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EDITED BY
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REVIEWED BY
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Cairo University, Egypt
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University of Cambridge,
United Kingdom

*CORRESPONDENCE
Armelle Charrie-Duhaut,
✉ acharrie@unistra.fr

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Adhesive coatings in naval archaeology: molecular and palynological investigations on materials from the Roman Republican wreck Ilovik–Paržine 1 (Croatia)

Armelle Charrie-Duhaut^{1*}, Quentin Couillebault², Igor Miholjek³
and Giulia Boetto²

¹Laboratoire de spectrométrie de masse des interactions et des systèmes (LSMIS), UMR 7140, CNRS, Strasbourg University, Strasbourg, France, ²Centre Camille Jullian (CCJ), CNRS, Aix Marseille University, Aix-en-Provence, France, ³Department for Underwater Archaeology, Croatian Conservation Institute, Zagreb, Croatia

Introduction: The construction of a vessel (from a boat to a large ship) and its maintenance requires waterproofing of its hull and protection against water corrosion and the aggression of microorganisms, worms and other pests. What could be more logical than using an easily accessible and applicable hydrophobic adhesive material? Many substances have been used over time such as resins, bitumen, plant tars, pure or mixed with beeswax, fats, inorganic elements. Pliny the Elder already mentions *zopissa*, a mixture of pitch and beeswax (*Natural History* XVI, 23). The strong expansion of shipbuilding between the 13th and 19th centuries generated a veritable industry of plant tars.

Methods: In this research work, a new interdisciplinary approach involving the combined use of molecular, palynological and statistical indicators has been implemented to characterize ancient waterproofing materials. This analytical strategy opens new fields of investigation in naval archaeology.

Results and discussion: Beyond the characterization of materials (nature, manufacturing processes, naval techniques, degree of alteration), it especially reveals information about the surrounding vegetation during the production or the application of the waterproofing material. This approach has been applied to the study of the protective coating of the Roman Republican wreck Ilovik–Paržine 1 (around the middle of the second c. BC) found in Paržine Bay (Ilovik Island, Croatia).

KEYWORDS

adhesive coating, Adriatic Sea, FTIR, GC-MS, Ilovik–Paržine 1 wreck, pitch, pollen analysis

1 Introduction

From the dugout canoe, the oldest found being the Mesolithic Pesse canoe (8,265 ± 275 BP) to today's powerful ships, there has been a significant evolution in naval techniques. This is closely linked to Human evolution, as humans have acquired new

technical knowledge to meet their needs of maritime and river transport. Very early on, assemblies of rushes, bark, and wooden planks were used, which then raised the problem of making boats waterproof. Numerous accounts have been found indicating the use of natural adhesive substances as a sealing agent for instance the cuneiform tablet XI (2100-1700 BC), recounting the Epic of Gilgamesh in Mesopotamia, indicates a precise description of a sealing process using bitumen (George, 2003). However, it was only in Antiquity with the writings of Pliny the Elder (*Natural History*, XVI, 21) that a true description of the use of organic materials in naval archaeology became available. Over time, organic adhesives have become more than just waterproofing agents; they also enable improved seaworthiness and better resistance to external subaquatic and marine aggressions.

If the construction woods of ancient ships are usually the subject of extensive study, little interest has been given to non-wooden materials, which were long considered secondary. The rise of archaeometry in the mid-20th century, a multidisciplinary approach, has made it possible to characterize these organic substances found in archaeological contexts (Charrié-Duhaut et al., 2009a). Methodological developments in chemical and physico-chemical analyses specifically adapted to the context, as well as the use of increasingly precise technologies, particularly in mass spectrometry, have led to numerous advances in our understanding of coatings. Structural and molecular analyses using Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS) provide access to the molecular signature of materials, whether pure or blended, altered or not. This signature, composed of diagnostic molecules linked to specific natural substance called biomarkers, makes it possible to determine the biological origin of the materials but also provides information on alteration processes, whether anthropogenic or natural. The information thus obtained documents the evolution of practices and know-how over time. R. Evershed was one of the first to publish his work on adhesives used to protect ship hulls (Evershed et al., 1985; Robinson et al., 1987). His study focused on coatings taken from the wreck of the Mary Rose, an English flagship sunk in the 16th century. Numerous traces of organic coatings discovered on shipwrecks, whether on construction materials, ropes, or in transported amphorae, from different periods (from Neolithic period to the present day) have subsequently been analyzed. A wide variability in composition was recorded depending on the geographical areas, the type of boat, and even the area of the hull where the adhesive is applied. Mixtures have sometimes been made to improve the properties of the coating (Charrié-Duhaut et al., 2009b; Duce et al., 2015) but the mechanism involved in wood-adhesive interactions remains the same. Frihart (2005) indicates that the process is primarily physical, not chemical. It involves impregnation and anchoring within the wood's pores, as well as weak intermolecular interactions.

In the context of naval archaeology in the north-eastern Adriatic, a new interdisciplinary approach was implemented to study the protective coating of the Roman Republican wreck Ilovik-Paržine 1 (around the middle of the second c. BC) found in Paržine Bay (Ilovik Island, Croatia). It relies on the unprecedented combined use of molecular, palynological and statistical indicators, and opens new research fields in naval

archaeology. State-of-the-art techniques (ATR-FTIR, GC-MS) remain key tools for determining the nature of the coatings and their state of alteration through the acquisition of structural and molecular data. In addition, new information concerning vegetation surrounding the production sites of the adhesive and the shipyards where it was applied, was provided through the study of pollen assemblages. In this multidisciplinary research work, the results of the various analyses are not simply juxtaposed but fully integrated into the historical reflection. This comprehensive approach allows to consider the ship as a whole, understanding the techniques used, the phases of its life, its movements, its environment, going far beyond a simple description of the materials.

2 The history of boat coatings through the lens of chemical analysis: state-of-the-art

The state-of-the-art presented in this paper is not intended to be exhaustive. It simply aims to demonstrate the significant role of adhesive materials in naval archaeology and their great diversity. The materials used must have certain properties: adhesiveness, hydrophobicity, local available, portable, storable and applicable. Given the strong dependence on available natural resources, local expertise has developed. To illustrate this point, the cases of the Middle East, the Atlantic, Mediterranean and Adriatic basins, as well as Asia, will be detailed.

The Middle East, in particular Mesopotamia, is a region rich in bitumen, where it could be found at the surface. The earliest evidence of bitumen as a boat coating dates back to the Ubaid period (4500-3700 BC). Molecular analyses of reed-bundle boat coating materials discovered at As-Sabiyah (5300-4900 BC, Kuwait) and Ra's al-Jinz (2500-2100 BC, Oman) revealed the presence of bitumen (Connan et al., 2005). The samples taken were in fact bitumen amalgams into which plant fibers had been incorporated to improve flexibility and tensile strength. The use of bitumen continued for many centuries. It was, for example, found as coating and luting material at the Al-Balid shipwreck (10th–15th century, Oman), boat that belongs to the tradition of sewn boats of the Indian Ocean (Connan et al., 2023). In this case also, a mixture with resins (Dipterocarpaceae and frankincense), fat or oil and mineral matter is mentioned.

In the Atlantic, Mediterranean and Adriatic basins, during Antiquity, conifer tars called pitch are frequently mentioned for the protection of ship hulls. This black sticky tar was produced by heating coniferous wood under oxygen-depleted conditions and can be used in shipbuilding and ship repair (Bailly, 2015). This use was quite widespread, as indicated by molecular analyses carried out on shipwrecks distributed throughout these geographical areas. Pitch was identified in the external coating of the hull of the Maa'gan Mikhael (Israël, 400 BC) (Connan and Nissenbaum, 2003). The coating on the sewn boat of Zambratija (1120-930 BC, Istria, Croatia) constituted the oldest evidence of the use of pitch in Adriatic region (Charrié-Duhaut, 2019). Pitch was also identified on Poreč 1 (94-72 BC, Istria, Couillebault et al., 2024) and Caska 1 (42-104 AD, Pag Island, Charrié-Duhaut, 2023), two sewn boats discovered on the north-eastern coast of Croatia and belonging to

the same architectural type, a sailing and rowing boat (Boetto, 2024). Always in Dalmatia, the shipwreck of Pakoštane (end of the fourth-beginning of the fifth c. AD, not published) attests the use of this type of coating on mortise-and-tenon built ships. Colombini et al. (2003) mention pitch as a waterproofing coating for river and sea vessels, whose wrecks have been discovered in the Roman port of Pisa and dated between the first c. BC and the seventh c. AD. Similarly, this tar was identified on some shipwrecks found along the French coast in the Mediterranean Sea (Wicha, 2005) and belonging to mortise-and-tenon built ships with frames that are internally lashed to the planking (Pomey and Boetto, 2019): Cap Béar 3 (third quarter of the first c. BC, Port-Vendres), Barthélémy B (25–50 AD, Saint-Raphael), Baie de l'Amitié (40–100 AD, Agde). It should also be mentioned that pitch was not only used on ships sailing on the seas but also on fluvial barges belonging to the Gallo-Roman Rhône-Saône tradition whose shipwrecks were discovered in Lyon Parc Saint-Georges (first and third c. AD, Connan and Charrié-Duhaut, 2010). Composite adhesives, mixing pitch and beeswax, have been identified on the graeco-archaic sewn ship Jules-Verne 7 (sixth c. BC, Marseille, Connan, 2002) and on the sewn barge Santa Maria di Padovetere (fifth c. AD, Comacchio, Italy, Beltrame et al., 2019). This mixture corresponds to what Pliny the Elder called “*zopissa*”. Other examples include mixtures of pitch combined with bitumen such as in the sailing ship Kyrenia (end of the fourth c. BC, Beck and Borromeo, 1990), or with clay and animal fibers in the naval ship Phanagoria (first c. BC, Taman Peninsula, Russia, Greshnikov et al., 2024). The use of pitch continued also after antiquity and, from the 13th century onwards, gave rise to a substantial “sticky business” (White and Stern, 2017; Burri, 2010). Among the main producing countries were France, Poland, Germany, Norway, Sweden, Finland, Russia and, at least from the 17th century onwards, North America (Loewen, 2005). Numerous shipwrecks have been discovered around the world with traces of adhesive coatings, either pure or in the form of a mixture of several components, but it is impossible to list them all here. We cite as an example: the shipwreck La Chrétienne E (16th c. AD, Cap Dramont, France, Bailly, 2015), the merchant ship Saint-Etienne (18th c. AD, Corsica, Charrié-Duhaut et al., 2009b), the Russian frigate Saint Nikolai (18th c., Finland, Reunanen et al., 1989).

