Document Version
Final published version

Citation (APA)
Łucejko, J. J., Bertelli, I., Costa, R., Ebert, B., Falcó, A., Ion, R. M., Kozowyk, P., Mojović, Z., Nardella, F., & More Authors (2026). Characterising terpenic plant resins, wood tars and pitches in heritage science: analytical methods and applications. *npj Heritage Science*, *14*(1), Article 162. https://doi.org/10.1038/s40494-026-02426-6

npj | heritage science

Review

https://doi.org/10.1038/s40494-026-02426-6

Characterising terpenic plant resins, wood tars and pitches in heritage science: analytical methods and applications

Check for updates

Jeannette Jacqueline Łucejko[1] ✉, **Irene Bertelli**[1,2], **Renata Costa**[3], **Bettina Ebert**[4], **Andreu Falcó**[5,6], **Rodica-Mariana Ion**[7,8], **Paul Kozowyk**[9], **Zorica Mojović**[10], **Federica Nardella**[11], **Alessandra Pecci**[5,6], **Erika Ribechini**[1], **Hannes Schroeder**[12], **Magdalena Zborowska**[13] & **Maria Perla Colombini**[1]

This review examines natural plant resins, wood tars and pitches in heritage science, focusing on their historical uses, chemical composition and analytical characterisation. Particular attention is given to diterpenoid and triterpenoid resins and to chemical transformations induced by ageing, degradation and thermal processing. The identification of diagnostic molecular markers supports the determination of botanical origins and technological practices, while an overview of complementary analytical methods highlights current challenges and perspectives.

The use of resin, tar and pitch in human history: a technological continuum

Plant-derived resins, tars, and pitches have been utilised since prehistory across diverse cultural and geographic contexts; this review focuses primarily on materials documented in European and Mediterranean archaeological and historical records[1]. These substances represent some of the earliest known technological innovations in human history, with a long and complex trajectory of use extending from the Palaeolithic period to the modern industrial era[2–8]. Birch tar, derived from *Betulaceae*, is the oldest known adhesive, with archaeological evidence from the European Lower Palaeolithic indicating its use approximately 200,000 years ago[8], and it may also have served as an insect repellent[9]. In the Scandinavian Iron Age, birch bark tar was employed as sealant for wooden containers[10]. While the exploitation of birch bark tar for hafting tools is ancient, the transition to resin and pitch or tar from *Pinaceae* trees marked a significant technological shift.

The production of wood tar, derived from resinous and non-resinous woody materials, was practiced by the Minoans around 3000 B.C.[11], and likely served as an essential commodity for ancient centres of power in Greece, Macedonia, Asia Minor and Egypt[12]. In ancient Egypt, plant resins were integral to embalming practices[13,14], and extensive records on the practical and ritual use of tar and tar-based materials were preserved in the Mouseion, Library of Alexandria, reflecting early understandings of chemical processing for medicinal and ritual use[15]. Medicinal uses of pine tar were documented by Hippocrates (460–370 BC) over 2400 years ago[3,5]. Likewise, Theophrastus (371–287 BC) and Gaius Plinius Secundus described the use of tar and tar water in their influential writings[16]. Due to its antiseptic properties, pine tar has been used for centuries in both human and veterinary medicine to treat skin conditions[5]. Archaeological evidence also indicates that plant resins and tars were used as chewing gums in the past. The use of aromatic plant resins as incense is well established, and analytical techniques have confirmed their presence in the archaeological record[17–20].

Pine resin and pine tar have a long history of use as protective coatings and sealants for wooden elements or ceramic vessels. In Roman times, pitch was primarily used for waterproofing ships, but also for storing and transporting food in amphorae and dolia[21–23]. Pine tar has historically been, and continues to be, applied as a protective and sacrificial coating on wooden structures, including medieval Norwegian stave churches, shingle roofs and wooden built heritage[6,7,24]. In Scandinavia, this practice remains active today, illustrating continuity of use across centuries[25]. In medieval Northern

---

[1]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy. [2]Department of Sciences of Antiquity, Sapienza University of Rome, Rome, Italy. [3]Faculty of Sciences (FCUP), University of Porto, Porto, Portugal. [4]Museum of Archaeology, University of Stavanger, Stavanger, Norway. [5]Archaeological and Archaeometric Research Unit (ERAAUB), Institute of Archaeology (IAUB) of the University of Barcelona, Barcelona, Spain. [6]Department of History and Archaeology, Faculty of Geography and History (INSA-UB), University of Barcelona, Barcelona, Spain. [7]Valahia University of Targoviste, Targoviste, Romania. [8]National Institute for Research & Development in Chemistry and Petrochemistry, Evaluation and Conservation of Cultural Heritage Research Group, Bucharest, Romania. [9]Department of Architectural Engineering and Technology, Delft University of Technology, Delft, The Netherlands. [10]Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Beograd, Serbia. [11]Amsterdam Institute for Life and Environment (A-LIFE), Section Chemistry for Environment and Health, Vrije Universiteit, Amsterdam, The Netherlands. [12]Globe Institute, Faculty of Health and Medical Sciences, University of Copenhagen, Copenhagen, Denmark. [13]Department of Chemical Wood Technology, Faculty of Forestry and Wood Technology, Poznań University of Life Sciences, Poznań, Poland.
✉e-mail: jeannette.lucejko@unipi.it

Europe, wood tar and resin-based adhesives were also used in the construction and maintenance of stone cathedrals[26,27]. Additionally, archaeological evidence indicates that tar and pitch were used in weaponry and medieval warfare, as components of incendiary devices such as firebombs[28,29].

Over the past millennium, one of the primary uses of tar has been as a caulking agent for waterproofing ships[6,30,31]. During the Viking Age, tar-soaked wool was commonly employed for this purpose, while planks and, occasionally, ropes were coated in tar[6]. This practice of waterproofing ships with tar continued throughout the Middle Ages and beyond, eventually giving rise to a significant tar export industry in Scandinavia[6]. By the early modern period, tar production had become large-scale and systematically organised, particularly in outland forest regions. Wood tar derived from pine trees emerged as one of Northern Europe's most valuable exports and played a central role in Sweden's economy for centuries. Likewise, the British colonies in North America capitalised on their abundant pine forests for tar production. Pine tar remained a globally traded and economically important commodity until the 19th century[32,33]. However, demand for tar declined with the transition to iron and steel shipbuilding, as its primary function, preserving wooden vessels from rot, became obsolete.

Throughout history, plant resins have been extensively used as binding media in lacquers, varnishes, paints and coatings. In some well-documented traditions, particularly in East and Southeast Asia, the botanical origin of lacquer materials is clearly defined. Analyses of archaeological Asian lacquerware reveal the use of a diverse range of plant-based lacquers based on exudates of the *Anacardiaceae* family, including urushi, which is derived from *Toxicodendron vernicifluum*, thitsi from *Melanorrhoea usitata*, and Vietnamese lacquer from *Toxicodendron succedaneum*[34,35]. Resins have also been widely employed in varnishes for fine and decorative arts, and natural resins continue to play a role in the conservation of artworks. In addition to diterpenoid resins such as pine and sandarac, triterpenoid resins and balsams (e.g. mastic, dammar, elemi, and benzoin) have been extensively used as varnish components, particularly in painting and decorative objects[36]. Notably, pine and sandarac resins were commonly used in the varnishes of some of the most renowned musical instruments, including those crafted by Stradivari[37,38]. Amber, a fossilised resin, was also historically employed in varnish formulations, especially in Northern and Eastern Europe[36,39,40].

The study of natural resins, tar and pitch within heritage science provides valuable insights into human evolution, technological innovation, specialised knowledge systems, trade networks, social organisation, cross-craft interactions, and international relations. Due to their molecular complexity and overlapping chemical signatures, accurate identification of these substances often requires specialised analytical techniques. Although largely supplanted by petroleum-based products in the 20th century, growing interest in sustainable and renewable alternatives has revitalised research into natural resins and tars. These investigations not only contribute to the reconstruction of historical technologies but also inform the development of bio-based alternatives for contemporary industrial applications.

Botanical origin and chemical composition of natural resins

From a chemical perspective, natural resins are highly complex mixtures whose composition varies according to the botanical source and reflects differences in terpenoid and phenolic constituents. The chemical composition of resins is highly complex and varies according to the genus and species of the source plant from which the resin is extracted. Natural resins are composed of mixtures of volatile and nonvolatile terpenoids and/or phenolic compounds. Terpenes and terpenoids, which form the largest and most diverse class of plant compounds, are complemented with additional functional groups that contribute to their chemical diversity. Terpenes are secondary metabolites, derived biosynthetically from concatenations of units of dimethylallyl diphosphate (DMAPP) and of its isomer isopentenyl pyrophosphate (IPP). Structurally, terpenes are often visualised as linked isoprene units, each consisting of 5 carbon atoms (C_5H_8)[39].

Figure 1 illustrates the two biosynthetic pathways leading to the formation of the basic structural unit of terpenoids. DMAPP acts as a primer to which IPP units can be added in sequential chain-elongation steps. These reactions, catalysed by prenyltransferase enzymes, connect isoprene units to one another. Geranyl diphosphate (GPP) may be folded into mono-, bi-, and tricyclic structures and subsequently modified to yield over 1000 distinct monoterpenes. Because the precursor farnesyl diphosphate (FPP) contains five additional carbon atoms, sesquiterpenes have many more types of cyclisation. The precursor geranylgeranyl diphosphate (GGPP) forms more than 3000 diterpene structures, typically featuring various oxygen-containing functional groups. Dimerisation of the C15 FPP leads to the formation of triterpenes, which include a wide variety of structural types such as dammarane, oleanane, hopane, ursane, lanostane, and lupane.

Mono- and sesquiterpenes are the volatile compounds responsible for the characteristic smell of resins. These compounds are also responsible for the fluid state of freshly exuded resin, as they are liquid at room temperature. For this reason, when a resin contains a high concentration of low molecular weight terpenes, it is referred to as an oleoresin[41]. Mono- and sesquiterpenes are distributed throughout various parts of the plant, including leaves, flowers, and bark. Generally, low molecular weight terpenes constitute the essential oils of resin. However, this designation is misleading because these terpenoids are neither essential to plant metabolism nor are they true oils; 'essential' refers to their essence or fragrance, while 'oil' describes their tactile properties[39]. High molecular weight terpenes are found with acidic or alcoholic functionalities and exhibit varying degrees of unsaturation. While isolated double bonds are generally reactive, the formation of aromatic or conjugated ring systems confers greater chemical stability; consequently, molecules containing aromatic rings are more stable than low molecular weight terpenes.

From a chemical perspective, plant resins are highly complex mixtures of mono-, sesqui-, di-, and triterpenes, which contain 10, 15, 20, and 30 carbon atoms per molecule, respectively. The volatile fraction of plant resins commonly contains both mono- and sesquiterpenes, while di- and triterpenes are rarely found together in the same nonvolatile resin fraction. Both di- and triterpenes co-occur only in a few genera of the large tropical rainforest angiosperm family *Burseraceae*. This allows for terpenoid resins to be broadly classified into two major groups: diterpenoid and triterpenoid resins[21,36,42]. In contrast to resins, the production process of tar and pitch leads to chemical modifications of the native terpenoids of the resin, including aromatisation, demethylation and decarboxylation. This results in the formation of new compounds with lower molecular weight and a high degree of aromatisation[43].

Analytical challenges in characterising resinous substances in heritage science

The chemical complexity of resins poses significant challenges for their analytical characterisation. Their composition varies widely depending on their origin, reflecting differences in the amounts and types of volatile and nonvolatile terpenoids and phenolic compounds, preservation state, and frequent association with other organic and inorganic components. The main challenges are:

- Complex composition: resins contain a high number of terpene compounds, which undergo degradation due to ageing, environmental exposure, and human activities (e.g., heating processes, such as in the production of tar and pitch).
- Low concentrations: organic materials are often present in minimal amounts compared to the inorganic matrices in which they are embedded.
- Coexistence with other organic substances: resins frequently appear alongside beeswax, oils, animal fats, and other organic materials in archaeological and historical objects, complicating identification.

Due to these complexities, specific analytical procedures are required to obtain meaningful information. Such characterisation

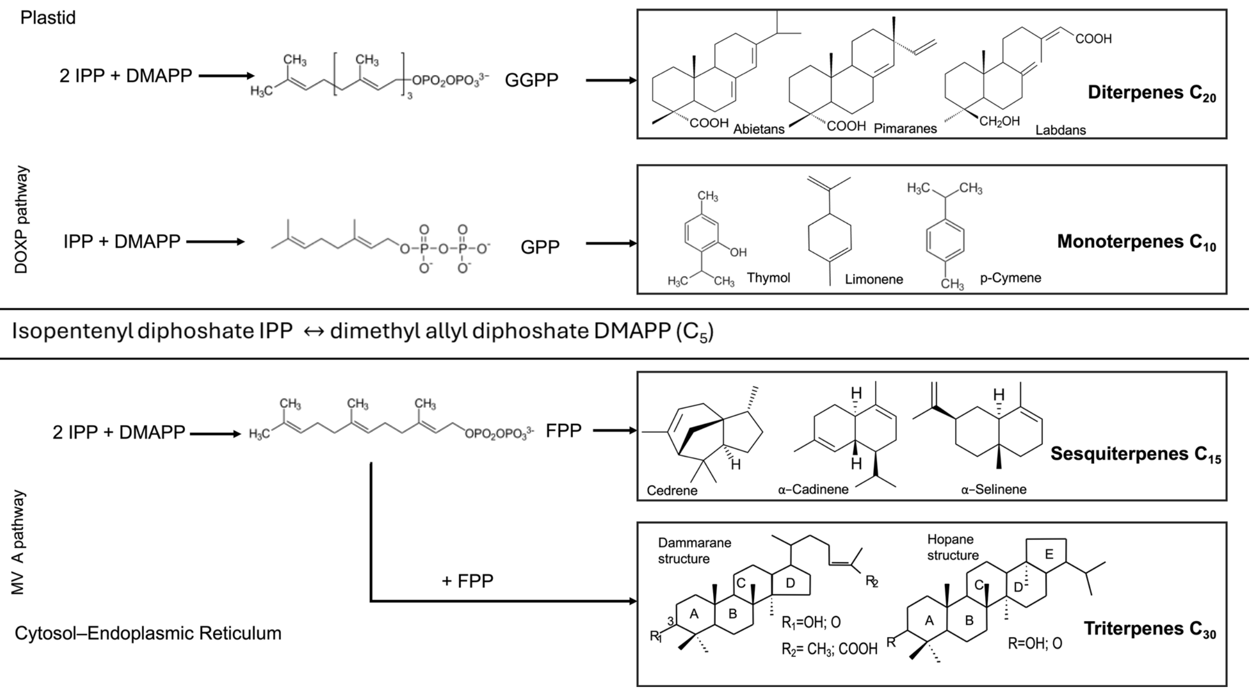


Fig. 1 | Overview of terpenoid biosynthesis through plastidial and cytosolic pathways and representative skeletal structures of major terpenoid classes. The figure illustrates the biosynthesis of terpenoids via the two principal metabolic routes: the plastidial 1-deoxy-D-xylulose-5-phosphate (DOXP) pathway and the cytosolic mevalonate (MVA) pathway. In plastids, the condensation of isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) leads to the formation of geranyl diphosphate (GPP), the precursor of monoterpenes (C_{10}), and geranylgeranyl diphosphate (GGPP), which gives rise to diterpenes (C_{20}). Representative diterpenoid skeletal types shown include abietane, pimarane, and labdane frameworks. Example monoterpenes illustrated are thymol, limonene, and p-cymene. In the cytosol and endoplasmic reticulum, IPP and DMAPP are converted into farnesyl diphosphate (FPP), the precursor of sesquiterpenes (C_{15}), exemplified by cedrene, α-cadinene, and α-selinene. The condensation of two FPP units leads to the formation of triterpenes (C_{30}), represented by dammarane- and hopane-type skeletons. Generic R substituents indicate structural variability within each terpenoid class. Carbon numbers for each class (C_{10}, C_{15}, C_{20}, C_{30}) are indicated to emphasize the isoprenoid building-block organization. Abbreviations: IPP, isopentenyl diphosphate; DMAPP, dimethylallyl diphosphate; GPP, geranyl diphosphate; FPP, farnesyl diphosphate; GGPP, geranylgeranyl diphosphate; DOXP, 1-deoxy-D-xylulose-5-phosphate; MVA, mevalonate pathway. Figure adapted from reference[39].

methods often rely on the identification of molecular markers (named also biomarkers)—diagnostically stable molecules that either remain intact in archaeological contexts or form through long-term ageing[17,44–47]. Identifying such molecular markers provides critical insights into:

- Botanical origin: determining the plant source of resins, tars, or pitches.
- Anthropogenic modifications: detecting intentional chemical alterations made before use or during the artefact's use history.
- Natural decay: understanding transformations and degradation processes due to environmental exposure and ageing.

By analysing these molecular markers, it is often possible to partially reconstruct the original composition of organic materials and gain insights into the processes that have altered them over time. Due to their volatility, mono- and sesquiterpenes are generally unsuitable molecular markers for identifying and classifying resins, as they are rarely found in ancient samples[36,44]. Additionally, quantifying low molecular weight terpenes cannot reliably determine the botanical source, as their concentrations do not directly correspond to those in the original plant. Over time, these compounds evaporate unevenly, further complicating analysis.

In contrast, high molecular weight terpenes often feature acidic or alcoholic functionalities and may undergo aromatisation; they exhibit greater chemical stability and are therefore more likely to persist over time. Increased aromaticity and varying degrees of unsaturation further enhance their stability. Increased aromaticity enhances molecular stability, making these compounds more likely to persist over time.

The chemical composition of terpenic plant resins

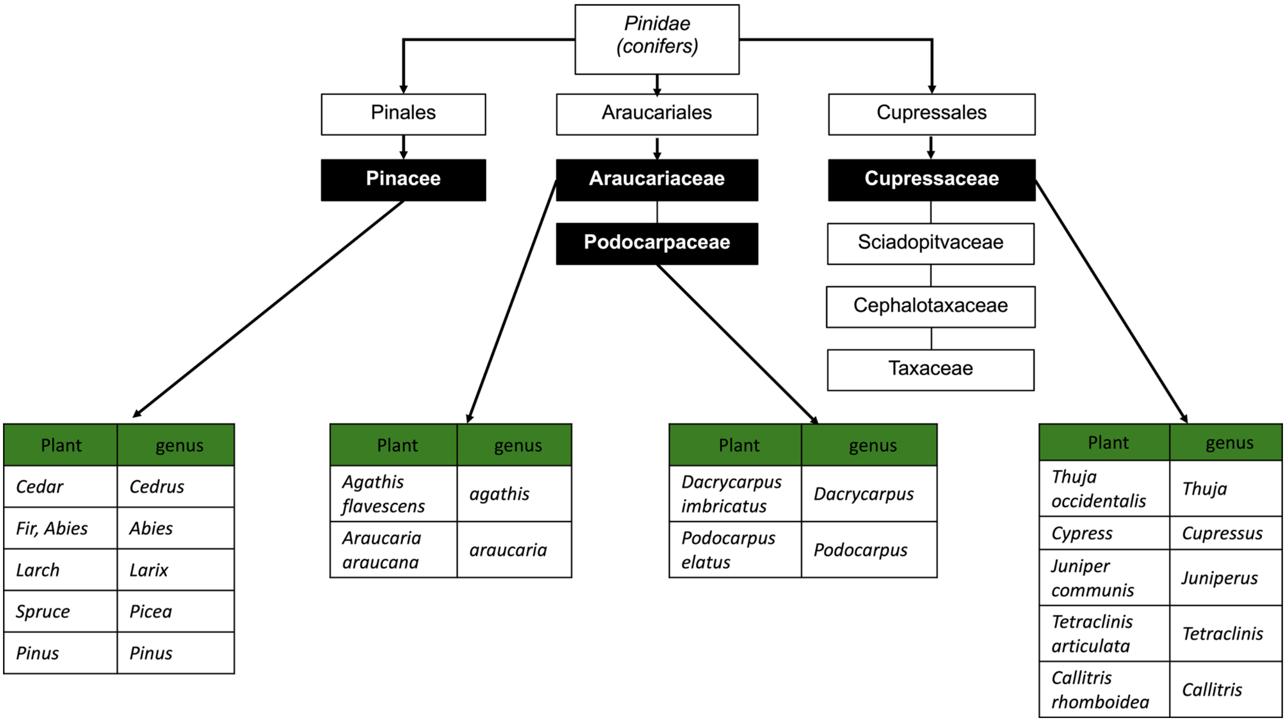
Diterpenoid resins

Diterpenoid resins are produced predominantly by conifers (subclass *Pinidae*), including both temperate and tropical taxa, and play an important role in the physical and chemical defence responses against invading organisms and pathogens. Figure 2 reports a simplified classification of conifers showing only the *Pinaceae*, *Araucariaceae*, *Cupressaceae*, and *Podocarpaceae* which produce resin in secretory structures. *Pinaceae* and *Cupressaceae* represent the largest family of conifer families, with an extensive natural distribution in the Northern Hemisphere.

Diterpenes in conifer resins are characterised by three main skeletal types (abietane, pimarane, and labdane) that vary quantitatively across different conifer families. These resins are characterised by a large volatile fraction (20–50%) with monoterpenes predominating over sesquiterpenes. Nonvolatile terpenes in conifers are primarily diterpene acids.

Diterpenes in conifer resins are characterized by a limited number of skeletal frameworks whose relative abundance varies among conifer families. Representative diterpenoid skeletons are shown in (Fig. 3).

Diterpenoid resins from *Pinaceae* consist of mixtures of tricyclic compounds, such as abietanes and pimaranes. Among the diterpenoid compounds found in resins, the most common are carboxylic acids. For abietanes, these acids include abietic, neoabietic, levopimaric, and palustric acids, which differ only in the position of the conjugated double bond, and all have an isopropyl substituent at carbon C13[48]. The pimaradiene acids (pimaric, sandaracopimaric, and isopimaric acids) are structurally related to the abietadiene acids but differ in their carbon skeleton, lacking conjugated double bonds and displaying a different arrangement of the methyl and vinyl group at C13[48].



Plant	genus
Cedar	*Cedrus*
Fir, Abies	*Abies*
Larch	*Larix*
Spruce	*Picea*
Pinus	*Pinus*

Plant	genus
Agathis flavescens	*agathis*
Araucaria araucana	*araucaria*

Plant	genus
Dacrycarpus imbricatus	*Dacrycarpus*
Podocarpus elatus	*Podocarpus*

Plant	genus
Thuja occidentalis	*Thuja*
Cypress	*Cupressus*
Juniper communis	*Juniperus*
Tetraclinis articulata	*Tetraclinis*
Callitris rhomboidea	*Callitris*

Fig. 2 | Taxonomic classification of conifers and principal resin-producing families and genera. The figure presents a simplified taxonomic scheme of conifers (Pinidae) highlighting the principal orders, families, and selected genera associated with resin production in specialized secretory structures. Three main orders are shown: Pinales, Araucariales, and Cupressales. Within Pinales, the family Pinaceae is indicated as a major resin-producing group and includes representative genera such as Cedrus (cedar), Abies (fir), Larix (larch), Picea (spruce), and Pinus. Within Araucariales, the families Araucariaceae and Podocarpaceae are identified as resin-producing groups. Representative genera include Agathis and Araucaria (Araucariaceae), as well as Dacrycarpus and Podocarpus (Podocarpaceae). Within Cupressales, the family Cupressaceae is highlighted as a resin-producing group and includes genera such as Thuja, Cupressus (cypress), Juniperus (juniper), Tetraclinis, and Callitris. Other families within Cupressales (Sciadopityaceae, Cephalotaxaceae, and Taxaceae) are shown for taxonomic context but are not emphasized as primary resin producers. Families capable of producing resin in specialized secretory structures are indicated by black boxes, whereas non-highlighted families are shown in light boxes. Arrows indicate hierarchical taxonomic relationships from subclass to order, family, and representative genera. The scheme is adapted from references. [222] and [223].

