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RESEARCH

Pyrotechnology and lipid biomarker variability in pine tar production

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Abstract

Tar or pitch produced from pine resin and wood played an important role in the past as an adhesive, waterproofing and medicinal product. However, the formation and biomolecular composition of pine tar produced only from resin under different combustion conditions (i.e., temperature and oxygen availability during heating) has not been as widely investigated as pine tar produced by dry distillation of wood or birch bark tar, for which an extensive literature is available. This lack of information hampers technological interpretations of biomolecular data obtained from organic residue analyses of archaeological pine tar products. In this study, we performed controlled laboratory heating sequences with pine resin (*Pinus canariensis*) at 150, 250, 350 and 450 ºC under both oxygenated and oxygen-limited conditions, and analyzed the products using gas chromatography-mass spectrometry (GC-MS). A control unheated resin sample was also analysed. We found that the formation of pine tar from resin occurs around 250–350 ºC under both oxygenated and oxygen-limited atmospheres. We also present and discuss the lipid biomarkers of pine resin and its combustion products according to changes in temperature and oxygen availability. Our reference data provide new information for the biomolecular identification of archaeological pine tar products and show potential for shedding light on the conditions in which tar was manufactured by ancient populations in different contexts.

Keywords Lipid biomarkers · Pine tar · Pine resin · Abietane-class diterpenoids · Methyl dehydroabietate · Anthropogenic combustion

Introduction

Tar or pitch is a dark coloured substance formed by the pyrolysis or combustion of biomass (Lobert and Warnatz 1993; Colombini and Modugno 2009; Li and Suzuki 2010; Adachi et al. 2019). It was commonly obtained in the past by hard-heating plant materials such as birch bark or conifer resin and wood (Colombini and Modugno 2009; Duce et al. 2015). It is among the oldest synthetically produced materials, dating back to the Middle Palaeolithic (Koller et al. 2001; Mazza et al. 2006; Niekus et al. 2019). Since then, tar has been widely used by ancient populations as a glue, a waterproofing agent and a drug for its adhesive, hydrophobic and medicinal properties, respectively (Colombini and Modugno 2009; Duce et al. 2015; Barnes and Greive 2017; Rageot et al. 2019).

In archaeology, the term "tar" usually refers to the initial dark-coloured viscous product obtained from the heating of resinous materials, while "pitch" is commonly used to refer to the thicker substance derived from further heating of the

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tar to drive off volatiles, and the materials derived from the dry distillation or pyrolysis of wood (Evershed et al. 1985; Pollard and Heron 2008; Kozowyk et al. 2020). However, in the literature the two terms occasionally convey ambiguity. Some authors employ the terms tar and pitch indistinctly or give them different meanings (Kozowyk et al. 2020 and references therein). For simplicity and for the purpose of this paper here we broadly use the term tar to refer to all dark-coloured viscous liquid or solid products obtained from the heating or pyrolysis of both resin and woody materials and that have been produced and used in the past for different purposes.

The investigation of past tar products has focused on its molecular identification in the archaeological record and on approaching the technical processes underlying its production and exploitation. Tar is an amorphous material requiring chemical analysis for its identification (Ribechini 2009). Lipid biomarker analysis through gas chromatography coupled with mass spectrometry (GC-MS) has shown to be an efficient technique for the characterization of archaeological tar residues (Colombini et al. 2005b; Ribechini 2009). Since the 1980s, GC-MS analyses of tar residues on different archaeological objects (e.g., stone tools, ceramics, bones), and in different contexts (e.g., kilns, shipwrecks, sediments) have contributed to a better understanding of plant exploitation in the human past (Evershed et al. 1985; Colombini et al. 2003; Pollard and Heron 2008; Abdel-Maksoud et al. 2021).

These studies have revealed that most archaeological tar products derive from birch (*Betula* spp.) and conifers (mainly *Pinus* spp.) (Mills and White 1987; Beck et al. 1997; Hjulström et al. 2006; Rageot et al. 2019), which are easily distinguished by GC-MS due to their different molecular fingerprints. Between these two kinds of tar, birch bark tar has received more attention in archaeological investigations due to its early and widespread occurrence in the prehistoric record. Its potential to shed light on the technical knowledge of Neanderthals and other prehistoric societies has resulted in extensive research (Koller et al. 2001; Niekus et al. 2019; Koch and Schmidt 2021). Thus, there is information on the chemical composition of birch tar (mainly pentacyclic triterpenes such as lupeol and betulin and their degradation markers), and its production process, which involves hard-heating treatments (i.e., between 220–500 ºC depending on the method), generally under reduced or limited-oxygen conditions (Rageot et al. 2019 and references therein; Koch and Schmidt 2021 and references therein), although its formation under oxygenated conditions is also possible (Schmidt et al. 2019).

Pine tar, usually produced through dry distillation of wood, has also played an important role in the past. Although the origin of this technology remains unknown, the first evidence of conifer tar production may date back to the European Neolithic (Ottaway 1992; Mitkidou et al. 2008; Rageot et al. 2019; Breu et al. 2023), becoming widespread in the archaeological record since Antiquity mainly as a waterproofing product to caulk the seams of ships and vessels (Robinson et al. 1987; Connan and Nissenbaum 2003; Colombini et al. 2003, 2005a; Romanus et al. 2009; Dimitrakoudi et al. 2011; Jerković et al. 2011; Bailly et al. 2016; Font et al. 2007). In the 16th to 19th centuries, pine tar production intensified exponentially, as large quantities of this product were demanded by European navies and commercial fleets (Evershed et al. 1985; Reunanen et al. 1989; Hjulström et al. 2006). Molecular identification of archaeological tar products from these historical contexts through the identification of pine tar biomarkers have played an important role in these investigations.

