

A resin nodule in the Cretaceous Garschella Formation from Langer Köchel (Bavaria, S Germany): possible origin and palaeogeographic provenance

Hubert Engelbrecht · Karl B. Föllmi ·
Ursula Baumer · Johann Koller

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Abstract A resin nodule was found in glauconite-rich detrital sediments of the Cretaceous Garschella Formation (Aptian to Albian) outcropping at Langer Köchel (Bavaria, S Germany). Gas chromatographic and mass spectrometric analyses of the fossil resin revealed dealkylation and the total defunctionalisation of its polycyclic constituents. Besides many unspecific components a specific one, *agathalene*, has survived. *Agathalene* also presents a strongly degraded product, but may have been derived from its natural precursor agathic acid, which is a very specific constituent (biomarker) of recent and fossil kauri resin. Although *agathalene* is a far less specific secondary biomarker, it indicates the botanic origin of the fossil resin nodule. Besides other potential producers of agathic acid, precursors of the present-day conifer species *Agathis dammara* and *A. australis* were distributed in a wider palaeophytogeographic range than today and might have been the botanical source of kauri resin. In view of the east–west directed Early Cretaceous surface current system of the Tethys ocean, the palaeogeographic provenance of the Werdenfels resin nodule probably was a mainland positioned further to the east or southeast of the Helvetic

shelf, to where it was transported probably by driftwood of the resin-producing *Agathis* sp.

Keywords Resin nodule · Amber · Garschella formation · Cretaceous · *Agathalene* · Palaeogeography

Introduction

In 1998, a cm-sized nodule of fossil amber was found in glauconitic sandstone of the Cretaceous Garschella Formation, which was exploited in the open-pit mine “Hartsteinwerk Werdenfels”, located on the southern flank of Langer Köchel near Garmisch-Partenkirchen in Southern Bavaria (Germany; 11°9'E, 47°38'N; Fig. 1b). This mine was active between 1927 and 1999 and afterwards the area was declared a geotope, part of the nature reserve “Murnau-Eschenloher Moos” (Glaser et al. 2008).

The fossil amber nodule—here referred to as Werdenfels resin nodule—was found in a heap of blasted rock boulders on the mine’s floor, which is now flooded. The rock surrounding the nodule allows the determination of the stratigraphic subunit of the Garschella Formation (see below). The importance and scientific value of this discovery is related to its uniqueness. The nodule described here is the first reported finding of amber in the Helvetic zone, to which the sedimentary units of Langer Köchel belong. In addition, amber may contain valuable information on its botanical source (Roghi et al. 2006) and on the environmental and climatic conditions of the terrestrial ecosystem at the time and place of its formation (Gianolla et al. 1998, Rasnitsyn and Quicke 2002). In this paper, we provide a short review of the stratigraphy at Langer Köchel and its palaeogeographic and palaeoenvironmental context, which is necessary for the proposed explanation of the

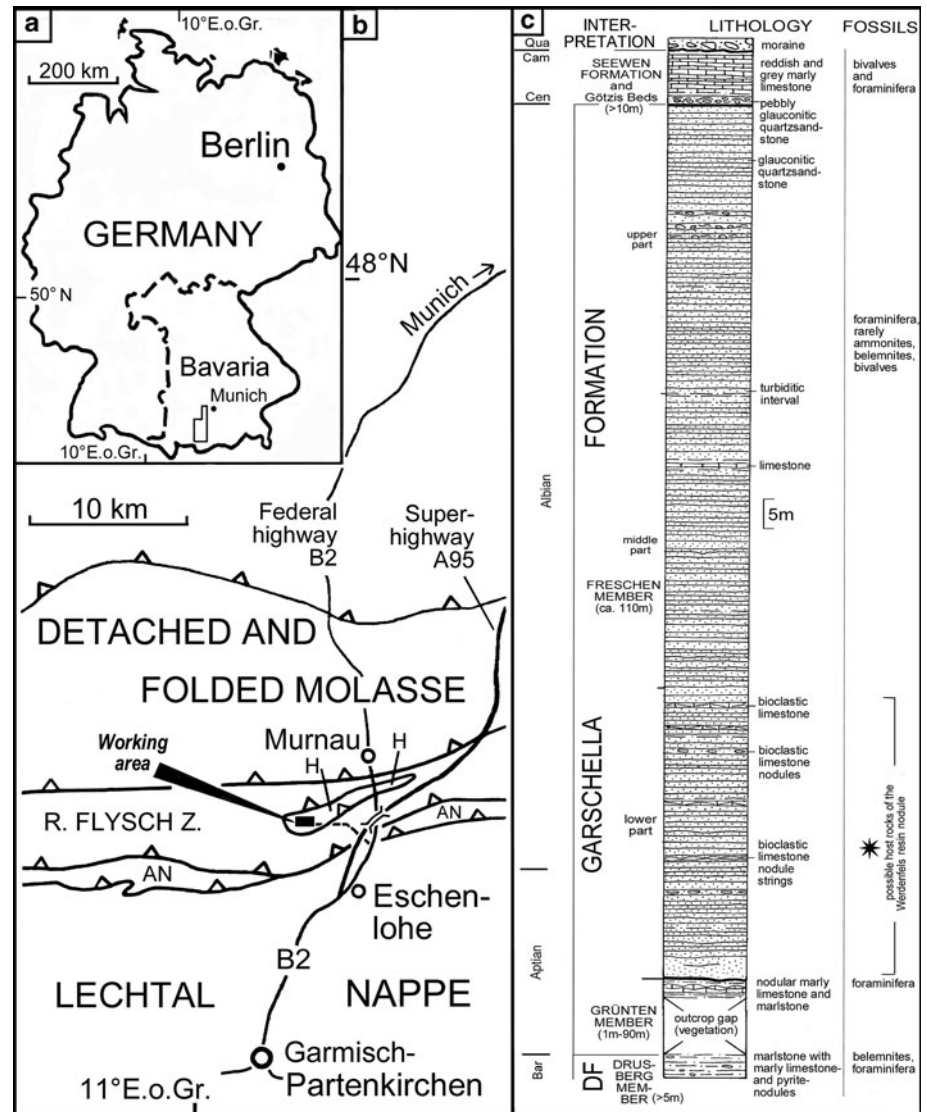
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H. Engelbrecht (✉)
Heßstraße 96, 80797 Munich, Germany
e-mail: hubertengelbrecht@umweltgeol-he.de