Over time, oxidation reactions lead to significant changes in the chemical composition of *Pinaceae* resins. In particular, abietic acid, a major component of fresh resin, is progressively converted into dehydroabietic acid, which becomes the dominant compound as the resin ages. Further oxidation in the presence of oxygen can yield secondary products such as 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid[30]. Figure 4 illustrates this oxidation pathway, along with the effects of thermal treatment on resinous *Pinus* wood[44,49].

In archaeological samples from Roman-age amphorae[49], the relative abundance of secondary oxidation products reflects a combination of thermally induced transformations during production and subsequent oxidative processes occurring after deposition. During tar manufacture, heating of resinous wood promotes aromatisation, demethylation, and decarboxylation of abietic and dehydroabietic acids, while long-term exposure to oxygen following burial further enhances oxidative alteration, leading to the formation of highly oxidised compounds.

Within the analysed assemblage, the occurrence of characteristic saturated abietane hydrocarbons in a single specimen suggests that limited reductive processes also took place. Such reductions are not related to the production stage, but are more plausibly associated with specific burial conditions, including reducing environments, elevated pressure, or microbial activity[50,51]. Overall, the close similarity in the molecular composition of the analysed pine tar residues supports the interpretation that pine tar was widely used as a waterproofing and sealing agent at multiple sites in northern Greece during the Roman period[49].

Strasbourg turpentine and Venice turpentine are aromatic, thick, viscous exudates obtained respectively from fir (*Abies* spp.) and larch (*Larix* spp.) trees primarily in central Europe. Both materials are composed mainly of resin acids (65–75%), a volatile oil fraction rich in monoterpenes (15–20%), and minor amounts of neutral resinous substances. Their chemical composition is very similar, and both have been used since the 16th century as an additive to oil paints.

Cupressaceae resin contains bicyclic compounds, such as labdanes[52]. These compounds have only two rings, with the remaining carbon atoms forming a linear side chain that often contains a highly reactive conjugated double bond, which readily undergoes polymerisation reactions. As a result, labdane-type diterpenoids are rarely preserved as free molecular species in aged resins, as they tend to be incorporated into polymeric networks, a behaviour also observed in copals and ambers[53,54].

Pinaceae and *Cupressaceae* contain distinct diterpenoid compounds that are widely used as molecular markers for the identification of conifer resin. In most cases, diterpenoid molecular markers patterns allow assignment at the family or genus level; however, species-level discrimination within the same is often challenging and not always reliable based on diterpenoid profiles alone. The main diterpenoid molecular markers reported for conifer resins are summarised in Table 1, based on data from literature[48,54–59].

Triterpenoid resins

Triterpenoid resins are primarily produced by angiosperms, particularly flowering plants. Some of the most notable plant families that produce triterpenoid resins, used in European and Mediterranean countries, include the *Burseraceae* family, which features genera like *Boswellia* (frankincense), *Commiphora* (myrrh), *Canarium luzonicum* (elemi) and the *Pistacia* and *Hopea* genus (mastic and dammar resin, respectively). These plants are, historically valued for medicinal, ceremonial, and aromatic purposes[60]. In many angiosperm resins, sesquiterpenes constitute the dominant fraction of the volatile components. In resins produced by members of the

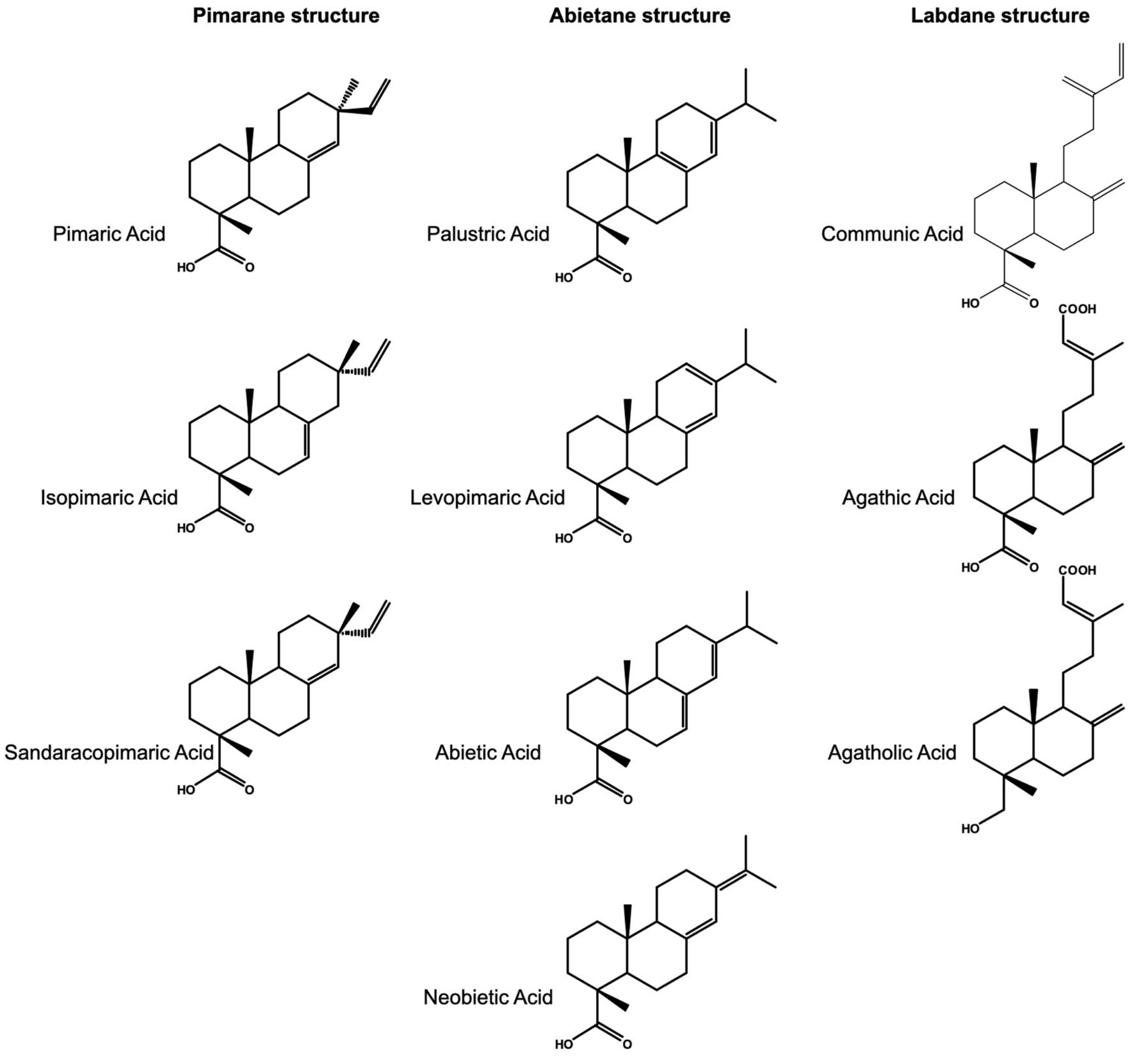


Fig. 3 | Representative chemical structures of major diterpenoid classes occurring in resins of the *Cupressaceae* and *Pinaceae* families. The figure shows selected examples of diterpenoid skeletons characteristic of conifer resins, organized according to the three principal structural classes: pimarane-type, abietane-type, and labdane-type frameworks. These diterpenoids are widely reported in resins of the *Cupressaceae* and *Pinaceae* families and constitute key molecular markers in heritage science investigations. The left column illustrates pimarane-type structures, including pimaric acid, isopimaric acid, and sandaracopimaric acid. These compounds share a tricyclic diterpenoid core with variations in double-bond position and stereochemistry. The central column presents abietane-type structures, including palustric acid, levopimaric acid, abietic acid, and neoabietic acid. Abietane diterpenoids are characterized by a rearranged tricyclic skeleton with conjugated double bonds and typically a carboxylic acid functional group. These compounds are among the most abundant constituents of *Pinaceae* resins. The right column displays labdane-type structures, including communic acid, agathic acid, and agatholic acid. Labdane diterpenoids possess a bicyclic core with an isoprenoid side chain and are particularly associated with *Cupressaceae* resins. Structural differences among the illustrated compounds reflect variation in double-bond configuration and functional groups such as carboxylic acid or hydroxyl moieties. All structures are shown as neutral skeletal formulas, highlighting the carbon framework and principal functional groups.

Dipterocarpaceae family, this high volatile content results in a more fluid resin consistency, making them suitable for medicinal applications and as fuel oil. In contrast, resins from *Pinus*, *Boswellia*, and *Pistacia*, have a higher proportion of nonvolatile components, resulting in a more viscous resin used for varnishes and protective coatings[36,39].

Chemically, triterpenoid resins are composed of mixtures of tetracyclic (dammarane and lanostane) and pentacyclic (ursane, oleanane, lupane, hopane) structures (Fig. 5), which serve as molecular markers for the botanical source[61]. These structures are typically functionalised as carboxylic acids, ketones, alcohols or lactones, depending on the plant species and degree of oxidation. For example, frankincense (olibanum) is particularly rich in pentacyclic boswellic acids, together with small amounts of cembrane-type diterpenoids[62]. Myrrh contains similar triterpenoid compounds (dammarane, polypodane, octanordammarane, cycloartane, oleanane, lupane, ursane, and lanostane), ketones, and esters, but in different proportions and with distinctive sesquiterpenoids contributing to its aroma[63]. Storax resin, also called benzoin, is obtained from the *Styrax officinalis* trees, native to upper Egypt. Storax contains triterpenoids along with styrene, stryacin, and cinnamic acid[44]. Mastic resin is characterised by the presence of hydroxydammarenone and a series of triterpenoid acids including oleanonic, moronic, isomasticadienonic, and masticadienonic acids, while notably lacking ursane-type compounds[64]. Dammar resin contains a high proportion of dammarane- and lanostane-type triterpenes, both as neutral and oxidised species, which tend to polymerise with age (Fig. 5).[44]

These complex mixtures are further complicated by degradation over time: initial oxidation reactions produce alcohols, ketones, and carboxylic acids that can undergo condensation reactions, forming oligomeric species of three or four terpenoid units. Over time, continued oxidation and radical reactions promote polymerisation, leading to high-molecular-weight oligomers[47]. In dammar and mastic resins, the formation of cross-linked polymeric networks—a common process occurring in resinous systems—together with the evaporation of more volatile sesquiterpenes, reduces solubility and makes the material harder. Such changes not only alter the mechanical properties of the resins hampering the extraction of molecular

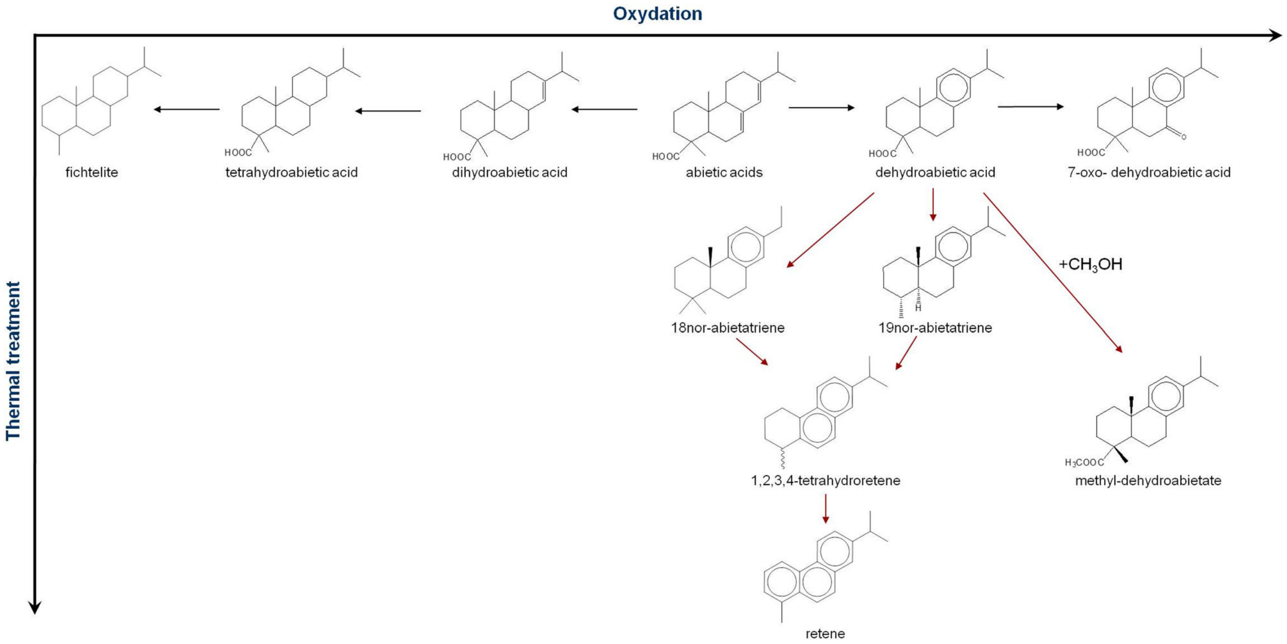


Fig. 4 | Oxidative and thermal transformation pathways of abietane-type diterpenoids in Pinus resin and resinous wood. The figure illustrates the principal oxidative and thermally induced transformation products of abietane-type diterpenoids occurring in Pinus resins and resin-rich wood. The horizontal axis (left to right) represents progressive oxidation, while the vertical axis (top to bottom) indicates increasing thermal treatment. Along the upper horizontal sequence, abietane diterpenoids undergo progressive oxidation from abietic acids to dehydroabietic acid and further to 7-oxo-dehydroabietic acid. Earlier reduction products, including dihydroabietic acid and tetrahydroabietic acid, are also shown, as well as fichtelite as a highly reduced derivative. Black horizontal arrows indicate oxidative interconversion pathways among these compounds. From dehydroabietic acid, additional transformation routes are depicted by red arrows. Thermal degradation and rearrangement processes lead to the formation of 18-nor-abietatriene and 19-nor-abietatriene, which can further aromatize to 1,2,3,4-tetrahydroretene and ultimately to retene under more intense thermal conditions. The formation of methyl dehydroabietate in the presence of methanol (CH_3OH) is also indicated. Red arrows therefore represent thermally driven reactions and decarboxylation/aromatization processes associated with heating and pyrolytic alteration. All structures are shown as skeletal formulas, emphasizing the progressive aromatization of the abietane core during oxidation and thermal maturation. The scheme is adapted from references.[44]and [49].

Table 1 | Main compounds in diterpenic resinous materials occurring in historical samples

Resinous materials	Main compounds	Ref
Pine resin from pine trees (genus *Pinus*, family Pinaceae)	Pimaradienic acids, abietadienic acids, dehydroabietic acid, di-dehydriabietic acid, 7-oxodehydroabietic acid, 15-hydroxy-dehydroabietic acid, 15-hydroxy-7-oxodehydroabietic acid	21,36
Venice turpentine from larch (*Larix*)	Pimaradienic acids, abietadienic acids, dehydroabietic acid, di-dehydriabietic acid, 7-oxodehydroabietic acid, 15-hydroxy-dehydroabietic acid, 15-hydroxy-7-oxodehydroabietic acid, epimanool, larixol, laryxyl acetate	36,56
Strasbourg turpentine from European silver fir (*Abies alba*)	Pimaradienic acids, abietadienic acids, dehydroabietic acid, di-dehydroabietic acid, 7-oxodehydroabietic acid, 15-hydroxy-dehydroabietic acid, 15-hydroxy-7-oxodehydroabietic acid, cis-abienol	39,218
Sandarac (*Tetraclinis articulata*), cypress and juniper resins	Pimaric acid, sandaracopimaric acid, isopimaric acids, agathic acid, isoagathic acid, cis- and trans-communic acid, totarol, manool, sugiol, pinifolic acid, ferruginol, callistric acid	36,201
Sandarac (*Callitris*)	Callitrisic acid, sandaracopimaric acid, 4-epi-pimaric acid, cis- and trans-communic acid, 12E-ozic acid	54,55,201
Manila copal from *Agathis philippinensis* (or *Agathis dammara*)	Pimaric acid, sandaracopimaric acid, isopimaric acids, cis- and trans-communic acids, agathic acid, agatholic acid	54
Labdanum resin (Cistaceae family)	Laurifolic, cistenolic, labdanolic acids, manoyloxide, *epi*- manoyloxide, 3-hydroxy manoyloxide and 3-acetoxy manoyloxide	58

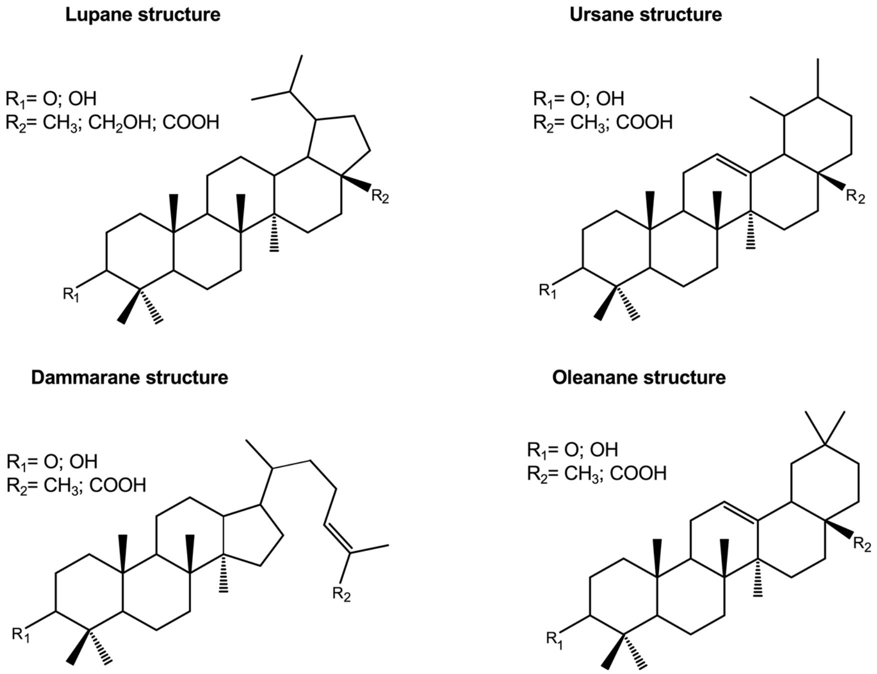
markers, but also complicate analytical characterisation, as the aged material no longer reflects the original molecular marker composition of the fresh resin. The main compounds of triterpenoid resin occurring in historical samples are reported in Table 2.

Production of wood tar and pitch and the chemical composition

During tar and pitch production, heating of wood or resinous plant material induces chemical transformations that result in compositions markedly different from the original feedstock[7,30,49,65,66].

Terminological ambiguity between tar and pitch persists in the literature, with inconsistent usage across disciplines. In this review, the term “wood tar pitch” is used to refer specifically to pitch obtained through the refinement of wood tar, and the botanical source of the material is specified whenever possible (e.g. pine tar, birch bark tar).

The chemical composition of wood tar and pitch depends heavily on the source material. More specifically, the composition of tar is dependent on the pyrolysis method (i.e. thermal degradation under oxygen-limited conditions), duration, temperature, and the type of initial wood used, including the age and growing conditions of the trees[67]. Wood tar mainly



Lupane structure

Ursane structure

Dammarane structure

Oleanane structure

Fig. 5 | Representative skeletal structures of the principal triterpene classes occurring in resinous materials. The figure presents the core carbon skeletons of the main structural classes of triterpenes identified in natural resins and resin-derived materials, including lupane-, ursane-, dammarane-, and oleanane-type frameworks. These pentacyclic triterpenoids are widespread in angiosperm resins and constitute important molecular markers in archaeological and heritage science studies. The lupane structure is characterized by a pentacyclic framework with a terminal isopropenyl substituent, while the ursane and oleanane structures display closely related pentacyclic cores differing in methyl group arrangement and double-bond position. The dammarane structure exhibits a tetracyclic core with a side chain, typical of dammar resins and related botanical sources. Generic substituents are indicated as R$_1$ and R$_2$ to represent structural variability within each class. For all four skeleton types, R$_1$ may correspond to oxygenated functionalities such as a carbonyl group (O) or hydroxyl group (OH), whereas R$_2$ may represent methyl (CH$_3$), hydroxymethyl (CH$_2$OH), or carboxyl (COOH) substituents depending on the specific compound. These variations account for the diversity of naturally occurring triterpenoids within each structural family. All compounds are shown as simplified skeletal formulas emphasizing ring connectivity, stereochemistry, and principal functional groups. Figure adapted from reference[44].

Table 2 | Main compounds of triterpenoid resins occurring in historical samples

Resin	Main compounds	Ref
Frankincense (or olibanum) *Boswellia* (family Burseraceae)	α-boswellic acid, β-boswellic acid, α 3-*O*-acetyl-a-boswellic, α. *O*-acetyl-β-boswellic, 11-keto-β-boswellic acid	62
Myrrh *Commiphora* spp. (Burseraceae)	commic acid C, commic acid D and commic acid E, α- and β-amyrin	63
Storax *Liquidambar* spp. (Altingiaceae)	α- and β-storesin, oleanonic acid, 3-epioleanolic acid, cinnamic acid	44
Mastic *Pistacia lentiscus* (Anacardiaceae)	moronic acid, masticadienonic acid, iso-masticadienonic acid, nor-olean-17-en-3one, tirucallol	64
Dammar Dipterocarpaceae (*Shorea*, *Dipterocarpus*, *Hopea*)	shoreic acid, 20,24-epoxy-25-hydroxy-dammaren-3-one, 20,24-epoxy-25-hydroxy-dammaren-3-olo, ursonic acid, ursonic aldehyde, oleanonic acid	44

consists of aromatic compounds and small oxygenated compounds deriving from the pyrolysis of the wood. However, different tree species have varying wood constituents (carbohydrates, cellulose, lignin, extractives) which behave uniquely during pyrolysis, influencing the final tar and volatile fractions (Fig. 6). Wood tars and pitches produced from resinous woods also contain compounds obtained from the aromatisation, demethylation and decarboxylation reactions of the terpenoids within the resin[68]. In some cases, this may make up a significant portion of the tar material[7]. Production methods vary widely, both temporally and geographically, and heavily influence the material composition. In general, until recently, little attention has been paid to prehistoric tar-production methods. Recent research has revealed that before the actual tar kilns, a series of funnel-shaped tar pits were used[6,7,69]. These were built close to the forest from primitive holes in the ground, and without an outlet pipe. Hence, continuous recovery of tar products was not possible, and the tar accumulated at the base of the pit, having to be recovered after burning.

Historic production can be divided into two categories:

- Autothermic: the reaction material that converts to tar also provides the heat to feed the reaction. Often, small pre-prepared pieces of wood rich in resin are located inside ovens/kilns and are burnt. Some oxygen is therefore required in the reaction chamber. Examples of this are medieval tar kilns, ovens or pits. These vary in both scale and collection location of the tar[6,7,70,71]. It is possible that birch bark tar was initially discovered and produced by an autothermic technique, where tar forms on a stone surface next to the ignited bark[72].
- Allothermic: production of wood tar and pitch relies on external fuel to heat the reaction material, and the reaction wood can be kept in a low-oxygen (oxygen-limited) atmosphere. Historically, allothermic production was often utilised during smaller 'domestic' manufacturing of tar, typically relying on a metal or ceramic vessel containing the reaction material.