Archaeological pine resin and tar lipid biomarker identification relies on modern reference samples. The main lipid constituent in fresh pine resin is abietic acid, although its oxidation products, such as dehydroabietic acid and 7-oxodehydroabietic acid (which can also derive from pimaric acids (Medeiros and Simoneit 2007)), may also occur in significant quantities due to diagenetic alteration (Colombini et al. 2005b; Pollard and Heron 2008). When resinous materials are heated, diterpenoid molecules undergo dehydrogenation, decarboxylation, methylation/demethylation, aromatization and dealkylation. These transformations give rise to the formation of new compounds of varying weight and aromaticity such as norabietatrienes (18-norabieta-8,11,13-triene and 19-norabieta-8,11,13-triene), retene, methyl dehydroabietate and phrenantrenes derivatives, among others (Fig. 1) (Pollard and Heron 2008; Colombini and Modugno 2009; Jerković et al. 2011; Duce et al. 2015). These compounds may be used as suitable pine tar biomarkers, and ratios of the proportions between them may provide technological information (i.e., combustion conditions and raw materials) (Evershed 1993; Beck et al. 1997; Pollard and Heron 2008). Other compounds such as anhydrosugars, alkyl guaiacols and alkyl guaiacyl dehydroabietates have also been proposed as useful wood tar biomarkers (Bailly et al. 2016 and references therein).

However, our knowledge on pine tar lipid biomarkers is based on contemporary laboratory-produced or purchased end-products, which are usually manufactured through dry distillation (pyrolysis) of wood or uncertain processes. A single study (Beck et al. 1997) analyzed the lipid composition of tar produced only from resin heated at different temperatures, but the authors also employed pyrolysis to produce tar. Laboratory resin-derived tar production experiments that control temperature and oxygen availability are lacking. Thus, pine tar formation and the biomolecular changes occurring during the tar production process under different combustion conditions are not well understood. Such knowledge gaps hamper technological interpretations

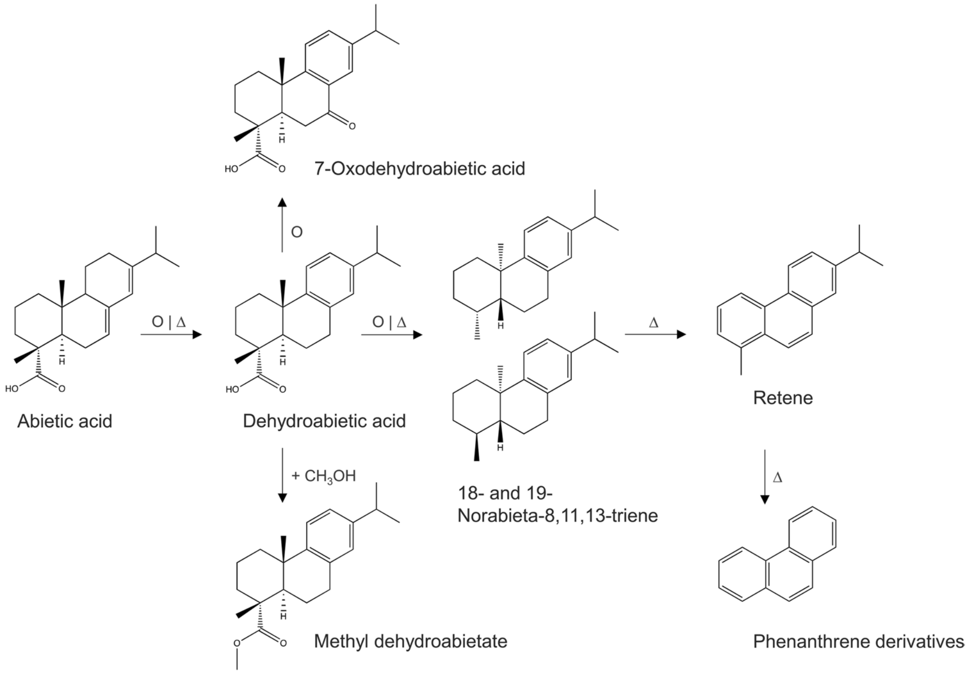

Fig. 1 Simplified scheme for the degradation pathway of the main abietane-class diterpenoids and aromatic derivatives. Δ (thermal alteration) and O (oxidative diagenesis) indicate the main processes governing molecular degradation as discussed in the text

of archaeological pine tar products based on biomolecular data. Bridging these gaps is crucial for identifying and better understanding the exploitation of pine resin and its pyrogenic products in different archaeological contexts. Although the anthropogenic transformation of resin into tar through heat has been documented ethnoarchaeologically in native American sites (Odegaard et al. 2014), archaeological evidence for this type of tar production remains scarce.

Here, we performed controlled laboratory heating sequences with pine resin (*Pinus canariensis*) at 150, 250, 350 and 450 ºC under both oxygenated and oxygen-limited conditions and analysed the products as well as a control unheated resin sample using gas chromatography-mass spectrometry (GC–MS). By contributing reference data for the formation of pine tar from resin according to temperature and oxygen availability, and for the chemical modifications that occur in the products under these different heating conditions, we aim to facilitate the identification and technological characterization of archaeological pine tar residues.