K. B. Föllmi
Institut de Géologie et Paléontologie, Université de Lausanne,
Anthropole, 1015 Lausanne, Switzerland

U. Baumer · J. Koller
Doerner Institut, Barerstraße 29, 80799 Munich, Germany

Fig. 1 a–b Geographical and geological setting of the working area. *H* Helvetic Zone, *R. Flysch Z.* Rhenodanubian Flysch Zone, *AN* Allgäu Nappe (after Doben et al. 1996). **c** Synthetic and schematic stratigraphic column of the Helvetic succession at Langer Köchel with indication (*asterisk*) of the suggested stratigraphic subgroup (lower part of the Freschen Member) where the Werdenfels resin nodule possibly comes from. Fossil content according to Zeil (1954) and data of H. Engelbrecht. *Thick line* erosional gap. Scale of lithology slightly exaggerated. *Bar* Barremian, *DF* Drusberg Formation, *Cen* Cenomanian, *Cam* Campanian, *Qua* Quaternary



origin of the Werdenfels resin nodule. Further, we present the results of the chemical investigations of the amber nodule. These data allow us to discuss its botanical origin, the pressure- and temperature overprint during its geological history, and its chemical relations to other Alpine occurrences. Finally some suggestions are proposed regarding the palaeogeographic provenance of the Werdenfels resin.

Methodology

Millimetre-sized splinters of the Werdenfels resin nodule were isolated, put into a small glass tube and analysed in the laboratory of the Doerner Institut in Munich. Two methods were used for the analysis of amber-like materials: gas chromatography combined with mass spectrometry (GC/MS) for separation and identification of the soluble

chemical constituents and Fourier transformation infrared spectroscopy (FTIR) to obtain a more general view of the whole sample (Koller et al. 1997). In total, approximately 4.5 mg were available. For GC/MS analysis about 1 mg was homogenized and extracted step-by-step by several organic solvents, i.e. isoctance, methanol, chloroform/methanol (7/3) and waterfree oxalic acid in methanol (10% w/v). The third solvent (chloroform/methanol) revealed to be most effective; however, only roughly 30% were soluble at best. Aliquots of these extracts (after evaporation of the solvents) and also of the remaining residues were treated with a solution of trimethyl sulfonium hydroxide (0.2 M TMSH in methanol) in order to convert carboxylic acid groups into their methylesters. The supernatant was injected after the reaction (30 min, 50°C). However, no carboxylic functionalities of resin acids and resin acid esters were observed in the soluble fraction. Since all other extracts did not contain relevant amounts of extracted

material, only the chloroform/methanol extracts were used for interpretation. All solutions were directly injected into an Agilent GC (former Hewlett Packard, model 6890). Injection temperature was at 250°C and injection was carried out in splitless mode. A DB-5ht-capillary column of J&W (15 m × 0.32 mm ID) with a (5%-phenyl)-methylpolysiloxane stationary phase (film thickness 0.1 µm) was used for separation. The initial oven temperature was kept at 55°C (T1) for 1 min and raised at a heating rate (R) of 11°C/min up to the final temperature of 350°C (T2). Helium 5.0 (purified) was used as carrier gas with a constant flow of 1.8 ml/min. A flame ionization detector (FID) was used for detection at a temperature of 380°C.

For peak identification, the same sample was again injected into a Hewlett Packard GC (model 5890, series II) combined with the Hewlett Packard quadrupole mass spectrometer (Model 5989 B; column DB-5ht, 30 m × 0.25 mm ID × 0.1 µm film thickness; temperature program T1 = 55°C, R = 14°C/min, T2 = 360°C; Helium 5.0 carrier gas; constant flow 1.0 ml/min, EI mode, scan range m/z 42–500).

FTIR analyses were performed with a Perkin Elmer 1760X spectrometer, coupled to a Spectra Tech IR-Microscope. For IR analysis a small splinter from the Werdenfels resin nodule was pressed onto a miniature diamond cell (Spectra Tech) and the resulting spectra were recorded between 4,000 and 700 cm^{-1} .

0.2 M *n*-trimethylsulfonium hydroxide in methanol was purchased from Macherey–Nagel, Postfach 101352, D-52313 Düren. All other solvents were LiChrosolve grade, purchased from VWR International GmbH, Hilpertstr. 20a, D-64295 Darmstadt. DB-5ht column (J&W) was purchased from Agilent Technologies Deutschland GmbH, Hewlett-Packard-Str. 8, D-76337 Waldbronn.

Geological and stratigraphical setting and palaeoenvironmental development

The lithostratigraphic succession at Langer Köchel is part of the Helvetic zone present in Southern Bavaria. In the study area (Fig. 1b), the Helvetic units of Langer Köchel are tectonic constituent of a triangle zone established at the external front of the Northern Calcareous Alps (Roeder 2009).