Conifer tar and pitch

During the last few millennia, conifers were one of the primary wood sources for producing wood tar and pitch. Pine was perhaps utilised more than any other wood type[67]. During the production process, the liquid tar together with various high-volatile compounds and a solid residue, charcoal, are formed. Pine tar is a dense, dark brown to black viscous liquid with a distinct empyreumatic odour of burnt organic matter. It is slightly soluble in water, but more soluble in common solvents like ethanol, acetone, and diethyl ether, as well as in caustic alkali solutions[5,73]. The chemical composition of pine tar is extremely complex, containing several hundred chemical components resulting from the concurrent presence of hemicelluloses, cellulose, lignin and a terpenoid fraction[67]. Retene is considered a stable end-product of these reaction pathways, while intermediates such as nor-abietatrienes, simonellite, and tetrahydroretene are formed during these processes. However, when the aim is to identify pine tar in archaeological finds, the terpenoid fraction, consisting of retene, tetrahydroretene, dehydroabietic methyl ester, and norabietane, is typically used as a diagnostic biomarker[45]. This is because terpenoids are generally more resistant to environmental degradation than many other classes of organic compounds[45].

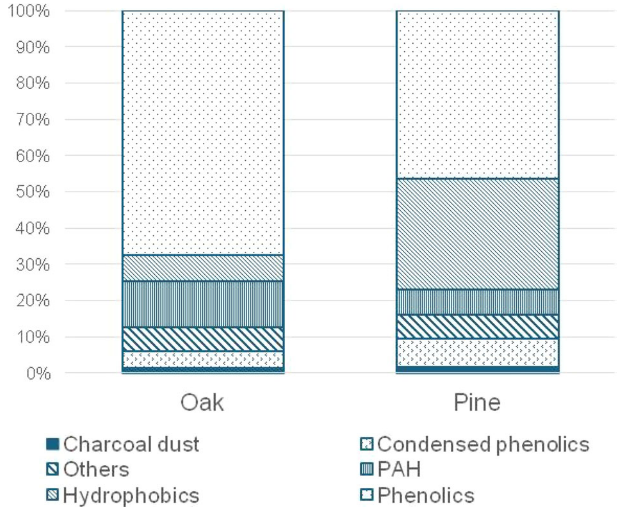


Fig. 6 | Comparative compositional distribution of major compound classes in oak and pine wood tars. The figure shows a stacked bar chart comparing the relative percentage composition of principal chemical fractions identified in oak and pine wood tars. The vertical axis represents relative abundance expressed as percentage (0–100%), and each bar corresponds to a different botanical source (oak and pine). The compositional fractions are distinguished by different fill patterns and colours. Charcoal dust is represented by a solid dark segment. "Others" are indicated by a diagonally hatched segment. Hydrophobic compounds are shown with a cross-hatched pattern and include steroids and fatty substances. Condensed phenolics are represented by a dotted pattern. Polycyclic aromatic hydrocarbons (PAHs) are shown with vertical line hatching. Phenolics are indicated by a lightly bordered segment. Oak tar is characterized by a higher proportion of condensed phenolics and phenolic compounds, whereas pine tar exhibits a greater relative abundance of hydrophobic components and polycyclic aromatic hydrocarbons. Minor fractions of charcoal dust and other components are present in both materials. PAH polycyclic aromatic hydrocarbon. Hydrophobics include steroids and fatty substances. Figure adapted from reference[224].

Since dehydroabietate and retene are considered molecular markers of resin heating, their presence can consequently be associated with the production of tar from resin-containing wood, or with the thermal processing of resin[74]. Alkyl guaiacyl dehydroabietates are formed from a reaction between dehydroabietic acid (a resin acid) and alkyl guaiacols (a wood pyrolysis product), and are proposed as a marker to differentiate conifer wood tar from heated resin[46]. Methyldehydrobietate, produced during heating, is also used as a marker for tar and pitch manufactured by the pyrolysis of wood. Interestingly, this compound is absent when the material is produced from a *Pinaceae* resin[30]. Figure 4 outlines the thermal and oxidation reactions occurring during the distillation of resinous wood originating from the *Pinaceae* family. Table 3 describes the molecular markers used for the chemical recognition of *Pinaceae* tar or pitch in archaeological samples.

The relative abundance of resin and fatty acids also correlates to temperature development during the tar production process. The first barrel of tar collected during traditional kiln production is subject to the lowest temperatures, for the shortest duration, and thus most closely resembles the composition of pure resin[24]. As temperatures and duration increase, and the second, third, and fourth barrels of tar are produced, there is a tendency for dehydrogenation and decarboxylation of components towards a higher degree of aromatisation of the cyclic compounds[75]. In general, this can be seen as a tendency for linoleic, oleic, pimaric, palustric, and abietic acid to decrease in abundance, while phenanthrene 2, 4, 5, 7-tetramethyl, podocarpa-1, 11, 13-trien-15-opic acid, and 13-isopropyl, methyl ester increase[75]. For example, the predominance of aromatised and decarboxylated compounds in tar sampled from the Mary Rose, coupled with a relative depletion of fatty and resin acids, has been interpreted as evidence for production at relatively high temperatures[76].

In addition to pine, other conifer species, such as *Cedrus libani*, have also been employed in the production of tar and pitch. However, their use is more limited, due to their restricted geographic distribution, and consequently, there is less available information regarding their composition. *Cedrus libani* is traditionally used in southern Turkey to produce tar for medicinal purposes, and such tar was found to consist of almost 50% sesquiterpenoids, in addition to hydrocarbons and other compounds[77]. Tar produced from the same conifer species under laboratory conditions varied considerably from the traditionally made tar, containing between 22.5 and 32.4% himachalol, a relatively volatile sesquiterpenoid that was not detected in traditional tar in the current study, likely due to post-production ageing and loss of volatile components. Furthermore, high and low molecular-weight hydrocarbons such as heptane, cyclohexane, and benzene account for 34% of the composition of traditionally-produced *Cedrus libani* tars, but were not detected at all in lab-produced tars[78]. This shows the differences that production method can have on tar composition, highlighting the caution that must be taken when producing or collecting modern reference material.

Birch bark tar and pitch

Birch bark tar molecular markers stem from the presence of pentacyclic triterpenoids in the bark: lupeol, betulin, betulinic acid, and erythrodiol[79]. Their degradation products are influenced by the method of production, allowing some insight into how the tar was produced. Soft heating markers, indicating lower temperatures and shorter heating times, include lupa-2,20(29)-diene, α-betulin I, lupa-2,20(29)-dien-28-ol (B395), lupa-2,20(29)-dien-28-ol (B396), olean-2,11-dien-28-oic acid, betulone, allobetulin, and betulinic acid, 28-acetate. Compounds indicated with the prefix "B"

Table 3 | Molecular markers of Pinaceae and Betulaceae tar and pitch occurring in archaeological samples

Pitch/tar	Main molecular markers	Ref
Pinaceae	retene, tetrahydroretene, norabietanes, methyldehydroabietate, didehydroabietic acid, dehydroabietic acid, 7-oxo-dehydroabietic acid, 7-oxo-abietic acid, 15-hydroxy-7-oxo-dehydroabietic acid, 15-hydroxy-dehydroabietic acid	30,46,74
Betulaceae	lupeol, lupenone, betulin, betulone, betulinic acid, lupa-2,20(29)-diene, lupa-2,20(29)-dien-28-ol, allobetulin, olean-2,11-dien-28-oic acid	44,79

Table 4 | Analytical methods to characterise resins, tar and pitch in heritage science

Analytical technique	Sample preparation	Type of information	Ref
FTIR and Raman	Powdering	• Screening for the presence of resins, tar and pitch by identifying their functional groups • Discrimination among diterpenoid and triterpenoid resins through different bands in the spectra • Assessment of oxidation, cross-linking and hydrolysis processes affecting the resin	66,84–92,210
NMR	Organic solvent extraction; Solid-state NMR is used to study cross-linked or insoluble resin structures.	• Molecular structure of terpenoids isolated from the resin • Discrimination between different classes of resins by characteristic proton and/or carbon shifts • Chemical changes monitoring	93–97
XRD	Powdering	• Crystalline structure and degree of crystallinity of the resin • Occurrence of thermal treatment (e.g. drying)	98,99
GC-MS and GCxGC-HRMS	Organic solvent extraction, alkaline or acid hydrolysis, derivatisation (silylation or methylation), head space analysis for volatile terpenes	• Identification of molecular markers and ageing products • Discrimination between different classes of resins, tar and pitch • Investigation of volatile terpenes	21,55,74,75,100–109
Py-GC-MS and EGA-MS	In situ derivatisation (optional)	• Discrimination between resin, tar and pitch • Identification of molecular markers and ageing products • Study of polymerised resins	110–114
HPLC-MS	Organic solvent extraction	• Discrimination between resin, tar and pitch • Identification of molecular markers and ageing products • Discrimination between different classes of resins • Identification of thermolabile terpenoids in a wider polarity range	60,61,115
CE	Dissolution in organic solvent (typically methanol)	• Discrimination between resin, tar and pitch • Identification of peak pattern for each resin type • Detection of specific resin acids through their migration times	116,117
Direct MS (DE-MS, DI-MS, DT-MS), MALDI-MS, SIFT-MS, FIA-MS	Dissolution in organic solvent (for some of the methods)	• Discrimination between resin, tar and pitch • Identification of resin type trough specific m/z signals	118–124
TGA and DSC	-	• Thermal stability • Occurrence of cross-linking • Amount of free terpenoids and oligomeric species	98,118,125

followed by a number refer to characteristic mass diagnostic ions (m/z) used for the identification of pentacyclic triterpenoids in GC-MS, rather than to distinct molecular species[80]. Strong heating markers, indicating higher temperatures and longer heating times, include double-degraded pentacyclic triterpenoids α-allobetulin, allobetul-2-ene, 3-oxoallobetulin, and hydrocarbon pentacyclic triterpenoids α-lupane (B337) and α-lupane (B360). Experimental birch bark tar contains primarily long-chain even-numbered saturated fatty acids, while unsaturated fatty acids are less abundant[5]. Long-chain dicarboxylic acids, ranging from $C_{16:0}$–$C_{24:0}$, are produced from the degradation of suberin in birch bark[17,81]. However, in experimental reproductions, dicarboxylic acids are only identified in tars produced by the autothermic ‘condensation’ technique, and are limited to hexadecanoedioic acid, and thus are not clearly related to suberin. A further marker of a high level of heating during birch bark tar preparation is the presence of esterification products. These compounds most likely originate from the esterification between triterpenoid compounds related to botulin, and fatty acids from suberin formed upon heating of birch bark[82].

While the identification of birch bark tar in general can be undertaken relatively securely, elucidating specific production strategies is much more difficult. Varying patterns in pentacyclic triterpenoid molecular markers, and soft and strong heating markers can be influenced by different production techniques. Yet, they also exhibit considerable intra-method variation[4,83]. Table 3 reports the molecular markers used for the chemical recognition of *Betulaceae* tar or pitch in archaeological samples.

Analytical methods for characterising plant resins, wood tars and pitches

There are numerous analytical methods that have been used to analyse terpenoids. These include spectroscopic methods, such as Fourier-transform infrared spectroscopy (FTIR)[66,84–88], Raman spectroscopy[89–92], nuclear magnetic resonance spectroscopy (NMR)[93–97], X-ray diffraction (XRD)[98,99] and chromatographic-mass spectrometric methods, such as gas chromatography coupled with mass spectrometry (GC-MS)[21,55,74,75,100–106], two dimensional gas chromatography coupled with high resolution mass spectrometry (GCxGC-HRMS)[107–109], analytical pyrolysis coupled with GC-MS (Py-GC-MS)[110–114], high performance liquid chromatography coupled with mass spectrometry (HPLC-MS)[60,61,115] capillary electrophoresis (CE)[116,117] and direct mass spectrometry methods[118–124]. Calorimetric methods, such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), have also been used to study natural resins along with tar and pitch[98,118,125]. Details are outlined in Table 4.

Table 5 | Key IR spectral features of terpenoid resins[84,90,131]

Band wavelength (cm^{-1})	Interpretation
Diterpenoid resins	
3383-3418	ν(O–H) stretching (hydrogen-bonded), associated with carboxylic acid groups (–COOH); characteristic for abietadiene-type resin acids (e.g., abietic, levopimaric and neoabietic acids)
2870-2940	ν(C–H) stretching of methyl ($–CH_3$) and methylene ($–CH_2–$) groups
1710–1730	ν(C = O) stretching of carboxylic acids and/or ester carbonyls (resin acids/esterified derivatives)
1610–1660	ν(C = C) stretching of unsaturated (alkenyl/aromatic-like) structures.
1380 -1449	$\delta(CH_3)$ and $\delta(CH_2)$ bending (deformation) vibrations, with variable relative intensities
1000–1300	ν(C–O) stretching (carboxylic acids/esters); contributions from C–O–O vibrations may occur in oxidized material (peroxides/ hydroperoxides)
Triterpenoid resins	
3410-3440 and 3400- 3450	ν(O–H) stretching (often hydrogen-bonded), attributed to hydroxyl groups (–OH)
2940 and 2960	ν(C–H) stretching of methyl ($–CH_3$) and methylene ($–CH_2–$) groups
1700-1720	ν(C = O) stretching of carbonyl-containing groups, including carboxylic acids (–COOH) and oxidized products (e.g., ketones/aldehydes)
1640	ν(C = C) stretching (unsaturated structures)
1440-1460	$\delta(CH_2)$ and $\delta(CH_3)$ bending vibrations
1050–1240	ν(C–O) stretching (alcohol/ether/carboxylic derivatives); may also include bands from hydroperoxides (–OOH)/ peroxy functionalities in oxidized resins

Spectroscopic techniques

Spectroscopic vibrational techniques. Spectroscopic vibrational techniques such as Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy are widely used as non-destructive screening tools for the investigation of resins and, more broadly, organic materials in cultural heritage contexts[84,89–93,113,126–129]. These methods primarily provide insight into the molecular structures and functional groups present within a sample, and typically do not require extensive sample preparation[130]. Although FTIR and Raman spectroscopy are generally regarded as non-destructive techniques, laboratory-based analyses often require micro-sampling or surface preparation (e.g. powdering or polishing), whereas truly non-invasive measurements are mainly achieved through in situ or portable instrumentation. In certain cases, they also allow for in situ analysis[84,127]. As preliminary analytical tools, FTIR and Raman spectroscopy are effective for detecting the presence of resinous substances in a sample. However, due to the frequent overlap of absorption bands, the definitive identification of the resin, tar or pitch often remains inconclusive. For instance, in reflectance FTIR analysis, the spectral markers of birch bark tar and pine wood tar overlap. Moreover, these markers are not exclusive, as their bands also correspond to bands associated with pine resin[99]. Table 5 summarises the principal spectral IR features of terpenoid resins, as compiled from existing literature[84,90,131]. The reported band ranges reflect commonly observed IR regions for these resin classes and may vary depending on resin composition, ageing state, and analytical conditions. As a significant example, Fig. 7 shows the FTIR spectra of a diterpenoid resin and a triterpenoid resin, allowing comparison of their absorption profiles under different artificial photoaging conditions. This provides a general picture of the ageing phenomenology of the terpenoid resins highlighting the temporal evolution of the oxidation and polymerization pathways.

FTIR and Raman spectroscopy are fundamental to the investigation of resin chemical structures. FTIR spectroscopy enables the identification of functional groups such as carbonyls (C = O), hydroxyls (O–H) and carbon-carbon double bonds (C = C). Characteristic bands in the mid-infrared range allow different types of resins to be distinguished. Raman spectroscopy provides information on aromatic structures, C–C vibrations, CH_2 and CH_3 groups, making it particularly useful in the analysis of low-fluorescence resins, especially diterpenoid resins such as pine and larch resins[91]. The use of a 1064 nm laser (NIR Raman) reduces the problem of fluorescence and allows the analysis of even the most extensively aged samples[87].

A flow chart based on FTIR and Raman spectroscopy was developed to distinguish between the main classes of natural resins (diterpenoid and triterpenoid resins), based on the presence of specific bands in the spectra: interestingly, Raman spectra of diterpenoid resins show a signal at around 3085 cm^{-1}, attributable to =C–H stretching vibrations of olefinic (C = C) groups, which is absent in the triterpenoid resins[89,90], thus providing a rapid tool to classify the resinous material. However, a reliable discrimination between diterpenoid and triterpenoid resins based on the use of Raman and FTIR relies on a combination of spectral features rather than a single band[90]. The C = O band near 1730 cm^{-1}, intensity of C–H deformations, and the presence or absence of aromatic C = C vibrations around 1600 cm^{-1} are particularly useful indicators. Even so, degradation can obscure some signals, requiring comparative analysis with reference samples and complementary techniques for reliable identification.

Although these spectral bands may not serve as definitive markers in highly degraded samples, their presence, absence, and relative intensity patterns provide a useful framework for spectral classification. The application of multivariate analysis, combined with comparisons to modern aged reference materials, enhances the reliability and interpretation of the results. For example, a study aimed at distinguishing between different *Bursera* resins from a range of species employed a chemometric approach incorporating FTIR in combination with multivariate principal component analysis (PCA) and linear discriminant analysis (LDA) methods. This study demonstrated success in predicting the botanical origin of the resins[132]. This chemometric FTIR-based classification approach can be applied to resin samples from other archaeological sites or museum collections worldwide for botanical identification.

FTIR and Raman spectroscopy are useful for investigating the ageing processes of natural resins, which primarily involve oxidation, cross-linking reactions, and hydrolysis[89,126,127,131]. These techniques can also be employed in combination with microscopy to enable imaging and mapping analysis[84]. The application of ATR-far-infrared spectroscopy and chemometric analysis of natural resins has also been reported in the literature[85]. According to this study, FarIR spectroscopy offers improved discrimination among various resin types, including sesquiterpene resins, diterpene resins, diterpene resins with polymerised communic acid, and triterpene resins, when compared to MidIR spectroscopy. However, FarIR spectroscopy is limited by its relatively low signal intensity and the challenges associated with conducting analyses at the microscopic scale. As such, it is best employed as a complementary technique alongside Raman spectroscopy and conventional FTIR spectroscopy in the MidIR region. A round robin study

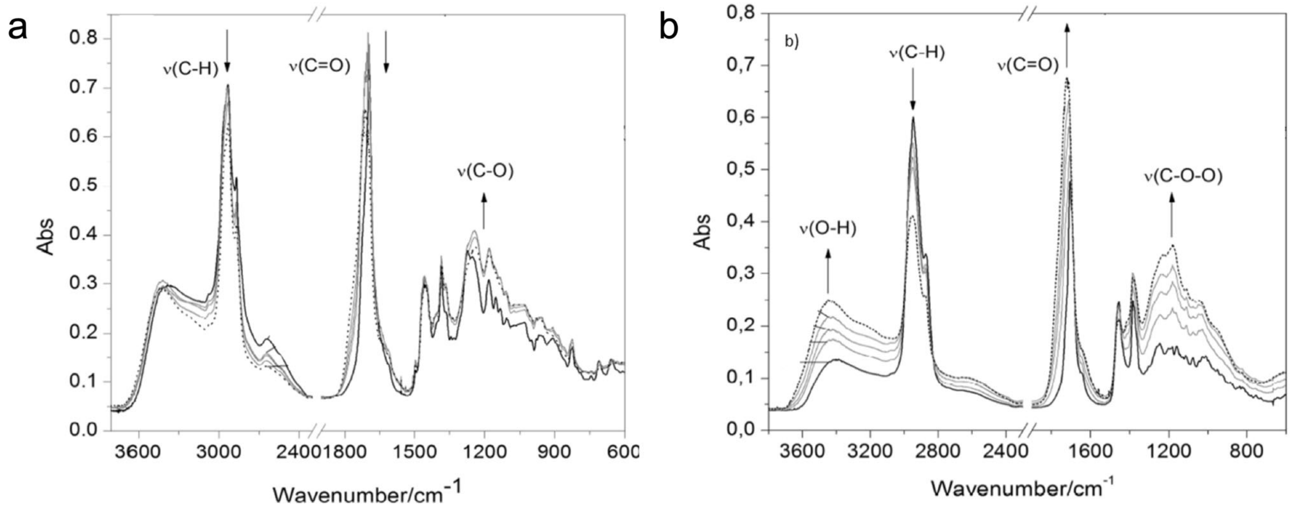


Fig. 7 | Fourier-transform infrared (FTIR) spectra of diterpenic and triterpenoid resins as a function of light exposure. Figure is adapted from[131] (Elsevier, 2016). The figure presents FTIR absorption spectra showing chemical changes induced by light exposure in two classes of natural resins. The horizontal axis represents wavenumber (cm^{-1}), and the vertical axis shows absorbance (Abs). Multiple overlaid spectra in each panel correspond to increasing durations of light exposure, illustrating progressive chemical modification. **a** FTIR spectra of a diterpenic resin (sandarac). Characteristic absorption bands include aliphatic C–H stretching vibrations around 2800–3000 cm^{-1}, carbonyl (C = O) stretching vibrations near 1,700 cm^{-1}, and C–O stretching bands in the region 1000–1300 cm^{-1}. Changes in band intensity and shape with light exposure indicate oxidation and structural modification of the diterpenoid matrix. **b** FTIR spectra of a triterpenoid resin (dammar). Prominent absorption features include O–H stretching vibrations around 3,200–3,600 cm^{-1}, aliphatic C–H stretching bands near 2800–3000 cm^{-1}, carbonyl (C = O) stretching near 1700 cm^{-1}, and C–O–O vibrations in the fingerprint region. Progressive spectral variations reflect photo-oxidative processes affecting the triterpenoid structure. FTIR Fourier-transform infrared spectroscopy, C–H carbon–hydrogen stretching, C = O carbonyl stretching, C–O carbon–oxygen stretching, O–H hydroxyl stretching, C–O–O peroxide-related vibrations. Figure adapted from reference. [131]. Copyright © 2016 Elsevier. Reproduced with permission.

Table 6 | Raman bands of selected plant resins (excitation wavelength 780 nm)[129]

Plant resin	Wavenumber, cm^{-1}
Colophony	1649,1631,1611,1565,1469,1442,1372,1302,1256,1233,1199,1133,1106,1070,1050,970,950,926.882,741,706,556,529,460,371,311
Sandarac	1645, 1450, 1362, 1301, 1244, 1195, 1140, 1093, 1046, 974, 930, 882, 747, 557, 518, 485, 447, 402, 360, 300, 237
Venice turpentine	1646, 1611, 1469, 1444, 1373, 1293, 1255, 1219, 1201, 1163, 1143, 1130, 1089, 1083, 1055, 1016, 996, 966, 946, 938, 926, 885, 840, 745, 712, 665, 649, 587, 563, 539, 478, 441, 374, 329, 234
Strasbourg turpentine	1649, 1613, 1441, 1372, 1327, 1303, 1231, 1201, 1183, 1166, 1137, 1105, 1083, 1049, 1013, 1000, 969, 951, 927, 905, 882, 840, 820, 769, 741, 708, 665, 644, 564, 479, 462, 371, 306, 222
Mastic	1708, 1639, 1458, 1312, 1175, 1096, 935, 711, 602, 552
Dammar	1655, 1452, 1315, 1198, 1179, 1027, 1001, 954, 938, 918, 830, 800, 761, 710, 674, 601, 582, 556, 529, 464, 412, 318

conducted across six conservation and research laboratories evaluated different embedding and polishing procedures used in ATR-FTIR analysis, revealing variability in the results[133]. When analysing multi-component samples, matrix effects and interferences from other materials can complicate interpretation and may lead to misinterpretation of the results.

Raman spectroscopy using long wavelength excitation has proven effective for obtaining spectra from archaeological resins excavated from a variety of sites and depositional environments. Degradation of the resin specimen can be identified in the spectral signatures, but distinction between triterpenoid resins such as *Pistacia terebinthus*, *Dipterocarpus alatus* and dammar resins remains difficult since these present very similar Raman spectra[91].

Table 6 presents the Raman frequencies of selected natural plant resins, acquired at 780 nm. All the resins exhibit at least one peak within the 1800–1500 cm^{-1} region, indicative of the presence of C = C double bonds[129].

