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Chemical analyses reveal dual functionality of Early Mesolithic birch tar at Krzyż Wielkopolski (Poland)

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ABSTRACT

Birch bark tar played an important role as an adhesive in the European Middle Palaeolithic and Mesolithic with key practical functions. For the Mesolithic in northern Europe, tar is suggested to have a variety of functions, including decorative, on various artefacts such as amber beads, antler and bone objects. However, no chemical characterisation has been conducted to confirm the organic composition of such decorations. To address this gap, we conducted organic residue analysis on archaeological samples taken from three artefacts excavated at the Early Mesolithic site Krzyż Wielkopolski (Poland). These include a wooden shaft, an antler point, and a perforated antler object with ornamental engravings. We further replicated two potential aceramic birch bark tar production techniques and employed Principal Component Analysis (PCA) for molecular differentiation. Our results show that birch bark tar served a dual functionality in tool hafting and ornamentation at Krzyż. We found compositional differences among archaeological samples, but comparing these results to experimental data presents significant challenges. Our findings shed light on birch bark tar versatility, and imply more widespread use of birch bark tar as a decorative element in the European Mesolithic than has hitherto been recognised.

1. Introduction

Birch bark tar (hereafter referred to as birch tar) is a material used for a variety of everyday purposes throughout prehistory. It is the earliest known human-made adhesive, employed by Neanderthals in the Middle Palaeolithic (Grünberg et al., 1999; Mazza et al., 2006; Niekus et al., 2019). In these early contexts, the use of other adhesive materials, for example bitumen, both in Europe (Schmidt et al., 2024) or in the near East (Boëda et al., 2008; Hauck et al., 2013), and Pinaceae resin in central Italy (Degano et al., 2019), is also evidenced. In subsequent periods, birch tar is continuously found in archaeological contexts up to the Medieval period (Hayek et al., 1990; Urem-Kotsou et al., 2018; Regert et al., 2019; Stacey et al., 2020; Rageot et al., 2021; Little et al., 2022; Bernardini et al., 2023; Ren et al., 2023; Koch et al., 2024b). This wider distribution of birch tar may partly be due to its strong adhesive properties (Kozowyk et al., 2017a; Schmidt et al., 2021, 2022; Koch and Schmidt, 2023), excellent preservation (Kozowyk et al., 2020) and

hydrophobic properties (Kabaciński et al., 2023). The oldest pieces of birch tar were used for the backing of stone tools (Mazza et al., 2006; Niekus et al., 2019; Schmidt et al., 2023), but it gained a more diverse functionality during the Mesolithic, notably in northern Europe (for an overview, see Little et al., 2022).

Mesolithic uses of birch tar include hafted composite tools and nondescript lumps, some bearing tooth imprints often interpreted as chewing marks (Aveling and Heron, 1999; Kashuba et al., 2019). Chemical analyses confirmed the use of birch tar as the hafting adhesive on osseous points (Aleo et al., 2023; Kabaciński et al., 2023), for flint inserts on bone (Vahur et al., 2011; Bjørnevad et al., 2019; Osipowicz et al., 2020) or wooden projectile points (Larsson et al., 2016). However, birch tar has been suggested not only to have a utilitarian purpose, but also to have been used as a decorative element. This suggestion has been made for various types of artefacts, such as amber beads, antler axes, bone axes, and daggers (for an overview, see Little et al., 2022). More specifically, multiple pieces of antler are reported as being decorated

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with a black resinous/tarry substance. This black residue sometimes fills an ornamental pattern engraved into the antler (Malmer and Magnusson, 1955, and references therein; Trąbska and Trybalska, 2017). Certain authors suggest birch tar to be the material filling these engravings. Only a small number of chemical characterisations were conducted on the preserved residues to identify their nature. Trąbska and Trybalska (2017) attempted to identify the dark black substance filling an ornamental pattern on an antler artefact from Rusinowo, dating to the Late Palaeolithic (~10700 BCE), using infrared spectroscopy followed by elemental analyses. The results, however, did not allow any organic adhesive material to be detected, and the residue was interpreted as ash remains. Sulgostowska (1997) reports spectral analyses on a black antler decoration, possibly indicating a wood tar of birch origin, however, details on the analysis or results are not given. Despite the growing corpus of accounts mentioning black decorative infills on different types of Mesolithic artefacts in northern Europe, there remains an absence of information on the origin and nature of the material used to enhance these engravings.

To address this gap, we conducted gas chromatography – mass spectrometry (GC–MS) on residues sampled from four artefacts discovered at the Early Mesolithic site Krzyż Wielkopolski, Poland (from here on referred to as Krzyż, see Fig. 1). The site is located on the lower northern terrace of the Noteć River with artefacts being recovered from its sandy terraces. The site has excellent organic preservation due to waterlogged conditions. Previous studies have already shown that birch tar was employed for hafting purposes at this site (Kabaciński et al., 2023). The discovery of additional artefacts with residues from the same site context, recovered during the 2019 excavation campaign, provides the opportunity to test whether birch tar was consistently used, and served more than hafting purposes. Black residues were identified on a wooden shaft, and antler point and a perforated antler object. The latter bears engraved patterns infilled with a black residue. In a first step, all three objects were sampled to identify the adhesive's composition and shed light on adhesive use and function in relation to different artefact

types. Secondly, we compared the tar's molecular signatures with experimentally produced birch tar samples made with aceramic techniques. Regarding the latter, previous studies have found molecular differences using ceramic production techniques (Rageot, 2015; Rageot et al., 2019), however, applying chemical analyses to aceramic production methods has shown significant challenges (Kozowyk et al., 2023; Schmidt et al., 2023; Chasan et al., 2024).