The work on Nanhai 1 shipwreck of the Southern Song Dynasty (1127–1279, China) demonstrates once again the variability in the composition of adhesives, which is highly dependent on available natural resources and on the know-how of shipbuilders (Liu et al., 2025). The waterproofing agent is a traditional composite material called “*nianliao*” consisting of tung oil, lime and hemp. In Southeast Asia, the available natural adhesive resource is the resin of Dipterocarpaceae, also called “*dammar*”. It has also been the subject of intensive trade (Berdin, 2020) and is still used today in Cambodia and Vietnam in the traditional construction of bamboo Thuyen Thung and wooden junks (Bui and Girard, 2008). Burger et al. (2009) remarkably illustrate the phenomena of culture integration and technology transfer. Samples from the M1J (16th century) Portuguese warship, which sank in the strait of Malacca in Malaysia, reveal three different compositions: pure dammar, dammar mixed with pitch, and dammar mixed with pitch and bitumen. As explained previously, in southern

Europe, pitch was commonly used as a coating, so it is not surprising to find it on a Portuguese ship. The latter, designed for long journeys, necessarily required maintenance. It is therefore highly probable that the sailors adopted the traditions and know-how of the countries where they had to carry out repairs: bitumen during their passage in the Persian Gulf and dammar in South Asia.

3 The Roman Republican wreck Ilovik–Paržine 1: general presentation

The shipwreck Ilovik–Paržine 1 was discovered in 2016 in Paržine Bay, located southeast of Ilovik Island in the Cres-Lošinj archipelago. The excavations conducted in 2017 by the Department for Underwater Archaeology of the Croatian Conservation Institute (Zagreb, Croatia) confirmed the site's significance through the discovery of amphora fragments, ballast stones, and hull remains assembled using the mortise-and-tenon fasteners. From 2018 to 2022, the wreck was the subject of five annual excavation campaigns as part of a collaboration between the Department for Underwater Archaeology of the Croatian Conservation Institute and the Adriboats program of the research laboratory Centre Camille Jullian (CNRS, Aix-Marseille University, Aix-en-Provence, France).

The wreck lies at a depth of 4 m and about 30 m from the seafront (Figure 1). The first two campaigns uncovered the complex of the ship's bow roughly oriented east-west, several trunks and amphoras belonging to the cargo mixed with some disjointed elements of the ship's structure. The campaigns from 2020 to 2022 focused on the stern area, discovered about 20 m east of the bow area. There the ship structure was relatively well-preserved underneath the ballast. The construction of the ship was initially dated around 170 BC by AMS radiocarbon analysis on a single wood sample from the hull. This date was then confirmed by samples taken on two of the trunks of the cargo and by the typology of amphoras (Miholjek and Boetto, 2021; Boetto et al., 2024).

The study of the ballast allowed to make suggestions about the origin of the shipyard. The ballast is composed of pebbles and stones belonging to carbonate sedimentary rocks. Sedimentary analyses revealed its highly homogeneous nature and identified the likely source as a beach near *Brundisium*, now known as Brindisi in the Apulia region (Italy), which was one of the most important ports on the Adriatic. Thus this ballast appears to be permanent and loaded at the time of the ship's construction (Fournier et al., 2024).

The analysis of various pieces of wood from the frame, planking and tenons carried out by Alba Ferreira Dominguez (Ipsa Facto, Marseille) identified five species (Boetto et al., 2024). Deciduous taxa are predominant, both in the main structure and in the assemblies, in particular elm (*Ulmus* sp.), but also deciduous oak (*Quercus* sp.), holm (*Quercus ilex* L.), ash (*Fraxinus* sp.), and a wood of a Rosaceae species (Rosaceae *maloideae*). The use of fir (*Abies* sp.) is low. The hull's waterproofing system consists of a thick layer of organic adhesive coating brushed onto the inside and outside of the hull. Samples were taken from this organic layer at different locations on the wreck and ten were selected for analysis (Table 1). The results



FIGURE 1
View of the excavation of the bow area of the Ilovik-Paržine 1 shipwreck. In the foreground, the cargo of logs and amphoras can be seen. Archaeologists are working near the structure of the bow complex (Adriboats © L. Damelet, CNRS/CCJ).

TABLE 1 List of samples collected on the Ilovik-Paržine 1 shipwreck (Adriboats © Q. Couillebault, AMU/CCJ).

Year of excavation	Reference code	Location on the wreck	FTIR and GC/MS	Palynological analysis
2018	PA 100	Fragment of disjointed planking N7, bow area	-	x
2018	PA 101	Planking, bow area	x	x
2018	PA 102	Planking, bow area	x	x
2021	PA 103	Inner face, keel, at the stern	x	x
2021	PA 104	Inner face, keel, at the frame station F155	x	x
2021	PA 105	Inner face, K7, between the frames F145-F144	-	x
2021	PA 108	Inner face, between the frames F162N, on the plank P33N	x	x
2021	PA 110	Inner face, between the frames F131-F132, on the plank P11N	-	x
2021	PA 111	Inner face, between the frames F130-F131, on the plank P15N	x	x
2021	PA 112	Inner face, between the frames F129-F130, on the plank P14N	x	x

are part of the doctoral research of Quentin Couillebault (2025, University of Aix-Marseille).

laboratory (with the collaboration of D. Kaniewski, UMR 5608, Toulouse, France).

4 The coating: materials and methods

4.1 FTIR spectroscopy and mass spectrometry

Structural and molecular analyses were carried out at SMIS laboratory (with the collaboration of A. Charrié-Duhaut, UMR 7140, Strasbourg, France) and pollen analysis in TRACES

The structural analyses by FTIR and molecular by GC-MS are performed on an organic extract prepared from 15 to 30 mg of archaeological sample. After fine grinding, the sample is extracted