Fourier transform Raman (FT-Raman) spectroscopy has been applied to the analysis of natural resins of archaeological significance, with a particular focus on distinguishing between diterpenoid and triterpenoid resins[89,91]. The spectra of both resin types exhibit numerous similar bands, making direct discrimination difficult. A comprehensive assessment aimed at identifying distinct vibrational bands that could serve as reliable markers for the differentiation of diterpenoid resins from triterpenoid resins, irrespective of their degradation state, revealed that the relative intensities of many characteristic bands change significantly with the degree of degradation. This variability reduces their utility as general diagnostic tools. In resins from the genus *Pinus*, a decrease in the relative intensity of the C = O stretching peak around ~ 1700 cm^{-1}, representing exocyclic carbonyl and carboxyl groups, was observed in matured resins. These bonds derive from labdanoid diterpene monomers whose concentrations are reduced through covalent incorporation into the macromolecular structure[53]. Nevertheless, certain position-specific bands were identified as more stable and could aid in distinguishing not only between diterpenoid and triterpenoid resins, but also between individual resin types within each group.

Infrared spectroscopy has proven to be a highly effective tool for studying birch bark tar, enabling non-invasive identification of its molecular components as well as the assessment of the material's degradation state[81]. A detailed FTIR spectral analysis of birch bark tar was made, highlighting characteristic absorption bands corresponding to compounds formed during pyrolysis, such as betulinic acid, betulin, and lupeol – typical pentacyclic triterpenoids. Key diagnostic bands include strong C = O carbonyl group absorptions (~ 1710–1730 cm^{-1}), C–H stretching vibrations in the region of 2850–2950 cm^{-1}, and a complex pattern of skeletal and functional group vibrations within the 1000–1450 cm^{-1} range. Due to the high sensitivity of IR spectroscopy, it is also possible to monitor chemical changes related to the sample's age, environmental exposure, or the specific production technique used (e.g. open vs. closed vessel). IR spectroscopy, especially when combined with comparative analysis of reference samples, provides valuable information not only on the composition of birch bark tar, but also on the technology of its production. This is highly relevant to archaeological research and the reconstruction of ancient craft techniques.

The use of non-destructive analytical methods to identify and differentiate pine tar and birch tar in archaeological adhesives is particularly valuable, as it not only confirms the organic nature of the material but also provides important evidence for distinguishing between tar sources[99]. However, the complexity of identifying archaeological tars is clear: birch bark and pine wood tar markers often overlap and are not unique; it is difficult to distinguish resin and tar from the native markers for pine wood, particularly using reflectance FTIR. Further research is needed to enrich the FTIR libraries reflectance spectra of weathered tar materials, to explore techniques for enhancing the quality of the spectra, and to identify vibrational modes characteristic of degradation markers that guarantee for tar production processes.

In conclusion, vibrational spectroscopic techniques are valuable tools for rapid non-destructive analyses, and with the availability of portable instruments, they can be applied directly at archaeological or historical sites. The recent development of user-friendly, affordable, and compact devices has led to a significant increase in their applications. However, the enthusiasm generated by the advantages of these techniques over other analytical tools must be tempered by a thorough understanding of the factors affecting their performance[128]. It is crucial to recognise their limitations and to consider how instrument characteristics, sample interrogation methods (e.g. ATR, transmission or reflectance FTIR, Raman spot size and penetration depth), and spectral data interpretation can influence the conclusions drawn from Raman and IR spectroscopic analyses.

X-ray diffraction (XRD). X-ray diffraction (XRD) was employed as a non-destructive analytical tool to support the identification and differentiation of adhesive materials, specifically archaeological pine wood tar and birch bark tar[99]. The technique was particularly effective for detecting crystalline phases, which provide information on inorganic inclusions and ordered degradation products that can assist in distinguishing between different tar types and production histories. In pristine experimental tars, the XRD patterns exhibited broad, blunt curves indicative of their predominantly amorphous, organic nature—around 21° 2θ for pine tar and 16°/41.5° for birch tar. However, weathering significantly diminished these amorphous signatures in experimental and archaeological samples, making verifying organic content solely through XRD more challenging. Instead, XRD was valuable for identifying crystalline components such as quartz, calcite, as well as additives like ochre (haematite) or environmental phases such as pyrite, which can form under reducing conditions associated with organic matter degradation in waterlogged or marine burial environments. While XRD alone could not distinguish between pine and birch tar, it played a crucial complementary role in confirming residue provenance, detecting additives, and assessing burial conditions, mainly when used with SEM-EDS and micro-FTIR analyses.

Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) is a powerful analytical technique used to investigate the molecular structure and composition of organic compounds, including natural resins and their degradation products.

As carbon and hydrogen are found in practically all organic compounds, NMR can be used on a wide range of materials, and is particularly important for the analysis of biomass materials and their transformation products[134]. ^{1}H, ^{13}C, ^{31}P are most frequently used in the analysis of materials from cultural heritage[135]. Importantly, NMR can be applied in both liquid and solid state, providing complementary information on molecular structures and transformations: liquid-state NMR has been widely used for soluble organic fractions such as resins, oils, and waxes[135], while solid-state NMR offers valuable insights into insoluble or partially degraded components in cultural heritage materials[136]. Compared with other common techniques, NMR spectra are more specific to peculiar chemical compounds than FTIR, allowing more unambiguous identification of resins[76,93] and gum resins[137]. An advantage of NMR is that it is non-destructive[134], however, compared to spectroscopic techniques such as FTIR and Raman, it generally requires larger sample amounts and, in many cases, solvent extraction, which can limit its application to precious archaeological materials[97]. However, NMR lacks the sensitivity and resolving power of FTIR. As such, it is often used in combination with other techniques.

NMR was used together with GC-MS and FTIR to classify pitch from the Mary Rose and an Etruscan shipwreck as originating from *Pinus sylvestris*[76]. Similarly, an analysis of Late Antique amphorae from underwater archaeological contexts by both GC-MS and ^{1}H NMR resulted in molecular markers for *Pinaceae* spp. resin or pitch in some of the amphorae[138]. However, in this study, most characterisation was achieved with GC-MS, while NMR primarily indicated the presence of lipids associated with olive oil[138]. ^{13}C NMR has distinguished between birch bark tar and birch sap, eliminating the latter as a possible material used in prehistoric adhesives[139]. NMR has also proven the use of *Pistacia* resin (mastic) in Roman funerary rituals[93]. ^{1}H and ^{13}C NMR was used to classify *Xanthorrhoea* resin from shipwrecks[136]. Statistical analyses have shown that ^{1}H NMR can clearly differentiate between resins, gum resins, and gums from both conifers and angiosperms[140]. Despite its suitability, the cost of instrumentation and complexity of spectra mean that there is both a lack of available equipment and expertise for NMR within archaeology[141], and it is consequently not used as frequently as other analytical techniques such as GC-MS and FTIR.

Thermoanalytical techniques

Understanding the thermal behaviour of complex organic materials such as natural resins, tars, and pitches—known for their chemical variability and sensitivity to environmental and processing conditions—is essential for evaluating their composition, stability, degradation pathways, and suitability for both technological and conservation applications[98]. These substances, often multicomponent and heterogeneous, exhibit a wide range of thermal events that require sensitive and multifaceted analytical approaches.

Thermal analysis (TA) offers a powerful framework for their investigation, tracking changes in mass, heat flow, mechanical properties, or gas evolution as a function of temperature[142]. Among the most widely employed techniques are thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA), as outlined in Table 7. These core methods are frequently coupled with complementary tools such as evolved gas analysis by mass spectrometry (EGA-MS) and Fourier-transform infrared spectroscopy (TG-FTIR), broadening the interpretive scope by linking thermal behaviour to molecular composition and structural evolution.

Together, these standalone and hybrid techniques offer an integrated analytical platform that is particularly effective in resolving the thermal, structural, and chemical complexity of resins and related materials used in the field of cultural heritage[143]. Owing to their high sensitivity and minimal sample requirements TA techniques are especially well-suited for the analysis of valuable or historically significant objects where material preservation is critical[144,145].

A significant portion of studies employing thermoanalytical techniques focuses on raw materials. This emphasis is particularly valuable, as the characterisation of fresh, unaltered substances provides a fundamental understanding of their baseline properties. When these raw materials are subjected to artificial or natural ageing processes, the resulting changes can

Table 7 | Overview of thermoanalytical techniques and their main analytical principles

Technique	Principle
Thermogravimetry (TG)	Measures the weight loss of a sample as it is heated, while the oxygen uptake curve provides insights into the oxidative stability of the sample
Derivative thermogravimetry (DTG)	Provides the rate of weight change with respect to temperature
Differential thermal analysis (DTA)	Measures the temperature at which certain physical or chemical transitions occur, such as phase changes (e.g. crystallisation or decomposition) or thermal expansions
Differential scanning calorimetry (DSC)	Examines the thermal transitions of materials, including their melting, crystallisation, and decomposition processes
Evolved gas analysis (EGA-MS)	Investigates the thermal behaviour of organic materials by monitoring the evolved gases from the sample in real-time during the heating process
Thermomechanical analysis (TMA)	Measures changes in physical properties (e.g. expansion or contraction) with temperature
Dynamic mechanical analysis (DMA)	Probes mechanical responses like expansion, softening, and viscoelasticity under thermal stress

Table 8 | Glass transition temperatures (Tg) of selected natural resins

Material	Source/type	Tg, °C	Ref
Dammar	Triterpenoid resin from *Dipterocarpaceae* trees in southeast Asia of the genera *Shorea*, *Balanocarpus*, or *Hopea*	60 67–75	150,219
Copal	Diterpenoid resins from *Trachylobium* species (Africa), *Hymenaea courbaril* (South America) and *Agathis australis* (New Zealand)	85.3	220
Mastic	Triterpenoid resin from the mastic shrub, *Pistacia lentiscus*, southern Europe and northern Africa	54 46.5 34.7	61,150,221
Pine resins	Oleoresinous exudate from *Coniferae* trees: longleaf pine (*Pinus palustris*), Cuban pine (P. caribaea), loblolly pine (*P. taeda*), cluster pine (*P. pinaster*), or Scots pine (*P. sylvestris*)	30	64
Sandarac	*Callitris quadrivalvis* native to Australia, and the sandarac tree *Tetraclinis articulata* native to northern Africa	63	150

be more precisely interpreted. Consequently, this approach offers critical insights into the degradation mechanisms observed in materials from cultural heritage objects, enabling more informed assessments of their conservation status and history[146–148].

Differential scanning calorimetry (DSC) provides particularly detailed insights into thermal transitions, enabling the distinction between various types of binding media based on their unique thermal fingerprints. This capability is especially valuable in conservation, where accurate identification of materials supports decisions on treatment strategies. DSC is also effective in detecting changes due to oxidation, polymerisation, or cross-linking, and plays a crucial role in assessing material ageing—observable through evolving thermal profiles, including the appearance of exothermic peaks related to network formation. Such analysis contributes not only to material identification but also to establishing the chronological framework of artefacts. Natural resins, typically used as varnishes, display distinct glass transition temperatures Tg and melting point ranges, commonly between 30–70 °C, making them visually and physically suitable for artistic applications[143].

Despite its utility, comparing Tg values across literature is often problematic due to methodological inconsistencies, limited available data, and variations in analytical conditions[149]. To address this, the International Confederation for Thermal Analysis (ICTA) established a standard protocol for Tg determination using DSC. Michael Schilling made a significant contribution in this area by applying the ICTA method to a range of polymeric conservation materials, including Sandarac resin[150]. His work highlighted the importance of standardised data for comparing materials and improving conservation practice reliability[150]. A standardised summary of Tg values for selected natural resins is provided in Table 8.

A large portion of thermoanalytical studies has focused on freshly harvested or raw resin materials. For instance, a study on *Pinus halepensis* resin employed TGA, DSC, FTIR, and XRD in combination with vapour sorption measurements to reveal how drying improves thermal stability and polymer ordering while reducing crystallinity due to volatile loss[98].

Dammar resin, a complex triterpenoid mixture, has been examined using TGA and TGA-FTIR to resolve its sesquiterpenoid, monomeric, and oligomeric fractions[118]. A more comprehensive chemical profile was later obtained through a multianalytical strategy combining thermoanalytical, chromatographic, and mass spectrometric methods (DE-MS, Py-GC-MS, FIA-ESI-MS, and GC-MS)[151]. This revealed that the oligomeric fraction consists of ester-linked triterpenoids, identical to the monomeric units, with evidence of oxidation-related carbonyl groups contributing to polymer formation.

Pine resin, historically used for waterproofing and adhesives and frequently found in archaeological contexts, has also been the subject of intensive thermoanalytical research[152–155]. Recent work on black pine, shore pine, rosin, and Baltic amber illustrates the value of integrating TGA, EGA-MS, FTIR, GC–MS, and dielectric testing to assess decomposition behaviour, composition, and suitability for applications in sustainable electronics and conservation[153]. Several recent studies have also focused on correlating the thermal properties of resins with their maturation or ageing state, often employing TGA, DSC, and FTIR on resins from diverse geographic sources[156,157]. These studies underscore the importance of standardised protocols and multitechnique approaches in building a reliable framework for the characterisation of both fresh and aged resin materials.

A recent study employed a combination of analytical techniques, including infrared spectroscopy and thermogravimetric analysis, to investigate structural and morphological changes in traditional binder resins, specifically mastic and colophony, when in contact with zinc-based pigments[158]. The analysis revealed a clear correlation between resin acidity and the early formation of zinc soaps, observed after just 7 hours of UV ageing. These interactions, along with the formation of metal oxalates, were shown to significantly impact the stratigraphy and visual integrity of painted surfaces. The study demonstrates the important role of thermoanalytical methods in identifying pigment–binder interactions and offers valuable insights into the mechanisms underlying chemical degradation in works of art.

Despite the broad applicability of thermal analysis, its application in archaeology remains underutilise. Few interesting papers are available and summarised as follows.

A multianalytical approach combining thermoanalytical techniques (DSC, TGA, TG-FTIR) with GC-MS was used to investigate the chemical-physical interactions between pine pitch and beeswax, materials often found together in archaeological adhesives[43]. Using an experimental archaeology framework, replicas of *Pinus sylvestris* pitch with varying proportions of beeswax were created and analysed. This same methodology was extended to the analysis of Zopissa, a historical adhesive of unknown composition, and to two archaeological adhesives recovered from opus sectile glass fragments excavated in Antinoopolis (4th–5th century AD). The study demonstrated the effectiveness of thermoanalytical techniques in quantifying pitch-to-additive ratios and detecting interactions between components. The findings support the hypothesis that artisans intentionally altered the chemical and physical properties of pitch by incorporating organic additives such as waxes or fats to enhance material performance.

The thermal behaviour of modern pine resin and amber, used here as a comparative reference material, was examined under controlled conditions using DSC to explore the relationship between thermal properties and material age[159]. The analysis revealed significant similarities in the thermal profiles of resin and geologically young amber, particularly the presence of large exothermic peaks associated with residual reactive compounds. These thermal features diminished in older amber samples, indicating that such reactive species likely diffused out or underwent slow chemical transformation over time. The study highlights the potential of DSC as a diagnostic tool for evaluating the maturation and thermal stability of both recent and fossilised resinous materials.

Investigation of the thermal behaviour and molecular composition of resin–beeswax mixtures used as adhesives in archaeological contexts was performed in another study[160]. Combining evolved gas analysis coupled with mass spectrometry (EGA-MS) and flow injection analysis–high resolution mass spectrometry (FIA-HRMS), the researchers explored how heating alters these complex organic mixtures[160]. EGA-MS revealed changes in thermal degradation patterns, and activation energies were estimated via isoconversional analysis. The results suggest that ancient adhesives underwent thermal pre-treatment, leading to the formation of new hybrid molecular species through interactions between resin diterpenes and beeswax compounds. These newly formed species were confirmed by high-resolution mass spectrometry, highlighting a sophisticated level of material preparation and technological intent in antiquity. This study demonstrates the value of thermoanalytical approaches, especially when integrated with molecular techniques, for reconstructing ancient manufacturing practices and understanding the evolution of organic adhesives in cultural heritage.

A comparative thermal study of natural resins from Russia, the Dominican Republic, Colombia, and Poland was undertaken to investigate the influence of geological age on thermal behaviour[157]. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to assess thermal stability, while FTIR spectroscopy provided structural and compositional insights. The results showed that resins of different origins exhibited distinct thermal responses, likely reflecting post-depositional alterations. TG analysis revealed higher thermal stability for the Dominican, Russian, and Colombian samples (228–300 °C). Complex thermal events in the DSC curves prevented reliable identification of glass transition temperatures. The study concluded that TG and DSC alone are inadequate for precise age determination of resins, though FTIR, particularly in the carbonyl region, may offer useful complementary information on resin maturation and chemical evolution.

While studies often focus on raw or artificially aged resins, their application to archaeological contexts remains comparatively limited. Standardised methods, such as those recommended by ICTA, are crucial for ensuring comparability of thermal data—especially Tg values—across studies. Continued integration of these approaches will be key to advancing the chemical understanding of complex organic materials in cultural heritage.

Chromatographic and mass spectrometric techniques

Chromatographic and mass spectrometric methods offer greater sensitivity than spectroscopic methods, enabling the identification of specific molecular markers that reveal the botanical origin of the plant from which the resin was obtained, along with specific ageing products[161]. For instance, the detection of dehydroabietic acid indicates pine resin, while boswellic acid is characteristic of frankincense. In addition, the detection of 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid indicate extensive oxidation of the resins[21]. Chromatographic methods can also shed light on the technologies employed for pitch and tar production. The identification of the methyl esters of abietane acids suggests that pitch was derived from the destructive distillation of resinous wood, a process during which gaseous methanol is generated and readily reacts with diterpenic acids to form methyl esters[44]. Moreover, the separative capabilities of chromatography enable the analysis of complex mixtures and facilitate the identification and quantification of trace components.

GC-MS is the most widely-used method for characterising resins, tar and pitch[36,44,66,105,113,162]. GC can separate terpenes and other compounds within complex mixtures, while MS detection provides unambiguous identification, thus offering comprehensive insight into a sample's chemical composition. GC-MS analysis requires sample pretreatment, usually involving organic solvent extraction to isolate the compounds of interest. The most commonly used organic solvents include chloroform, methanol, hexane and diethyl ether, and the extraction process may be assisted by ultrasound and/or microwave techniques[100,163,164]. In some cases where polymerised resins are insoluble in organic solvents, acid or alkaline hydrolysis may be employed[165]. Additionally, derivatisation reactions such as methylation and silylation are performed prior to the analysis to improve the volatility and detectability of polar and thermolabile terpenes[166]. Trimethylsilylating (TMS) reagents such as BSTFA (N,O-bis(trimethylsilyl) trifluoracetamide) are widely used for the derivatisation of resinous materials, as they produce TMS esters of terpenes with characteristic mass spectra and diagnostic fragment ions[167]. Thermochemolysis using tetramethylammonium hydroxide (TMAH) is also commonly applied, particularly for the analysis of acidic and polymerised resin components[168,169].

Figures 8, 9 present example chromatograms for birch bark tar and pine pitch, respectively, with their identified compounds. The chemical pretreatment applied to the two samples differed: the birch bark tar extract (Fig. 8) was prepared following the extraction procedure described in[119], whereas the pine pitch sample (Fig. 9) was processed according to the method reported in[43].

To enhance analytical sensitivity and improve compound separation in the mixture, GCxGC-HRMS can be employed. This method expands the range of detectable compounds and is particularly suitable when resins and tar are present alongside other components[107,170–172]. The technique is particularly useful in paleo-metabolomic analysis[109] where paleo-molecules were extracted using functionalised films and then analysed by both monodimensional and comprehensive GCxGC-MS. Interestingly, in such a study, monodimensional GC-MS analysis did not reveal the presence of triterpenoids, while bidimensional GCxGC analysis revealed penta- and tetra-cyclic triterpenes from resins of *Pistacia* species as oleanane-type molecules (as β-Amyrin, Olean-18-en-3-ol), and triterpenoids with a dammarane skeleton (Dammaran-3-one, 20,24-epoxy-25-hydroxy)[109]. In this study, the presence of *Pistacia* and other triterpenoid compounds led the authors to deduce that the "recipe" used for embalming was expensive and typically reserved for royalty or extremely wealthy nobles and notables.

Volatile resin fractions can also be investigated by GC-MS by performing headspace solid phase microextraction (HS-SPME), which allows preconcentration and sampling of the volatile species on a fibre[173–177]. The compounds collected by the fibre are then desorbed in the GC system.