Materials and methods

Chemicals and consumables

Solvents and standards were used as received, without further purification. Dichloromethane (purity ≥ 99.8%), methanol (purity ≥ 99.9%), hexane (purity ≥ 97%), and ethyl acetate (purity ≥ 99.7%) Chromasolv® for HPLC grade were provided by Honeywell (Seelze, Germany). Sand of 50–70 mesh particle size and silica gel technical grade, pore size 60 Å, 70–230 mesh 63–200 µm were provided by Sigma-Aldrich (Madrid, Spain). Silylating mixture N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) + trimethylchlorosilane (TMCS) 99:1 v/v were supplied by Sigma-Aldrich. Milli-Q water was deionized by using a Milli-Q gradient system A10 (Millipore, Bedford, MA, USA). Sand and silica gel were combusted at 550 °C for 3 h before the use.

Due to the high variety of molecules found, representative compounds were selected to quantify the analytes. Anthracene (CAS: 120-12-7, purity 100%), methyl abietate (CAS: 127-25-3 mg/L in DCM, purity 100%) and coprostanol (CAS: 360-68-9, purity 98%) were acquired from Sigma-Aldrich. Sigma Aldrich also provided acenaphthene-d10 (CAS: 15067-26-2, purity 99%), 5α-androstane (CAS: 438-22-2, purity ≥ 99.9%) and 5α-androstan-3β-ol (CAS: 1224-92-6, purity 100%) used as internal standards (IS). Individual stock solutions in DCM at 400 mg/L were prepared and diluted to produce working mixtures.

Pasteur pipettes and glass wool were from VWR International (Barcelona, Spain). Non-volumetric glassware was automatically washed and thermally disinfected at 93 °C, dried at 120 °C for 1 h and combusted at 550 °C during 3 h. Volumetric glassware was cleaned in an ultrasonic bath initially with Derquim + universal detergent (Panreac-AppliChem, Barcelona, Spain) (10 min), then with tap water (10 min), and finally with Milli-Q water (10 min). Then, volumetric material was rinsed five times with MeOH.

Samples

Resin was collected from a dead pine tree (*Pinus canariensis*) in the pinewood forest of Arico (Tenerife, Canary Islands) at ~1600 m-high altitude in October 2020 (Fig. S1). The tree was located far from any road or anthropogenic contamination sources. Only resin that naturally oozed out from the trunk of the tree was taken. The samples were collected wearing nitrile gloves, packed in aluminium foil, and stored at −20 ºC until further treatment.

Experimental setup

The resin samples (0.3035–9.9888 g, Table S1) were introduced and heated in Al foil-lined ceramic crucibles (4.2 cm diameter × 2.4 cm height) under both oxygenated and oxygen-limited conditions at 150, 250, 350 and 450 ºC during 1 h in a muffle furnace, applying a ramp rate of 26 ºC/min (Kuo et al. 2008). Oxygen-limited conditions were achieved by wrapping the crucibles with Al foil before heating (Wiesenberg et al. 2009; Jambrina-Enríquez et al. 2018). After heating, the combustion products were cooled down overnight in the closed muffle furnace. Mass loss (%) was calculated by weighing the samples together with the crucibles before and after combustion. Subsequently, the samples were removed from the Al foil-lined crucible for lipid extraction.

Lipid extraction, analysis and quantification

Lipid extraction and GC-MS analysis were conducted at the Archaeological Micromorphology and Biomarkers Laboratory (University of La Laguna, Tenerife, Spain) following the procedure described by Jambrina-Enríquez et al. (2018, 2019). Lipids were extracted from unheated and heated resin samples (0.2247–0.6111 g) with dichloromethane/methanol (DCM:MeOH, 9:1, v:v) by ultrasonic extraction (3 × 30 min) followed by centrifugation (3 × 10 min at 4700 rpm) and filtered through annealed glass wool and glass microfiber filter. Since no tar was not obtained by heating the resin at 450 ºC during 1 h under both oxygenated and oxygen-limited conditions, these samples were discarded from the lipid analysis.

An aliquot of the total lipid extract (TLE) was fractionated into different polarity fractions through a silica gel column filled with glass wool, 0.1 g pure quartz sand and 1 g of activated silica using several organic solvents mixtures (Table 1). Linear hydrocarbons (fraction 0) were eluted with 3/8 of column dead volume (DV ≈ 1.5 mL) in hexane and discarded. Then, four fractions were eluted for analysis: fraction 1 (aromatics), eluted with 2DV in hexane:DCM (8:2, v/v), fraction 2 (ketones, esters and aldehydes), eluted with 2DV in DCM, fraction 3 (alcohols, terpenes and steroids), eluted with 2DV in DCM/ethyl acetate (EtOAc) (1:1, v/v), and fraction 4 (fatty acids, diols and other more polar compounds), eluted with 2DV in MeOH. All the fractions were dried under a N_2 flow.