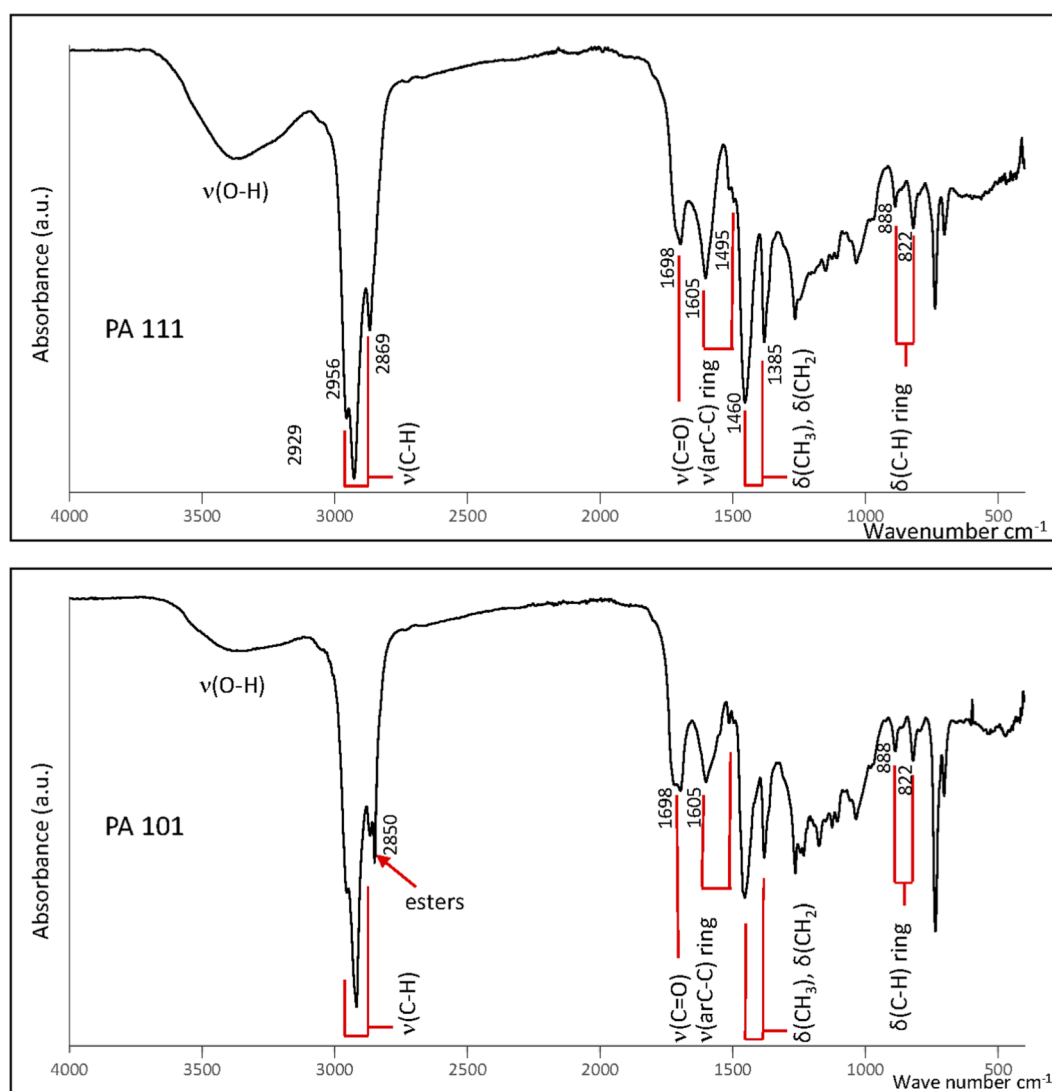


FIGURE 2
FTIR spectra from PA111 and PA 101 organic extracts.

by ultrasound for 5 minutes with dichloromethane/methanol DCM/MeOH (60:40). This operation is repeated three times. The combined solvent extracts, forming the total organic extract, were concentrated by evaporation and split into three parts (for FTIR, for GC-MS and to be conserved). The GC-MS part is filtered through silica (DCM/MeOH eluent) to remove any traces of insoluble matter. After evaporation, the extract is then subjected to a trimethylsilylation using N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% triméthylchlorosilane (TMCS) (2 h, 70 °C in pyridine) before analysis.

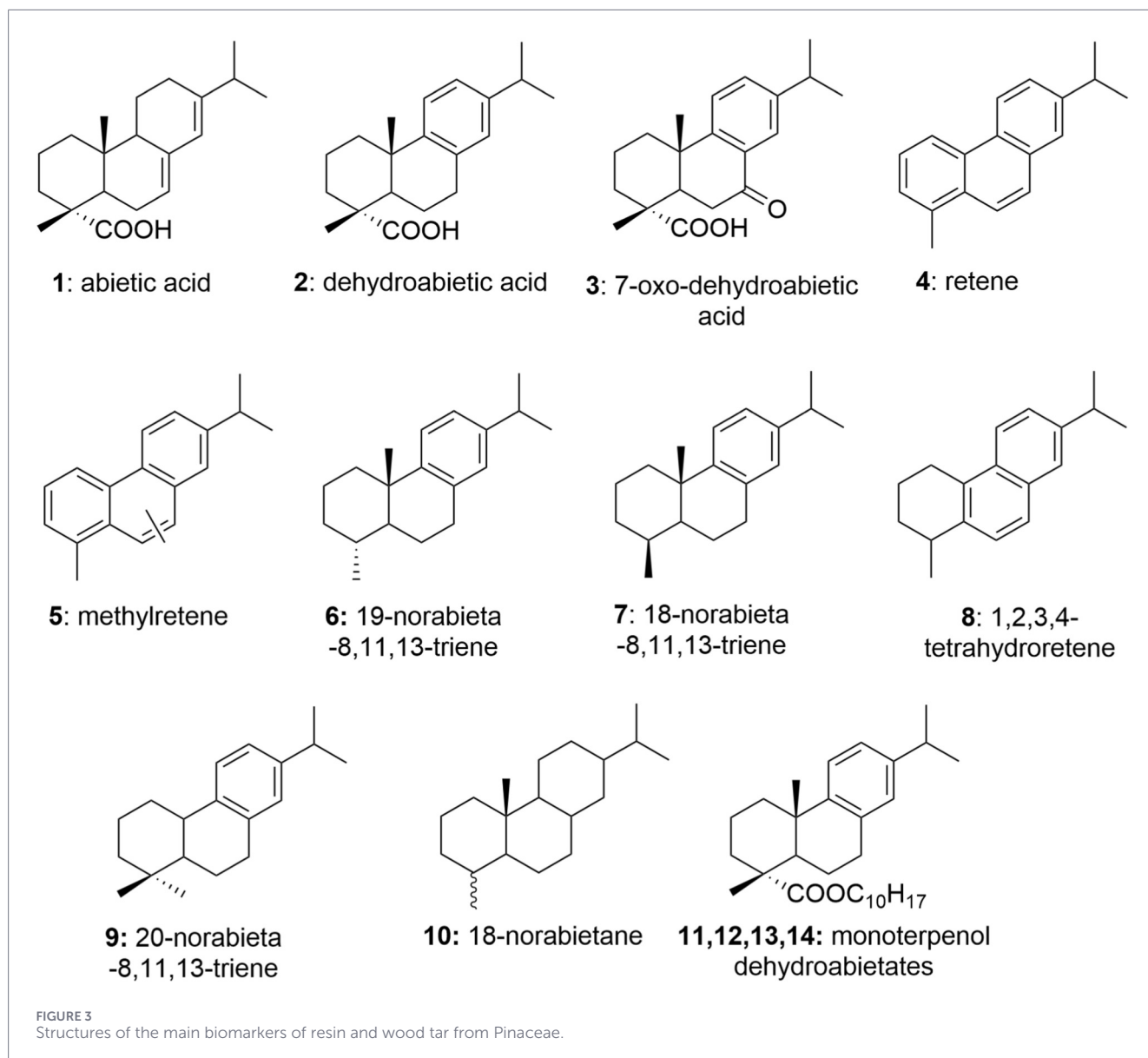
Infrared measurements were recorded on the organic extracts using a Spectrum Two spectrometer from Perkin Elmer with UATR diamond accessory in mode attenuated total reflectance (ATR). Spectra (4,000 to 400 cm^{-1} , spectral resolution 4 cm^{-1}) were processed with Perkin Elmer Spectrum software.

The GC/MS system consists of an Agilent 8,890 chromatographer tandem with an Agilent 5977B MSD. Gas

chromatographic separations were operated on a HP5-MS column (30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness) with H_2 constant flow of 1.5 mL min^{-1} and a temperature gradient of 40 °C for 2 min, then 10 °C/min until 100 °C, then 4 °C/min up to 320 °C for 30 min. The mass spectrometer was operating in the electron impact mode (EI) at 70 eV. The temperature of the source was set at 210 °C. Molecules are identified by comparing their mass spectrum with reference mass spectra available in NIST, in the literature, or in the internal LSMIS library.

4.2 Pollen analysis

The superficial layers are mechanically separated to extract the palynomorphs from the central part of the samples and eliminate any recent contamination. The adhesive coating is dissolved using sulfuric acid and then with a trichloroethylene-acetone mixture. The samples are then prepared according to a modified version of Fægri



and Iversen (1989). The cold hydrochloric acid attack (HCl 35%) is omitted since the carbonates had already been removed with sulfuric acid. Hydrofluoric acid (HF, 70%) is used to remove silica through the formation of fluorosilicates. These are then removed by treatment with hot hydrochloric acid (HCl, 35%) at 50 °C. Non-sporo-pollinic organic matter is removed with hot potassium hydroxide (KOH 10%). Nitric acid with drops of hydrochloric acid was used to eliminate the residual organic matter. Acetolysis was not carried out. The residue obtained is diluted in glycerin and mounted between a slide and a coverslip.

The pollen grains are counted using an Olympus microscope and identified from books (Fægri and Iversen, 1989; Moore et al., 1991; Punt and Blackmore, 1991), atlases (Reille, 1992; 1995; 1998), and reference slides. The mean pollen sum is 151 pollen grains, with a minimum of 8 and a maximum of 236 grains. The median value is 163 pollen grains, with the 25th percentile at 109 grains and the 75th percentile at 211 grains. The mean number of taxa is 24, with

a minimum of 7 and a maximum of 36 taxa. The median value is 25 taxa, with the 25th percentile at 21 taxa and the 75th percentile at 29. The results of our palynological analyses are presented in the form of detailed pollen diagrams (see §4.3.). Pollen frequencies are based on the terrestrial pollen sum, excluding local helophytes, macrophytes and spores of non-vascular cryptogams. The frequencies of aquatic taxa are calculated by adding local helophytes and macrophytes to the terrestrial pollen sum.

The data are analysed using PAST 4 software (version 1.0). The relative abundance of each taxon across the ten samples is depicted using box plots. Biological data are further examined through a neighbor-joining cluster analysis (descending type) to generate a dendrogram, where the branches represent ecological distances between taxon groups. The analysis employed Correlation as the similarity measure and Final branch as the root. Each cluster is summed to produce pollen-derived vegetation patterns (PdVs). A spindle diagram is then used to visualize the distribution of

TABLE 2 List of detected (+) and undetected (–) biomarkers and abietic acid/DHA ratio. The ratios are calculated from the peak areas on the chromatogram.