To better understand possible aceramic production processes, we replicated two of the most frequently discussed aceramic production methods: the condensation method (Schmidt et al., 2019; Blessing and Schmidt, 2021) and the raised structure (Kozowyk et al., 2017b; Schenck and Groom, 2018). We did this to narrow down the production technique that might have been employed at Krzyż, while also assessing any potential differences in production linked to the adhesive function, i.e. hafting versus decoration.

2. Materials and methods

2.1. Archaeological samples

We sampled three artefacts discovered during the 2019 excavation at the site Krzyż Wielkopolski 7 in western Poland (Fig. 1), dated to the late Preboreal-Boreal period. A more detailed description of the site context is given in the supplementary material. Two artefacts are likely components of composite tools or weapons. These include a wooden pine (*Pinus* subg. *Pinus*) shaft with black residue towards its proximal end (KRZYŻ-7-2019/23, depicted in Fig. 2b), and an antler point covered by a thicker black substance, primarily on its proximal end (KRZYŻ-7-2019/86). The latter bears a flat impression on one side, suggesting it might have been hafted (left image in Fig. 2a). On the opposite side of the antler point, the residue reveals evenly spaced imprints on its surface (right image in Fig. 2a). The point and shaft discussed here were discovered in different and distant trenches, hence certainly relate to different objects. The third sample was taken from a perforated object



Fig. 1. Map indicating site location of Krzyż Wielkopolski (credit: J. Kabaciński).



Fig. 2. Artefacts with visible residue from Krzyż. (a) Antler point with residues and possible ligature imprint on one side (KRZYŻ-7-2019/86); (b) wooden shaft with residues on its proximal end (KRZYŻ-7-2019/23); (c) fragment of perforated antler object, decorated with engraved patterns that are filled with a black residue (KRZYŻ-7-2019/178, the close-up image is to scale, the smaller image of the entire artefact is not).

crafted from deer antler, featuring ornamental incisions filled with black residue (KRZYŻ-7-2019/178, Fig. 2c). For details on the wood and osseous technology, see the [supplementary material](#). To assess the preservation of biomarkers we sampled bark from a birch trunk recovered in trench T1/2022, dated to the Boreal period, and compared it to a modern bark sample (*Betula pendula*) (for photographs, see Fig. S5 of the [supplementary material](#)). To permanently record the shape of the antler

artefact and the ornamental pattern, it was scanned using a 3D Artec Spider and 3D models were created using Artec Studio v.16. The scan is publicly available at the data repository NAKALA (<https://doi.org/10.34847/nkl.0e8as770>).

2.2. Experimental samples

We conducted an experimental program with the aim of comparing two aceramic birch tar production methods and their molecular signature. For this, we produced 20 reference samples with the two most frequently discussed aceramic birch tar production techniques: the raised structure (Osipowicz, 2005; for details on the production method, see Kozowyk et al., 2017b; Schenck and Groom, 2018) and the condensation method (for details on the production method, see Schmidt et al., 2019). Although more production methods are currently debated (Kozowyk et al., 2017b; Koch and Schmidt, 2022; Chasan et al., 2024), these two have very opposite production parameters that may result in the most significant influence on molecular composition. This is because the raised structure tar is produced in oxygen-depleted, allotherm conditions, whereas tar obtained through condensation is produced autotherm and in open air. In brief, the condensation method consists of directly burning birch bark next to a tilted river cobble onto which the tar then condenses. The raised structure consists of a two-chamber set-up. An upper, earthen dome contains birch bark, and a fire is lit around this sealed dome. Below this, a second underground chamber with a receptacle serves to contain the tar that drips down during the process. Ten samples were produced with each method. Details and images of the tar production can be found in the [supplementary material](#). The raised structures were conducted simultaneously with the aim to reduce variability, with the temperature monitored in 3 of the setups.