After the addition of 1 µL of acenaphthene-d10 (400 mg/L in DCM) to F1 and 3 µL of 5α-androstane (400 mg/L in DCM) to F2 as internal standards (IS), the volumes were completed to 50 and 150 µL DCM, respectively. An aliquot of the fractions 3 and 4 were combined and silylated (in DCM) with 100 µL of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) + trimethylchlorosilane (TMCS) 99:1 v/v at 80 ˚C for 60 min and using 3 µL of 5α-androstan-3β-ol (400 mg/L in DCM) as IS. Subsequently, the extracts were dried under a N_2 flow and reconstituted with 150 µL DCM before analysis.

All lipid fractions were analysed twice using a gas chromatography (GC) system coupled to a single quadrupole (Q) mass spectrometer (MS) (GC-Agilent 7890B, MSD Agilent 5977A) equipped with a multimode injector (MMI) and a HP-5 ms capillary column ((5%-phenyl)-methylpolysiloxane phase, 30 m length × 0.25 mm i.d., 0.25 mm film thickness). The GC was programmed to an initial temperature of 70 ºC for 2 min heated with a heating rate of 12 ºC/min to 140 ºC and to a final temperature of 320 ºC with a heating rate of 3 ºC/min and held for 15 min. Helium was used as the carrier gas with a flow of 1 mL/min. The multimode injector was held at a split ratio of 5:1 at an initial temperature of 70 ºC during 0.85 min and heated to 300 ºC at a programmed rate of 720 ºC/min. The MS operated in full-scan mode (*m/z*

Table 1 Lipid fractionation procedure

Fraction number	Main lipid compounds	Elution volume	Mobile phase	Derivatization method	Internal standard
0 (Discarded)	Linear hydrocarbons	3/8 dead volume (DV)	Hexane	-	-
1	Aromatics	2 DV	Hexane:DCM (8:2, v/v)	Not derivatized	Acenaphthene-d10
2	Ketones, esters and aldehydes	2 DV	DCM	Not derivatized	5α-androstane
3	Alcohols, terpenes and steroids	2 DV	DCM: EtOAc (1:1, v/v)	Silylation	5α-androstan-3β-ol
4	Fatty acids, diols and other more polar compounds	2 DV	MeOH	Silylation	5α-androstan-3β-ol

Table 2 Total concentrations (μg/gsample) of abietic acid, dehydroabietic acid, 7-oxodehydroabietic acid, methyl dehydroabietate, 18-norabieta-8,11,13-triene, 19-norabieta-8,11,13-triene and retene present in the unheated resin sample and in the products resulting from heating resin at 150, 250 and 350 °C under oxygen-limited and oxygenated conditions. The fragment ions selected for the quantification of the compounds and the lipid fractions in which they mainly eluted are also indicated. d: detected (concentration below the limit of quantification); nd: not detected

Compound	Lipid fraction	Fragment ions (*m/z*)	Unheated resin	Oxygen-limited conditions			Oxygenated conditions		
				150 °C	250 °C	350 °C	150 °C	250 °C	350 °C
Abietic acid (TMS)	3–4	302, 259, 287	8340.66 ± 59. 87	7006.29 ± 46.04	5185.14 ± 5.63	616.89 ± 54.70	19,844 ± 124.64	3831.04 ± 29.92	nd
Dehydroabietic acid (TMS)	3–4	239, 357, 372	9595.58 ± 51.12	8890.41 ± 41.25	8556.87 ± 87.74	8477.12 ± 20.11	21,265.41 ± 123.79	8521.55 ± 82.90	1960.18 ± 118.63
7-Oxodehydroabietic acid (TMS)	3–4	253, 268, 386	2222.28 ± 82.87	3096.68 ± 58.78	4488.63 ± 21.72	4693.29 ± 56.70	4905.25 ± 86.07	4656.94 ± 106.74	689.36 ± 77.52
Methyl dehydroabietate	2	239, 299, 314	1268.71 ± 26.13	424.13 ± 8.64	185.40 ± 3.66	424.84 ± 3.28	697.69 ± 9.21	160.21 ± 1.17	285.25 ± 1.16
18-Norabieta-8,11,13-triene	1	241, 159, 256	1.40 ± 0.03	9.41 ± 0.03	12.11 ± 0.07	10.71 ± 0.08	2.16 ± 0.03	0.93 ± 0.02	10.46 ± 0.04
19-Norabieta-8,11,13-triene	1	241, 159, 256	0.08 ± 0.01	1.71 ± 0.01	4.02 ± 0.06	7.02 ± 0.01	0.08 ± 0.01	0.36 ± 0.01	9.78 ± 0.02
Retene	1	219, 234, 205	d	0.93 ± 0.03	27.71 ± 0.01	29.00 ± 0.21	0.11 ± 0.04	5.35 ± 0.06	28.90 ± 0.51

40–580), with an electron ionization energy of − 70 eV and temperatures of 280 °C, 230 °C, and 150 °C for transfer line, ion source, and Q, respectively.