<i>Ilovik–Paržine 1</i>	PA 101	PA 102	PA 103	PA 104	PA 108	PA 111	PA 112
Abietic acid 1	+	+	–	+	+	+	+
Dehydroabietic acid (DHA) 2	+	+	+	+	+	+	+
$\frac{1}{2}$ ratio	0.16	0.22	0	0.1	0.15	0.12	0.08
7-Oxo-DHA 3	–	–	–	–	–	–	+
Retene 4	+	+	+	+	+	+	–
Methylretene 5	+	+	+	+	–	+	+
19-Norabietatriene 6	+	–	–	–	–	–	–
18-Norabietatriene 7	–	–	–	–	–	–	–
Tetrahydroretene 8	–	+	–	–	+	+	–
20-Norabietatriene 9	+	+	+	+	+	+	+
18-Norabietane 10	–	–	+	–	+	+	–
Monoterpenols déhydroabietates 11,12,13,14	+	+	+	+	+	+	+
Levogluconan	+	–	–	–	–	–	–
Wax esters	+	–	–	–	–	–	–
Sulfur	–	–	–	–	–	–	–
Linear alcohols	+	+	+	+	+	+	+
Linear acids	–	+	+	+	+	+	+
β -sitosterol	+	+	+	+	+	+	+

Bold numbers refer to the reference number of the biomarker in Figure 3.

PdVs across the samples. Subsequently, a principal component analysis (PCA) is conducted to evaluate sample ordination by identifying major variations in the PdV scores. The PCA illustrates the distribution of the samples along the first two components, which account for 68.9% of the total variance. A biplot PCA is chosen, with a convex hull drawn around the points. A classical cluster analysis (descending type, Correlation as the similarity measure and Paired group as algorithm) is performed to calculate a dendrogram, where the branches represent environmental distances between the samples.

5 Results and discussion

5.1 Structural analysis

In the literature on coating analysis in naval archaeology, Fourier Transform InfraRed spectroscopy is frequently used. This analytical technique is simple to implement and allows the identification of present organic functional groups. It has been proven very useful for preliminary analyses of large sample corpora in order to better classify materials with common characteristics and to establish a pre-selection for

molecular analyses. Access to the functional groups improves our understanding of the chemical structure of the compounds but will not make available precise structural identification leading to the compositional diagnosis, which will then be carried out by GC/MS.

The FTIR spectra obtained for the different organic extracts from the shipwreck Ilovik–Paržine 1 are similar (Figure 2, example of PA 111). The observed absorbance profiles correspond to those presented in the literature for Pinaceae tars (Colombini et al., 2003; Font et al., 2007; Izzo et al., 2013). The hydrocarbon skeleton of diterpenes (three-ring structures) is responsible for the strong stretching vibration bands at 2,956, 2,929 and 2,869 cm^{-1} of the C-H from methyle and methylene groups and their bending bands at 1,460 and 1,385 cm^{-1} . The presence of carboxylic acids is indicated by several bands: a wide band in V between 3,600 and 2,500 cm^{-1} (absorption of the O-H stretching from acid), a band at 1,698 cm^{-1} (stretching vibration of carbonyl from acid). Stretching and deformation vibrations of aromatic rings are clearly visible on the spectra respectively at 1,605, 888 and 822 cm^{-1} and at 1,495 cm^{-1} . Thus, all FTIR spectra from shipwreck Ilovik–Paržine 1 point out organic products rich in oxygen groups (particularly acidic groups) and highly aromatic. Only the spectrum of PA 101 differs slightly (Figure 2). It includes

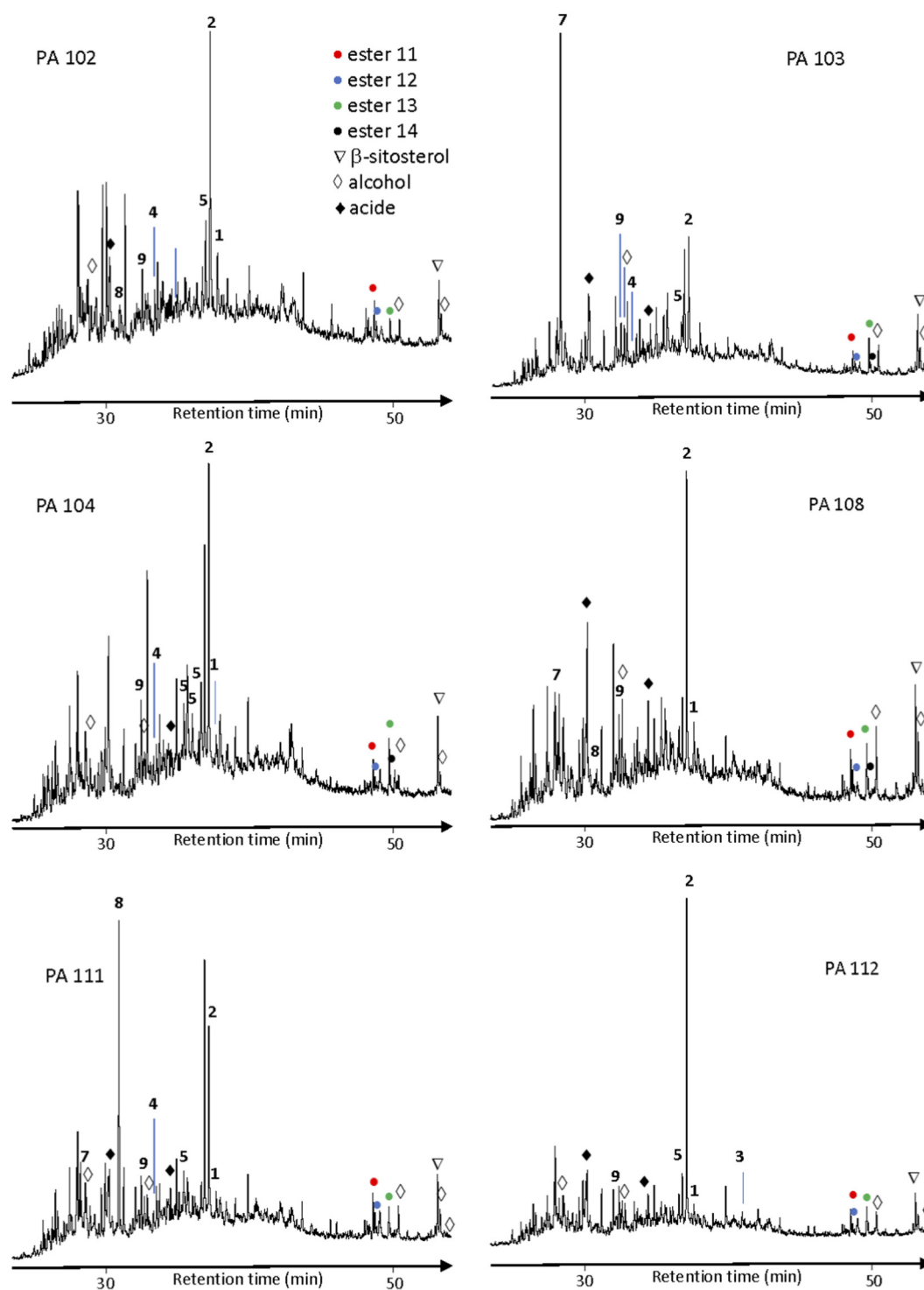


FIGURE 4
GC/MS profile (EI 70 eV) of the silylated organic extracts from PA 102, 103, 104, 108, 111 and 112.

all the characteristics mentioned previously but a shoulder is observed at $2,850\text{ cm}^{-1}$. According to Colombini et al. (2003), it would be characteristic of esters and could correspond to beeswax. A different composition can therefore be suggested for this sample.

5.2 Molecular analysis

The molecular approach based on precise structural identification of molecules present in organic extracts made from coating samples provides a molecular fingerprint of these. This

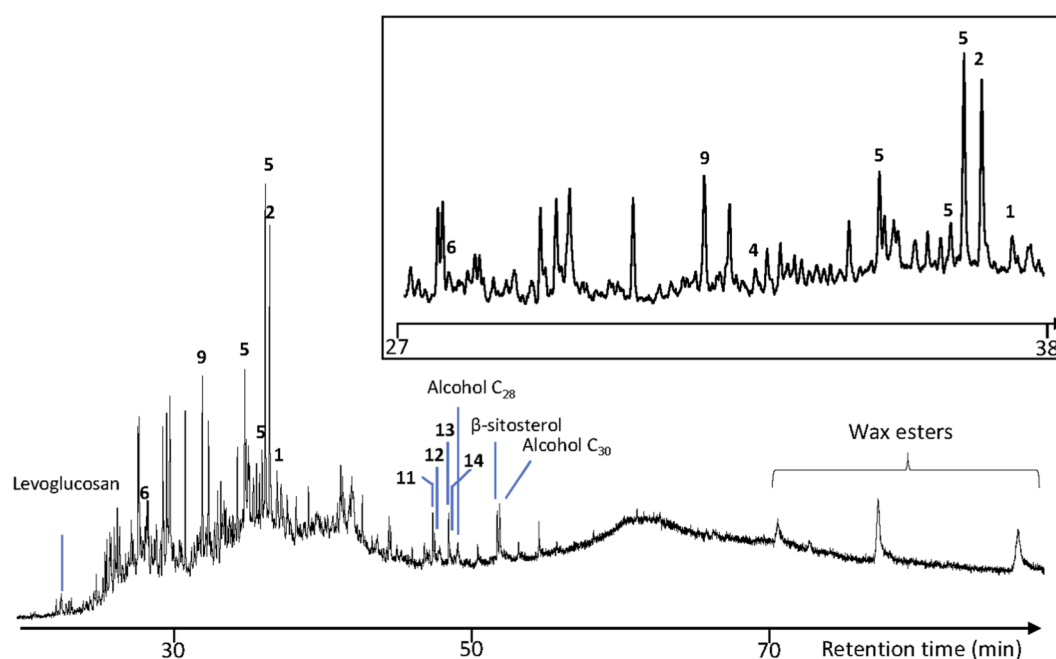


FIGURE 5
GC/MS profile (EI 70 eV) of the silylated organic extract from PA101.

