

UNVEILING THE ANCIENT CRAFT: RESIN USE IN THE ROMAN ERA AT THE *VILLA* OF PLA DE L'HORTA (GIRONA)

Desvelando el antiguo oficio: el uso de resina en época romana en la villa del Pla de l'Horta (Girona)

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ABSTRACT : In the heart of the historical exploration of the Roman *villa* of Pla de l'Horta, an archaeological site that has unveiled extensive data about ancient wine production and other economic activities in the Antiquity, we can offer new data of interest. Among its many productive facets, one endeavour stands out, the use of resin during the Roman period. This article delves into the origin and use of resin in this Roman settlement, founded at the end of the Republican era and abandoned in the fifth century AD, with a focus on the late Roman phase, where we have detected the use of pitch in the *dolia* of one warehouse. Using anthracological and chemical data, we demonstrate the use of pitch as bitumen to prepare and protect vessels for their use as oil storage. The use of resin as a material for the preparation, maintenance, and repair of large-format ceramic containers is discussed here.

Keywords: Roman *villa*; Biomarkers; Organic Residues; Anthracology; *dolia*.

RESUMEN: En el marco de la vertiente productiva de la *villa* romana del Pla de l'Horta, un yacimiento que ha revelado abundantes datos sobre la producción vinícola y otras actividades económicas de la Antigüedad, podemos aportar nuevos datos de interés. Entre sus múltiples facetas productivas, destaca una actividad: el uso de la resina en la época romana. Este artículo profundiza en el origen y el uso de la resina en este asentamiento romano, fundado a finales de la época republicana y abandonado en el s. V d. C., centrándose en la fase tardorromana, en la que hemos detectado el uso de brea en los *dolia* de un almacén. Utilizando datos antracológicos y químicos, demostramos el uso de la brea como betún para preparar y proteger los recipientes destinados al almacenamiento de aceite. Se considera aquí el uso de resina como material para la preparación, el mantenimiento y la reparación de recipientes cerámicos de gran formato.

Palabras clave: *villa* romana; biomarcadores; residuos orgánicos; antracología; *dolia*.

1. Introduction and objectives¹

In the past, humans extensively utilized substances such as resins, tars, and bitumens. Analyzing the remnants of these materials can provide insights into their botanical origins, acquisition methods, preparation processes, and geographical sources. The examination of natural resins and their derivatives represent a well-established domain within organic residue analysis (Evershed, 2008a: 905-906). Classical references², describe the use of pitch in container maintenance and preparation, potentially to enhance flavours, particularly in wines, favoured in classical times (Orengo *et al.*, 2013: 803). Numerous modern studies on amphoric materials have highlighted the presence of a blackish substance permeating food containers: pitch (Martínez and Petit, 1998: 265; Colombini *et al.*, 2005; Evershed *et al.*, 1985; Mills and White, 1994; Regert *et al.*, 2003; Robinson *et al.*, 1987; Van den Berg *et al.*, 2000). These materials find widespread use and are discovered either as amorphous deposits or in association with various archaeological artefacts (Evershed, 2008a: 905-906).

The process of pitch production involved a specialized furnace structure with a conical boiler and an external combustion chamber, designed to heat resinous wood, releasing resin after vaporizing water (Soutou, 1959: 87-88; Orengo *et al.*, 2013: 806; Mangas and Novillo, 2014: 268). There are several studies on Roman-era pitch production in the Iberian Peninsula. We may include the MPCV project in the southeastern Andorra Pyrenees and case studies from regions like Causses in the French Massif Central, Haut-Forez, Sanguinet Lake in Landes, Alsace's Oberbronn, and East Middle

Sweden (Orengo *et al.*, 2013: 806; Ejarque *et al.*, 2010; Loir, 1940; Viré, 1943; Albenque, 1947; Trintignac, 2003; Renaud, 1963; Balsan, 1951; Ulrich, 1939; Hjulström *et al.*, 2006). These diverse investigations collectively contribute to a richer understanding of pitch-related practices and industries during the Roman period.