The sedimentary deposits at Langer Köchel are interpreted as equivalents of the distal deepening-upward succession defined by Linder et al. (2006) and will be described in detail in an upcoming paper. The Freschen Member (Fig. 1c), which contains the Werdenfels resin nodule, lies on top of the Grünten Member with a sharp erosional unconformity (Fig. 2) and starts with a subunit consisting of medium to coarsely grained, dark olive, grey



Fig. 2 Erosional unconformity between the Grünten Member (alternance of nodular marly limestones and marlstones to the *right side*) and the Freschen Member (very thickly bedded calcareous quartz sandstones to the *left side*). Strike and dip of stratification is 182/87 (Clar value). View to the west. Scale bar 1 m. The marlstone boundary layer (64 cm thick) in the centre of the figure contains a microfauna of Aptian age (Engelbrecht, unpublished data)

to dark grey, medium to thickly bedded calcareous and glauconitic quartz sandstone layers containing rare millimetric phosphatic grains. The uppermost parts of the layers are locally bioturbated and display mm-thin, blackish, phosphatized ichnolites, which possibly represent *Paleo-phycus* sp. and *Thalassinoides* sp. burrows. Occasionally, up to 40 cm thick, light grey, often contorted layers and nodule strings consisting of coarsely grained and impure, bioclastic limestone are intercalated in the lower third of this sequence (Fig. 3). In the middle third of this unit, fine to medium grained, laminated and/or massive, up to several dm-thick quartz sandstone layers prevail. The upper third of this succession is separated by several dark grey, up to 30 cm thick, silty to sandy marlstone strata, which are persistent on a km-scale. At the base of this interval, a graded intercalation similar to an incomplete Bouma sequence T_{A-D} is present. In the upper part of this interval, several dm- to m-thick horizons including cm- to dm-thick, sub-rounded and rounded sandstone pebbles and boulders occur. In addition, white, light grey and black coloured, laterally inpersistent and convoluted, cm-sized chert horizons are occasionally present. The overall thickness of the Freschen Member is approximately 110 m. Its age at this locality is not determined because of the lack of age-diagnostic fossils. Identical lithologies present in the quarry Moosberg 4 km to the east-northeast contained a fauna consisting of ammonites, inoceramids and benthic foraminifera, which was classified by Zeil (1954) as Late Aptian to Middle Albian.

In palaeogeographic reconstructions, the Helvetic sedimentary units are attributed to the northern Tethyan margin



Fig. 3 Bioclastic limestone nodules in coarse grained, calcareous, thick bedded quartz sandstone layers of the lower third of the Freschen Member in the Eastern part of the quarry at 705 m elevation. Strike and dip of stratification is 160/52 (Clar value). View to the east. Scale bar 1 m

(Wyssling 1986; Bollinger 1988). Climate evolution during the late Early Cretaceous is observed in palaeoecological and stable-isotope patterns from coeval pelagic environments (Erba and Tremolada 2004; Steuber et al. 2005; Forster et al. 2007) and in the patterns of terrestrial plant diversification (Heimhofer et al. 2005). According to currently favoured models, climate development during this period was strongly influenced by extensive flood-basalt extrusions, which formed large igneous provinces such as the Kerguelen and Ontong-Java Plateau (Coffin and Eldholm 1994) and affected general greenhouse conditions by the release of primordial volcanogenic CO₂ (Wortmann et al. 2004). Under these circumstances, the northern Tethyan epicontinental carbonate platform was forced to react to eustatic sea-level rise (Christie-Blick 1990) and increased input of detrital material and nutrients, and drowned during the Aptian (Föllmi et al. 2007).

Results

Description and tentative stratigraphic location of the fossil resin nodule

The maximum diameter of the approximately oval shaped Werdenfels resin nodule is 4.3 cm (Fig. 4). The nodule is highly transparent and its colour is bright and light yellow; only mm-scaled domains are white-opaquely coloured. The finder reported that when it was found it showed a light bluish glimmer when exposed to the sunlight. Numerous randomly oriented joints and micro-fractures are indicative of intensive brittle deformation. A few gas bubbles and other particles <0.1 mm have been identified. The fossil

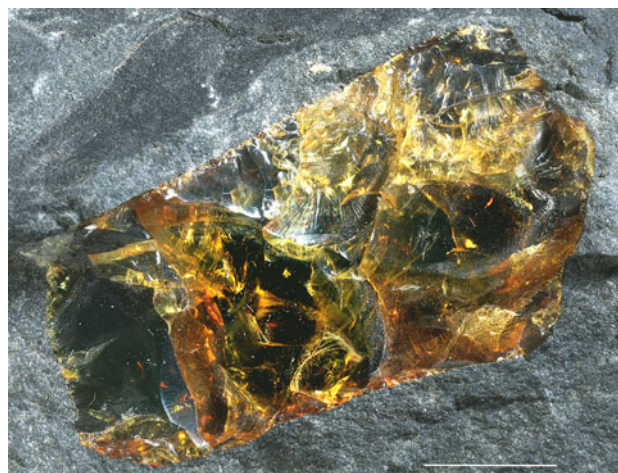


Fig. 4 Close-up view of the Werdenfels resin nodule. Scale bar 1 cm. Foto by Sybille Forster, Bayerische Staatsgemäldesammlungen (BStGS). Publication with written permission (21 February 2008) of the owner, Schloßmuseum Murnau (Germany)

resin nodule is regarded as pristine, because no distinguishing marks of redeposition were identified. Its host rock consists of medium- to coarse-grained, dark greenish to dark grey, slightly micaceous, well-sorted, finely layered calcareous quartz sandstone, which is tentatively attributed to the lower part of the Freschen Member. The sedimentary interfaces bear numerous trace fossils (*Paleophycus* sp.). A small fragment of a belemnite has further been observed.