2.3. Gas chromatography – Mass spectrometry

The sampled residues were analysed following established methods for archaeological adhesives (Rageot et al., 2019, 2021; Koch et al., 2024b). Samples were crushed and weighed. Tetratriacontane (*n*-C34, 10 µL of 2 mg/mL cyclohexane solution) served as the first internal standard. Sample powders underwent solvent extraction using dichloromethane (DCM) at a ratio of 2–3 mg/mL and two 15-minute sonication cycles. A DCM blank sample was included to check for in-laboratory contamination. A 100 µL aliquot was taken from each sample and dried under nitrogen flow. Each subsample was then derivatized using 50 µL of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 10 µL of DCM, and 2 µL of pyridine (heated for 60 min at 70 °C). After drying the aliquot under nitrogen flow, 90 µL DCM were added. Hexadecane (*n*-C16, 10 µL of a 0.2 mg/mL cyclohexane solution) was added as the second internal standard before injection into an Agilent J&W HP-5MS GC Column 30 m x 0.32 mm x 0.25 µm film thickness). The inlet temperature was set at 300 °C. The oven temperature was programmed to increase from 50 °C (with a 2-minute hold time) to 150 °C at a rate of 10 °C/min and then directly raised to 320 °C at a rate of 4 °C/min, maintaining this temperature for 15 min. GC–MS analyses used a Shimadzu GC 2010 PLUS in splitless injection mode with a column flow of 6 mL/min. Mass spectra were recorded with a Shimadzu QP2010 ultra (electron ionization at 70 eV, *m/z* range 50–950). Compound identification was done through comparison with the NIST library and published data (Ekman, 1983; Hayek et al., 1990; Aveling and Heron, 1998; Rageot, 2015). Internal standards were only added to the experimental samples. The raw GC–MS files of the archaeological and experimental reference samples are publicly available at the data repository NAKALA (<https://doi.org/10.34847/nkl.0e8as770>).

2.4. Statistical analysis

The peak integrals of all identified molecular compounds were extracted from the total ion chromatograms of the archaeological and reference tar samples. The relative abundance of each molecule was calculated to the sum of peak integrals of all identified compounds (for the main compound families detected, see Table 1). The relative abundances served as variables for Principal Component Analysis (PCA). Four

Table 1

Compound categories as used for statistical analysis (PCA). A full list of compounds identified in the archaeological and experimental samples can be found in the supplementary material.

Birch tar biomarkers	Birch tar degradation markers	Fatty acids/diacids
Betulin	Betulone*	Azelaic acid
Lupeol	Lupenone*	Hexadecanoic acid
Betulinic acid	Lupa-2,20(29)-diene	Heptadecanoic acid
Erythrodiol	Lupa-2,20(29)-dien-28-ol	<i>trans</i> -9-Octadecenoic acid
	Allobetulin	Octadecanoic acid
	28-oxoallobetul-2-ene	Eicosanoic acid
	Allobetul-2-ene	Heneicosanoic acid
		<i>cis</i> -13-Docosenoic acid
		Docosanoic acid

*also natural degradation markers found in minor amounts in birch bark, but increased amount through oxidation during birch tar production

different PCA's were made using different combinations of variables: 1) birch tar bio- and degradation markers and fatty acids/diacids (*n* = 20), 2) birch tar bio- and degradation markers (*n* = 11), 3) only birch tar degradation markers (*n* = 7) and 4) only fatty acids/diacids (*n* = 9). The compound categories used for PCA are listed in Table 1.

3. Results

3.1. Chemical identification of archaeological samples

All archaeological samples yielded molecular constituents characteristic of birch tar. The residues from the antler point, wooden shaft and antler decoration contained varying combinations of triterpenoid compounds, including bark biomarkers betulin and lupeol, as well as natural degradation markers associated with oxidation, such as betulone. Lupenone is biomarker, but its amount can increase through oxidation during birch tar production (Ekman, 1983). Degradation markers specifically linked to the production of tar from birch bark, 28-oxo-allobetul-2-ene and allobetulin, align with prior identifications of birch tar (Rageot et al., 2019). Our samples contained a range of saturated and unsaturated fatty acids and diacids, which might be related to the decomposition of suberin during the production (Ekman, 1983). However, the exact origin of these acids and diacids remains unclear for now. Minor traces of diterpenoid compounds (<1% of all identified compounds) including dehydroabietic acid, abietic acid, tetrahydroretene and retene, were identified in all archaeological samples. In addition, we found cholesterol and two derivatives (cholesta-3,5-dien-7-one and cholesta-4,6-dien-3-ol) in the sample taken off the antler decoration (Fig. 3). This sample has a lower abundance of triterpenoid compounds (73 %) and a higher abundance of fatty acids (17 %) compared to the other archaeological tars (Table 2). Cholesterol and its degradation markers might indicate the presence of a fatty substance of animal origin. We further note the presence of a homologous compound series (indicated through asterisk in Fig. 23, mass spectra of each compound in Fig. S4 of the [supplementary material](#)). These elute at retention times 36.04, 37.82 and 39.23, with a possibly related compound eluting at 30.67. The *m/z* 204 and 217 are characteristic for sugar compounds, possibly derived from cellulose (Bae et al., 2012). Levoglucosan, for example, has previously been identified in experimentally made birch tar samples, and could hence be linked to the production process (Kozowyk et al., 2023). The chromatograms for samples KRZYZ-7–2019/86 and KRZYZ-7–2019/23, and a list of identified compounds can be found in the [supplementary material](#).