Analytical pyrolysis (Py-GC-MS) is particularly useful for analysing high molecular mass molecular markers with high boiling points and low solubility in organic solvents. It is also applied to the study of complex polymers, including resins and their thermal degradation products[178]. Specific molecular markers or "fingerprints" from pyrolysed resins are detected using Py-GC-MS to determine the botanical source and geographical origin of the material[87]. To enhance the chromatographic behaviour of acidic compounds, pyrolysis experiments can be performed with *in situ* derivatisation[179]. Tetramethylammonium hydroxide (TMAH) methylates diterpenic acids, but can also cause side reactions, such as isomerisation, dehydration and nitrogen incorporation, especially in compounds with

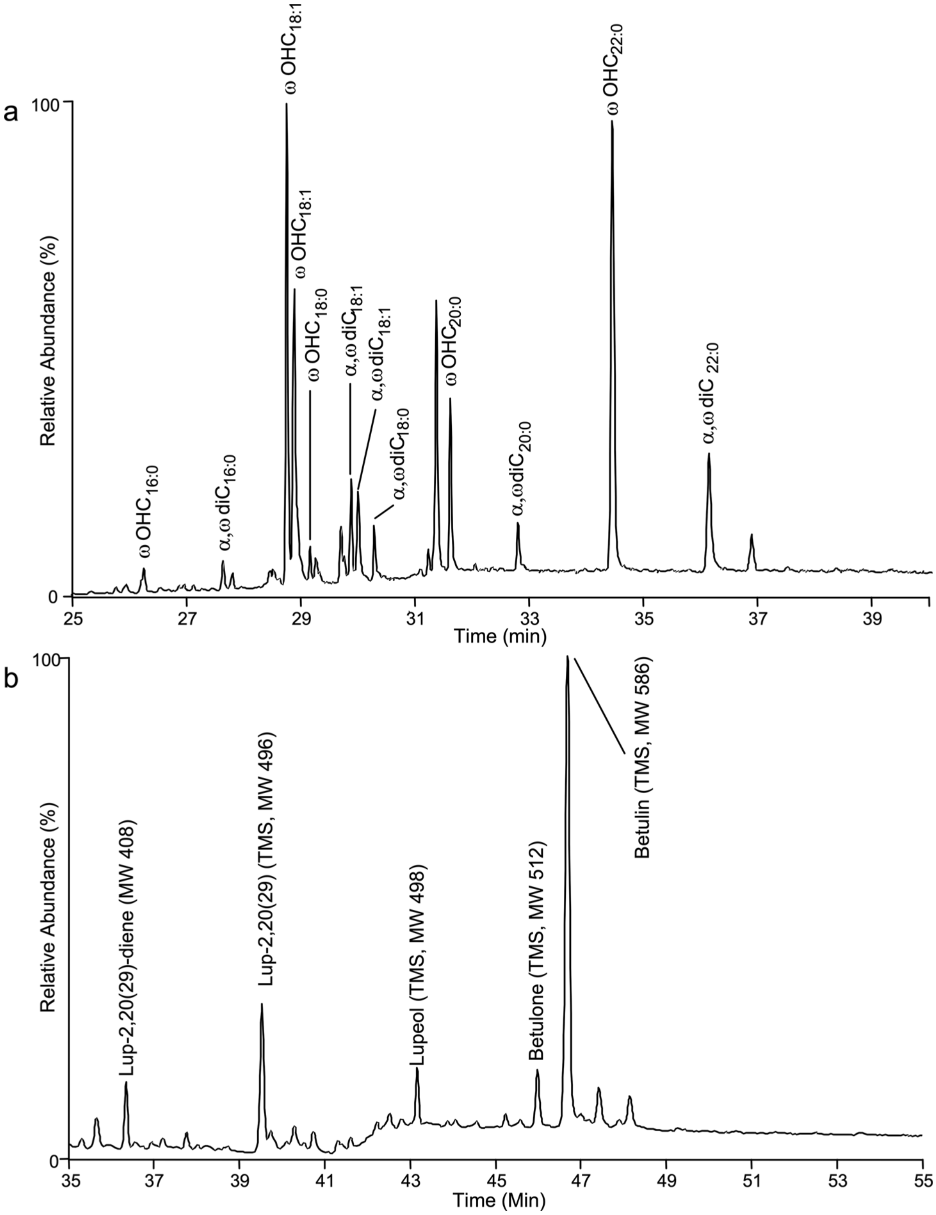


Fig. 8 | Gas chromatography–mass spectrometry (GC–MS) chromatograms of acid and neutral fractions of birch bark tar and corresponding identified compounds. The figure presents GC–MS chromatograms of birch bark tar separated into acid (**a**) and neutral (**b**) fractions. The horizontal axis represents retention time (minutes), and the vertical axis shows relative abundance (%). Peak labels correspond to compounds identified by mass spectrometry. **a** Chromatogram of the acid fraction. The dominant peaks correspond to long-chain ω-hydroxy fatty acids and α,ω-dicarboxylic acids, including ω-hydroxyhexadecanoic acid (ω-OHC$_{16}$:0), α,ω-dicarboxyhexadecanoic acid (α,ω-diC$_{16}$:0), ω-hydroxyoctadecanoic acid (ω-OHC$_{18}$:0), α,ω-dicarboxyoctadecanoic acid (α,ω-diC$_{18}$:0), and related homologues. Additional peaks correspond to unsaturated and shorter-chain analogues. These compounds are characteristic suberin-derived constituents of birch bark and are diagnostic markers of birch bark tar. **b** Chromatogram of the neutral fraction. Major components include lupane-type triterpenoids such as lup-2,20(29)-diene, lupeol (detected as its trimethylsilyl derivative), betulone (trimethylsilyl derivative), and betulin (trimethylsilyl derivative). Molecular weights (MW) are indicated for selected compounds. The predominance of lupane-type triterpenes is consistent with the botanical origin of the tar from Betula species. GC–MS gas chromatography–mass spectrometry, TMS trimethylsilyl derivative, MW molecular weight, α,ω-diC alpha,omega-dicarboxylic acid, ω-OH omega-hydroxy fatty acid. Figure adapted from reference[119].

carbonyl or hydroxyl groups[168]. On the other hand, hexamethyldisilazane (HMDS) is a milder derivatisation reagent. Analytical pyrolysis is also useful in the identification of birch bark tar, since birch bark contains high amounts of a lipid material, suberin[162,180]. During pyrolysis, suberin decomposes into monocarboxylic fatty acids, while suberan, the highly insoluble aliphatic macromolecule found in the outer layer of birch bark, breaks down to produce straight-chain alkenes and alkanes[181]. Thus, the identification of fatty acids, series of straight-chain alkenes and alkanes, and triterpenoids by Py-GC-MS lead to the confirmation of birch bark tar[112]. Figure 10 shows a characteristic pyrolitic profile obtained by Py-GC-MS for birch bark tar in presence of HMDS as the derivatization agent. This sample is part of a broader dataset analyzed in the published work[182]. Interestingly, the pyrogram differs from the chromatogram presented in (Fig. 7), reflecting the structural modifications induced by pyrolytic reactions during analysis, as well as the different sample fractions accessed by the two approaches: GC–MS after alkaline saponification targets extractable and hydrolysable components, whereas Py-GC-MS also probes insoluble macromolecular fractions through thermal fragmentation[112]. In this context, alkaline saponification mainly releases ester-bound components of suberin, whereas Py-GC-MS enables the thermal fragmentation of the highly insoluble aliphatic macromolecule suberan. Nevertheless, diagnostic compound classes characteristic of birch bark tar remain identifiable. The Fig. 10 highlights these through Extracted Ion Chromatograms (EICs) corresponding to alkanes and alkenes (m/z 85 and 83), aliphatic carboxylic acids (m/z 117), and triterpenoid compounds (m/z 189 and 203)[182].

HPLC analysis coupled with MS is an effective analytical method for studying terpenoids from diverse biological sources, offering detailed structural analysis of the compounds[61,115]. This method enables the identification of thermolabile species and extends the range of detectable polar compounds, especially when combined with atmospheric pressure ionisation sources such as atmospheric pressure chemical ionisation (APCI), electrospray ionisation (ESI), and atmospheric pressure photoionisation (APPI).

A methodology based on HPLC–MS–APPI was developed to successfully classify 26 resins of varying botanical origin using MS fingerprints as taxonomic criteria[183]. This approach proved particularly effective, as APPI showed greater efficiency and higher sensitivity for neutral triterpenoids that do not ionise readily with ESI.

Direct MS methods, such as direct inlet mass spectrometry (DI-MS)[122], direct exposure mass spectrometry (DE-MS)[17,104,105,119] and direct temperature resolved mass spectrometry (DT-MS) allow quick and sensitive analysis of resinous substances with minimal or no sample preparation[17,119]. They

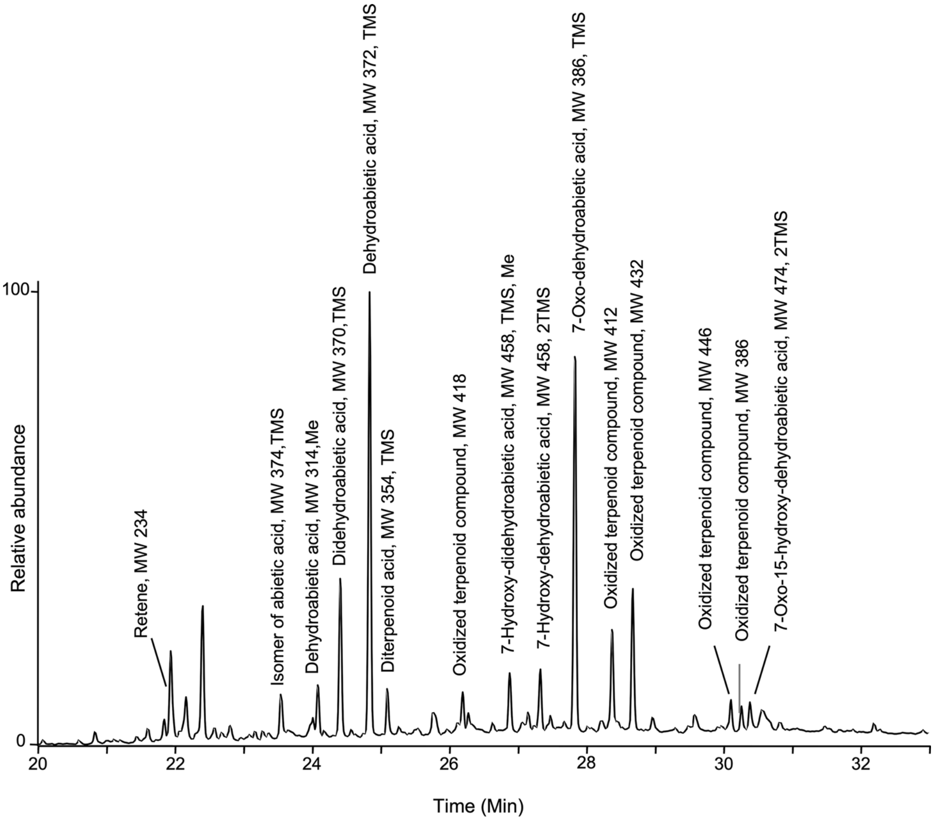


Fig. 9 | Gas chromatography–mass spectrometry (GC–MS) chromatogram of pine pitch residue heated at 300 °C under airflow. The figure shows the GC–MS chromatogram of a pine pitch residue subjected to thermal treatment at 300 °C under airflow conditions. The horizontal axis represents retention time (minutes), and the vertical axis shows relative abundance (%). Labelled peaks correspond to compounds identified by mass spectrometry and illustrate the chemical transformations occurring during heating. Early-eluting peaks include retene (molecular weight (MW) 234), a polycyclic aromatic hydrocarbon formed through aromatization and decarboxylation of abietane-type diterpenoids. Intermediate retention times show diterpenoid acids and their derivatives, including isomers of abietic acid (MW 374, trimethylsilyl (TMS) derivative), dehydroabietic acid (MW 370, TMS derivative), dihydroabietic acid, and related oxidized diterpenoids. Additional peaks correspond to oxidation products such as 7-hydroxy- and 7-hydroxy-8-dehydroabietic acids (detected as TMS derivatives), oxidized diterpenoid compounds (MW 412 and MW 432), and 7-oxo- and 15-hydroxy-dehydroabietic acid (MW 474, TMS derivative). The presence of methylated derivatives (Me) is also indicated. The chromatographic profile reflects progressive oxidation, aromatization, and thermal degradation of abietane-type resin acids during heating in oxidative conditions. GC–MS gas chromatography–mass spectrometry, MW molecular weight, TMS trimethylsilyl derivative, Me methyl group. Figure adapted from reference[43].

provide chemical profiles of each material, and by analysing standard compounds it is possible to establish the characteristic ions that contribute to identifying the presence of natural resins and discriminating between different types of resins and tar[121,184].

Other methods that involve mass spectrometry to study resinous materials are MALDI-MS[122–124], SIFT-MS[185–187] and FIA-MS[49,118,150]. As for direct MS methods, these approaches are quick and sensitive and require minimal sample preparation. By identifying typical m/z signals it is possible to distinguish between diterpenoid and triterpenoid resins and to investigate their ageing products.

Capillary electrophoresis (CE)

Capillary electrophoresis encompasses a group of analytical separation techniques that have found widespread application across clinical, environmental, food and forensic sciences, with a growing number of publications each year[188]. In heritage science, CE has been applied to the analysis of plant material (waxes, resins, drying oils, and plant gums), animal origin materials (animal glues)[189], as well as dyes and inks[190] in historical samples. Several studies have utilised CE to separate and identify diterpenoids and pentacyclic triterpenoids in plant materials[191], and it is a promising technique for the analysis of cultural heritage samples[192,193]. Though it offers benefits such as short analysis times, high resolution, and minimal sample and reagent volume requirements, CE struggles to differentiate compounds with similar charge-to-mass ratios. To improve separation and to increase resolution, additives like cyclodextrins, surfactants, and organic solvents are often incorporated in practical applications[194]. The most commonly used additives are: Cyclodextrins (CDs); Surfactants such as sodium dodecyl sulphate (SDS). Buffer selection and its pH optimisation significantly influence the ionisation of the analytes, and consequently their electrophoretic mobility.

CE for the analysis of diterpenoid resins in historical samples has been performed[116,117]. In one such study, the background electrolyte (BGE) consisted of a borate buffer at pH 9.25, with methyl-β-cyclodextrin and sulfobutylether-β-cyclodextrin as modifiers[117]. This enabled the detection of diterpenoid compounds in natural resins in museum objects[117]. Cyclodextrines facilitated the analysis of neutral compounds by CE, but triterpenoid resin compounds, being insoluble in aqueous solution, could not be characterised. In another study, a BGE was also introduced for the separation of 11 resin acids, including 3 chlorinated ones from the wastewater from pulp mills[195].

CE has the advantage of requiring minimal sample pre-treatment. However, its main limitation lies in the demanding nature of the detection process: although analyte identification is facilitated by their distinct spectral properties, each analyte necessitates a separate calibration curve, thereby increasing the analytical workload.

While data on the characterisation of triterpenoids in archaeological resins by CE is currently unavailable, the method has been successfully applied to detect triterpenoids in herbs and plant resins:

- Micellar electrokinetic capillary chromatography (MEKC), using alcohol as an organic modifier and sodium dodecyl sulphate (SDS) as the surfactant, enabled the separation of oleanolic acid and ursolic acid, two natural triterpenoids in herbs[196].
- Separation and detection of triterpenoids and flavonoids in *Swertia mussotii* Franch. was achieved by capillary zone electrophoresis with a borate/phosphate buffer (pH 9.5) and b-cyclodextrin as an additive[197].
- Capillary electrochromatography (CEC), a hybrid technique that combines HPLC and CE, improved the characterisation of *Boswellia serrata* resin, successfully separating six acidic triterpenes[191].

Compared to gas chromatography (GC) and high-performance liquid chromatography (HPLC), CE offers faster analytical procedures, requires similar small sample amounts, and delivers high selectivity. However, its main limitations are its applicability only to charged or ionisable

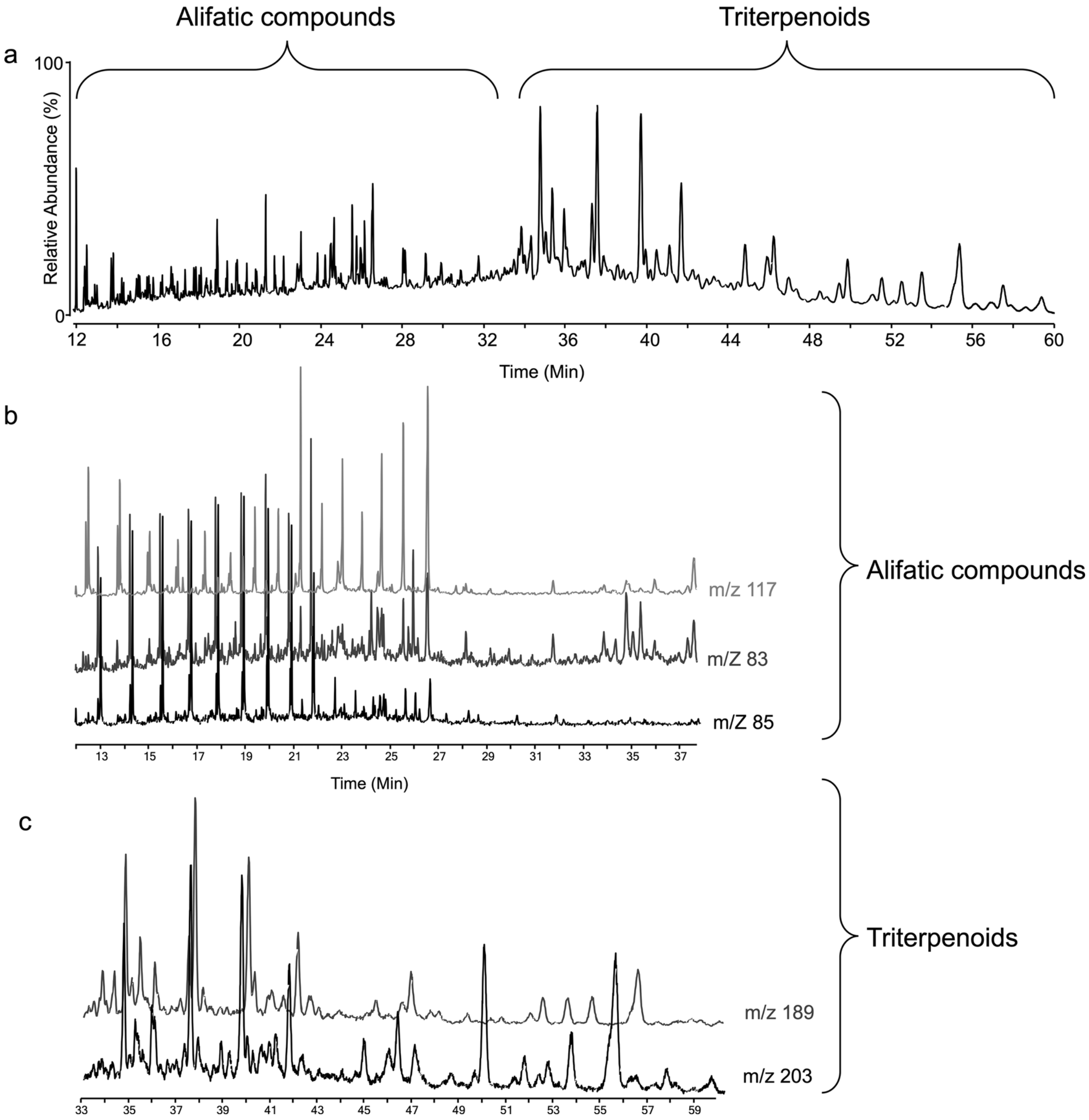


Fig. 10 | Pyrolysis gas chromatography–mass spectrometry (Py-GC–MS) profile of an archaeological birch bark tar sample and selected extracted ion chromatograms (EICs). The figure shows the pyrolytic profile obtained by Py-GC–MS analysis of an archaeological birch bark tar recovered from a Neolithic sickle. Hexamethyldisilazane (HMDS) was used as a derivatization agent prior to analysis. **a** Total ion chromatogram (TIC) of the sample. The horizontal axis represents retention time (minutes), and the vertical axis shows relative abundance (%). The early-eluting region (approximately 12–30 min) is dominated by aliphatic compounds, whereas the later region (approximately 33–60 min) is characterized by triterpenoid compounds derived from birch bark constituents. **b** Extracted ion chromatograms (EICs) corresponding to aliphatic components. The trace at m/z 85 and m/z 83 highlights alkanes and alkenes, while the trace at m/z 117 corresponds primarily to aliphatic carboxylic acids and related derivatives. These ions are diagnostic fragments commonly associated with long-chain aliphatic compounds. **c** Extracted ion chromatograms (EICs) for triterpenoid constituents, shown at m/z 189 and m/z 203. These fragment ions are characteristic of lupane-type triterpenoids and related degradation products typical of birch bark tar. Py-GC–MS pyrolysis gas chromatography–mass spectrometry, EIC extracted ion chromatogram, TIC total ion chromatogram, HMDS hexamethyldisilazane, m/z mass-to-charge ratio. Figure adapted from reference[182].

compounds (except in MEKC), as well as the complexity associated with optimising experimental parameters.

Ancient DNA analysis

In recent years, ancient DNA (aDNA) analysis has emerged as a complementary approach to spectroscopic and chromatographic methods for the study of resins, tars, and pitches[198,199]. Using shotgun metagenomics and reference-based approaches, short and degraded DNA fragments preserved within materials can be matched to modern genomes to identify their botanical origin at the species or genus level—for example, birch DNA recovered from birch tar. In addition to confirming the main substrate, DNA analysis can also reveal other plant or animal species present, shedding light on additives that may have been intentionally included to modify the properties of the tar or pitch, such as pine resin, beeswax, or fibrous plant material. Beyond the materials themselves, chewed resins and mastics have yielded traces of human DNA, which can provide information on the genetic ancestry, sex, and kinship of the individuals who used them[198,199], as well as fragments of oral microbial DNA that inform on past health, diet, and the composition of ancient microbiomes. Together, these applications illustrate how aDNA studies can extend the interpretive scope of heritage science, offering molecular evidence for both the biological sources of resinous materials and their role in past human practices.

However, the application of aDNA analysis to resins, tars, and pitches faces challenges. DNA preservation is highly variable and influenced by environmental conditions, burial chemistry, and the thermal processing involved in tar or pitch production, often resulting in very low yields. The short fragment size and damaged nature of aDNA also increase the risk of misidentification, especially given gaps and biases in current genomic reference databases. Contamination from modern DNA introduced during collection, conservation, or laboratory processing represents an additional risk. For these reasons, robust authentication criteria and cautious interpretation are essential, and DNA results must be evaluated alongside chemical and archaeological evidence to avoid false positives and overinterpretation.

Ancient DNA approaches, while not yet routine, hold considerable potential as a complement to established analytical techniques. By directly identifying plant taxa and revealing the presence of additives or use-related biological signals, metagenomic analyses can enrich our understanding of the technological recipes and cultural practices associated with resins, tars, and pitches. Continued methodological refinement is likely to establish aDNA as a valuable tool within heritage science in the coming years.

Challenges and considerations in analytical characterisation

Although many of the analytical techniques discussed in this review are commonly described as non-destructive, it is important to distinguish between non-destructiveness and non-invasiveness. Generally, FTIR, Raman, and XRD require micro-sampling or surface preparation under laboratory conditions, unless portable instrumentation is used, which is still only seldom employed in archaeology. NMR typically requires larger sample quantities and, in many cases, solvent extraction. While the techniques mentioned above are not inherently destructive, chromatographic and thermoanalytical techniques always involve extensive sample pretreatment. These practical constraints must be carefully considered when selecting appropriate methods for the analysis of valuable or limited archaeological materials.

Reference materials for accurate comparison and data interpretation

For all analytical methods discussed, the use of reference resinous materials of known origin or preparation process is critical for accurate analysis. These reference materials consist of well-characterised samples with established chemical profiles, serving as benchmarks for comparing unknown resin samples[200]. Additionally, chemometric approaches such as hierarchical cluster analysis (HCA) and principal component analysis (PCA), described in the following section, enhance data processing, improve the classification and identification of resin types, and aid in determining the botanical origin of the resins[17,85].

The composition of resinous materials is complex and remains only partially understood, due to the diversity of plant species that produce resins, and their sensitivity to environmental factors such as climate and soil conditions. For instance, modern samples of sandarac resin often exhibit systematic deviations in composition compared to the resin exuded by *Tetraclinis articulata*, the historical source of authentic sandarac which are frequently attributed to adulteration[201]. Furthermore, resin composition can change over time through oxidation or polymerisation processes. Given that environmental conditions and ageing can significantly alter chemical compositions, many research laboratories develop reference libraries of resinous materials that have been artificially aged using standardised protocols[202,203]. To ensure the accuracy and reliability of analytical measurements, these artificially aged materials must be homogeneous and stable.

Because certified reference materials (CRMs) are not commercially available in this field, such laboratory-produced materials, with thoroughly documented properties, are invaluable for round-robin exercises, and are essential for maintaining consistency and comparability of results across different laboratories and over time. Unfortunately, few examples of such procedures are reported in the literature[169,204,205], and these reference materials often remain accessible only to a limited number of researchers.

As noted above, reference collections of resins and tars are available in only a few research laboratories. Botanical museums, however, may serve as an additional valuable source of well-documented plant materials. Unfortunately, access to such historical collections is often highly restricted due to the need for sampling. Nevertheless, when sampling is permitted, this approach can offer essential insight into the chemistry of natural materials[206]. Notably, quality control assessments of natural resins—both on the contemporary market and in select historical collections—frequently reveal issues such as impurities, adulteration, and mislabelling[207].

Data processing approaches

The spectral signatures of plant resins and tars are influenced by a range of factors, including species, variety, age, environmental conditions, and chemical composition, among others. The application of preprocessing techniques, designed to eliminate irrelevant information and enhance the computing efficiency of mathematical models, has proven effective in successfully classifying these materials and discriminating between the different groups[208]. The use of spectroscopic and chromatographic data combined with multivariate methods and statistics is an efficient way to differentiate plant materials. The main problem of this approach is the need to perform multiple analysis of reference materials to construct a chemometric model.

Principal component analysis (PCA) and linear discriminant analysis (LDA) of FTIR spectra has successfully been used to determine the botanical origins of resins from archaeological Aztec samples[132], and to classify archaeological adhesives from Eastern Europe and the Urals[209]. Similarly, PCA has been applied to FTIR spectra to differentiate Palaeolithic birch tar production strategies from Königsaue, Germany[69,210]. PCA of FT-Raman spectroscopy has been used to discriminate resins from other natural organic materials of cultural heritage interest[90], while hierarchical cluster analysis (HCA) applied to FTIR data has enabled the differentiation of Australian plant exudates at both genus and species levels[211]. Partial least squares (PLS) regression has been employed to develop quantitative predictive models based on near infrared spectra, allowing the quantification of the main chemical components of resins. This chemometric approach provides a direct analytical tool for the rapid quality control of *Pinus pinaster* resin in the tapping industry[212]. More generally, the integration of spectroscopic data (FTIR, Raman), chromatography, and thermal analyses with multivariate chemometric methods (e.g. PCA, PLS) enables more robust classification and interpretation, particularly for samples characterised by complex degradation histories[87].