The objectives of this study focus on determining what products were stored or contained in *dolia*-type containers in a warehouse dating from the late empire. Although this is not an objective *per se*, we believe it is interesting to establish a possible relationship between the contents of *dolia*-type containers and their connection to agricultural production and the economic activities of the settlement. What work processes should we consider to be directly or indirectly related to the agricultural activities of the *villa*, if we have evidence of this, and what implications do complementary activities have for the immediate landscape of what we understand to be the fundus of the *villa*. It is also important to understand what type of secondary products were indispensable for conservation, maintenance, etc. in relation to food storage spaces. We want to demonstrate how, through various analyses and studies, we can explain a strategy for obtaining resin: on the one hand, we sought to determine the tree taxa used to obtain this product and the procedures employed. We also investigated whether there was a specific space in the *villa* for resin production. On the other hand, we want to determine what it was used for: on what surfaces or utensils and for what purpose this product was used, in a suburban productive context such as that of the Roman *villa* we are studying.

2. The villa and the warehouse of Pla de l'Horta. Context

The villa of Pla de l'Horta is located in the town of Sarrià de Ter, 4.5 km from the current city of Girona. Sheltered by the eastern slope of the Montagut hill and it faces the small plain that opens to the west. This villa occupies a gently sloping terrain

¹ Research Project *Territori, paisatge i espais productius en un entorn suburbà: la vil·la romana del Pla de l'Horta* (ref. ARQ001SOL-184-202) granted by the Generalitat of Catalunya and *Diacronía de los territorios y paisajes de Emporion/ Emporiae y Gerunda durante la Antigüedad-DyLan* (ref. PID2023-148337NA-I00) granted by the Ministry of Science and Innovation of the Government of Spain.

² Columella (xii, 4 and 18); Pliny the Elder (xiv, 16, 25 and 27; xvi, 22 and 53; xxiii, 1 and xxiv, 47); Oribasius (vii, 28); Scribonius (201) and Vitruvius (ii, 9, 13).

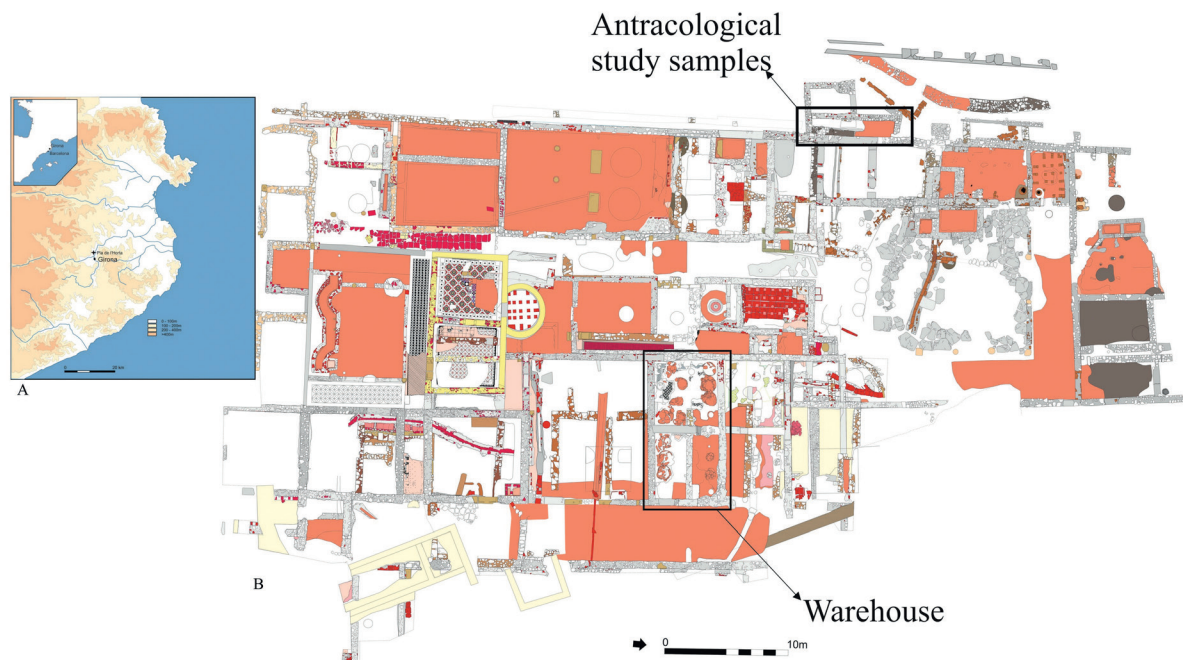


FIG. 1. Pla de l'Horta: A) geographical position of the site; B) general plan of the site.

that extends to the ford where one of the branches of the *Via Augusta* crossed the Ter River (Fig. 1).