3.2. Chemical signatures of Boreal versus modern bark

The chromatograms of both bark samples are shown in Fig. S5 of the [supplementary material](#). The modern bark sample (*Betula pendula*)

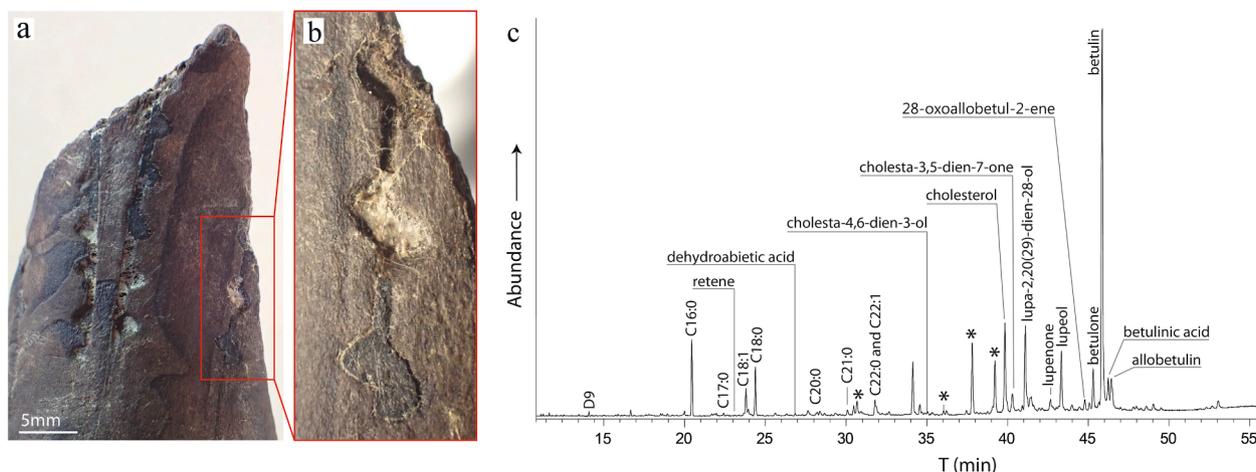


Fig. 3. Results obtained from the black residue filling the engraved decorative pattern on the antler object (KRZYZ-7-2019/178). (a) Photograph of the decorative pattern with black residue filling some of the elements (red frame indicates sampling location before sampling). (b) Close up photograph of the sampled location after sampling (residue was taken from upper half circles). (c) Chromatogram of black substance filling the decorative pattern on the antler. DX = Diacids (X = carbon n), CX:Y = Fatty acids (X = carbon n, Y = n of unsaturations). Asterisk indicates an unidentified homologous compound series (for mass spectra see Figure S4 in the Supplementary Information). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Relative percentages of main molecular families identified in archaeological samples and experimental samples (the latter show average values for each set of 10 experiments). Note that unidentified compounds are not included in the calculation. Lab ID (for the archaeological samples) refers to the sample ID used in the laboratory, but the sample ID is used throughout this study.

Samples	Lab ID	Triterpenoid markers [%]	Fatty acids/diacids [%]	Diterpenoid markers [%]	Cholesterol + derivatives [%]
KRZYZ-7-2019/86 (antler point)	TK8360	97	2	< 1	0
KRZYZ-7-2019/23 (wooden shaft)	TK8363	98	2	< 1	0
KRZYZ-7-2019/178 (antler decoration)	TK8362	73	17	< 1	10
Condensation method	CM01-10	91	8	0	0
Raised structure	RS01-10	85	14	0	0

