may result from different phyto genesis, from age difference and other structure of macromolecule.
2. Similarity demonstrated of the chemical structure and some properties of both discussed resins analyzed by different methods, is not a sufficient basis to state that these resins come from trees belonging to families of close kinship. The similarity of structures may prove, however, that the plant sources attributed them (trees from families: Dipterocarpaceae and Burseraceae) secrete resins of similar composition, intended for similar physiological and protective purposes (conditioned by high temperatures climatic zones: subtropical and tropical one).
3. Without sufficient substantiation of common name *glessite* for European and Asian resins under discussion, it should be not entitled to use this name in the case of Asian resin. For this resin the already existing name *dammar* seems to be more adequate.
4. The most probable reason of simultaneous occurrence of components in resins known as typical for angiosperm and gymnosperm trees seems to be pollutions by one of these group of compounds caused by migration of resin components or tree juices to the deposition environment, especially into soils, having a high adsorption capacity. Under favorable conditions, some of these compounds can be released from the soil and then go to other resins, giving thus the interpretation troubles for researchers.
5. Dammar only has found place in the actual classification of fossil resins – but not glessite. The classification should be supplemented therefore but after a series of additive investigations for samples from various deposition places, especially these where glessite is isolated to avoid an influence of components of other resins in sediment.

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Dr. hab. ANIELA MATUSZEWSKA
Silesian University, Dept. of Earth Sciences, Faculty of Geochemistry, Mineralogy and Petrography
Katedra Geochemii, Mineralogii i Petrografii
ul. Będzińska 60,
PL-41-200 Sosnowiec
E-Mail: aniela.matuszewska@us.edu.pl