FTIR analysis of the whole fossil resin

The FTIR spectrum of a tiny resin splinter of the amber nodule is presented in Fig. 5. The investigated sample contains the whole fossil resin, i.e. its soluble and insoluble fractions. Unfortunately, the resulting spectrum is not very characteristic and the recognition by direct comparison with known spectra of other fossils resins was not possible.

Nevertheless, to a very limited extent some combined negative and positive interpretations seem to be feasible and promising. If the characteristic bands of functional

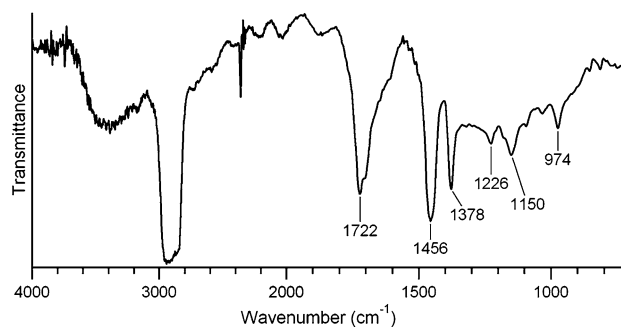


Fig. 5 Fourier transformation infrared spectrum of the Werdenfels resin nodule. Reference: Ursula Baumer and Johann Koller, Doerner Institut

groups are known, the absence of these functionalities could be established (Vandenberg et al. 1980) by negative interpretations. For example, the carboxylic groups of diterpenoid resin acids and resin acid esters show carbonyl stretching vibrations at about $1,740\text{ cm}^{-1}$ (most intense), $1,240$ and $1,020\text{ cm}^{-1}$ (only for resin acid ester). In the Werdenfels nodule, the presence of resin acids and resin acid esters seems to be very unlikely.

Aromaticity has to be confirmed by the presence of bands between $1,500$ and $1,600\text{ cm}^{-1}$ and C–H vibration in the range between $3,000$ and $3,100\text{ cm}^{-1}$. Since the spectrum does not contain any bands in these regions, considerable aromaticity can be excluded too. The IR-region between $1,630$ to $1,690\text{ cm}^{-1}$ and $3,000$ to $3,100\text{ cm}^{-1}$ is associated with olefinic vibration (C=C and C–H stretching). Again, since no bands are present in these regions, unsaturated compounds may be eliminated. By the same way—i.e. since no oxygen–hydrogen–stretching band is present between $3,100$ and $3,700\text{ cm}^{-1}$ —OH-functionalities may be excluded too.

A very special feature used for negative and positive interpretation is the so called “Baltic shoulder”. According

to Beck et al. (1965), this phenomenon occurs in the range between $1,175$ and $1,250\text{ cm}^{-1}$ only within Baltic ambers. Since the spectrum in Fig. 5 does not contain this “shoulder”, any similarity or relationship between Baltic and the Werdenfels resin nodule must be excluded.

A positive interpretation of the spectrum of the Werdenfels nodule is only possible in the region of $2,800$ to $3,000\text{ cm}^{-1}$. There, the strongest bands by far are noted. They all belong to the C–H stretching vibration of saturated hydrocarbon groups within the molecules. From this spectrum we may conclude, that the Werdenfels nodule does either not contain any aromatics, olefinic and carboxylic functionalities or only in abundances, which are too small (<5%) to be detected by FTIR. According to this FTIR-spectrum, saturated components must prevail in the fossil resin.

GC/MS analysis of the soluble parts of the fossil resin

GC/MS analyses were conducted only with the soluble fraction of the fossil resin ($\sim 30\%$). The results of these analyses are presented in the form of a gas chromatogram