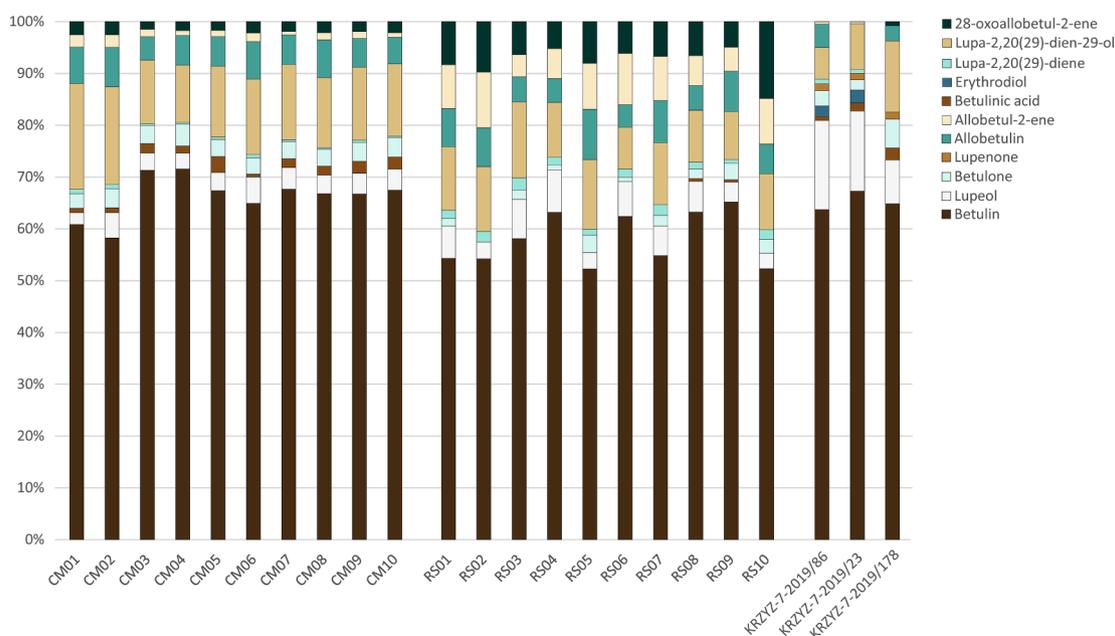


Fig. 4. Relative percentages of birch tar related compounds (as of the sum of all birch tar bio- and degradation markers). CM = Condensation method tar, RS = Raised structure tar, KRZYZ-7-2019/86 = Antler point tar, KRZYZ-7-2019/23 = Wooden shaft tar, KRZYZ-7-2019/178 = Antler decoration tar.

consists in the majority of the biomarkers betulin and lupeol, and to a lesser extent betulonic acid. We further detected betulone, which forms through oxidation from betulin, and sitosterol. This is in line with previous analyses of modern birch bark (Ukkonen and Erä, 1979; Aveling and Heron, 1998). The bark recovered from the Boreal layer in Krzyż shows the presence of the same biomarkers (betulin, lupeol and betulonic acid), and the oxidised products betulone and lupenone (oxidation product forming from lupeol). The commonly referenced biomarker erythrodiol (for example in Ekman, 1983) could not be identified, and lupa-2,20(29)-dien-28-ol (previously mentioned by Aveling and Heron, 1998) was not detected. Ekman (1983) reports erythrodiol as a biomarker of birch bark, but as shown by two previous studies (Hayek et al., 1990; Aveling and Heron, 1998) and the results of this study, it is not always present in modern, or archaeological birch bark. It remains unclear if the absence of some biomarkers is due to environmental influences, degradation, or to the genus, which we could not identify for the Boreal bark.