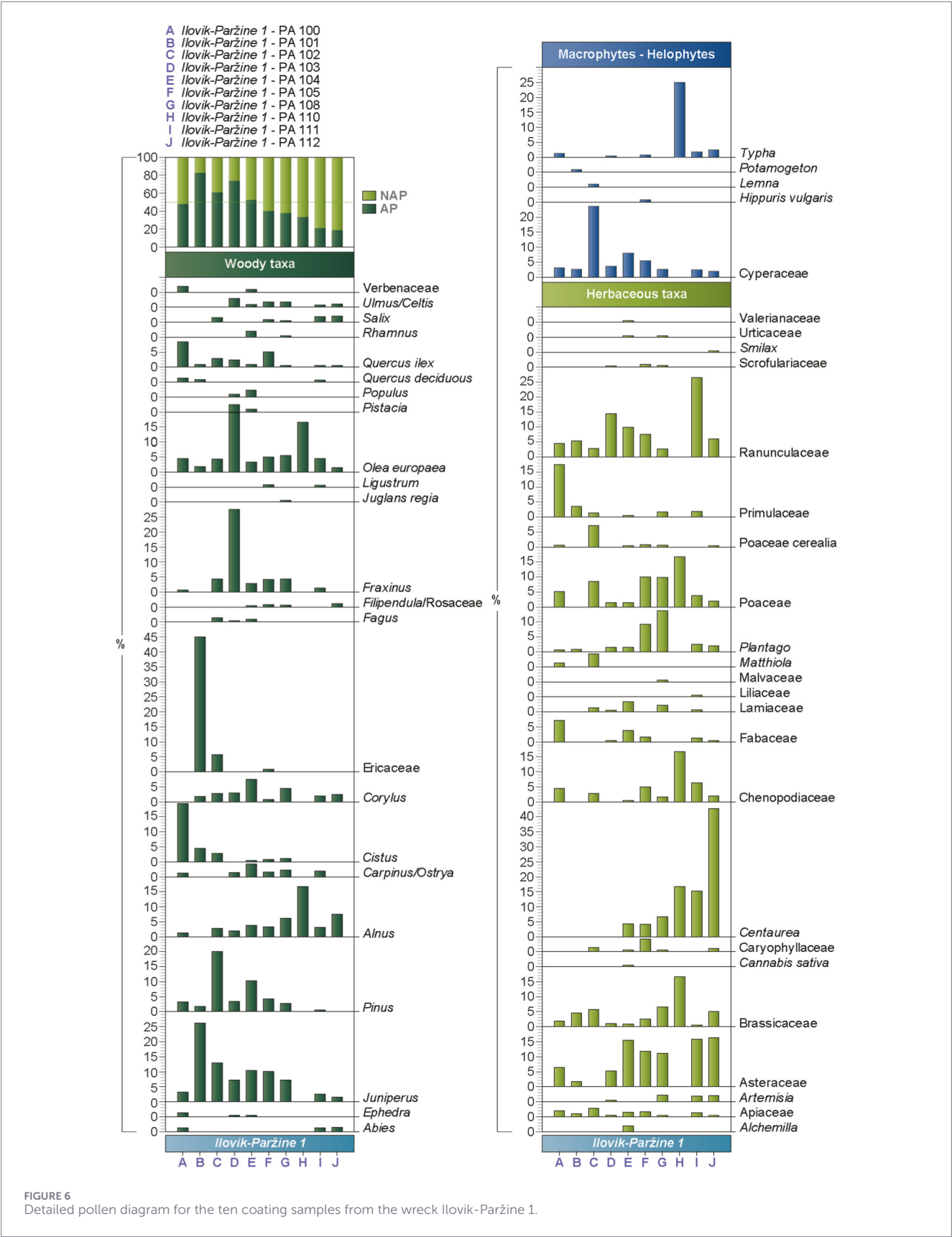
fingerprint includes ubiquitous components, diagnostic compounds for each natural substance as well as their transformation products. The distribution of diagnostic markers makes it possible to identify the biological origin of natural substances present in adhesives but also to improve our understanding of the processes involved during their manufacture, use or after their give up in the environment.

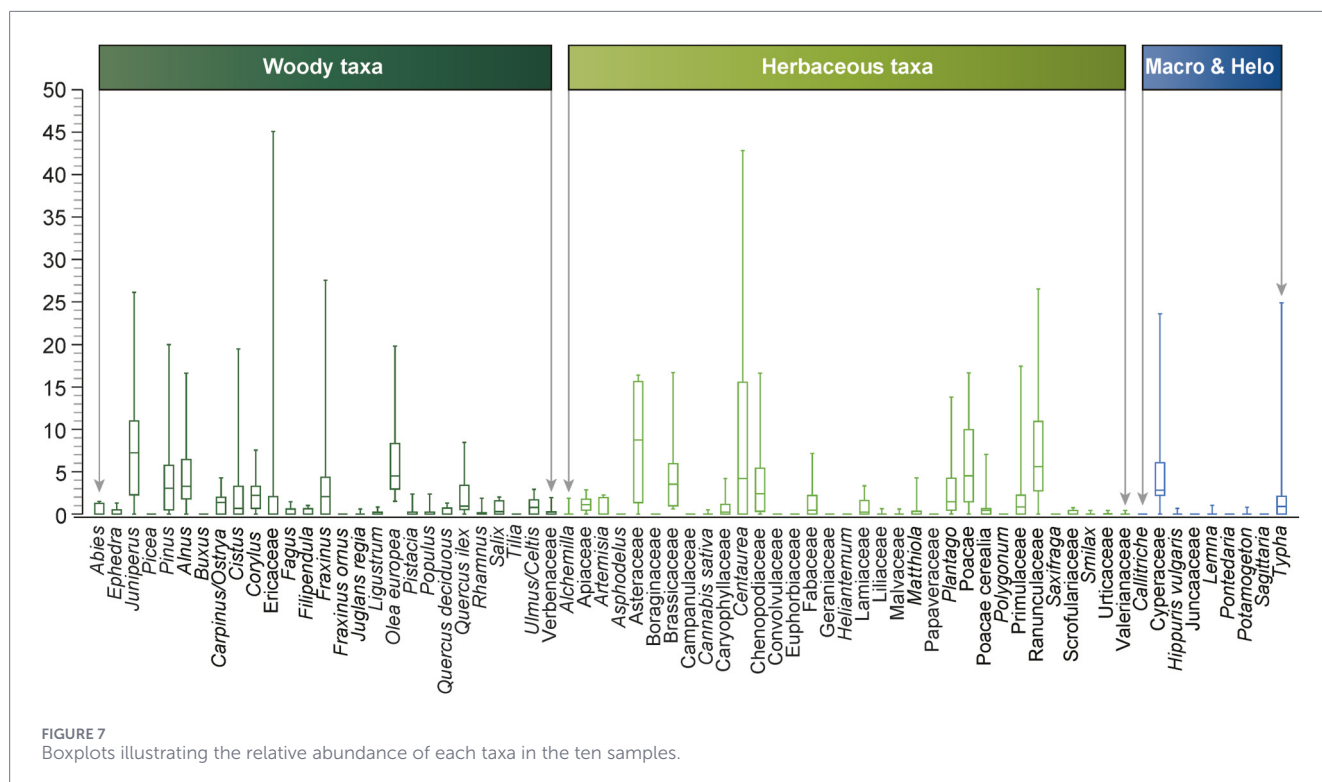
The seven GC/MS profiles of the wreck are predominantly dominated by diterpene markers derived from abietic acid **1** (Figure 3; Table 2). This molecular family is characteristic of conifer species and more specifically from the Pinaceae family. Their presence suggests that the analyzed adhesives contain a Pinaceae derivative, resin or tar. Resin is the natural exudate that flows out after the tree is incised. Conifer tar, also called pitch, is produced by the pyrolytic treatment of wood under oxygen-depleted conditions. This wood consists of resin (2%–5%), cellulose (40%–50%), lignin (20%–35%) and hemicellulose (25%–35%). The pyrolysis of wood yields a sticky tar, chemically composed of diterpene structures and organic compounds resulting from the thermal decomposition of the wood's macromolecular constituents (cellulose, lignin, and hemicellulose). The profiles obtained are very rich in components essentially with diterpene structure (Figures 4, 5). Some compounds that are ubiquitous in plants are also present (linear acids and alcohols, β -sitosterol). The profiles also present an unresolved complex molecular background UCM ("bump" under the peaks of the chromatogram). This UCM corresponds to a set of compounds that are not separated by gas chromatography. These molecules are co-eluting and appear superimposed on the chromatogram, giving the impression of significant background noise. Such an observation was initially made in geochemistry on biodegraded oils, and the presence of a UCM is interpreted as a sign of intense biodegradation (Gough and Rowland, 1990). The same process applies to plant tars.