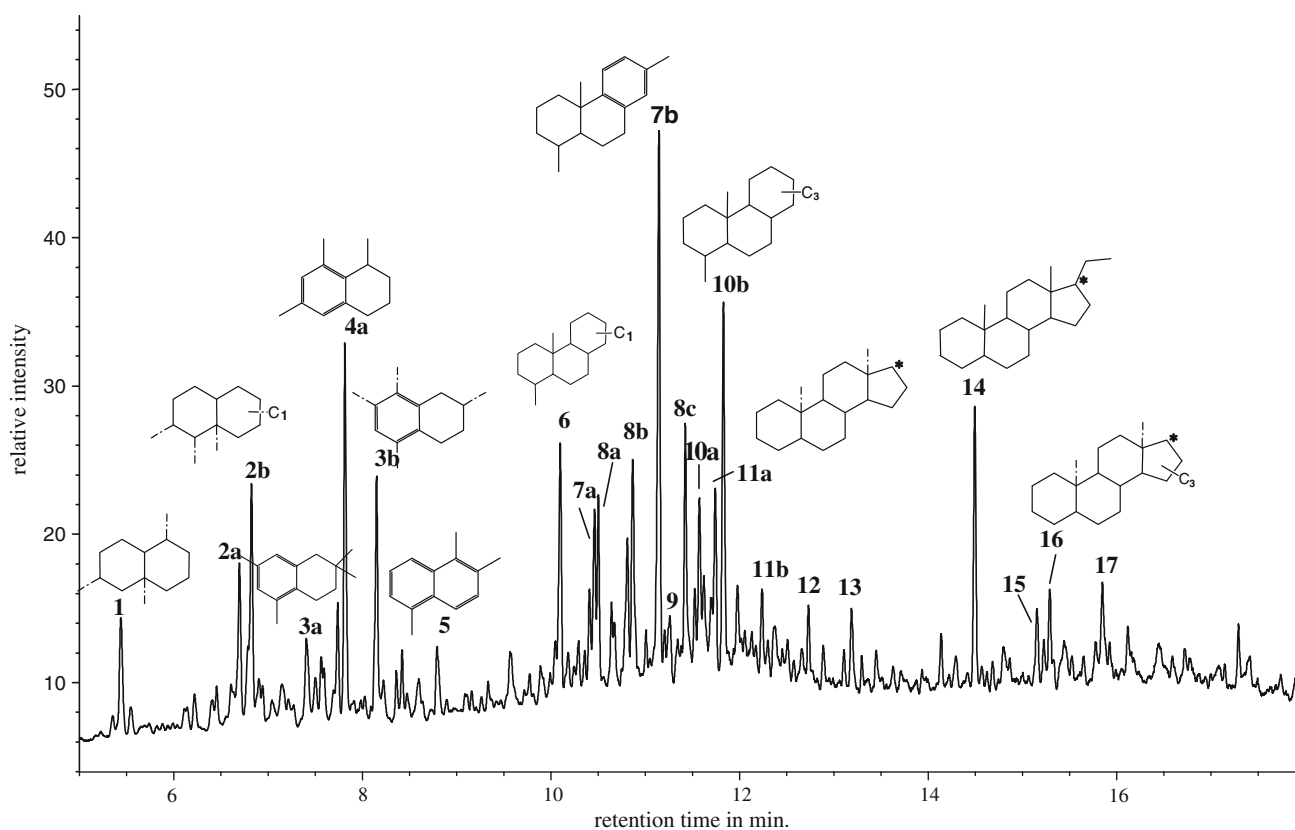


Fig. 6 Gas chromatogram of the chloroform/methanol (7/3 volume ratio) extract. Compounds indicated with a number are identified (or tentatively identified). The structures of several dicyclic and tricyclic hydrocarbons are determined by a combination of different methods using the mass spectra of the respective compounds. These are partly based upon library search (NIST, WILEY), literature research

(Bendoraitis 1974; Gallegos 1984; Richardson and Miller 1987) and extrapolation of the mass spectral fragmentation of known compounds. Structures below the numbers below. The C_{17} -position of the cholestane skeleton is marked by asterisks. The positions of side groups or chains figured as dashed lines are not ensured. Reference: Ursula Baumer and Johann Koller, Doerner Institut

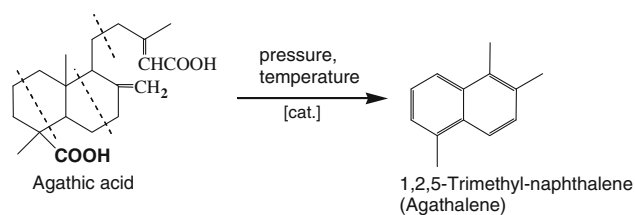


Fig. 7 Catalytic decarboxylation, dealkylation and aromatization of agathic acid (labdanoid type) due to the impact of elevated pressure as described by Ruzicka and Hosking (1930). Reference: Ursula Baumer and Johann Koller, Doerner Institut

of the chloroform/methanol extract in Fig. 6 and are summarized in Table 1. Three groups of wholly (or partially) saturated polycyclic hydrocarbons are observed, which consist of dicyclic terpanes (or terpenes), tricyclic terpanes (or terpenes) and tetracyclic steranes.

The dicyclic hydrocarbons contain components with three or four methyl side groups. They were classified by their degree of saturation into decalins (fully saturated), tetralins (one aromatized ring) and naphthalenes (fully aromatized). There exist at least six decalins and five tetralins. However, only one fully aromatized product could be observed in the Werdenfels resin nodule, 1,2,5-trimethylnaphthalene (*agathalene*, Fig. 6, no. 5), which is described as a decarboxylation, dealkylation and aromatization product of agathic acid (Fig. 7; Ruzicka and Hosking 1930; Noller 1960; Thomas 1969).

The tricyclic hydrocarbons include perhydro-phenanthrenes and octahydro-phenanthrenes, both with three, four or five methyl side groups. The majority of these constituents (perhydro-phenanthrenes) is composed of saturated hydrocarbons. A minority (octahydro-phenanthrenes) is partially aromatized, i.e. consists of the tri-unsaturated analogues (with one aromatized ring) of the saturated hydrocarbons.

The tetracyclic steranes are all based on a cholestane skeleton with shortened or even missing side chains at the C₁₇-position (Fig. 6). They consist exclusively of saturated tetracyclic hydrocarbons without any unsaturation or functional group.

On the whole, GC/MS analyses confirm the results of FTIR analysis: no carboxylic, hydroxylic or olefinic functionalities could be observed, aromatics are only present in small amounts and saturated hydrocarbons are clearly dominating.

Discussion

Biological origin of the fossil resin nodule and its degradation

The dicyclic and tricyclic hydrocarbons of the first and second group represent strongly aged and degraded

resinous products, which in most cases can not be related to their natural precursors in the recent resins. Further, they may be contained in many different fossil resins, even in some of the Alpine ambers (Beck et al. 1996). Because of these very unspecific characteristics they are often not noted.