3.3. Experimental aceramic tar

The temperature measured in three of the raised structures is shown

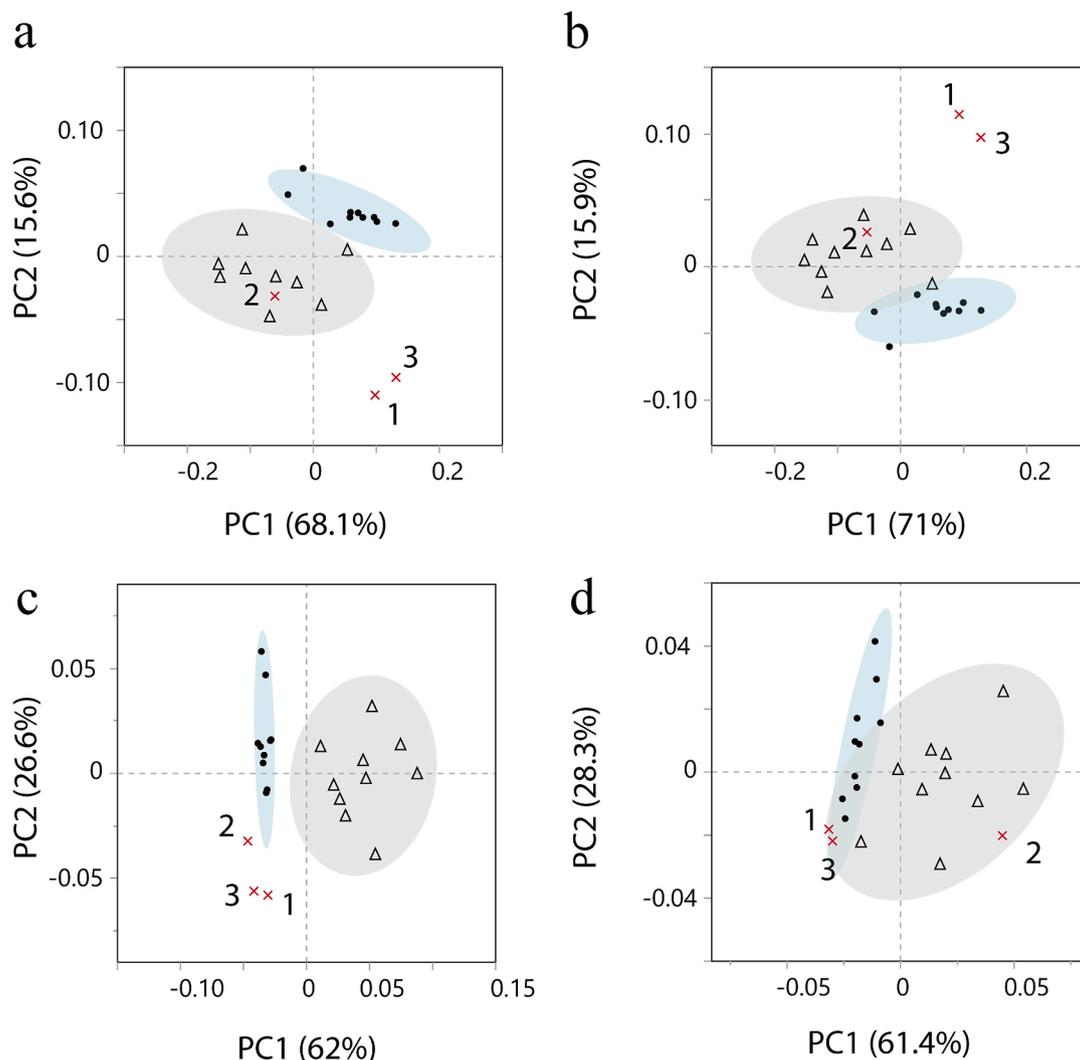


Fig. 5. PCA plots showing the molecular variation (as calculated from relative abundances) among experimental and archaeological samples using different sets of variables: a) all birch tar bio and degradation markers + fatty acids/diacids ($n = 20$) b) all birch tar bio- and degradation markers ($n = 11$), c) natural and anthropogenic birch tar degradation markers ($n = 7$) and d) fatty acids/diacids ($n = 9$). Experimental samples: ● = Condensation method, Δ = Raised structure. × (red) = Archaeological samples: 1 = KRZYŻ-7-2019/86 (antler point), 2 = KRZYŻ-7-2019/178 (antler decoration), 3 = KRZYŻ-7-2019/23 (wooden shaft). Ellipses show 95 % confidence intervals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Statistical comparison (PCA)

PCA allowed us to identify differences between the two experimentally reproduced tar types (CM and RS). The two groups form distinct clusters indifferent to which of the four sets of variables was used to perform the analyses (Fig. 5). RS tar and CM tar can thus be differentiated using birch tar bio- and degradation markers and the fatty acid/diacid profile, or only one of these compound groups. Fig. 5a-b shows a similar differentiation of the archaeological samples in regards to the two experimental groups based on the complete set of triterpenoids and fatty acids/diacids (Fig. 5a) and only the triterpenoid compounds (Fig. 5b). Here, the tar sample from the antler decoration plots with the RS whereas the other two samples from the antler point and wooden shaft are grouped together but apart from the experimental samples. However, when using only the degradation markers found in the birch tars, the opposite can be observed. Fig. 5c shows the tar from the antler decoration plotting slightly closer with the CM. If we use only the fatty acid/diacid profile to differentiate our samples, the reference samples still form clusters but the confidence ellipses slightly overlap. The antler tar lies within the RS and the other two archaeological tars lie in the interface of the two groups. These plots show that depending on which molecular groups (different molecular families but also within triterpenoids) are used for PCA, a different result is obtained. A trend can be seen within the archaeological samples, always differentiating between the antler decoration tar versus the antler point and wooden shaft tars. The latter two plot together indifferently of the variables used, suggesting they are molecularly more similar to each other than to the antler tar. In three of the PCA's (Fig. 5a-c), the two hafting tars plot entirely outside of the confidence intervals of either of the production method clusters. This means that they do not fall within the range of variation of both methods.

4. Discussion

4.1. Limitations and perspectives in molecular differentiation of birch tar production methods

Based on a set of experimental birch tar samples using production methods with ceramics (double-pot and single pot), previous studies showed that specific molecular markers are only found in *per descensum* production systems (Rageot, 2015; Rageot et al., 2019). Three recent studies have tested whether this difference can be found in aceramic birch tar production methods relying on similar principles (Kozowyk et al., 2023; Schmidt et al., 2023; Chasan et al., 2024), but characteristic markers are either not present in the experimental samples or their abundance is too variable to be confidently used for differentiation. This limitation in aceramic conditions hence calls for a different approach. Kozowyk et al. (2023) applied PCA to differentiate four aceramic production methods using a sample set of 7 samples. The authors state that the sample size is likely the reason for inter- and intra-method variation for most compounds, limiting the differentiation between production methods relying on similar principles. Our results, using an increased sample size per method, also show that the CM and RS can be reliably differentiated using different sets of variables (e.g. biomarkers, degradation markers, fatty acids/diacids). Albeit increasing the sample size, we also observe a higher variability in the RS samples (as already shown by Kozowyk et al., 2023). Still, the molecular difference between these methods should be sufficient to identify an archaeological sample if it was made with a similar method. In a recent study, Chasan et al. (2024) showed that when comparing the aceramic methods with the molecular signature of archaeological samples, the choice of variables significantly influenced the outcome of a PCA. Our results stand in line with this finding. By using fatty acids and triterpenoid compounds (Fig. 5a), only triterpenoids (Fig. 5b) or only fatty acids/diacids (Fig. 5d), it seems that the antler decoration tar is molecularly similar to the RS. However, if plotted only with triterpenoid degradation markers (Fig. 5c), it clusters

closer to the CM. Similarly, the hafting tars seem to plot entirely separate from both techniques, which might suggest a completely different method to having been used. Their fatty acid/diacid signature, however, more closely aligns with the CM (Fig. 5d). As a result, we argue that modern experimentally produced birch tar samples can be differentiated, because these have been produced in similar conditions and have undergone only limited post-production degradation caused by natural or anthropogenic factors. It seems all the more challenging to compare archaeological samples to these experimentally replicated tars. This is partly due to anthropogenic alteration of tar through cooking and reuse, but also the unknown degree of degradation over thousands of years through environmental influences and diagenetic processes. Such effects can alter the molecular signature to a point where it no longer resembles its original composition. A recent study using spectroscopic methods to differentiate aceramic tar production, based on molecules that only undergo limited taphonomic processes (in birch tar: suberin), showed that Palaeolithic tar at Königsau was made in an underground, oxygen-depleted condition (Schmidt et al., 2023). Using infrared spectroscopy, in addition to molecular characterisation, may provide a promising approach to fully characterise archaeological birch tar artefacts.