Thus, the profiles obtained for non-altered or freshly prepared pitch (Couillebault, 2025; Bailly, 2015) exhibit no UCM. Consequently, the presence of these UCMs on the GC/MS profiles corresponding to the wreck Ilovik–Paržine 1 indicates significant alteration. Moreover, the profiles obtained for non-altered or freshly prepared pitch show a reduced peak number corresponding to the main diagnostics biomarkers that will be considered in this study on the wreck Ilovik–Paržine 1.

Among the diterpenic acids likely to be present, dehydroabietic acid **2** (DHA) is predominant or highly represented in all samples (Figures 4, 5). Abietic acid **1** is only present in small proportions or absent (PA 103), and its isomers are absent. The abietic acid/DHA ratios are typical of pitch profiles (0 for PA 103 and between 0.08 and 0.15) (Bailly, 2015). However, a resin that has undergone alteration or heat treatment may have a resin acid profile and an abietic acid/DHA ratio similar to that of pitch. In PA 112, 7-oxo-DHA **3**, an oxidation product of DHA **2**, is clearly identified, suggesting degradation processes mainly associated with natural ageing.

During heat treatment exceeding 300 °C, decarboxylation and aromatization reactions on resin acids lead to the formation of diterpenic aromatic hydrocarbons. Retene **4** was found in all samples (except PA 112), as well as methylretenes **5** (except PA 108). These compounds indicate complete aromatization of abietane-derived diterpenes and heat treatment having exceeding 300 °C. They are formed by thermal degradation via a decarboxylation reaction of dehydroabietic acid **2** forming norabietatrienes **6** and **7**, followed by their progressive aromatization into retene **4** and to the formation of alkyl derivatives **5** by the migration of a methyl group. Tetrahydrotetene **8**, often cited in the literature, was not identified in all samples (Table 2). All samples contain mixed esters





of monoterpenols and DHA (compounds 11,12,13,14, molecular weight 436 Da, major fragment m/z 137).

Different processes occur concomitantly in the distribution of the previously mentioned biomarkers, including the manufacturing process with more or less intense heating (temperature, heating time) and alteration. Distinguishing between them remains difficult. As an example of this complexity, 18-norabietane **10** is identified in PA 103, PA 108, and PA 111. Its proportions vary depending on the thermal stress experienced by the tars. Post-production or post-landfill diagenetic alterations may also explain its presence (Bailly, 2015). Nevertheless, the omnipresence of 20-norabietatriene **9** would suggest extensive alteration of all the samples (Bailly, 2015). The predominance of methylretenes compared to retene reflects their selective preservation during diagenetic alteration processes. The ratio between diterpenic acids and aromatic hydrocarbons indicates the predominance of acids, but this ratio remains low and can be considered an indicator of significant alteration.

In light of the preceding data, there is no doubt that these adhesives are the product of intense heating of a natural substance originating from the conifer family. Heated resin? Pitch? Markers of wood heat treatment specific to pitches, such as methoxyphenols and their esters, or guaiacyl dehydroabietates (Bailly et al., 2016) have not been identified. Only sample PA101 contains an anhydrous sugar, levoglucosan, thus confirming the presence of pitch. This compound is a common degradation product resulting from the pyrolysis of lignin and cellulose (Zhang et al., 2013).

Molecular analyses also show that the PA 101 coating contained an additional substance added to the pitch. Long-chain palmitic acid esters, commonly called wax esters, were identified (characteristic fragment m/z 257, predominance of even-

numbered terms with chains containing more than 40 carbon atoms) (Figure 5). Wax esters are characteristic biomarkers of beeswax. PA101 would therefore be a mixture of pitch and beeswax. Adding wax modifies the mechanical and physical properties of the adhesive (Bertelli et al., 2023). Pitch tends to become brittle when cold, and adding wax improves the adhesive's flexibility while further increasing its hydrophobic nature. This additive also reduces the adhesive's viscosity when hot, making it easier to apply.

5.3 Pollen and statistical analysis

Molecular analyses of adhesives used in shipbuilding make it possible to precisely define their composition and to specify their degree of alteration as well as the processes of degradation involved in order to better ensure their preservation and restoration. An obvious lack of biomarkers exists to accurately define the botanical species of conifers from which pitch was prepared. Similarly, it is very difficult to specify the place of production of this pitch, as well as the location of the ship's place of construction or of refitting. Isotopic analyses, usually very useful for defining biological or geographical origin, have been conducted but the results remain laborious to interpret (Bailly, 2015). A complementary approach is promising: the characterization of pollen-derived assemblages in coating. Adhesive by definition, these materials can function as traps for surrounding pollens during their manufacture and use in the construction or restoration of ships. The trapped pollens are then themselves protected within the adhesive layer. Some studies mention this approach, which is still not very widespread (Muller, 2004; Andrieu-Ponel et al., 2014; Andrieu-Ponel, 2019; Marlier et al., 2019; Couillebault et al., 2023), but there is still a lack of data to support statistical approaches. The presence of

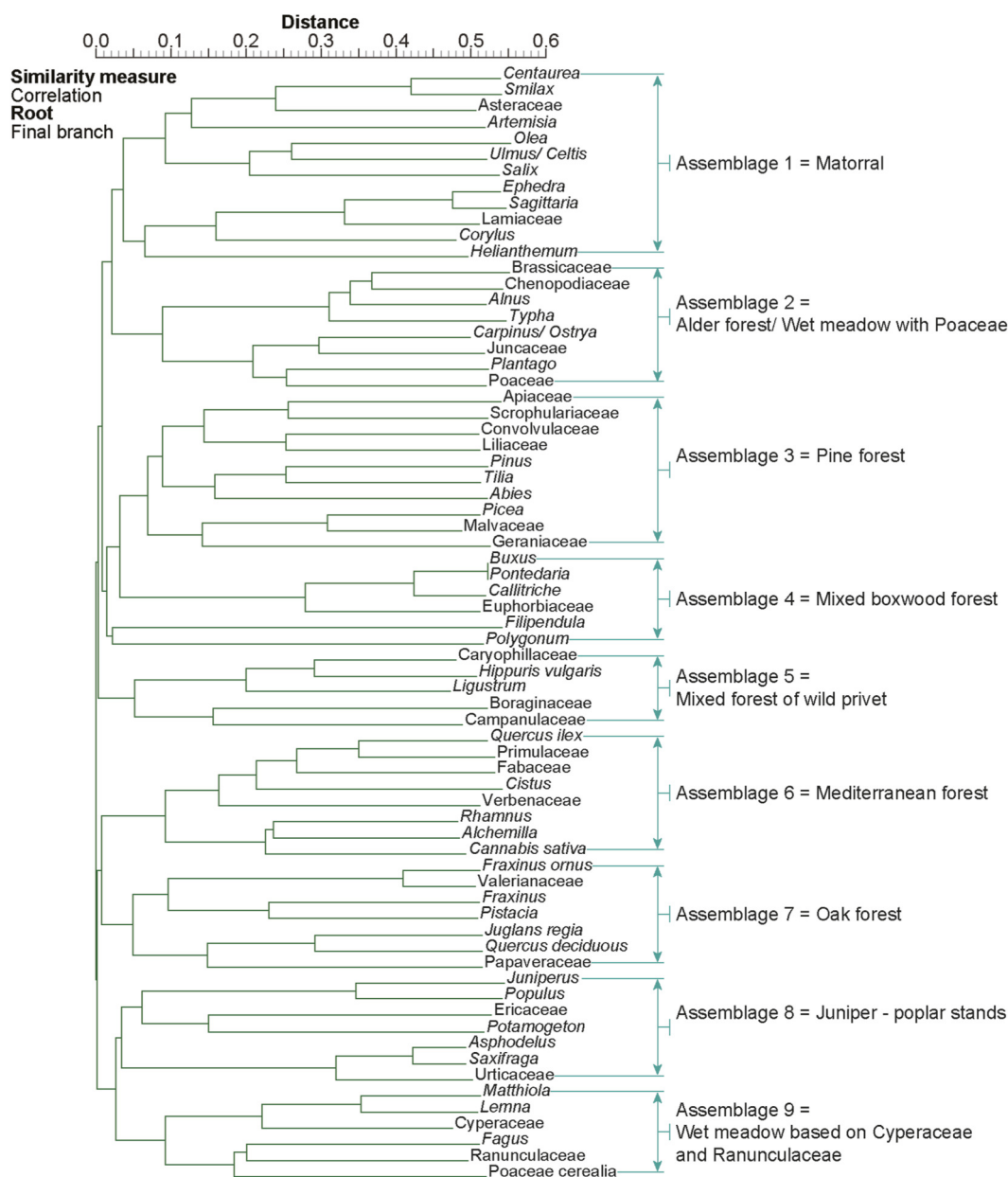


FIGURE 8

Pollen-based clusters from Ilovik-Paržine 1. Neighbour joining cluster analysis (descending type, Correlation as the similarity measure, Final branch as root) used to determine the pollen assemblages.

pollens was studied in the waterproofing adhesive from the wreck Ilovik-Paržine 1.