The only component of interest, the trimethylnaphthalene (TMN)-isomer *agathalene*, is also the only fully aromatized one. It is found together with other TMN isomers in high abundances in crude oils and sediments (Strachan et al. 1988, Alexander et al. 1992, Yessalina et al. 2006). There it was interpreted as a degradation product originating from higher plants (angiosperms), i.e. as a product of “structural degradation of oleanone-type triterpenoids” (Strachan et al. 1988). The TMN-fraction isolated from crude oils and sediments, however, always contains a great variety of TMN-isomers. This is clearly not the case with the Werdenfels resin nodule, where only one isomer, 1,2,5-TMN, was identified. Ruzicka and Hosking (1930) produced this specific 1,2,5-TMN called *agathalene*, from agathic acid and no other isomers were reported. Agathic acid is a characteristic and major constituent of the recent resins of kauri pines (Araucariaceae) and also of their fossil derivatives (kauri copals, Thomas 1969). It is therefore used as a biomarker for the trunk resins from the family Araucariaceae (e.g. *Agathis*, *Araucaria*). *Agathalene*, which is produced by defunctionalization, dealkylation and aromatization processes from agathic acid therefore serves as a secondary biomarker and gives an indication for the botanical source (Thomas 1969, p. 611) of the Werdenfels nodule.

Today, agathic acid only occurs in natural resins of subtropical-tropical zones (Langenheim 1995), which are presently produced in large quantities by *Agathis australis* and *A. dammara* (Farjon and Waters 2006; Beveridge and Bergin 2006), two tropical conifer species of the Araucariaceae (Van den Burgh 2006; de Laubenfels 2006). A tropical origin of the Werdenfels resin nodule is also supported by the absence of diterpenoid resin acids of the abietane and pimarane type, which are produced at present in large quantities by non-tropical conifer species.

The constituents identified in the Werdenfels resin nodule show some similarities to shale oils (Gallegos 1984) and to the saturated fraction of crude oils (Strachan et al. 1988, Richardson and Miller 1987). Some of these components are also present in trace amounts in lignite and hard coal (Oelert and Lenart 1975). The Werdenfels nodule also contains tetracyclic sterane components (Fig. 6), which are unknown in the exudations of resin-producers. They probably represent decarboxylation products of two steroid acids, the pregnane acid (C₂₂) and the cholenic acid (C₂₄). Products based on the same tetracyclic skeleton, but with fully developed side chains at the C₁₇-position, were identified in crude oils (Rullkötter 1984). For example,

Table 1 Identification and mass spectral data (m/z -fragments) of the constituents of the Werdenfels resin nodule

Type	Identification	Molecular formula	Molecular weight	Peak no.	Fragments m/z (top ten)
Dicyclic terpanes	Trimethyl-decalin	C ₁₃ H ₂₄	180	1	165 (100), 109 (78), 81 (50), 95 (47), <u>180</u> (36), 55 (27), 137 (27), 67 (23), 110 (20), 123 (14)
	Tetramethyl-decalins (4 possible isomers, only two shown in Fig 6)	C ₁₄ H ₂₆	194	2a	179 (100), 109 (51), 95 (40), 123 (37), 81 (35), <u>194</u> (35), 82 (33), 83 (32), 55 (23), 110 (21)
				2b	109 (100), <u>194</u> (39), 95 (32), 123 (26), 110 (26), 81 (25), 82 (22), 55 (17), 124 (17), 69 (15)
Dicyclic terpenes	Tetramethyl-tetralins (2 isomers)	C ₁₄ H ₂₀	188	3a	132 (100), <u>188</u> (41), 117 (36), 159 (27), 173 (17), 131 (16), 133 (14) 174 (11), 129 (11), 115 (10)
				3b	173 (100), <u>188</u> (22), 133 (14), 174 (13), 158 (9), 145 (7), 128 (6), 129 (6), 143 (6), 131 (5)
	Trimethyl-tetralins (3 possible isomers, only one shown in Fig. 6)	C ₁₃ H ₁₈	174	4a	159 (100), <u>174</u> (32), 160 (14), 131 (13), 144 (10), 129 (10), 128 (9), 146 (7), 115 (6), 173 (6)
	1,2,5-Trimethyl-naphthalene (agathalene)	C ₁₃ H ₁₄	170	5	155 (100), <u>170</u> (99), 153 (27), 152 (20), 115 (12), 154 (11), 171 (11), 169 (11), 128 (11), 156 (11)
Tricyclic terpanes/terpenes	Trimethyl-perhydrophenanthrene	C ₁₇ H ₃₀	234	6	109 (100), 163 (97), 95 (71), 81 (55), 110 (47), 219 (45), 164 (43), 67 (42), <u>234</u> (38), 55 (37)
	Octahydro-trimethyl-phenanthrene (2 isomers)	C ₁₇ H ₂₄	228	7a	213 (100), 131 (75), <u>228</u> (35), 157 (29), 214 (19), 185 (16), 143 (12), 132 (10), 128 (7), 141 (7)
				7b	131 (100), 213 (80), 157 (35), <u>228</u> (31), 214 (14), 143 (13), 132 (11), 128 (10), 142 (9), 185 (9)
	Tetramethyl-perhydrophenanthrenes (3 isomers)	C ₁₈ H ₃₂	248	8a	109 (100), 177 (71), 95 (62), 81 (60), 233 (44), 69 (38), 55 (35), <u>248</u> (35), 67 (34), 110 (31)
				8b	177 (100), 109 (60), 95 (39), 81 (38), 110 (37), <u>248</u> (31), 178 (23), 55 (20), 67 (20), 69 (18)
				8c	109 (100), <u>248</u> (70), 81 (52), 95 (49), 110 (42), 55 (30), 67 (26), 124 (26), 82 (25), 233 (23)
Octahydro-tetramethyl-phenanthrene	C ₁₈ H ₂₆	242	9	227 (100), 157 (53), 143 (48), 131 (47), 171 (44), <u>242</u> (32), 145 (28), 158 (27), 228 (20), 128 (19)	
Pentamethyl-perhydrophenanthrenes (2 isomers)	C ₁₉ H ₃₄	262	10a	233 (100), 109 (24), 123 (23), 137 (22), 95 (21), <u>262</u> (20), 97 (20), 81 (19), 234 (18), 232 (16)	
			10b	233 (100), 123 (45), 109 (34), 81 (28), 227 (28), 95 (27), 137 (24), 55 (21), 145 (20), <u>262</u> (15)	
Tetracyclic steranes	'Androstane' (2 isomers)	C ₁₉ H ₃₂	260	11a	245 (100), 109 (93), 131 (90), 241 (87), 81 (69), 95 (66), <u>260</u> (62), 163 (53), 108 (52), 231 (49)
				11b	245 (100), 227 (64), 209 (48), 242 (41), <u>260</u> (40), 163 (33), 172 (28), 81 (24), 95 (23), 109 (23)
	Allopregnane	C ₂₁ H ₃₆	288	14	<u>288</u> (100), 273 (81), 217 (63), 109 (44), 81 (44), 95 (34), 67 (31), 289 (25), 55 (24), 218 (22)
	Methyl-allopregnane	C ₂₂ H ₃₈	302	15	189 (100), 217 (50), 95 (48), 81 (45), 67 (43), 123 (41), 69 (35), <u>302</u> (34), 109 (33), 55 (28)
Not identified	Not identified	–	256	12	131 (100), 241 (82), 157 (38), 233 (23), <u>256</u> (22), 171 (20), 143 (17), 242 (17), 145 (16), 132 (14)
	Not identified	–	274	13	227 (100), 145 (78), 242 (44), 171 (32), <u>274</u> (24), 228 (16), 209 (15), 143 (15), 128 (13), 146 (13)
	Not identified	–	316	16	282 (100), 129 (38), 109 (28), 163 (28), 283 (26), 104 (23), 95 (21), 164 (20), 130 (18), <u>316</u> (11)
	Not identified	–	324	17	309 (100), 132 (51), 105 (46), 119 (39), 310 (30), 81 (29), <u>324</u> (28), 145 (26), 173 (25), 199 (22)