PCA applied to GC-MS data is a valuable tool for identifying the chemical similarities and differences between samples. For example, PCA has revealed distinct compositional clusters among amphorae from archaeological sites in Pisa (Italy) and Fayum (Egypt), differentiated by the relative abundance of oxidised abietanes[21]. The Fayum samples exhibited a higher degree of oxidation, likely due to the region's hot and dry climate, in contrast to the waterlogged conditions in Pisa. While environmental factors may explain the variation in oxidised diterpenic acids, the relatively elevated amounts of retene in the Egyptian amphorae suggest that pitch production in this case involved higher temperatures and longer processing times.

PCA of GC-MS data has also highlighted compositional differences in tars used for distinct purposes at the Mesolithic site of Krzyz Wielkopolski (Poland), as well as among tars from four Iron Age sites[163,213]. PCA has been integrated with other multivariate techniques, such as partial least squares regression and discriminant analysis (PLS-DA) to differentiate resins in historic lacquered objects[201], and to classify tars derived from various tree species[139]. Additionally, discriminant projection (DP) has been used to identify birch bark tar adhesives on copper age arrowheads. PCA applied to DE-MS mass spectral data has successfully grouped different triterpenoid resins into clusters, including samples from a 200,000-year-old birch bark tar artefact[17]. Furthermore, PCA combined with SIFT-MS has demonstrated significant potential for distinguishing organic materials in archaeological objects. In one such study, the interpretation of the mass spectrometric data, supported by statistical data analysis, shed new light on the chemical composition of the organic residues preserved in 50 vessels from the grave goods of Kha and Merit, housed in the Museo Egizio (Turin, Italy)[186]. This non-destructive analytical approach provides a unique opportunity to complement, confirm and expand archaeological interpretations regarding the uses of archaeological vessels and jars.

Resins derived from tropical trees, such as Manila copal, sandarac, South American copal, and Congo copal, all of which were frequently used in finishing layers on decorative objects until the early 20th century, have been compared using multivariate analysis[214]. This has identified specific molecular markers which aid in the identification of copals in resinous lacquer formulations[214]. PCA and cluster analysis have also been applied to NMR- derived variables to distinguish resins produced by the conifer families *Araucariaceae*, *Cupressaceae*, and *Pinaceae* from those originating from the angiosperm family *Fabaceae*[140].

Experimental studies have highlighted difficulties in applying chemometric approaches to a single material, due to the difficulty of precisely replicating chemical compositions, and the limited understanding of natural degradation processes[4,83]. For instance, in a PCA plot of over 100 samples, archaeological birch tar samples are clustered more closely with materials containing beeswax and cellulose introduced through conservation, than with modern experimental birch tars[209]. Accelerated degradation experiments for reference samples are recommended when applying biomolecular profiles of fresh plant material to interpret ancient samples[215]. In the case of copal, however, burial conditions, cleaning, and conservation have only a minor impact on its molecular composition[132].

Regardless of the material, chemometric techniques such as PCA should always be complemented by detailed spectral interpretation to reduce the risk of misclassification[209].

Data preprocessing prior to PCA varies across different studies, complicating the comparison of results[216]. For example, FTIR data may be normalised using peak heights, baseline-corrected, or processed with algorithms such as standard normal variate (SNV), or multiplicative signal correction (MSC). PCA may be performed on complete absorbance spectra, on first or second derivatives, including hundreds or thousands of variables (wavenumbers), or on selected peaks or spectral ranges, depending on the material under investigation[69,90,209,216]. Similarly, GC-MS data may be treated with log10 transformations to reduce discrepancies in relative abundances of components[214], reduced by selecting data from specific mass ranges[17], or by selecting peaks with the highest fisher ratio (FQ)[217].

Given this variability, it is essential to consider the approaches previously employed, and to clearly document the data processing techniques prior to conducting any multivariate or statistical analyses of spectral and chemometric results.

Conclusion and perspectives

The study of plant resins, tars, and pitches highlights their extraordinary significance throughout human history. These substances were employed across millennia for a wide range of technological, functional, ritual, and medicinal purposes, spanning from the hafting of Palaeolithic tools to the waterproofing of Viking ships, from embalming practices in Egypt to the application of artistic varnishes in Europe and Asia. Employed on nearly every continent, plant resins and their derivatives remained in continuous use until the 19th century and, in some cases, persist into the present day, making them some of the most enduring technologies in human history.

These materials have been identified in diverse archaeological contexts, including the hafting of stone tools, sealing and repairing pottery, gluing inlays, creating mosaics, colouring or infilling ceramic decorations, caulking ships, preserving wooden structures, repairing stone buildings, in medical and food preservation applications, and even as chewing gum. Their chemical complexity and variability, combined with the transformations induced by time, environmental exposure, ageing and human manipulation, make their analysis a particularly challenging yet rewarding domain within heritage science.

It is important to recognise that heritage materials are inherently complex, and this complexity is further complicated by the varying preservation characteristics of the different substances and the influence of environmental conditions. Modern organic substances differ significantly from ancient ones, which are typically degraded and may follow diverse degradation pathways. Analytical techniques can offer insights into the intentional mixing of various substances, including plant byproducts, beeswax, and animal fats, used to achieve specific functional properties. These tailored compositions enhance the performance of the final products for a wide range of applications, including cosmetics and waterproofing.

While a multi-technique analytical approach is essential for accurately identifying the composition of ancient resinous mixtures, the use of well-characterised and aged reference materials, in combination with chemometric approaches, significantly enhances both the identification of components and the interpretation of degradation processes over time.

The analytical methods reported in this overview demonstrate great potential for detecting resinous materials and, when contextualised with historical information, can illuminate their complex and varied uses throughout history. It is important to emphasise that no single analytical technique can provide a complete picture. Instead, the integration of multiple methods enables a more comprehensive understanding of the past. A multi-analytical approach is essential: spectroscopic methods provide rapid, non-invasive screening; chromatographic and mass spectrometric techniques identify molecular markers and degradation products; thermoanalytical methods reveal material stability and interactions; NMR provides structural insights; and, increasingly, ancient DNA analysis complements chemical data with biological evidence. Each analytical technique has its own strengths and limitations, which are summarised in Table 9, alongside future directions and emerging perspectives in the field. Figures 1–5

Despite significant advances, several critical challenges persist in the study of resinous cultural heritage materials. These challenges are primarily related to degradation processes, the scarcity of certified reference materials, and the inherent complexity of mixtures in which resins often co-exist with waxes, oils, or fats. The most pressing issues include:

- the lack of standardised reference materials—both fresh and artificially aged—which limits comparability across laboratories and hinders reproducibility.
- the need for advanced data processing methods (chemometrics, multivariate statistics, machine learning) to effectively manage complex mixtures and overlapping spectral signals.
- the necessity of interdisciplinary collaboration, integrating analytical chemistry with allied disciplines, to ensure that analytical results are properly contextualised and interpreted Figs. 6–10

To address the current challenges, several key developments are urgently needed. These include the creation of comprehensive libraries of modern, aged, and experimentally produced resinous substances; the advancement of chemometric approaches capable of managing complex mixtures and overlapping signals; and the adoption of interdisciplinary approaches that integrate analytical chemistry with archaeology, history, conservation, and molecular biology to ensure meaningful contextualisation of the results.

Looking ahead, the integration of chemical, spectroscopic, thermoanalytical, and genetic data will significantly improve our ability to reconstruct ancient recipes, production techniques, and cultural practices. A multi-analytical strategy not only facilitates the identification of original raw materials but also enhances our understanding of degradation pathways and post-depositional alterations. Beyond heritage science, such research holds broader implications for sustainable materials science, as historical natural products may inspire the development of modern eco-friendly alternatives.

In conclusion, the characterisation of resins, tars, and pitches deepens our understanding of ancient technologies and cultural practices, while simultaneously offering innovative directions for contemporary science and sustainable materials development. The cross-disciplinary study of these

Table 9 | Strengths, limitations, and perspectives of analytical techniques applied to resins, tars, and pitches

Analytical technique	Advantages	Disadvantages	Perspectives
FT-IR and Raman	Fast, non-destructive, require minimal or no sample preparation; allow detection of functional groups (C = O, O–H, C = C) and provide spectral fingerprints of resins; portable instruments enable in situ fieldwork; effective for preliminary classification of diterpenoid vs. triterpenoid resins	Strong overlap of bands in complex mixtures; difficult to distinguish degraded samples due to loss or masking of signals; results often require comparison with modern or artificially aged reference materials	Integration with chemometrics (PCA, PLS, LDA) for species-level classification; expansion of spectral libraries with experimentally aged resins and tars; development of more sensitive portable devices for non-invasive field applications
XRD	Non-destructive; identifies crystalline phases and mineral contaminants; effective for detecting additives (ochre, calcite, quartz) or environmental inputs; complements FTIR and SEM-EDS	Poor sensitivity to amorphous organic phases (most resins and tars); cannot reliably distinguish botanical origin; weathering reduces diagnostic features	Combined use with FTIR, Raman and microscopy to strengthen identification; more systematic application to assess preservation conditions of archaeological contexts
NMR	Provides detailed structural data at molecular level; distinguishes resin families (diterpenoid vs. triterpenoid); solid-state NMR suitable for cross-linked, insoluble materials; non-destructive	High cost and low availability of instruments; requires relatively large sample quantities and extraction compared to FTIR and Raman and MS-based methods; complex spectra demand advanced expertise	Valuable for studying polymerisation and cross-linking in aged materials; integration with GC-MS and FTIR for robust multi-technique approaches; expansion of NMR databases of natural resins
Thermoanalytical techniques (TG, DSC, DTA, DMA, TMA, EGA-MS)	High sensitivity, require only milligrams of material; track stability, oxidation, polymerisation, and resin–additive interactions; useful to detect thermal fingerprints and glass transition temperatures (Tg)	Lack of standardised protocols complicates comparison of results; degradation processes alter thermal profiles, complicating interpretation	Adoption of ICTA standards for thermal analysis; broader application to archaeological adhesives and complex mixtures; integration with FTIR and GC-MS to reconstruct ancient processing technologies
Chromatographic and mass spectrometric techniques (GC-MS, GCxGC-HRMS, Py-GC-MS, HPLC-MS)	Most powerful methods for biomarker detection and botanical assignment; identify production technologies (heating regimes, distillation); sensitive to low-concentration compounds; Py-GC-MS allows analysis of insoluble or polymerised residues	Require destructive sampling and derivatisation; susceptible to degradation-related loss of volatile compounds; complex interpretation of mixtures	Expansion of biomarker libraries including artificially aged and experimentally produced tars; increased use of multidimensional GCxGC-HRMS for complex mixtures; integration with non-invasive sampling protocols (SPME, micro-extraction)
Capillary electrophoresis	High separation efficiency, fast analysis, low solvent and sample consumption; low cost compared to LC-GC; allows analysis of specific resin acids in historical samples	Limited to charged/ionisable species; optimisation of buffers and additives needed; not yet widely applied to archaeological materials	Further development of CE-MS and capillary electrochromatography (CEC); promising for diterpenoid profiling in museum samples; potential use as a complementary low-cost screening method
DNA analysis	Provides direct taxonomic identification of plant sources; detects additives and exogenous materials; chewed resins yield human and microbial DNA, offering insight into health, diet, ancestry, and cultural practices	Preservation highly variable; yields often low and fragmentary; significant contamination risk; requires genomic reference databases that are as yet incomplete	Rapidly evolving field with potential to complement chemical analysis; standardisation of authentication protocols essential; in future could provide routine botanical and cultural information alongside chemical biomarkers

natural substances continues to bridge past and future, revealing both human ingenuity and the enduring potential of natural products.

Data availability

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

Code availability

No custom code was used in this study.

Received: 28 October 2025; Accepted: 2 March 2026;

References

1. Pollard, A. M., Heron, C. & Gillard, R. D. in *Archaeological Chemistry* (eds A. Mark Pollard, C Heron, & R. D. Gillard) 7, 235-269 (The Royal Society of Chemistry, 2008).
2. Al-Hassani, S. T. S., Woodcock, E., Saoud, R., Foundation for Science, T. & Civilisation. *1001 Inventions: Muslim Heritage in Our World*. (Foundation for Science Technology and Civilisation, 2007).
3. Alén, R. & Yhdistys, S. P.-i. *Biorefining of Forest Resources*. (Paper Engineers' Association/Paperi ja Puu Oy, 2011).
4. Aleo, A. et al. A multi-analytical approach reveals flexible compound adhesive technology at Steenbokfontein Cave, Western Cape. *J. Archaeol. Sci.* **167**, 105997. https://doi.org/10.1016/j.jas.2024.105997 (2024).
5. Barnes, T. M. & Greive, K. A. Topical pine tar: History, properties and use as a treatment for common skin conditions. *Australas. J. Dermatol* **58**, 80–85, https://doi.org/10.1111/ajd.12427 (2017).
6. Hennius, A. Viking Age tar production and outland exploitation. *Antiquity* **92**, 1349–1361, https://doi.org/10.15184/aqy.2018.22 (2018).
7. Tintner, J. et al. Pitch oil production – An intangible cultural heritage in Central Europe. *J. Anal. Appl. Pyrolysis* **159**, 105309. https://doi.org/10.1016/j.jaap.2021.105309 (2021).
8. Mazza, P. P. A. et al. A new Palaeolithic discovery: tar-hafted stone tools in a European Mid-Pleistocene bone-bearing bed. *J. Archaeol. Sci.* **33**, 1310–1318, https://doi.org/10.1016/j.jas.2006.01.006 (2006).
9. Siemssen, T., Hearne, K. & Rigterink, S. Midge-Infested Wetlands and. *Coevol. Birch Tar. Use Late Pleistocene Neanderthals* https://doi.org/10.17863/CAM.118226 (2024).
10. Nordby, C. C. in *Holding it all together: Ancient and modern approaches to joining, repair and consolidation* (eds Ambers J., C. Higgitt, L. Harrison, & D. Saunders) p. 54-60 (Archetype 2009).
11. Meiggs, R. *Trees and Timber in the Ancient Mediterranean World*. 2009/02/16 edn, 34 (Clarendon Press, 1982).
12. Regert, M. et al. Birch-bark tar in the Roman world: the persistence of an ancient craft tradition?. *Antiquity* **93**, 1553–1568, https://doi.org/10.15184/aqy.2019.167 (2019).

13. Łucejko, J., Connan, J., Orsini, S., Ribechini, E. & Modugno, F. Chemical analyses of Egyptian mummification balms and organic residues from storage jars dated from the Old Kingdom to the Copto-Byzantine period. *J. Archaeol. Sci.* **85**, 1–12, https://doi.org/10.1016/j.jas.2017.06.015 (2017).
14. Evershed, R. P. & Clark, K. A. in *The Handbook of Mummy Studies: New Frontiers in Scientific and Cultural Perspectives* (eds DH Shin & R Bianucci) 653-715 (Springer Singapore, 2021).
15. Metwaly, A. M. et al. Traditional ancient Egyptian medicine: A review. *Saudi J. Biol. Sci.* **28**, 5823–5832, https://doi.org/10.1016/j.sjbs.2021.06.044 (2021).
16. Pliny (the Elder). in *libri XII-XVI* IV (Heinemann, 1960).
17. Modugno, F., Ribechini, E. & Colombini, M. P. Chemical study of triterpenoid resinous materials in archaeological findings by means of direct exposure electron ionisation mass spectrometry and gas chromatography/mass spectrometry. *Rapid Commun. Mass Spectrom.* **20**, 1787–1800, https://doi.org/10.1002/rcm.2507 (2006).
18. Pollard, A. M., Batt, C. M., Stern, B. & Young, S. M. M. *Analytical Chemistry in Archaeology*. (Cambridge University Press, 2007).
19. Pollard, A. M. & Heron, C. *Archaeological Chemistry*. (RSC Publishing, 2008).
20. Rageot, M. et al. Management systems of adhesive materials throughout the Neolithic in the North-West Mediterranean. *J. Archaeol. Sci.* **126**, 105309. https://doi.org/10.1016/j.jas.2020.105309 (2021).
21. Colombini, M. P., Giachi, G., Modugno, F. & Ribechini, E. Characterisation of organic residues in pottery vessels of the Roman age from Antinoe (Egypt). *Microchem. J.* **79**, 83–90, https://doi.org/10.1016/j.microc.2004.05.004 (2005).
22. Pecci, A., Cau Ontiveros, M. Á & Garnier, N. Identifying wine and oil production: analysis of residues from Roman and Late Antique plastered vats. *J. Archaeol. Sci.* **40**, 4491–4498, https://doi.org/10.1016/j.jas.2013.06.019 (2013).
23. Pecci, A. et al. Wine consumption in Bronze Age Italy: Combining organic residue analysis, botanical data and ceramic variability. *J. Archaeol. Sci.* **123**, 105256. https://doi.org/10.1016/j.jas.2020.105256 (2020).
24. Egenberg, I. M., Holtekjølen, A. K. & Lundanes, E. Characterisation of naturally and artificially weathered pine tar coatings by visual assessment and gas chromatography-mass spectrometry. *J. Cult. Herit.* **4**, 221–241, https://doi.org/10.1016/S1296-2074(03)00048-7 (2003).
25. Lindblad, L., Fredriksson, N. & Källbom, A. *Challenges in Pine Tar Production and Practices for Sustainable Preservation of Swedish Wooden Heritage*. (2021).
26. Ebert, B. Learning from the Past: Rediscovering Traditional Medieval Wood Tar Adhesives for Sustainable Stone Conservation and Built Heritage. *Stud. Conserv.* **69**, 63–71, https://doi.org/10.1080/00393630.2024.2339728 (2024).
27. Ebert, B. & Bjelland, T. in *Working Towards a Sustainable Past* (ed J. Bridgland) 1-9 (ICOM-CC, 2023).
28. Atzbach, R. in *Castles at War : The Danish Castle Research Association "Magt, Borg og Landskab"* (eds R Atzbach, L Meldgaard Sass Jensen, & L Plith Lauritsen) (Dr. Rudolf Habelt, 2015).
29. Demuth, V. NOTHAW – ein hansischer Hafen bei Avaldsnes an einer maritimen Schlüsselstelle der norwegischen Westküste. *Skyllis* **23**, 14–24 (2023).
30. Colombini, M. P., Giachi, G., Modugno, F., Pallecchi, P. & Ribechini, E. The characterization of paints and waterproofing materials from the shipwrecks found at the archaeological site of the Etruscan and Roman harbour of Pisa (Italy). *Archaeometry* **45**, 659–674, https://doi.org/10.1046/j.1475-4754.2003.00135.x (2003).
31. Ravn, M. Viking-Age War Fleets: Shipbuilding, resource management and maritime warfare in 11th-century Denmark *Maritime Culture of the North 4*. *Int. J. Nautical Archaeol.* **46**, 226–227, https://doi.org/10.1111/1095-9270.12231 (2017).
32. Loewen, B. Resinous Paying Materials in the French Atlantic, AD 1500–1800. History, Technology, Substances. *Int. J. Nautical Archaeol.* **34**, 238–252, https://doi.org/10.1111/j.1095-9270.2005.00057.x (2005).
33. Moll, F. The history of wood-preserving in shipbuilding. *Mar. 's. Mirror* **12**, 357–374, https://doi.org/10.1080/00253359.1926.10655387 (1926).
34. Heginbotham, A. & Schilling, M. in *East Asian Lacquer: Material Culture, Science and Conservation* (eds S Rivers, R Faulkner, & B Pretzel) 92-106 (Archetype Publications, 2011).
35. Schilling, M. R., Heginbotham, A., van Keulen, H. & Szelewski, M. Beyond the basics: A systematic approach for comprehensive analysis of organic materials in Asian lacquers. *Stud. Conserv.* **61**, 3–27, https://doi.org/10.1080/00393630.2016.1230978 (2016).
36. Mills, J. S. & White, R. Natural Resins of Art and Archaeology Their Sources, Chemistry, and Identification. *Stud. Conserv.* **22**, 12–31, https://doi.org/10.2307/1505670 (1977).
37. Kasprzok, L., Fabbri, D., Rombolà, A. G., Rovetta, T. & Malagodi, M. Identification of organic materials in historical stringed instruments by off-line analytical pyrolysis solid-phase microextraction with on-fiber silylation and gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrolysis* **145**, 104727. https://doi.org/10.1016/j.jaap.2019.104727 (2020).
38. Rovetta, T. et al. The case of Antonio Stradivari 1718 ex-San Lorenzo violin: History, restorations and conservation perspectives. *J. Archaeol. Sci.: Rep.* **23**, 443–450, https://doi.org/10.1016/j.jasrep.2018.11.010 (2019).
39. Langenheim, J. H. *Plant resins: Chemistry, Evolution, Ecology, and Ethnobotany* (Timber Press Inc., 2003).
40. Seyfullah, L. J. et al. Production and preservation of resins – past and present. *Biol. Rev.* **93**, 1684–1714, https://doi.org/10.1111/brv.12414 (2018).
41. Celedon, J. M. & Bohlmann, J. Oleoresin defenses in conifers: chemical diversity, terpene synthases and limitations of oleoresin defense under climate change. *N. Phytol.* **224**, 1444–1463, https://doi.org/10.1111/nph.15984 (2019).
42. Messina, F. et al. Diterpenoids and triterpenoids from the resin of Bursera microphylla and their cytotoxic activity. *J. Nat. Prod.* **78**, 1184–1188, https://doi.org/10.1021/acs.jnatprod.5b00112 (2015).
43. Duce, C. et al. Thermal degradation chemistry of archaeological pine pitch containing beeswax as an additive. *J. Anal. Appl. Pyrolysis* **111**, 254–264, https://doi.org/10.1016/j.jaap.2014.10.020 (2015).
44. Colombini, M. P. & Modugno, F. in *Organic Mass Spectrometry in Art and Archaeology* 1-36 (John Wiley & Sons, Inc.), 2009).
45. Connan, J. & Nissenbaum, A. Conifer tar on the keel and hull planking of the Ma'agan Mikhael Ship (Israel, 5th century BC): identification and comparison with natural products and artefacts employed in boat construction. *J. Archaeol. Sci.* **30**, 709–719, https://doi.org/10.1016/S0305-4403(02)00243-1 (2003).
46. Bailly, L., Adam, P., Charrié, A. & Connan, J. Identification of alkyl guaiacyl dehydroabietates as novel markers of wood tar from Pinaceae in archaeological samples. *Org. Geochem.* **100**, 80–88, https://doi.org/10.1016/j.orggeochem.2016.07.009 (2016).
47. van der Doelen, G. A., van den Berg, K. J. & Boon, J. J. Comparative Chromatographic and Mass-Spectrometric Studies of Triterpenoid Varnishes: Fresh Material and Aged Samples from Paintings. *Stud. Conserv.* **43**, 249–264, https://doi.org/10.2307/1506734 (1998).
48. Perveen, S. & Al-Taweel, A. *Terpenes and Terpenoids*. (IntechOpen, 2018).
49. Dimitrakoudi, E. A. et al. Characterization by Gas Chromatography—Mass Spectrometry of Diterpenoid Resinous Materials in Roman-