Besides these limitations, our study provides insight into the compositional differences between archaeological samples. We argue that it may be possible to compare archaeological samples with each other using a molecular approach, given that these have likely undergone similar environmental changes, or originate from the same or similar archaeological contexts. This being the case for the three birch tar samples identified here, hafting tars are more similar to each other but different from the tar used for decorative purposes. The differentiation between the samples can be related to both presence and absence, as well as the varying abundances of specific triterpenoid bio- and degradation markers, and fatty acids/diacids. It remains unclear why the abundances vary; it might be due to factors such as the initial production conditions of the tars or post-production treatments, such as cooking or rendering the tar into a more liquid state. For example, it is known that hafting tar requires specific mechanical properties which can be enhanced through cooking (Schmidt et al., 2022). Kabaciński et al. (2023) compared the composition of hafting birch tar (also from Krzyż) to an experimentally made birch tar in slow heating conditions (max. 350° C), which would, according to previous experimentations (Rageot et al., 2019, 2021) produce a liquid tar with low viscosity. It is unclear whether such tar would suffice for hafting purposes and if it does not, it may explain the use of ligatures for additional binding of composite tools at Krzyż. As an alternative explanation, Kabaciński et al. (2023) propose the use of birch tar for its hydrophobic properties (i.e. waterproofing the tool), which might be especially useful if used in aquatic environments (Koch et al., 2024a). Tar which is not used for hafting but only for decoration, may not require the same mechanical properties, as it “only” needs to adhere to the object. Due to the small sample size of archaeological material in this study, we cannot predict whether the same molecular difference would be observed in a larger sample set. What our data allows is to provide a new working hypothesis. A future study on additional decorated and hafted artefacts, from the same contexts/site and other northern European Early Mesolithic sites, is needed to test this assumption.

4.2. Our results in line with previous data on Mesolithic hafting adhesives

Previous chemical analyses on a bone implement discovered at Krzyż found that birch tar was used as a hafting agent to attach a bone point to a wooden shaft, strengthened by bast ligatures (Kabaciński et al., 2023). Birch tar as a hafting adhesive is known from multiple Mesolithic contexts across northern Europe. These hafting contexts may vary, as some objects consist of different component materials, such as bone, wood or stone (Aveling and Heron, 1998; Vahur et al., 2011; Larsson et al., 2016; Bjørnevad et al., 2019; Osipowicz et al., 2020; Aleo et al., 2023; Kabaciński et al., 2023). Our findings of birch tar on an antler point and

wooden shaft therefore fall in line with current knowledge of Mesolithic adhesives in composite hafting technologies. In our case, the point and wooden shaft were found in distant trenches and certainly represent different artefacts, however, they could be linked to the same time period (late Preboreal-Boreal). Ligatures are underlying the birch tar on the implement presented in [Kabaciński et al. \(2023\)](#), and we may hypothesise that the parallel grooves left in the thick tar layer on the point ([Fig. 3a](#) and [Fig. S7a-b](#)) could also be left behind by ligatures attaching two components, in this case however, on top of the tar. Similar composite tools are reported at the contemporary site Friesack in northern Germany ([Gramsch, 1991, 2000](#)). The latter have not yet been subjected to chemical analyses but the use of birch tar for hafting purposes at Krzyż ([Kabaciński et al., 2023](#); and this study) helps strengthen our understanding of the use of the same organic adhesive (birch tar in particular) and hafting technologies in the Early Mesolithic of the north European Plain.

In our samples, we further detected minor traces which might be indicative of a conifer resin/tar (<1%), but we cannot exclude contamination from fire fuel using pine wood. Use of conifer resin is known from earlier (see [Degano et al., 2019](#)) and later contexts ([Mittkidou et al., 2008](#); [Rageot et al., 2019](#)), but clear evidence from the Mesolithic is lacking (see [Croft et al., 2018](#) for an exception). The North European Plain during the Early Holocene was covered by birch and pine forests with some deciduous trees, including elm and hazel ([Ralska-Jasiewiczowa et al., 2004](#)), suggesting an availability of pine resin. This is also supported by the numerous finds of pine wood artefacts at Krzyż ([Kabaciński et al., 2023](#)). Nevertheless, our results, along with the prevalent evidences of birch tar in Mesolithic Europe, suggest that birch tar was preferred over conifer resins, possibly due to its strong adhesive properties and hydrophobicity, as suggested by [Kabaciński et al. \(2023\)](#).