Detailed pollen diagram (Figure 6) and evaluation of the relative abundance of each taxa (Figure 7) were carried out on the ten coating samples from the wreck. The cluster analysis (Figure 8) and the spindle diagram (Figure 9) indicate that the coating samples from Ilovik-Paržine 1 reflect a high diversity of environments. These analyses allow to define four distinct clusters into which the ten samples are distributed. The first group is represented solely by the sample PA 100, which is dominated by a Mediterranean forest of *Q. ilex*, *Cistus*, and *Primulaceae*. Other major PdVs identified in this group include an alder forest and

a wet meadow with *Poaceae* and *Chenopodiaceae*, as well as a matorral with *Olea europaea* and *Asteraceae*. The second group, illustrated by PA 101, displays fewer Mediterranean forest taxa and is dominated by *Juniperus* and *Ericaceae*. The third group, represented by the sample PA 102, is characterized by a wet meadow of *Cyperaceae*. This group also includes a pine forest, an alder forest with a wet meadow of *Poaceae*, *Chenopodiaceae*, and *Brassicaceae*, as well as *Juniperus* patches. The remaining samples belong to the fourth group, which is characterized by the dominant PdVs corresponding to a matorral with *O. europaea*, *Corylus*, *Asteraceae*, *Centaurea*, an alder forest, and a wet meadow with *Poaceae*, *Brassicaceae*, *Chenopodiaceae*, *Plantago*, and *Ranunculaceae*. PA

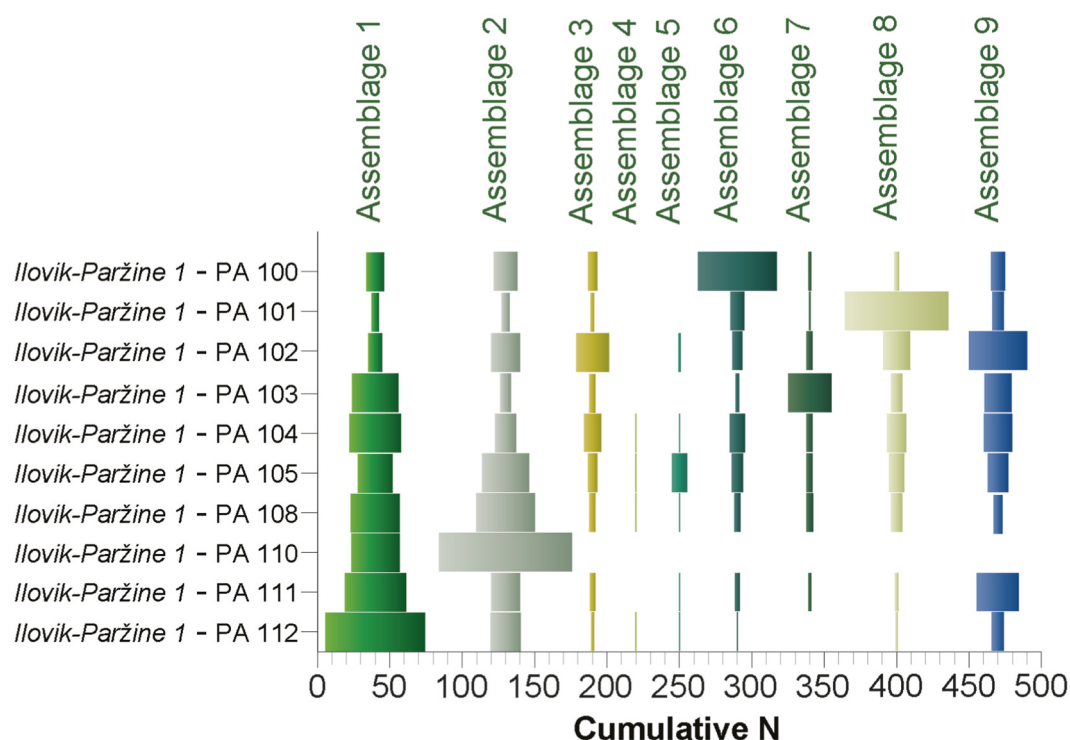


FIGURE 9
Spindle diagram depicting the distribution of pollen-derived vegetation patterns (PdVs) from each sample.

103 is distinguished by the presence of a deciduous oak forest and a reduced presence of alder forest and wet meadow. For PA 104, PA 111, and PA 112, the dominant PdV is the matorral, whereas the alder forest and wet meadow are more prevalent in PA 105, PA 108, and PA 110.

The PCA reveals the main PdVs structuring the Ilovik-Paržine 1 samples, with a distribution that slightly differs from the groupings identified previously. PA 100 and PA 102 are primarily arranged according to the Mediterranean forest PdV. However, PA 102 is less represented by this assemblage, positioning it at an intermediate level between the dominant PdVs. Consequently, PA 100 and PA 102 are distinct, as supported by the cluster. PA 101 is the only sample that aligns with the juniper-dominated stands. PA 103 and PA 104 are ordered by the deciduous oak forest and the wet meadow dominated by Cyperaceae and Ranunculaceae. PA 105, PA 108, and PA 110 are associated with the alder forest and wet meadow of Poaceae. PA 111 and PA 112 are arranged according to the shrubland PdV. The cluster analysis suggests an alternative distribution for the last seven samples. Thus, PA 103 is distinct from the others, while the remaining samples (PA 104, PA 105, PA 108, PA 110, PA 111, and PA 112) are grouped together (Figures 10, 11).

The distribution of these statistical analyses highlights a zoning of samples within the wreck Ilovik-Paržine 1 and suggests that the ship undergone four to five distinct batches of coatings. The cluster analysis indicates homogeneity in the coatings at the stern and in the central part of the ship, while it distinguishes three distinct batches at the bow (PA 100, PA 101, PA 102). The PCA identifies two batches at the bow (PA 100 and PA 102; PA 101), two batches

in the central zone (PA 105, PA 108, and PA 110; PA 111 and PA 112), and a single batch in the stern area (PA 103 and PA 104). These zonations likely reflect either successive repairs made to different parts of the vessel according to specific needs, or the use of materials from different sources during the construction or refurbishment of the ship.

The landscapes revealed by the palynological analyses are characteristic of the Mediterranean coastline and valleys, including its forests and matorral (*Q. ilex*, *Pinus*, *Cistus*, *Corylus*, *Ericaceae*, *Juniperus*, *O. europaea*). The low-relief areas are dominated by deciduous oak forests, with *Quercus*, *Carpinus*, and *Ulmus*. The presence of *Alnus* and *Fraxinus* indicates riparian vegetation, which may be found near the coast or in the nearby hinterland. Although *Abies* and *Fagus* are present in small proportions, these taxa suggest proximity to mountainous regions. This vegetation is typical of the north-eastern Adriatic littoral, which is in close proximity to mountain ranges such as the Učka and Čičarija ranges in Istria, and the Velebit mountain range in Dalmatia (Horvat et al., 1974; Bognar, 1996). Based on these preliminary results, it is reasonable to hypothesize that the studied coatings were produced and/or applied on the eastern Adriatic coast, where the shipwreck was discovered.

However, the micropaleontological, petrographic, sedimentological, diagenetic, and geochemical analyses of the ballast stones from Ilovik-Paržine 1 suggest that the ship was constructed near Brundisium/Brindisi (Fournier et al., 2024). Comparisons with reference sites in the Apulia region, such as Lake Alimini Piccolo near Lecce (Di Rita and Magri, 2009) and the Salpi Lagoon in the Tavoliere Plain near Manfredonia (Susini et al., 2022),