Reference: Ursula Baumer and Johann Koller, Doerner Institut

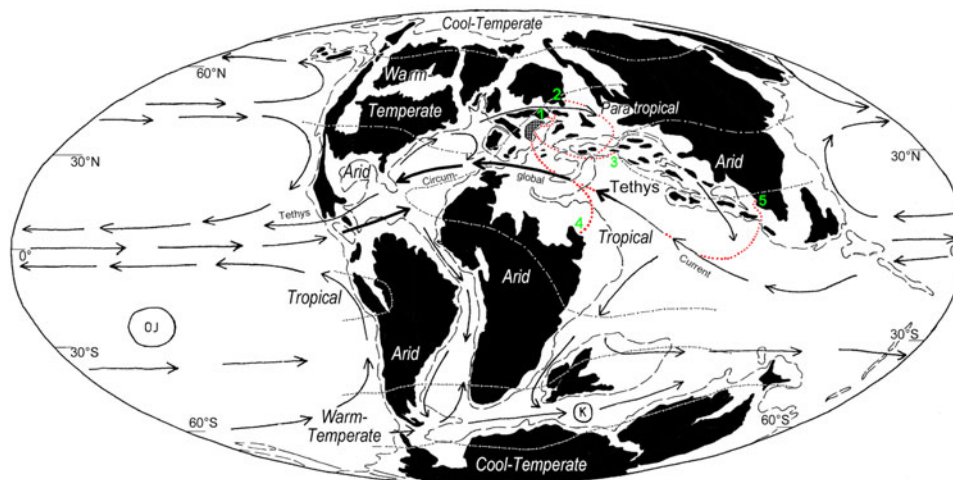


Fig. 8 Global palaeogeographic map for the Early Albian (105 Ma) after Blakey (2008) and including climate zones of Scotese (2000) and marine surface currents of Pucéat et al. (2005). Areas in black: continental mainlands and adjacent island arcs; *thinly dashed lines*: shelf break; *arrows*: marine surface currents; small *dash-dotted lines* delineations of climate zones; *hatched zone*: depositional area of the Helvetic; *dotted lines* potential source areas and implied driftways of the Werdenfels resin nodule, controlled by the Tethys Circumglobal Current. Possible source areas of the Werdenfels resin nodule: (1)

East European mainland and islands with *Agathoxylon pannonicum* (Philippe et al. 2006); (2) Litoral area at the margin of the Ukrainian shield (Zherikhin and Eskov 1999); (3) Coastal region of an island which supplied the depositional area of the Nahr Umr Formation (Savkevich et al. 1990); (4) Levantine mainland with *A. levantensis* (Poinar et al. 2004); (5) Litoral area in Myanmar (Cruickshank and Ko 2003). Encircled areas show the approximate positions of deposits of the large igneous provinces: OJ Ontong-Java (125–120 Ma); K Kerguelen (118 Ma) (Larson and Erba 1999; Ogg et al. 2004)

tetracyclic- C_{24} -carboxylic acids based on the cholestane-skeleton found in Californian crude oils were interpreted as the biomarkers for C_{24} -bile acids of lower animals (Oelert and Lenart 1975). Since the steranes found in the Werdenfels nodule are non-regular, i.e. strongly aged and degraded, it is proposed that they were already imported into the fresh Werdenfels resin nodule and may represent degraded relics of organic inclusions in, or of colonists on the Werdenfels resin nodule; equivalent palaeomicrohabitats were described by Ascaso et al. (2005). Another possible source of the degraded steranes might have been early- or syndiagenetically circulating formation waters containing steroids, which were partially absorbed by the Werdenfels nodule.