Lipid compounds were identified using the NIST mass spectra library, published mass spectra data, and the order of elution reported in the literature for isomers (e.g., Evershed et al. 1985; Simoneit and Mazurek 2007; Duce et al. 2015). The concentrations of the main abietane-class compounds (i.e., abietic acid, dehydroabietic acid, 7-oxodehydroabietic acid, methyl dehydroabietate, 18-norabieta-8,11,13-triene, 19-norabieta-8,11,13-triene and retene, which were chosen here as key compounds because they are the most diagnostic compounds of pine resin and tar (Modugno and Ribechini 2009)) (Fig. 1) were quantified using instrumental calibration curves based on analyte peak area/IS peak area ratios. Those calibration curves were obtained by injecting three times six increasing concentrations ($n = 6$) for each standard compound (anthracene for F1, methyl abietate for F2, and coprostanol for F3-4) and the concentrations for the IS indicated before. Those standards were selected due to their similar retention times to the quantified compounds. The compound areas were taken in the EIC (extracted ion chromatogram) mode by selecting the three most specific and intense fragments of the compounds (Table 2). The concentrations were normalised to sample weight and expressed as μg of individual compound per gram of sample (μg/g sample). Other compounds were only identified, and their presence/absence is presented in the Supplementary Information.

Results and discussion

The formation conditions of pine tar

Our resin heating sequences under both oxygenated and oxygen-limited conditions yielded similar products, producing recognizable amounts of tar between 250 and 350 °C (Fig. 2b, c, f, g). These tar products are distinguished as a black, shiny, homogeneous substance, solid at room temperature, and viscous and sticky when warming. However, only small masses of this homogeneous tar product were formed at 350 °C under oxygenated conditions (Fig. 2g). The main product formed under these combustion conditions was visibly charred, and is brittle and flaky in texture, possibly an unsuitable end-product. In contrast, combustion at lower temperatures, i.e., 150 °C, under both oxygenated and oxygen-limited conditions produced brownish, translucent resin (Fig. 2a, e). High temperatures, i.e., 450 °C, resulted in the formation of matt, non tar-like residues of different texture according to oxygen conditions (Fig. 2d, h). A limited oxygen supply during heating at 450 °C produced black, soot-like residues (Fig. 2d), while the full availability of oxygen

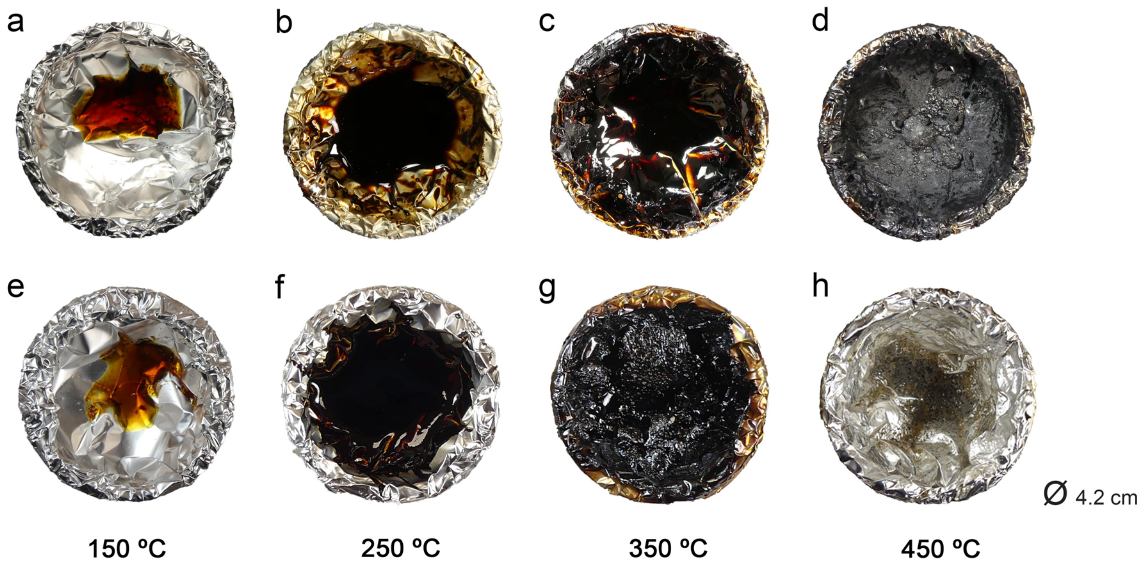

Fig. 2 Al foil-lined ceramic crucibles (4.2 cm diameter × 2.4 cm height) with resin heated (1 h) at different temperatures under oxygen-limited (**a**, **b**, **c**, **d**) and oxygenated (**e**, **f**, **g**, **h**) conditions

during combustion at the same temperature resulted in the formation of greyer, flakier, ashy residues (Fig. 2h).

As expected, mass loss increased with rising temperatures under both conditions (oxygenated and oxygen-limited) but was more significant under oxygenated conditions (Fig. 3; Table S1). This can be explained by oxygen enhancing the combustion process and higher volatilization of the resin in uncovered crucibles. Greater resin mass loss under oxygenated combustion suggests a higher efficiency of tar production under oxygen-limited conditions.

Comparing our results with previously published data, Beck et al. (1997) reported pine tar formation through *Pinus halepensis* resin pyrolysis after 30 min using the kettle method at 300, 350, 400 and 450 °C. Similarly, Colombini et al. (2005b) reported tar production from *Pinus sylvestris* resin through pyrolysis at 600 °C. Although the physical structures of these products are not described, the discrepancy with our data regarding to the formation of tar at 450 °C and 600 °C is probably related with their use of pyrolysis where the airflow is fully restricted during heating (i.e., a reduced atmosphere), preventing the tar from burning. Thus, limitation of oxygen supply during resin heating would enable tar formation at higher temperatures. This is congruent with our tar produced at 350 °C, where the samples under oxygenated conditions resulted in a highly charred, tar-like product (Fig. 2). The different resin heating times employed between those works and ours may also be related to this discrepancy. Whether the differences observed between our data and those cited above are also influenced by the raw material (i.e., different pine species) remains unclear.