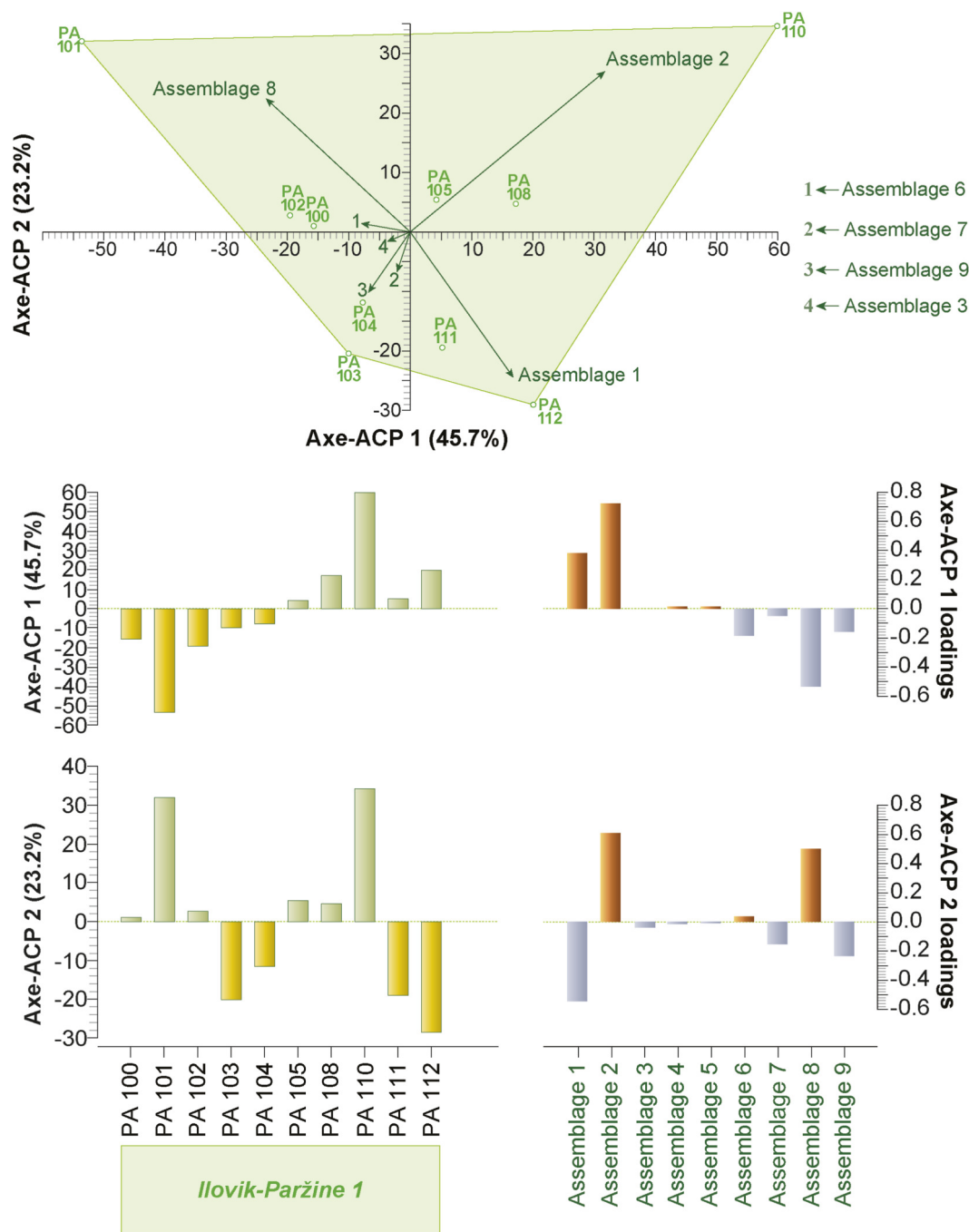


FIGURE 10
Principal component analysis (PCA) depicts the distribution of samples according to major changes in the PdV-scores.

reveal a correspondence with several samples from Ilovik-Paržine 1 (PA 103, PA 104, PA 105, PA 108, PA 110, PA 111, PA 112), due to the high abundance of herbaceous taxa (Asteraceae, Chenopodiaceae, Centaurea, Poaceae, and Plantago), which are associated with agro-pastoral practices, as well as the presence of Apiaceae, Brassicaceae, and *Olea europaea*. These data suggest that some of the coatings from Ilovik-Paržine 1 were either produced and/or applied at the shipyard, so not so far from *Brundisium*/Brindisi.

PA 100, whose assemblage is dominated by Mediterranean forest species such as *Quercus ilex*, *Cistus*, and Primulaceae, could have originated from Istria or Dalmatia (Sostarič, 2005), or more broadly from the western Mediterranean coast. Due to the significant presence of juniper-dominated communities, PA 101 and PA 102 might have originated from the vicinity of Naronia (Southern Dalmatia, Croatia, Figure 12). Indeed, environmental studies conducted in the Neretva Valley, particularly near the modern town of Vid, built on the ruins of the ancient city and

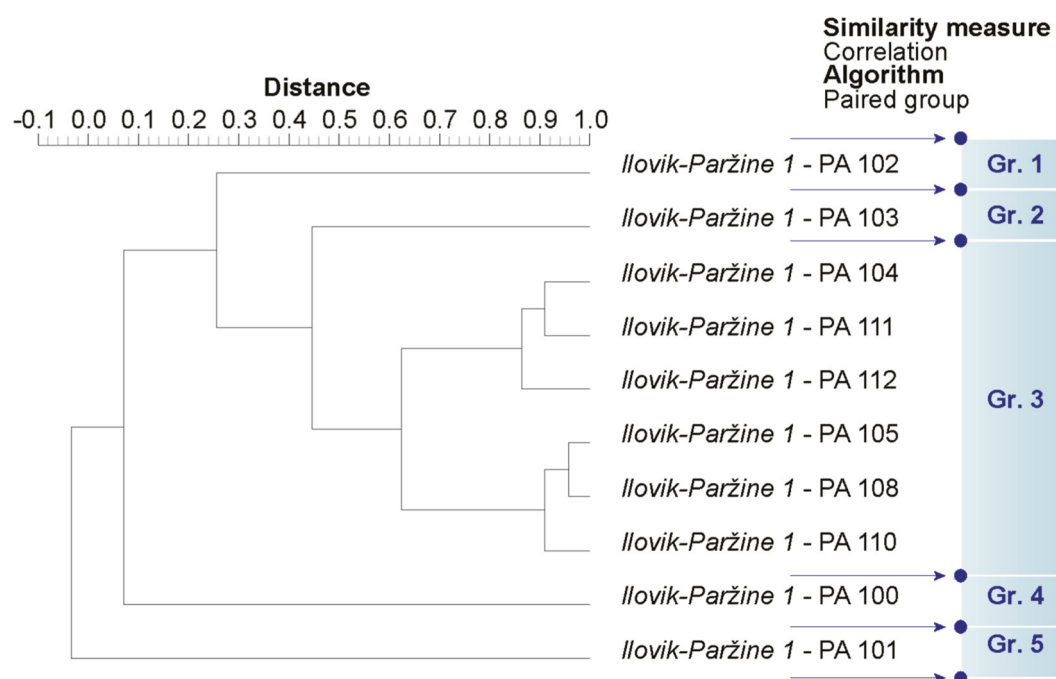


FIGURE 11

Classical cluster analysis (descending type, correlation as the similarity measure and Paired group as algorithm) representing the environmental assemblages.

port of Naron, indicate an expansion of *Juniperus* during the Roman period, from the second-first centuries BC to the fifth-sixth centuries AD (Brande, 1989). These samples may reflect localized repair actions on the ship's hull while it was sailing in the Adriatic Sea.

Thus, the coatings from the ship Ilovik-Paržine 1 appear to have multiple origins, reflecting not only the possible location of its shipyard but also different locations associated with maintenance and repair activities carried during its voyages.

6 Conclusion

The use of adhesives coating based on wood tars, either pure or mixed, has continued over the centuries, making the study of these materials an integral part of nautical archaeology and more broadly, of the history of shipbuilding techniques and the history of navigation.

Analyses of the waterproof coatings on the Ilovik-Paržine 1 wreck demonstrated the potential of an original multidisciplinary approach to studying these adhesive coatings commonly used in shipbuilding. Molecular analyses show that the main component of all the analyzed samples was a product resulting from the heat treatment of resin or wood from conifers (pitch). In contrast, palynological analyses show greater variety in pollen distribution, probably reflecting both the environmental contexts associated with the pitch production site and the pitch application sites, such as shipyards, repair yards, or ship navigation zone. The adhesive

PA 101 stands out as a notable exception, being a mixture of pitch and beeswax, and was distinctly identified through both cluster analysis and PCA. The results intersect and confirm the uniqueness of this sample. This type of composition corresponds to the *zopissa* used by the Greek shipbuilders (Pliny the Elder, *Natural History*, XVI, 23). Its identification at Ilovik-Paržine 1 is particularly interesting, especially in relation to the hypothesis that the shipyard was located near *Brundisium*/Brindisi, i.e., in an area where there was significant contact with the Greek colonies of southern Italy (Figure 12).

Palynological and statistical analyses of the coatings show promising leads for locating the geographical origin of the production and application areas of the pitch, as well as providing clues about sailing zone of the ship. Ilovik-Paržine 1 was a sailing ship intended for maritime transport in the Adriatic Sea and also in more distant maritime areas. The wreck presents four to five distinct batches of coatings, according to statistical analyses. The cluster analysis indicates homogeneity of the coatings at the stern and midships, while distinguishing three batches at the bow. The PCA identifies two batches at the bow, two midships, and one at the stern. These zonations reflect either successive repairs or the use of batches from different sources during construction or refitting. Molecular analyses, on the other hand, show homogeneity but this does not imply a single origin of the pitch, rather a similar nature and production technique. Palynology indicates that the origin of the majority of the coatings is to be found near the port of *Brundisium*/Brindisi, place of construction of the ship according to the results of sedimentological analyses carried out on the ballast.



FIGURE 12
Map showing the location of the wreck Ilovik-Paržine 1 and the places mentioned (Basemap: V. Dumas, CNRS/CCJ).

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

AC-D: Investigation, Writing – review and editing, Methodology, Conceptualization, Validation, Writing – original draft, Supervision. QC: Supervision, Writing – review and editing, Methodology, Conceptualization, Writing – original draft, Investigation, Validation. IM: Investigation, Writing – original draft, Funding acquisition. GB: Investigation, Conceptualization, Validation, Supervision, Writing – original draft, Writing – review and editing, Methodology.

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Conflict of interest

The author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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