Fossil resins originate from resinous exudations of resin-rich trees. These at least partially acidic products travel through different degrees of degradation and alteration in the course of their geological history. Due to these processes, neutral products may be formed by diterpenoid resin acids (Koller et al. 1997). Amber-like resins therefore consist of both acidic and neutral constituents (see also contributions in Anderson and Crelling 1995). The proportion of acidic to neutral constituents, however, may vary widely and probably reflects the differences in the geological processes (Beck et al. 1996). Acidic and neutral constituents were found in almost all ambers of the European Alps (Beck et al. 1996; Vavra 1996; Schmidt 2003). Surprisingly, the Werdenfels nodule contains only neutral

and no acidic constituents and even bicyclic degradation products of these possible acidic constituents (e.g. *fichtelite*) are clearly missing, thus revealing a quite different geographical provenance and geological history. Moreover, the neutral components identified in the Werdenfels nodule also differ from other known types of amber. In our experience, tetracyclic steranes do not belong to the constituents of amber-like fossil products. Additionally, the di- and tricyclic hydrocarbons, which are most probably common to many amber-like fossils also differ in their degrees of aromaticity. In the Alpine ambers (Beck et al. 1996), partly-unsaturated polycyclic hydrocarbons prevail over the saturated ones. In the Werdenfels nodule, in contrast, the saturated polycyclic hydrocarbons clearly dominate, thus again revealing a different geological history.

Finally, we conclude that this fossil resin was never exposed to strong heat, because strong heating of fossil organic matter (“smouldering”) would have produced a tar, mainly consisting of aromatic compounds (Collin and Zander 1983). The Werdenfels resin nodule, however, contains only tiny amounts of one aromatic compound. Additionally, the dominating saturated components reveal that this amber nodule was never exposed to oxygen. These results match the degree of degradation analyzed in organic matter present in the Helvetic units, encountered in the nearby drilling sites Vorderriß 1 and Hindelang 1 (Teichmüller and Teichmüller 1978; Hiltmann et al. 1995).

The constituents of the Werdenfels nodule reveal its geological history: dealkylation and defunctionalisation most probably reflect long phases of elevated pressure. The Helvetic units in Southern Bavaria were exposed to Alpine deformation, as it can be inferred from the intense deformation style (unpublished data of Engelbrecht) and from the fact that the units are allochthonous (e.g., Müller 1985, Huber and Schwerd 1995). In addition, this complicated the identification of the biological origin of the Werdenfels resin.

Palaeogeographical provenance

The depositional area of the Werdenfels resin nodule—the Late Aptian—Albian distal Helvetic shelf—was situated near the northern margin of the Early Cretaceous Tethys realm. According to Brenner (1976), Pantic and Burger (1981) and Hochuli (1981), this zone and its adjacent mainlands lay in the spheres of influence of two floral provinces: the subtropical and warm temperate South Laurasian floristic region and the tropical, but semi-arid Northern Gondwana one. These climate conditions, which evolved towards the Cenomanian to tropical-hot and humid conditions (Heimhofer et al. 2005), favoured thermophile conifer species to grow at the shores and on the adjacent inland (see Wilde and Goth 1987; Batten and Wenben 1987; Voronova 1989). The palynofloristic element *Araucariacites*, probably produced by *Agathis yallournensis* COOKSON et DUIGAN 1951 (Balme 1995), also occurred in the terrestrial northern Gondwana province (Dulic 2002). Poinar and Poinar (2003) suggested that *Agathis* was a palaeobotanic key species of Cretaceous forests.

The faint traces of the secondary biomarker *agathalene* (Fig. 6, no. 5) detected in the Werdenfels nodule point to *Agathis* of the family Araucariaceae as a possible botanical source.

We propose that the Werdenfels resin nodule was transported by driftwood into the Tethys ocean, thereby taking advantage of the presumed intensified river runoff. The increased outflow of terrigenous materials was distributed onto the northern Tethyan margin by westbound long-shore currents (Pucéat et al. 2005). These conditions raised the likelihood of mobilisation, raft-transportation and deposition of drop stones by driftwood to the distal Helvetic realm. The presence of a powerful E-W directed surface current system (Tethys Circumglobal Current) impinging the northern Tethyan margin (Fig. 8) postulated by different authors favours its origin from a source area to the east or southeast of the Helvetic realm. Philippe et al. (2006) mentioned a few localities of Early Cretaceous wood relics in terrestrial deposits of eastern Europe, such as the occurrence of *Agathoxylon pannonicum* (GREGUSS) BARALE, BARBACKA & PHILIPPE of Aptian or Albian age at

the locality Lábatlan (Hungary) and *Agathoxylon* sp. of Late Aptian age at the locality Tata (Hungary). According to Zherikhin and Eskov (1999), fossil resin fragments occur together with wood and bark pieces in Aptian deposits present in the Voronezh anticline. Other possible source areas are indicated in Fig. 8. We favour the northern Tethyan margin in eastern Europe as a potential source area (see numeral 1 in Fig. 8), since clasts consisting of gneiss, mica-schist and quartzite—found in the Garschella Formation present in western Austria and central Switzerland—were already shown to have most likely originated from this area (Föllmi 1989; Föllmi and Gainon 2008).

Furthermore, Murray et al. (1994) proved long-distance oceanic transport of fossil resin nodules.

To conclude, the palaeogeographic provenance of the Werdenfels resin nodule probably was a mainland positioned further to the east or southeast of the Helvetic shelf, to where it was probably transported on driftwood of the resin-producing *Agathis* sp. by the east–west directed Early Cretaceous surface current system of the Tethys ocean.

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