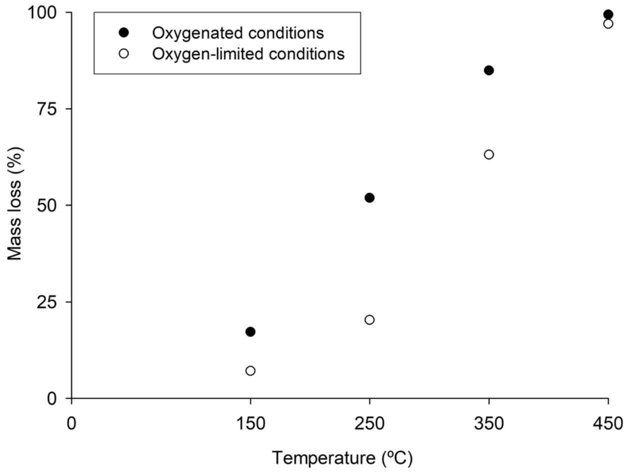

Fig. 3 Resin mass loss percentages for each heating temperature under oxygen-limited and oxygenated conditions

Other authors have reported pine tar samples produced up to 700 °C (Duce et al. 2015). However, these tar samples were produced from wood rather than from resin through dry or destructive distillation-type processes. Egenberg et al. (2002) also studied this tar production method as performed in a traditional Nordic kiln and reported tar products at lower temperatures (100–380 °C). However, since the raw material and system production system are different than ours, their tar formation values cannot be compared with our experimental data from the technological point of view. Also, the temperatures reported by Egenberg et al. (2002) are referred to as “average temperature while collected” rather than tar formation temperatures.

Our experimental data show that pine tar products are technologically simple to manufacture from resin, as high temperatures or oxygen supply control are not indispensable. Unlike wood tar production, specific building structures are not required either. Recent experiments have shown similar results for birch bark tar production (Schmidt et al. 2019; Koch and Schmidt 2022). In this sense, from the technological point of view, pine resin-derived tar could have been manufactured at least since the Middle Palaeolithic, in which combustion structures reached temperatures higher than 250 ºC (Mallol et al. 2013; Herrejón Lagunilla et al. 2019; Leierer et al. 2020) and the use of pine resin has been documented (Degano et al. 2019). Resin containers could be easily replaced by cobbles or by the use of other heating techniques. Unintentional production of pine resin-derived tar in hearths fuelled by resinous pine wood, which are common in Mediterranean Middle Palaeolithic context is also plausible (Cnuts et al. 2017). However, to our knowledge, no conifer tar production evidence has been reported for the Palaeolithic but only the use of resin (Degano et al. 2019).

It should be noted that the quality of our experimental tar produced under both oxygenated and oxygen-limited conditions as adhesive or waterproofing products remains untested. Future mechanical tests on our experimental tar products (alone and/or with additives) (e.g., Kozowyk et al. 2017; Schmidt et al. 2019) are called for. Also, further experiments at shorter temperature ranges (less than 100 ºC) and monitoring the effects of heating time would add greater detail to our dataset and help bridge our current knowledge gaps on pine tar formation.

Biomarker variability in pine tar production

Table 2 shows the total concentrations of the main abietane-class molecules (i.e., abietic acid, dehydroabietic acid, 7-oxodehydroabietic acid, methyl dehydroabietate, 18-norabieta-8,11,13-triene, 19-norabieta-8,11,13-triene and retene) present in the unheated resin sample and in the products resulting from resin heating at 150, 250 and 350 ºC under oxygenated and oxygen-limited conditions. Additional compounds identified are presented in Supplementary Table S2.

The unheated pine resin sample exhibited high concentrations of dehydroabietic acid, followed by lesser amounts of abietic acid and 7-oxodehydroabietic acid. 18-norabieta-8,11,13-triene, 19-norabieta-8,11,13-triene and retene were present in lower concentrations. Methyl dehydroabietate was also identified in significant quantities in the unheated resin.

Heating the resin samples modified the chemical composition of the original material. As temperature increased, dehydrogenation, decarboxylation, aromatization, methylation and dealkylation modifications were observed in the diterpenoid molecules regardless of the degree of oxygen availability during combustion. From the unheated resin to the tar produced at 350 ºC, the abundance of aromatics (18-norabieta-8,11,13-triene, 19-norabieta-8,11,13-triene and retene) generally increased with rising temperature under both oxygenated and oxygen-limited conditions. Under oxygenated conditions, the abundances of abietic acid, dehydroabietic acid and 7-oxodehydroabietic acid increased at 150 ºC and subsequently decreased with temperature. However, at 350 ºC, abietic acid was not found. In contrast, when oxygen was limited, the quantities of abietic acid and dehydroabietic acid decreased as temperature rose. In the case of 7-oxodehydroabietic acid, its abundance increased with temperature under these conditions. Unexpectedly, methyl dehydroabietate was also identified in the heated resin samples, decreasing its concentration at 150 ºC and even more at 250 ºC, and increasing at 350 ºC, under both oxygenated and oxygen-limited conditions.