Age Amphorae from Northern Greece. *Eur. J. Mass Spectrom.* **17**, 581–591, https://doi.org/10.1255/ejms.1155 (2011).
50. Meyers, P. A., Leenheer, M. J. & Bourbonniere, R. A. Diagenesis of vascular plant organic matter components during burial in lake sediments. *Aquat. Geochem.* **1**, 35–52, https://doi.org/10.1007/BF01025230 (1995).
51. Leppänen, H., Kukkonen, J. V. K. & Oikari, A. O. J. Concentration of retene and resin acids in sedimenting particles collected from a bleached kraft mill effluent receiving lake. *Water Res* **34**, 1604–1610, https://doi.org/10.1016/S0043-1354(99)00313-9 (2000).
52. Grötzinger, K., Birkemeyer, C., Kuzminska, M. & Rauwald, H. Isolation and identification of antispirochetal labdane-type manoyloxides from Cistus creticus L. by novel TLC-extractor/MS and GC/MS. *Planta Med*. **76**, P245, https://doi.org/10.1055/s-0030-1264543 (2010).
53. Saitta, E. T. & Kaye, T. G. Experimental maturation of pine resin in sediment to investigate the formation of synthetic copal and amber. *Sci. Rep.* **15**, 7627. https://doi.org/10.1038/s41598-025-89448-5 (2025).
54. Scalarone, D., Lazzari, M. & Chiantore, O. Ageing behaviour and analytical pyrolysis characterisation of diterpenic resins used as art materials: Manila copal and sandarac. *J. Anal. Appl. Pyrolysis* **68-69**, 115–136, https://doi.org/10.1016/S0165-2370(03)00005-6 (2003).
55. Simoneit, B. R. T., Cox, R. E., Oros, D. R. & Otto, A. Terpenoid Compositions of Resins from *Callitris* Species (*Cupressaceae*). *Molecules* **23**, 3384, https://doi.org/10.3390/molecules23123384 (2018).
56. Scalarone, D., Lazzari, M. & Chiantore, O. Ageing behaviour and pyrolytic characterisation of diterpenic resins used as art materials: colophony and Venice turpentine. *J. Anal. Appl. Pyrolysis* **64**, 345–361, https://doi.org/10.1016/S0165-2370(02)00046-3 (2002).
57. Dietemann, P., Miller, K. V., Höpker, C. & Baumer, U. On the Use and Differentiation of Resins from Pinaceae Species in European Artworks Based on Written Sources, Reconstructions and Analysis. *Stud. Conserv.* **64**, S62–S73, https://doi.org/10.1080/00393630.2019.1568678 (2019).
58. Rauwald, H. W., Liebold, T., Grötzinger, K., Lehmann, J. & Kuchta, K. Labdanum and Labdanes of Cistus creticus and C. ladanifer: Anti-Borrelia activity and its phytochemical profiling☆. *Phytomedicine* **60**, 152977. https://doi.org/10.1016/j.phymed.2019.152977 (2019).
59. De Pascual Teresa, J., Urones, J. G., Marcos, I. S., Barcala, P. B. & Garrido, N. M. Diterpenoid and other components of Cistus laurifolius. *Phytochemistry* **25**, 1185–1187, https://doi.org/10.1016/S0031-9422(00)81577-0 (1986).
60. Mathe, C., Culioli, G., Archier, P. & Vieillescazes, C. High-Performance Liquid Chromatographic Analysis of Triterpenoids in Commercial Frankincense. *Chromatographia* **60**, 493–499, https://doi.org/10.1365/s10337-004-0417-3 (2004).
61. Xu, C., Wang, B., Pu, Y., Tao, J. & Zhang, T. Techniques for the analysis of pentacyclic triterpenoids in medicinal plants. *J. Sep. Sci.* **41**, 6–19, https://doi.org/10.1002/jssc.201700201 (2018).
62. Mannino, G., Occhipinti, A. & Maffei, M. E. Quantitative Determination of 3-O-Acetyl-11-Keto-βBoswellic Acid (AKBA) and Other Boswellic Acids in Boswellia sacra Flueck (syn. B. carteri Birdw) and Boswellia serrata Roxb. *Molecules* **21**, 1329, https://doi.org/10.3390/molecules21101329 (2016).
63. Hanus, L. O., Rezanka, T., Dembitsky, V. M. & Moussaieff, A. Myrrh-Commiphora chemistry. *Biomed. Pap. Med Fac. Univ. Palacky. Olomouc Czech Repub.* **149**, 3–27, https://doi.org/10.5507/bp.2005.001 (2005).
64. Colombini, M. P., Modugno, F., Silvano, F. & Onor, M. Characterization of the Balm of an Egyptian Mummy from the seventh century B.C. *Stud. Conserv.* **45**, 19–29, https://doi.org/10.2307/1506680 (2000).
65. Dufour, A. et al. Comparison of two methods of measuring wood pyrolysis tar. *J. Chromatogr. A* **1164**, 240–247, https://doi.org/10.1016/j.chroma.2007.06.049 (2007).
66. Izzo, F. C., Zendri, E., Bernardi, A., Balliana, E. & Sgobbi, M. The study of pitch via gas chromatography–mass spectrometry and Fourier-transformed infrared spectroscopy: the case of the Roman amphoras from Monte Poro, Calabria (Italy). *J. Archaeol. Sci.* **40**, 595–600, https://doi.org/10.1016/j.jas.2012.06.017 (2013).
67. Alén, R. in *Chemistry for Biomass Utilization 200-251* (De Gruyter, 2024).
68. Nicholson, P. & Shaw, I. *Ancient Egyptian Materials and Technology*. 105 (Cambridge University Press, 2009).
69. Schmidt, P. et al. Production method of the Königsaue birch tar documents cumulative culture in Neanderthals. *Archaeol. Anthropol. Sci.* **15**, 84, https://doi.org/10.1007/s12520-023-01789-2 (2023).
70. Rageot, M. et al. Birch bark tar production: Experimental and biomolecular approaches to the study of a common and widely used prehistoric adhesive. *J. Archaeol. Method Theory* **26**, 276–312, https://doi.org/10.1007/s10816-018-9372-4 (2019).
71. Risbøl, O., Hennius, A. & Hennius, J. S. Socio-economic aspects of early iron age wood tar production in Scandinavia. *J. Field Archaeol.* 1-11 https://doi.org/10.1080/00934690.2025.2525682 (2025).
72. Schmidt, P. et al. Birch tar production does not prove Neanderthal behavioral complexity. *Proc. Natl. Acad. Sci.* **116**, 17707–17711, https://doi.org/10.1073/pnas.1911137116 (2019).
73. Paghdal, K. V. & Schwartz, R. A. Topical tar: back to the future. *J. Am. Acad. Dermatol* **61**, 294–302, https://doi.org/10.1016/j.jaad.2008.11.024 (2009).
74. Davara, J., Jambrina-Enríquez, M., Rodríguez de Vera, C., Herrera-Herrera, A. V. & Mallol, C. Pyrotechnology and lipid biomarker variability in pine tar production. *Archaeol. Anthropol. Sci.* **15**, 133, https://doi.org/10.1007/s12520-023-01829-x (2023).
75. Egenberg, I. M., Aasen, J. A. B., Holtekjølen, A. K. & Lundanes, E. Characterisation of traditionally kiln produced pine tar by gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrolysis* **62**, 143–155, https://doi.org/10.1016/S0165-2370(01)00112-7 (2002).
76. Robinson, N., Evershed, R. P., Higgs, W. J., Jerman, K. & Eglinton, G. Proof of a pine wood origin for pitch from Tudor (Mary Rose) and Etruscan shipwrecks: application of analytical organic chemistry in archaeology. *Analyst* **112**, 637–644, https://doi.org/10.1039/AN9871200637 (1987).
77. Kurt, Y., Suleyman Kaçar, M. & Isik, K. Traditional Tar Production from Cedrus libani A. Rich on the Taurus Mountains in Southern Turkey. *Econ. Bot.* **62**, 615–620, https://doi.org/10.1007/s12231-008-9023-x (2008).
78. Kurt, Y. & Isik, K. Comparison of Tar Produced by Traditional and Laboratory Methods. *Stud. Ethno-Med.* **6**, 77–83, https://doi.org/10.1080/09735070.2012.11886423 (2012).
79. Hua, Y., Bentley, M. D., Cole, B. J. W., Murray, K. D. & Alford, A. R. Triterpenes from the Outer Bark of Betula nigra. *J. Wood Chem. Technol.* **11**, 503–516, https://doi.org/10.1080/02773819108051090 (1991).
80. Witte, L. in *Gas Chromatography/Mass Spectrometry* (eds H Ferdinand Linskens & J F. Jackson) 134-145 (Springer Berlin Heidelberg, 1986).
81. Schmidt, P. & Koch, T. J. The molecular composition of birch tar and its infrared spectrum. *Archaeol. Anthropol. Sci.* **16**, 193, https://doi.org/10.1007/s12520-024-02102-5 (2024).
82. Perthuison, J., Schaeffer, P., Debels, P., Galant, P. & Adam, P. Betulin-related esters from birch bark tar: Identification, origin and archaeological significance. *Org. Geochem.* **139**, 103944. https://doi.org/10.1016/j.orggeochem.2019.103944 (2020).
83. Kozowyk, P. R. B., Baron, L. I. & Langejans, G. H. J. Identifying Palaeolithic birch tar production techniques: challenges from an experimental biomolecular approach. *Sci. Rep.* **13**, 14727. https://doi.org/10.1038/s41598-023-41898-5 (2023).

84. Prati, S., Sciutto, G., Bonacini, I. & Mazzeo, R. New Frontiers in Application of FTIR Microscopy for Characterization of Cultural Heritage Materials. *Top. Curr. Chem.* **374**, 26. https://doi.org/10.1007/s41061-016-0025-3 (2016).
85. Prati, S., Sciutto, G., Mazzeo, R., Torri, C. & Fabbri, D. Application of ATR-far-infrared spectroscopy to the analysis of natural resins. *Anal. Bioanal. Chem.* **399**, 3081–3091, https://doi.org/10.1007/s00216-010-4388-y (2011).
86. Shillito, L. M., Almond, M. J., Wicks, K., Marshall, L.-J. R. & Matthews, W. The use of FT-IR as a screening technique for organic residue analysis of archaeological samples. *Anal. Mol. Biomol. Spectrosc.: Basics Appl.* **72**, 120–125, https://doi.org/10.1016/j.saa.2008.08.016 (2009).
87. Natkaniec-Nowak, L., Drzewicz, P., Stach, P., Mroczkowska-Szerszeń, M. & Żukowska, G. The overview of analytical methods for studying of fossil natural resins. *Crit. Rev. Anal. Chem.* **54**, 2754–2776, https://doi.org/10.1080/10408347.2023.2200855 (2024).
88. Lucejko, J. J., Lluveras-Tenorio, A., Modugno, F., Ribechini, E. & Colombini, M. P. An analytical approach based on x-ray diffraction, fourier transform infrared spectroscopy and gas chromatography-mass spectrometry to characterize Egyptian embalming materials. *Microchem. J.* **103**, 110–118, https://doi.org/10.1016/j.microc.2012.01.014 (2012).
89. Brody, R. H., Edwards, H. G. & Pollard, A. M. Fourier Transform-Raman spectroscopic study of natural resins of archaeological interest. *Biopolymers* **67**, 129–141, https://doi.org/10.1002/bip.10059 (2002).
90. Daher, C., Paris, C., Le Hô, A.-S., Bellot-Gurlet, L. & Échard, J.-P. A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes. *J. Raman Spectrosc.* **41**, 1494–1499, https://doi.org/10.1002/jrs.2693 (2010).
91. Edwards, H. G. M. & Ali, E. M. A. Raman spectroscopy of archaeological and ancient resins: Problems with database construction for applications in conservation and historical provenancing. *Anal. Mol. Biomol. Spectrosc.: Basics Appl.* **80**, 49–54, https://doi.org/10.1016/j.saa.2011.01.030 (2011).
92. Nafie, L. A. Recent advances in linear and nonlinear Raman spectroscopy. Part XIV. *J. Raman Spectrosc.* **51**, 2354–2376, https://doi.org/10.1002/jrs.6025 (2020).
93. Bruni, S. & Guglielmi, V. Identification of archaeological triterpenic resins by the non-separative techniques FTIR and 13C NMR: The case of Pistacia resin (mastic) in comparison with frankincense. *Anal. Mol. Biomol. Spectrosc.: Basics Appl.* **121**, 613–622, https://doi.org/10.1016/j.saa.2013.10.098 (2014).
94. Lambert, J. B., Wu, Y., Kozminski, M. A. & Santiago-Blay, J. A. Characterization of eucalyptus and chemically related exudates by nuclear magnetic resonance spectroscopy. *Aust. J. Chem.* **60**, 862–870, https://doi.org/10.1071/CH07163 (2007).
95. Lambert, J. B., Wu, Y. & Santiago-Blay, J. A. Taxonomic and chemical relationships revealed by nuclear magnetic resonance spectra of plant exudates. *J. Nat. Prod.* **68**, 635–648, https://doi.org/10.1021/np050005f (2005).
96. Silva, E. O., Tavares, M. I. B., Bathista, A. L. B. S., Filho, N. P. & Nogueira, J. S. High-resolution carbon-13 nuclear magnetic resonance study of natural resins. *J. Appl. Polym. Sci.* **86**, 1848–1854, https://doi.org/10.1002/app.11099 (2002).
97. Spinella, A., Chillura Martino, D. F. & Meo, P. L. in *The Environment in a Magnet: Applications of NMR Techniques to Environmental Problems* Vol. 32 (eds P Conte, D F Chillura Martino, & P Lo Meo) 381 - 398 380 (Royal Society of Chemistry, 2024).
98. Favvas, E. P., Kouvelos, E. P., Papageorgiou, S. K., Tsanaktsidis, C. G. & Mitropoulos, A. C. Characterization of natural resin materials using water adsorption and various advanced techniques. *Appl. Phys. A* **119**, 735–743, https://doi.org/10.1007/s00339-015-9022-6 (2015).
99. Despotopoulou, M. et al. Testing non-destructive spectrometric methods for the identification and distinction of archaeological pine wood tar and birch bark tar. *J. Archaeol. Sci. Rep.* **56**, 104571. https://doi.org/10.1016/j.jasrep.2024.104571 (2024).
100. Cartoni, G., Russo, M. V., Spinelli, F. & Talarico, F. G. C.-M. S. characterization and identification of natural terpenic resins employed in works of art. *Ann. di Chim.* **94**, 767–782, https://doi.org/10.1002/adic.200490098 (2004).
101. Mompo, M. et al. Setting up a natural resin collection to identify an archaeological black pitch sample. *ACTA IMEKO* **13**, 1–6, https://doi.org/10.21014/actaimeko.v13i2.1834 (2024).
102. Otto, A. & Simoneit, B. R. T. Chemosystematics and diagenesis of terpenoids in fossil conifer species and sediment from the Eocene Zeitz formation, Saxony, Germany. *Geochim. Cosmochim. Acta* **65**, 3505–3527, https://doi.org/10.1016/S0016-7037(01)00693-7 (2001).
103. Otto, A., Simoneit, B. R. T. & Rember, W. C. Resin compounds from the seed cones of three fossil conifer species from the Miocene Clarkia flora, Emerald Creek, Idaho, USA, and from related extant species. *Rev. Palaeobot. Palynol.* **126**, 225–241, https://doi.org/10.1016/S0034-6667(03)00088-5 (2003).
104. Ribechini, E., Modugno, F., Baraldi, C., Baraldi, P. & Colombini, M. P. An integrated analytical approach for characterizing an organic residue from an archaeological glass bottle recovered in Pompeii (Naples, Italy). *Talanta* **74**, 555–561, https://doi.org/10.1016/j.talanta.2007.06.026 (2008).
105. Ribechini, E., Modugno, F., Colombini, M. P. & Evershed, R. P. Gas chromatographic and mass spectrometric investigations of organic residues from Roman glass unguentaria. *J. Chromatogr. A* **1183**, 158–169, https://doi.org/10.1016/j.chroma.2007.12.090 (2008).
106. Thurman, E. M. in *Comprehensive Analytical Chemistry* 90 (eds Imma Ferrer & E. Michael Thurman) 197-233 (Elsevier, 2020).
107. Lebedev, A. T., Polyakova, O. V., Artaev, V. B., Mednikova, M. B. & Anokhina, E. A. Comprehensive two-dimensional gas chromatography-high resolution mass spectrometry with complementary ionization methods in the study of 5000-year-old mummy. *Rapid Commun. Mass Spectrom.* **35**, e9058. https://doi.org/10.1002/rcm.9058 (2021).
108. Zhu, Y. et al. Characterization of nitrogen-containing compounds in coal tar and its subfractions by comprehensive two-dimensional GC × GC-TOF and ESI FT-ICR mass spectrometry based on new separation method. *Fuel Process. Technol.* **227**, 107125. https://doi.org/10.1016/j.fuproc.2021.107125 (2022).
109. Barberis, E., Manfredi, M., Ferraris, E., Bianucci, R. & Marengo, E. Non-invasive paleo-metabolomics and paleo-proteomics analyses reveal the complex funerary treatment of the early 18th dynasty dignitary NEBIRI (QV30). *Molecules* **27**, 7208, https://doi.org/10.3390/molecules27217208 (2022).
110. Chiavari, G., Fabbri, D., Mazzeo, R., Bocchini, P. & Galletti, G. C. Pyrolysis gas chromatography-mass spectrometry of natural resins used for artistic objects. *Chromatographia* **41**, 273–281, https://doi.org/10.1007/BF02688040 (1995).
111. Puchinger, L., Sauter, F., Leder, S. & Varmuza, K. Studies in organic archaeometry VII - differentiation of wood and bark pitches by pyrolysis capillary gas chromatography (PY-CGC). *Ann. di Chim.* **97**, 513–525, https://doi.org/10.1002/adic.200790034 (2007).
112. Ribechini, E., Bacchiocchi, M., Deviese, T. & Colombini, M. P. Analytical pyrolysis with in situ thermally assisted derivatisation, Py(HMDS)-GC/MS, for the chemical characterization of archaeological birch bark tar. *J. Anal. Appl. Pyrolysis* **91**, 219–223, https://doi.org/10.1016/j.jaap.2011.02.011 (2011).
113. Ribechini, E., Orsini, S., Silvano, F. & Colombini, M. P. Py-GC/MS, GC/MS and FTIR investigations on Late Roman-Egyptian adhesives

from opus sectile: New insights into ancient recipes and technologies. *Anal. Chim. Acta* **638**, 79–87, https://doi.org/10.1016/j.aca.2009.02.004 (2009).

114. Scalarone, D. & Chiantore, O. in *Organic Mass Spectrometry in Art and Archaeology* 327-361 (2009).
115. van der Doelen, G. A. et al. Analysis of fresh triterpenoid resins and aged triterpenoid varnishes by high-performance liquid chromatography-atmospheric pressure chemical ionisation (tandem) mass spectrometry. *J. Chromatogr. A* **809**, 21–37, https://doi.org/10.1016/S0021-9673(98)00186-1 (1998).
116. Dell'mour, M., Findeisen, A., Kaml, I., Baatz, W. & Kenndler, E. Capillary Electrophoresis as Analytical Method for the Characterisation of Natural Diterpenoid Resins in Artistic and Historic Works: A Comparison with Gas Chromatography. *The Open Analytical Chem. J.* **2** (2008). https://doi.org/10.2174/1874065000802010067
117. Findeisen, A., Kolivoska, V., Kaml, I., Baatz, W. & Kenndler, E. Analysis of diterpenoic compounds in natural resins applied as binders in museum objects by capillary electrophoresis. *J. Chromatogr. A* **1157**, 454–461, https://doi.org/10.1016/j.chroma.2007.05.010 (2007).
118. Bonaduce, I. et al. Terpenoid Oligomers of Dammar Resin. *J. Nat. Prod* https://doi.org/10.1021/acs.jnatprod.5b00916 (2016).
119. Colombini, M. P., Modugno, F. & Ribechini, E. Direct exposure electron ionization mass spectrometry and gas chromatography / mass spectrometry techniques to study organic coatings on archaeological amphorae. *J. Mass Spectrom.* **40**, 675–687, https://doi.org/10.1002/jms.841 (2005).
120. Choi, K. H. et al. Molecular-level investigation of coal-tar pitch treated by air blowing: Revealing the restructure of aromatic compounds via radical reactions. *Carbon* **203**, 377–385, https://doi.org/10.1016/j.carbon.2022.11.022 (2023).
121. Prokes, L. & Hložek, M. Identification of some adhesives and wood pyrolysis products of archaeological origin by direct inlet mass spectrometry. *Chem. Anal. (Wars., Pol.)* **52**, 700–713 (2007).
122. Teearu, A. et al. Method development for the analysis of resinous materials with MALDI-FT-ICR-MS: novel internal standards and a new matrix material for negative ion mode. *J. Mass Spectrom.* **52**, 603–617, https://doi.org/10.1002/jms.3943 (2017).
123. Vahur, S. et al. Analysis of dammar resin with MALDI-FT-ICR-MS and APCI-FT-ICR-MS. *J. Mass Spectrom.* **47**, 392–409, https://doi.org/10.1002/jms.2971 (2012).
124. Zhang, W., Andersson, J. T., Räder, H. J. & Müllen, K. Molecular characterization of large polycyclic aromatic hydrocarbons in solid petroleum pitch and coal tar pitch by high resolution MALDI ToF MS and insights from ion mobility separation. *Carbon* **95**, 672–680, https://doi.org/10.1016/j.carbon.2015.08.057 (2015).
125. Martín, Y., García, R., Solé, R. A. & Moinelo, S. R. Structural characterization of coal tar pitches obtained by heat treatment under different conditions. *Energy Fuels* **10**, 436–442, https://doi.org/10.1021/ef950208j (1996).
126. Nevin, A. et al. Assessment of the ageing of triterpenoid paint varnishes using fluorescence, Raman and FTIR spectroscopy. *Anal. Bioanal. Chem.* **395**, 2139–2149, https://doi.org/10.1007/s00216-009-3005-4 (2009).
127. Casadio, F., Daher, C. & Bellot-Gurlet, L. Raman spectroscopy of cultural heritage Materials: Overview of applications and new frontiers in instrumentation, sampling modalities, and data processing. Top. Curr. Chem. 374. https://doi.org/10.1007/s41061-016-0061-z (2016).
128. de Faria, D. L. A. & Edwards, H. G. M. in *Raman Spectroscopy in Archaeology and Art History: Volume 2* (eds P Vandenabeele & H Edwards) 314-343 (The Royal Society of Chemistry, 2018).
129. Vandenabeele, P. et al. Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art. *Anal. Chim. Acta* **407**, 261–274, https://doi.org/10.1016/S0003-2670(99)00827-2 (2000).
130. Edwards, H. G. M., Vandenabeele, P. & Colomban, P. in *Raman Spectroscopy in Cultural Heritage Preservation* 1-5 (Springer International Publishing, 2023).
131. Ciofini, D., Striova, J., Camaiti, M. & Siano, S. Photo-oxidative kinetics of solvent and oil-based terpenoid varnishes. *Polym. Degrad. Stab.* **123**, 47–61, https://doi.org/10.1016/j.polymdegradstab.2015.11.002 (2016).
132. Piña-Torres, C. et al. An analytical strategy based on Fourier transform infrared spectroscopy, principal component analysis and linear discriminant analysis to suggest the botanical origin of resins from Bursera. Application to archaeological Aztec Samples. *J. Cult. Herit.* **33**, 48–59, https://doi.org/10.1016/j.culher.2018.02.006 (2018).
133. Prati, S. et al. Evaluation of the effect of six different paint cross section preparation methods on the performances of Fourier Transformed Infrared microscopy in attenuated total reflection mode. *Microchem. J.* **103**, 79–89, https://doi.org/10.1016/j.microc.2012.01.007 (2012).
134. Bernardinelli, O. D., Novotny, E. E., de Azevêdo, E. R. & Colnago, L. A. in *Analytical Techniques and Methods for Biomass* (ed S Vaz Jr) 147-176 (Springer Nature Switzerland, 2025).
135. Spyros, A. in *Modern Magnetic Resonance* (ed Graham A. Webb) 221-232 (Springer International Publishing, 2018).
136. Ghisalberti, E. L. & Godfrey, I. M. Application of nuclear magnetic resonance spectroscopy to the analysis of organic archaeological materials. *Stud. Conserv.* **43**, 215–230, https://doi.org/10.2307/1506731 (1998).
137. Lambert, J. B. et al. Characterization of phenolic plant exudates by nuclear magnetic resonance spectroscopy. *J. Nat. Prod.* **84**, 2511–2524, https://doi.org/10.1021/acs.jnatprod.1c00522 (2021).
138. Tanasi, D., Greco, E., Pisciotta, F. & Hassam, S. Chemical characterization of organic residues on Late Roman amphorae from shipwrecks off the coast of Marsala (Trapani, Italy). *J. Archaeol. Sci.: Rep.* **40**, 103241. https://doi.org/10.1016/j.jasrep.2021.103241 (2021).
139. Sauter, F. & Puchinger, L. Archaeometry of birch bark pitch. *Archaologisches Korrespondenzblatt* **48**, 595–604, https://doi.org/10.11588/ak.2018.4.75396 (2018).
140. Lambert, J. B., Heckenbach, E. A., Wu, Y. & Santiago-Blay, J. A. Characterization of plant exudates by principal-component and cluster analyses with nuclear magnetic resonance variables. *J. Nat. Prod.* **73**, 1643–1648, https://doi.org/10.1021/np100318n (2010).
141. High, K. E. & Penkman, K. E. H. A review of analytical methods for assessing preservation in waterlogged archaeological wood and their application in practice. *Herit. Sci.* **8**, 83. https://doi.org/10.1186/s40494-020-00422-y (2020).
142. Turi, E. A. *Thermal Characterization of Polymeric Materials*. (Academic Press, 1981).
143. Maines, C. A. & de la Rie, E. R. Size-exclusion chromatography and differential scanning calorimetry of low molecular weight resins used as varnishes for paintings. *Prog. Org. Coat.* **52**, 39–45, https://doi.org/10.1016/j.porgcoat.2004.06.006 (2005).
144. Odlyha, M. in *Handbook of Thermal Analysis and Calorimetry* Vol. 2 (eds Michael E. Brown & Patrick K. Gallagher) 47-96 (Elsevier Science B.V., 2003).
145. Pires, J. & Cruz, A. J. Techniquesof thermal analysis applied to the study of cultural heritage. *J. Therm. Anal. Calorim.* **87**, 411–415, https://doi.org/10.1007/s10973-004-6775-0 (2007).
146. Ion, R. M. & Vasilievici, G. Thermoanalytical analysis of sacidava ceramics. *Sci. Bull. Valahia Univ. - Mater. Mech.* **21**, 18–22, https://doi.org/10.2478/bsmm-2025-0003 (2025).