4.3. Implications of our data for decorative residues observed in Mesolithic contexts

Decorated objects, often made of antler or bone, but also amber beads, are well-known in Mesolithic contexts, characterised through geometrical patterns or scenes engraved into the artefact's surface. Multiple studies mention the presence of a resinous or tar-like substance filling these decorative engravings ([Malmer and Magnusson, 1955](#), and references therein; [Sulgostowska, 1997](#); [Petersen, 2013](#); [Molin et al., 2014](#); [Toft and Petersen, 2016](#); [Trąbska and Trybalska, 2017](#); [Little et al., 2022](#)). As a consequence, determining whether a residue was purposefully used to infill decorative engravings is challenging. [Pionka \(2003\)](#) suggests that the dark infill was used to highlight the ornamental patterns on antler objects. An alternative hypothesis, in at least some cases, is that hafting material remained stuck within the incised grooves, as suggested for the bone dagger from Motala, Sweden ([Molin et al., 2014](#)). [Petersen \(2013\)](#) mentions birch tar to fill engraved decorations on an amber pendant of the Maglemose culture in Denmark, but no specifics on the analyses undertaken are provided. Other studies have identified a residue as ash remains ([Trąbska and Trybalska, 2017](#)). The perforated antler from Krzyż, along with similarly decorated bone and antler artefacts dated to the Mesolithic (a similar decorated antler is presented in [Sulgostowska, 1997](#)), presents a more homogenous filling of the engraved lines and half-circles (see [Fig. 3b](#) and [Fig. S7c-d](#)). Furthermore, no indication of hafting or residue on other parts of these decorated antlers are visible. To our knowledge, we provide the first clear chemical identification confirming the use of birch tar for ornamental purposes on antler in the Mesolithic.

It remains unclear, based on our analyses, whether the relatively high amount of cholesterol and its degradation markers in our sample might suggest an intentional mixture with an animal-derived fat or animal glue. Their absence in the antler point's tar make it unlikely that these components originate from the antler itself. Animal glues (made from bone or hide collagen) are rarely discovered in archaeological contexts, likely due to their water solubility ([Kozowyk et al., 2020](#)). The

mixture with birch tar might enhance its preservation, as can be hypothesised for DNA preservation in archaeological birch tar ([Jensen et al., 2019](#); [Kashuba et al., 2019](#)). At the Neolithic site La Draga, Spain, [Rageot et al. \(2021\)](#) found a similar signal of cholesterol and one of its degradation markers in combination with birch tar. At La Draga it was found on a marble bracelet, but it is not clear whether its function was to assemble or decorate the object. Some additives, for example beeswax, are known to act as a plasticiser ([Gaillard et al., 2015](#)) and, if added to plant-based adhesives, it was shown to increase the adhesive's mechanical strength ([Kozowyk et al., 2016](#)). In the case of the antler piece here, adding an animal fat could have provided a more malleable glue which could facilitate the filling of the engravings and also enhance its visual appearance. A thorough investigation on the molecular signature of experimentally composed glues (birch tar with animal fat, or glue), together with tests on its adhesive properties and water-solubility will help us understand the meaning behind these findings in archaeological samples. Our findings provide a promising outlook for future analyses on engraved artefacts recovered from Mesolithic contexts, whilst confirming birch tar was used for ornamental purposes as early as the Early Mesolithic. This yields potential to evaluate the chronological persistence of birch tar use as a decorative element from the Mesolithic onwards, up to the Roman antiquity ([Regert et al., 2019](#)).

5. Conclusion

While previous studies have shown that birch tar was used as a hafting agent at Krzyż, our results broaden this understanding of birch tar functionality to encompass use as a decorative element. This finding is significant because it encourages a closer look for similar decorated objects of the Mesolithic. If a stronger research focus is put on identifying decorative residues, and analytical methods are applied for their characterisation, we can broaden our understanding of birch tar use in the European Mesolithic beyond strictly utilitarian functions. Identifications of birch tar with evidence of animal fat or glue might further allow us to differentiate between adhesive technologies, and identify the advantages such a mixture yields. We show the limitations for the use of biomolecular approaches to characterise archaeological birch tar artefacts in relation to their production techniques. We advocate for caution when comparing the molecular composition of modern experimental tar samples to archaeological ones, especially considering the taphonomic influences are likely to be different or unknown. We propose, however, that a comparison might be possible between archaeological artefacts from the same site or if their archaeological context is similar. Our results have revealed molecular differences between birch tar used for hafting purposes and tar used for decoration. Such variation in function needs to be further tested in future studies drawing on larger sample sets. We argue that a deeper knowledge of the diversity of uses of tar within the Mesolithic material world has real potential to provide new insight into the technological, as well as artistic, choices people made in the production and use of birch tar.

CRedit authorship contribution statement

Tabea J. Koch: . **Jacek Kabaciński:** Writing – review & editing, Resources, Investigation, Funding acquisition. **Auréade Henry:** Writing – review & editing, Visualization, Investigation. **Benjamin Marquibelle:** Writing – review & editing, Visualization, Investigation. **Aimée Little:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Rebecca Stacey:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Martine Regert:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data will be publicly accessible on an online data repository.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jasrep.2024.104591>.

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