Although several papers have reported the occurrence of abietic acid as a major compound in fresh (bleed) pine resin (Colombini et al. 2005b; Pollard and Heron 2008), the dominance of dehydroabietic acid in our unheated sample, as well as a significative abundance of 7-oxodehydroabietic acid may be explained by the effect of resin exposure to oxygen while ageing (Colombini et al. 2005b). This process may oxidize abietic acid (and other abietanoic acids or pimaric acids) to form oxidative products such as dehydroabietic acid and 7-oxodehydroabietic acid according to the degradation pathway of diterpenoids with abietane skeletons (Medeiros and Simoneit 2007; Modugno and Ribechini 2009) (Fig. 1). In this sense, the richness of 7-oxodehydroabietic acid in our sample suggests a high degree of oxidation for the diterpenoid compounds, with the addition of two oxygen atoms (Duce et al 2015). The occurrence of 18-norabieta-8,11,13-triene, 19-norabieta-8,11,13-triene and retene in the sample is also probably related with oxidative diagenesis, deriving from abietane-type diterpenoids by microbial degradation or abiotic alterations that may occur in aerobic environments (Wakeham et al. 1980; Simoneit et al. 1986; Otto et al. 2007; Menor-Salván et al. 2010). All these chemical modifications in the resin compounds are consistent with the resin being collected from a pine that probably died several years beforehand.

As suggested by previously published data (Beck et al. 1997), thermal modifications of abietane-class diterpenoids (e.g., dehydrogenation, decarboxylation, methylation) may yield information for the technological interpretation of archaeological pine tar residues. The tar samples (resin heated between 250–350 ºC under both oxygenated and oxygen-limited conditions) yielded a hight abundance of aromatics (Table S2) and the highest concentration of retene among the samples, corroborating the usefulness of this compound to identify tar (Table 2). The formation of this compound usually requires sufficient temperature to induce aromatization of the resin diterpenoids (Robinson et al. 1987; Evershed 1993; Modugno and Ribechini 2009), especially in tar produced only from resin (Odegaard et al. 2014). Odegaard et al. (2014) have shown that when the resin is heated without a woody component, FTIR spectra aromatic bands are observed at temperatures above 210 ºC, which is in agreement with the significant increase in retene at 250 ºC. Norabietatrienes' abundance increases according to temperature rising, especially under oxygen-limited conditions, also indicates the potential of these compounds as thermometric indicators in resin-derived tar production, although the occurrence of these compounds may also be related to diagenetic alterations as discussed above. Lesser abundances of norabietatrienes and retene in the products resulting from resin heating under oxygenated conditions are probably related with a greater volatilization of these compounds in uncovered crucibles. Also, some authors have postulated that the formation of aromatics such as retene usually occurs in oxygen-limited combustion (Weser et al. 1998).

We found major differences between the lipid profiles of tar produced under oxygenated and oxygen-limited conditions at 350 ºC. At this temperature, under oxygenated conditions abietic acid disappeared and scant concentrations of dehydroabietic acid and 7-oxodehydroabietic acid were found. Higher degradation of these compounds under oxygenated combustion at 350 ºC is probably related with a higher oxygen supply during combustion (Duce et al. 2015). This is congruent with a high presence of phenanthrene derivatives and other retene derivatives in tar produced at 350 ºC, especially under oxygenated conditions, as these compounds are formed by further degradation of retene through dealkylation (Radke et al. 1982; Tan et al. 2006; Jerković et al. 2011) (Table S1). Phenanthrene derivatives have been well documented in traditionally produced and archaeological pine tar (Egenberg et al. 2002; Hanuš and Ben-Yehoshua 2013). Also, the brittle, charred texture of the tar produced at 350 ºC under oxygenated conditions also point towards a major thermal oxidative process for this tar product.

Although methyl dehydroabietate may be present in unheated resin from different pine species in scant quantities (Lu et al. 1975; Hjulström et al. 2006), this compound has not been documented in pine tar produced only from resin in other experimental works (Beck et al. 1997). Together with other pyrolytic abietane-type products such as retene, the occurrence of significant relative quantities of methyl dehydroabietate has been widely accepted as a proxy of pine tar production from wood through dry distillation rather than from heating only resin, associating its formation with the reaction of diterpenoid acids with methanol (i.e., methylation) released by the wood during hard heating (Beck et al. 1997; Colombini et al. 2005b; Hjulström et al. 2006; Pollard and Heron 2008; Modugno and Ribechini 2009). As lipid compounds were identified using specific ions (*m/z*) from published mass spectra data and the NIST mass spectra library, misidentification of methyl dehydroabietate (*m/z* 239, 299, 314; NIST matching percentage greater than 90%) in our samples is unlikely (Fig. 4). Likewise, as methylation-derivatization method was not used, the natural occurrence of methyl esters in our samples is assumed (Egenberg et al. 2002). The decrease in concentration of methyl dehydroabietate at 150 and 250 ºC under both oxygenated and oxygen-limited conditions could reflect the compound's thermal degradation. Although unclear, one explanation for the methanol source needed for the natural methylation of dehydroabietic acid in the absence of wood could be the uptake of methanol by the sampled resin from emissions of the decaying plant matter (Warneke et al. 1999). Also, we cannot rule out that the inconsistency that exists in the literature on the presence/absence of methyl dehydroabietate in pine resin (Lu et al. 1975; Beck et al. 1997; Colombini et al. 2005b; Hjulström et al. 2006) is due to methodological issues. Other naturally-methylated compounds such as methyl isopimarate, methyl sandaracopimarate, methyl abietate or methyl 6-dehydroabietate have also been identified in some of the heated resin samples (Table S1).