147. Ion, R. M. et al. Thermal and mineralogical investigations of historical ceramic. *J. Therm. Anal. Calorim.* **104**, 487–493, https://doi.org/10.1007/s10973-011-1517-6 (2011).
148. Ion, R.-M. et al. Thermal analysis of Romanian ancient ceramics. *J. Therm. Anal. Calorim.* **102**, 393–398, https://doi.org/10.1007/s10973-009-0226-x (2010).
149. Biroš, J., Larina, T., Trekoval, J. & Pouchlý, J. Dependence of the glass transition temperature of poly (methyl methacrylates) on their tacticity. *Colloid Polym. Sci.* **260**, 27–30, https://doi.org/10.1007/BF01447672 (1982).
150. Schilling, M. R. The glass transition of materials used in conservation. *Stud. Conserv.* **34**, 110–116, https://doi.org/10.2307/1506226 (1989).
151. De Falco, F. et al. A thermoanalytical insight into the composition of biodegradable polymers and commercial products by EGA-MS and Py-GC-MS. *J. Anal. Appl. Pyrolysis* **171**, 105937. https://doi.org/10.1016/j.jaap.2023.105937 (2023).
152. Cabaret, T., Boulicaud, B., Chatet, E. & Charrier, B. Study of rosin softening point through thermal treatment for a better understanding of maritime pine exudation. *Eur. J. Wood Wood Products* **76**, 1453–1459, https://doi.org/10.1007/s00107-018-1339-3 (2018).
153. Coppola, M. E. et al. Pinaceae pine resins (black pine, shore pine, rosin, and baltic amber) as natural dielectrics for low operating voltage, hysteresis-free, organic field effect transistors. *Glob. Chall.* **7**, 2300062. https://doi.org/10.1002/gch2.202300062 (2023).
154. Frances, M. et al. Effect of heat treatment on Pinus pinaster rosin: A study of physico chemical changes and influence on the quality of rosin linseed oil varnish. *Ind. Crops Prod.* **155**, 112789. https://doi.org/10.1016/j.indcrop.2020.112789 (2020).
155. Cabaret, T., Gardere, Y., Frances, M., Leroyer, L. & Charrier, B. Measuring interactions between rosin and turpentine during the drying process for a better understanding of exudation in maritime pine wood used as outdoor siding. *Ind. Crops Prod.* **130**, 325–331, https://doi.org/10.1016/j.indcrop.2018.12.080 (2019).
156. Pagacz, J., Naglik, B., Stach, P., Drzewicz, P. & Natkaniec-Nowak, L. Maturation process of natural resins recorded in their thermal properties. *J. Mater. Sci.* **55**, 4504–4523, https://doi.org/10.1007/s10853-019-04302-0 (2020).
157. Pagacz, J., Stach, P., Natkaniec-Nowak, L., Naglik, B. & Drzewicz, P. Preliminary thermal characterization of natural resins from different botanical sources and geological environments. *J. Therm. Anal. Calorim.* **138**, 4279–4288, https://doi.org/10.1007/s10973-019-08157-0 (2019).
158. Calà, E. et al. The characterization of natural resins and a study of their degradation in interactions with zinc oxide pigment. *Materials* **17**, 5416, https://doi.org/10.3390/ma17225416 (2024).
159. Jablonski, P., Golloch, A. & Borchard, W. DSC-measurements of amber and resin samples. *Thermochim. Acta* **333**, 87–93, https://doi.org/10.1016/S0040-6031(99)00101-X (1999).
160. Bertelli, I., Mattonai, M., La Nasa, J. & Ribechini, E. Study of thermal behavior and molecular composition of mixtures of resinous materials and beeswax found as adhesives in archaeological finds. *J. Anal. Appl. Pyrolysis* **171**, 105936. https://doi.org/10.1016/j.jaap.2023.105936 (2023).
161. Peters, K. E., Walters, C. C. & Moldowan, J. M. *The Biomarker Guide: Volume 2: Biomarkers and Isotopes in the Petroleum Exploration and earth History*. 2 edn, 2 (Cambridge University Press, 2005).
162. Ribechini, E., Mangani, F. & Colombini, M. P. Chemical investigation of barks from broad-leaved tree species using EGA-MS and GC/MS. *J. Anal. Appl. Pyrolysis* **114**, 235–242, https://doi.org/10.1016/j.jaap.2015.06.001 (2015).
163. Koch, T. J. et al. Chemical analyses reveal dual functionality of Early Mesolithic birch tar at Krzyż Wielkopolski (Poland). *J. Archaeol. Sci.: Rep.* **57**, 104591. https://doi.org/10.1016/j.jasrep.2024.104591 (2024).
164. Colombini, M. P., Andreotti, A., Bonaduce, I., Modugno, F. & Ribechini, E. Analytical strategies for characterizing organic paint media using gas chromatography/mass spectrometry. *Acc. Chem. Res.* **43**, 715–727, https://doi.org/10.1021/ar900185f (2010).
165. Chiavari, G. & Prati, S. Analytical pyrolysis as diagnostic tool in the investigation of works of art. *Chromatographia* **58**, 543–554, https://doi.org/10.1365/s10337-003-0094-7 (2003).
166. Blau, K. & Halket, J. M. *Handbook of Derivatives for Chromatography*. Second edition edn, (John Wiley and Sons, 1993).
167. Rontani, J. F. & Aubert, C. Trimethylsilyl transfer during electron ionization mass spectral fragmentation of some ω-hydroxycarboxylic and ω-dicarboxylic acid trimethylsilyl derivatives and the effect of chain length. *Rapid Commun. Mass Spectrom.* **18**, 1889–1895, https://doi.org/10.1002/rcm.1567 (2004).
168. Pastorova, I., van der Berg, K. J., Boon, J. J. & Verhoeven, J. W. Analysis of oxidized diterpenoid acids using thermally assisted methylation with TMAH. *J. Anal. Appl. Pyrolysis* **43**, 41–57, https://doi.org/10.1016/S0165-2370(97)00058-2 (1997).
169. van Keulen, H. Gas chromatography/mass spectrometry methods applied for the analysis of a Round Robin sample containing materials present in samples of works of art. *Int. J. Mass Spectrom.* **284**, 162–169, https://doi.org/10.1016/j.ijms.2009.03.007 (2009).
170. Cnuts, D. et al. Fingerprinting glues using HS-SPME GC×GC–HRTOFMS: A new powerful method allows tracking glues back in time. *Archaeometry* **60**, 1361–1376, https://doi.org/10.1111/arcm.12364 (2018).
171. Guo, X.-H. et al. Molecular characterization of a middle/low-temperature coal tar by multiple mass spectrometries. *Fuel* **306**, 121435. https://doi.org/10.1016/j.fuel.2021.121435 (2021).
172. Perrault, K. A. et al. A new approach for the characterization of organic residues from stone tools using GC×GC-TOFMS. *Separations* **3**, 16, https://doi.org/10.3390/separations3020016 (2016).
173. Hamm, S., Bleton, J., Connan, J. & Tchapla, A. A chemical investigation by headspace SPME and GC-MS of volatile and semi-volatile terpenes in various olibanum samples. *Phytochemistry* **66**, 1499–1514, https://doi.org/10.1016/j.phytochem.2005.04.025 (2005).
174. Hamm, S., Bleton, J. & Tchapla, A. Headspace solid phase microextraction for screening for the presence of resins in Egyptian archaeological samples. *J. Separative Sci.* **27**, 235–243, https://doi.org/10.1002/jssc.200301611 (2004).
175. Hamm, S., Lesellier, E., Bleton, J. & Tchapla, A. Optimization of headspace solid phase microextraction for gas chromatography / mass spectrometry analysis of widely different volatility and polarity terpenoids in olibanum. *J. Chromatogr. A* **1018**, 73–83, https://doi.org/10.1016/j.chroma.2003.08.027 (2003).
176. Regert, M., Alexandre, V., Thomas, N. & Lattuati-Derieux, A. Molecular characterisation of birch bark tar by headspace solid-phase microextraction gas chromatography-mass spectrometry: A new way for identifying archaeological glues. *J. Chromatogr. A* **1101**, 245–253, https://doi.org/10.1016/j.chroma.2005.09.070 (2006).
177. Lokker, A., Stefanuto, P.-H., Cnuts, D., Rots, V. & Focant, J.-F. Optimization of dynamic headspace sampling conditions for the identification of paleolithic adhesives. *Separation Sci* **7**, e202400085. https://doi.org/10.1002/sscp.202400085 (2024).
178. Ma, X.-M., Lu, R. & Miyakoshi, T. Application of pyrolysis gas chromatography/mass spectrometry in lacquer research: A review. *Polymers* **6**, 132–144 (2014).
179. Chiavari, G., Fabbri, D. & Prati, S. Characterisation of natural resins by pyrolysis - silylation. *Chromatographia* **55**, 611–616, https://doi.org/10.1007/BF02492910 (2002).
180. Holloway, P. J. The composition of suberin from the corks of *Quercus suber* L. and *Betula pendula* roth. *Chem. Phys. Lipids* **9**, 158–170, https://doi.org/10.1016/0009-3084(72)90011-4 (1972).

181. Nip, M. et al. Analysis of modern and fossil plant cuticles by Curie point Py-GC and Curie point Py-GC-MS: Recognition of a new, highly aliphatic and resistant biopolymer. *Org. Geochem.* **10**, 769–778, https://doi.org/10.1016/S0146-6380(86)80014-6 (1986).
182. Bertelli, I. et al. What doesn't meet the eye: Molecular insights into adhesive technologies of Neolithic harvesting tools from Central-North Italy. *Archaeol. Anthropol. Sci.* **17**, 168, https://doi.org/10.1007/s12520-025-02280-w (2025).
183. Rhourrhi-Frih, B. et al. Classification of natural resins by liquid chromatography–mass spectrometry and gas chromatography–mass spectrometry using chemometric analysis. *J. Chromatogr. A* **1256**, 177–190, https://doi.org/10.1016/j.chroma.2012.07.050 (2012).
184. Scalarone, D., Van Der Horst, J., Boon, J. J. & Chiantore, O. Direct-temperature mass spectrometric detection of volatile terpenoids and natural terpenoid polymers in fresh and artificially aged resins. *J. Mass Spectrom.* **38**, 607–617, https://doi.org/10.1002/jms.470 (2003).
185. Guerrini, C. et al. Focusing on Volatile Organic Compounds of Natural Resins by Selected-Ion Flow Tube-Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* **33**, 1465–1473, https://doi.org/10.1021/jasms.2c00042 (2022).
186. La Nasa, J. et al. Archaeology of the invisible: The scent of Kha and Merit. *J. Archaeol. Sci.* **141**, 105577. https://doi.org/10.1016/j.jas.2022.105577 (2022).
187. La Nasa, J. et al. SIFT-ing archaeological artifacts: Selected ion flow tube-mass spectrometry as a new tool in archaeometry. *Talanta* **207**, 120323. https://doi.org/10.1016/j.talanta.2019.120323 (2020).
188. Palmblad, M., van Eck, N. J. & Bergquist, J. Capillary electrophoresis - A bibliometric analysis. *TrAC Trends Anal. Chem.* **159**, 116899. https://doi.org/10.1016/j.trac.2022.116899 (2023).
189. Kaml, I. & Kenndler, E. Characterization of natural organic binding media in museum objects by capillary electrophoresis. *Curr. Anal. Chem.* **3**, 33–40, https://doi.org/10.2174/157341107779314226 (2007).
190. Ahmadi, S., Craig, D. B. & Goltz, D. M. Micellar electrokinetic chromatography with laser-induced fluorescence detection for separation of red and yellow historical dyes. *Chromatography* **1**, 9–23 (2014).
191. Ganzera, M., Stöggl, W. M., Bonn, G. K., Khan, I. A. & Stuppner, H. Capillary electrochromatography of boswellic acids in Boswellia serrata Roxb. *J. Sep. Sci.* **26**, 1383–1388, https://doi.org/10.1002/jssc.200301562 (2003).
192. Doménech-Carbó, M. T. Novel analytical methods for characterising binding media and protective coatings in artworks. *Anal. Chim. Acta* **621**, 109–139, https://doi.org/10.1016/j.aca.2008.05.056 (2008).
193. Stuart, B. H. in *Analytical Techniques in Materials Conservation* 296-340 (2007).
194. Saverwyns, S. & Berghe, I. V. in *Analytical Archaeometry* (eds H Edwards & P Vandenabeele) 0 (The Royal Society of Chemistry, 2012).
195. Luong, J. H. T., Rigby, T., Male, K. B. & Bouvrette, P. Separation of resin acids using cyclodextrin-modified capillary electrophoresis. *Electrophoresis* **20**, 1546–1554 (1999).
196. Qi, S., Ding, L., Tian, K., Chen, X. & Hu, Z. Novel and simple nonaqueous capillary electrophoresis separation and determination bioactive triterpenes in Chinese herbs. *J. Pharm. Biomed. Anal.* **40**, 35–41, https://doi.org/10.1016/j.jpba.2005.06.003 (2006).
197. Gao, R. et al. Simultaneous determination of oleanolic acid, ursolic acid, quercetin and apigenin in Swertia mussotii Franch by capillary zone electrophoresis with running buffer modifier. *Biomed. Chromatogr.* **29**, 402–409, https://doi.org/10.1002/bmc.3290 (2015).
198. Jensen, T. Z. T. et al. A 5700 year-old human genome and oral microbiome from chewed birch pitch. *Nat. Commun.* **10**, 5520. https://doi.org/10.1038/s41467-019-13549-9 (2019).
199. White, A. E. et al. Ancient DNA and biomarkers from artefacts: insights into technology and cultural practices in Neolithic Europe. *Proc. R. Soc. B: Biol. Sci.* **292**, 20250092. https://doi.org/10.1098/rspb.2025.0092 (2025).
200. Matheson, C. D. & McCollum, A. J. Characterising native plant resins from Australian Aboriginal artefacts using ATR-FTIR and GC/MS. *J. Archaeol. Sci.* **52**, 116–128, https://doi.org/10.1016/j.jas.2014.08.016 (2014).
201. Decq, L. et al. Quality control of natural resins used in historical European lacquer reconstructions with some reflections on the composition of sandarac resin (Tetraclinis articulata (Vahl) Mast. *J. Anal. Appl. Pyrolysis* **158**, 105159. https://doi.org/10.1016/j.jaap.2021.105159 (2021).
202. Dellaportas, P., Papageorgiou, E. & Panagiaris, G. Museum factors affecting the ageing process of organic materials: review on experimental designs and the INVENVORG project as a pilot study. *Herit. Sci.* **2**, 2. https://doi.org/10.1186/2050-7445-2-2 (2014).
203. Timoncini, A., Brattich, E., Bernardi, E., Chiavari, C. & Tositti, L. Safeguarding outdoor cultural heritage materials in an ever-changing troposphere: Challenges and new guidelines for artificial ageing test. *J. Cult. Herit.* **59**, 190–201, https://doi.org/10.1016/j.culher.2022.12.003 (2023).
204. Colombini, M. P. et al. A round robin exercise in archaeometry: analysis of a blind sample reproducing a seventeenth century pharmaceutical ointment. *Anal. Bioanal. Chem.* **401**, 1847–1860, https://doi.org/10.1007/s00216-011-5105-1 (2011).
205. Deghetaldi, K. The Organic Analysis of Artworks: Early Challenges and Future Directions. *West. Assoc. Art. Conserv.* **34**, 12 (2012).
206. Georgiou, R. et al. Disentangling the chemistry of Australian plant exudates from a unique historical collection. *Proc. Natl. Acad. Sci.* **119**, e2116021119. https://doi.org/10.1073/pnas.2116021119 (2022).
207. Ebert, B. & Schilling, M. R. A technical analysis of paint media used in twentieth-century Vietnamese lacquer paintings. *Stud. Conserv.* **61**, 52–67, https://doi.org/10.1080/00393630.2016.1227051 (2016).
208. de Carvalho Lopes, D. & Steidle Neto, A. J. in *Comprehensive Analytical Chemistry* Vol. 80 (eds João Lopes & Clara Sousa) 105-125 (Elsevier, 2018).
209. Chen, S. et al. Classification of archaeological adhesives from Eastern Europe and Urals by ATR-FT-IR spectroscopy and chemometric analysis. *Archaeometry* **64**, 227–244, https://doi.org/10.1111/arcm.12686 (2022).
210. Kozowyk, P. R. B., Poulis, J. A. & Langejans, G. H. J. Suberin-related Bands Identified with FTIR are Unreliable to Differentiate Neanderthal Tar Production Strategies. *J. Paleolithic Archaeol.* **8**, 41, https://doi.org/10.1007/s41982-025-00249-8 (2025).
211. Mann, A. K., Appadoo, D., Lenehan, C. E. & Popelka-Filcoff, R. S. Combining ATR far- and mid-infrared spectroscopy to distinguish native Australian plant exudates for cultural heritage analysis. *J. Archaeol. Sci.* **176**, 106167. https://doi.org/10.1016/j.jas.2025.106167 (2025).
212. Rubini, M. et al. Comparison of the performances of handheld and benchtop near infrared spectrometers: Application on the quantification of chemical components in maritime pine (Pinus Pinaster) resin. *Talanta* **221**, 121454. https://doi.org/10.1016/j.talanta.2020.121454 (2021).
213. Koch, T. J. et al. Differences in birch tar composition are explained by adhesive function in the central European Iron Age. *PLoS One* **19**, e0301103, https://doi.org/10.1371/journal.pone.0301103 (2024).
214. Decq, L. et al. Nontargeted pattern recognition in the search for pyrolysis gas chromatography/mass spectrometry resin markers in historic lacquered objects. *Anal. Chem.* **91**, 7131–7138, https://doi.org/10.1021/acs.analchem.9b00240 (2019).
215. Huber, B., Vassão, D. G., Roberts, P., Wang, Y. V. & Larsen, T. Chemical Modification of Biomarkers through Accelerated

Degradation: Implications for Ancient Plant Identification in Archaeo-Organic Residues. *Molecules* **27**, 3331, https://doi.org/10.3390/molecules27103331 (2022).

216. Medeghini, L., Mignardi, S., De Vito, C. & Conte, A. M. Evaluation of a FTIR data pretreatment method for Principal Component Analysis applied to archaeological ceramics. *Microchem. J.* **125**, 224–229, https://doi.org/10.1016/j.microc.2015.11.033 (2016).
217. Hayek, E. W. H. et al. GC/MS and chemometrics in archaeometry. *Fresenius. J. Anal. Chem.* **340**, 153–156, https://doi.org/10.1007/BF00324471 (1991).
218. Van den Berg, K. J., Boon, J. J., Pastorova, I. & Spetter, L. F. M. Mass spectrometric methodology for the analysis of highly oxidized diterpenoid acids in old master paintings. *J. Mass Spectrom.* **35**, 512–533 (2000).
219. Whitten, J. et al. *Varnishes and Surface Coatings: Low Molecular Weight Varnishes*, <https://www.conservation-wiki.com/wiki/Varnishes_and_Surface_Coatings:_Low_Molecular_Weight_Varnishes> (1997).
220. Umekar, M. J. & Yeole, P. G. Characterization and evaluation of natural copal gum-resin as film forming material. *Int. J. Green Pharmacy* 2. https://doi.org/10.22377/ijgp.v2i1.394 (2008).
221. Morkhade, D. M. Evaluation of gum mastic (Pistacia lentiscus) as a microencapsulating and matrix forming material for sustained drug release. *Asian J. Pharm. Sci.* **12**, 424–432, https://doi.org/10.1016/j.ajps.2017.05.002 (2017).
222. Birkett, A. *Conifer Families Evolution and Distribution*, <https://www.treeguideuk.co.uk/conifer-families/> (2025).
223. Ran, J.-H., Shen, T.-T., Wu, H., Gong, X. & Wang, X.-Q. Phylogeny and evolutionary history of Pinaceae updated by transcriptomic analysis. *Mol. Phylogenet. Evol.* **129**, 106–116, https://doi.org/10.1016/j.ympev.2018.08.011 (2018).
224. Ku, S. & Mun, S. P. Characterization of pyrolysis tar derived from lignocellulosic biomass. *J. Ind. Eng. Chem.* **12**, 853–861 (2006).

Acknowledgements

This work was supported by the European Union COST Action Eu-PoTaRCh (CA22155—Network for Forest By-Products: Charcoal, Resin, Tar, Potash), including Virtual Mobility grants E-COST-GRANT-CA22155-99374d6a and E-COST-GRANT-CA22155-21c99766. Participation of P. Kozowyk and B. Ebert was supported by the Research Council of Norway through the NFR project Sticking Stones (project no. 344868). The funders had no role in the design of the study, the collection, analysis, or interpretation of data, or in the writing of the manuscript.

Author contributions

Conceptualisation: J.J.L., M.P.C.; Writing—original draft: I.B., R.C., B.E., A.F., R-M.I., P.K., J.J.L., Z.M., D.N., A.P., E.R., H.S., M.Z., M.P.C.; Writing—review & editing: I.B., R.C., B.E., A.F., R-M.I., P.K., J.J.L., Z.M., D.N., A.P., E.R., H.S., M.Z., M.P.C.; Project administration: M.P.C.; Supervision: M.P.C.

Competing interests

M.P.C. is an Editorial Board Member of Heritage Science. She was not involved in the journal's review of, or decisions related to, this manuscript. The authors declare no competing financial or non-financial interests.

Additional information

Correspondence and requests for materials should be addressed to Jeannette Jacqueline. Łucejko.