Because of the occurrence of methyl dehydroabietate in our samples, some caution is needed when matching the presence of this compound in archaeological tar residues with pine tar production through dry distillation of woody materials, especially when low total concentrations of this compound are present and the archaeological context is unclear regarding tar production technology such as the Palaeolithic contexts where no specific tar production structures have been documented. Thus, we recommend quantifying and working with total concentrations rather than only with the relative abundances of the tar biomarkers, as has been the case up to now in archaeological research concerning pine tar products. Other compounds such as alkyl guaiacols or alkyl guaiacyl dehydroabietates (Bailly et al. 2016) therefore have greater potential for the identification of wood tar and its differentiation from tar produced by heating resin, as none of these biomarkers were found in our samples. Also, as methyl dehydroabietate may be found in unheated resin, its single presence should not be used as pyromarker. In this sense, our findings agree with the interpretation of the Middle Palaeolithic lithic residues from Sant'Agostino cave (Italy) as Pinaceae resin rather than tar, based on the presence of methyl dehydroabietate but no aromatics such as retene (Degano et al. 2019). However, the original presence of retene, which could have been volatilized or degraded through time, cannot be ruled out.

Future analyses of resin and tar samples (ideally also from other *Pinus* species) in different states of degradation, as well as further experiments at smaller temperature and heating ranges, as proposed before, are needed to expand our reference data and shed more light on the degradation pathway of abietane-class compounds during resin-derived tar

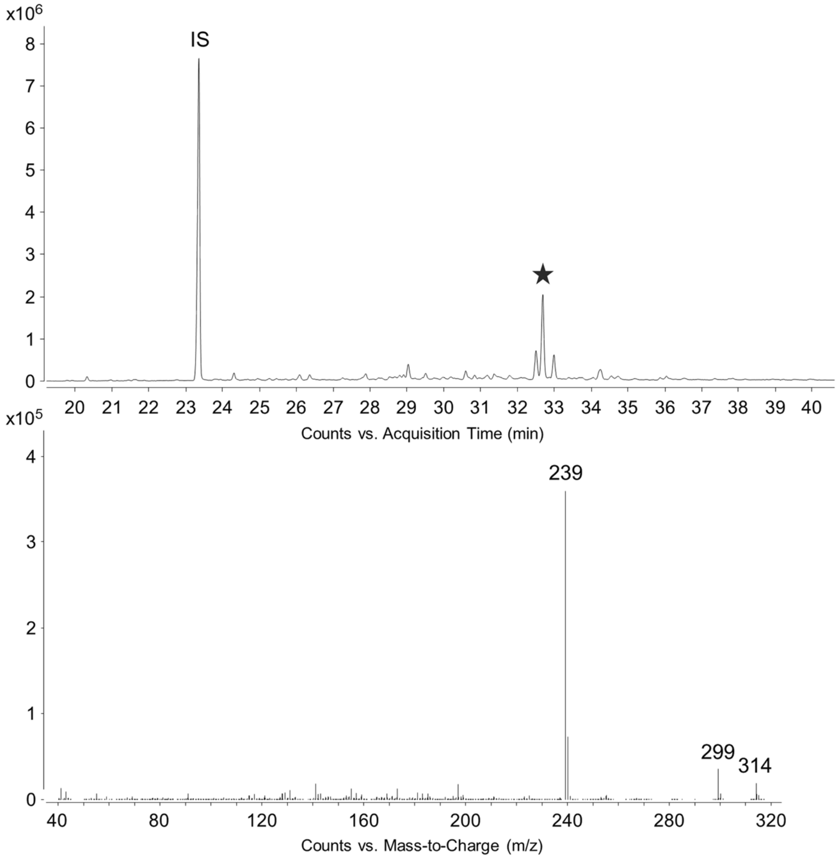

Fig. 4 Partial total ion chromatogram of lipid fraction 2 from resin heated at 350 ºC under oxygen-limited conditions indicating (black star) the methyl dehydroabietate peak (above) and its mass spectra (below)

production and diagenesis. This is crucial for understanding the chemical alterations that resin and tar products undergo under different diagenetic conditions and facilitate its identification in archaeological contexts.

Conclusions

Our controlled laboratory heating sequences have shown that the formation of pine tar produced through heating resin occurs around 250–350 ºC under both oxygen-limited and oxygenated conditions, although the former conditions were found to be more efficient in tar production. As temperature increased, dehydrogenation, decarboxylation, aromatization, methylation and dealkylation modifications were observed in the diterpenoid molecules under both oxygen-limited and oxygenated conditions, with the formation of retene as the main thermometric indicator of tar production. The hitherto undocumented occurrence of methyl dehydroabietate in pine tar produced by heating resin alone entails that some caution is needed when matching the presence of this compound in archaeological residues with tar produced through dry distillation of wood. Overall, our experiments provide new reference data for the identification and interpretation of pine tar residues preserved in archaeological contexts, highlighting their potential as proxies of technology and plant use among past human societies. Expanding our pyrotechnological and biomolecular data in the future will shed light on the degradation and formation processes of abietane-class molecules under different diagenetic and combustion conditions, as well as on the quality and suitability of resin-derived tar.

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Declarations

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