The archaeological site has been the subject of extensive research since 2008, during which time it has been established that it presents six significant construction phases. The earliest phase, which dates back to the mid-first century BC, was followed by a series of reforms during the Augustan, Flavian, and Severan periods. A restructuring of the productive sector, dated to the late 3rd century, while the final period of change occurred in the 4th century until the abandonment of the villa in the 5th century. The excavation has facilitated comprehension of a substantial portion of the area corresponding to the *pars urbana* of the Roman villa, in addition to some of the structures within the productive zone. Of particular interest is the discovery of a *torcularium*, which, in conjunction with a series of deposits, has led to the conclusion that wine production constituted a significant economic activity at the villa. But not the only one (Costa and Palahí, 2019b: 131-164).

In the late phase of the villa³, several rooms situated on the northern side of the residential area evolved into a storage facility for *dolia*. Initially, these spaces were part of the Augustan villa and underwent remodelling during the Severan period, functioning as private apartments or *diaetae* associated with the grand central *oecus*. Two separate sets of apartments were accessible from the eastern *ambulacrum* of the peristyle. Each apartment would consist of an entry corridor, a small adjoining room, and, at the far end, a bedroom or living area. Originally, each room boasted a mosaic floor, while the access corridor was paved with *opus signinum* adorned with *tesserae*, characteristic of the Augustan architectural style (Palahí, 2019: 187). Upon integrating these apartments into the productive complex, 4th century AD the walls separating the corridors from the small adjoining rooms were demolished. In one of these areas (south), they

³ For in-depth knowledge of the site, consult Costa *et al.*, 2019 and 2023.

installed six *dolia*, while the smaller room to the north was converted into a kitchen (Fig. 2). Similar uses were allocated to the two large rear rooms. The southern one was repurposed into a warehouse, alongside the adjoining access room, as previously mentioned, while the northern one served as a utility space, although the discoveries within did not distinctly define its function. Consequently, on the southern side of the warehouse, remnants of a significant portion of these containers are preserved. However, in two instances, only remnants of the small pits dug into the mosaic floor to fix *dolia* have endured. The *dolia* that remained in place flattened due to the collapse of the room's ceiling. The primary reason for this considerable destruction is that, during their installation, the pieces were not buried beneath the rooms subsurface. The overlaying mosaics, walls from earlier phases, and other structures made it unfeasible to create sufficiently deep pits. Instead, shallow cavities were formed to

house the bases of the *dolia*. The stability for the pieces was ensured by their mutual support against each other and the walls of the warehouse, leaving a narrow circulation passage. The best-preserved pieces are those located at the room's corners and near the perimeter walls, benefiting from the protection offered by these structures. The extended longevity of these containers may be attributed to the considerable cost and logistical challenges of replacing them within the confined warehouse space. The identification of lead staples used for repairing walls implies sustained and protracted usage and the necessity of routine maintenance and reparations.

It's noteworthy that, apart from the pieces found *in situ*, remnants of a small fractured *dolium*, displaced and fallen to the side, were also recovered. There are indications that the warehouse experienced a minor fire, particularly affecting the access area and leading to the partial collapse of the ceiling (Costa and Palahí, 2019a: 61). This warehouse



FIG. 2. Digital orthophoto of the *dolia* warehouse.

cannot be associated with any immediate structure or space for transformation or pressing, unlike other examples in the region (Salido, 2017: 259). The excavation of these rooms did not yield data pinpointing the exact time of the transformation of these residential spaces into warehouses, beyond a 4th-century AD context (Costa and Palahí, 2019b: 221). The conversion of spaces from the *pars urbana* into *dolia* warehouses or any other industrial-type structure is not an uncommon phenomenon. Similar chronologies document this process in numerous other *villae*, not only in the Iberian Peninsula—one relatively close example being Torre Llauder (Prevosti and Clariana, 1992: 64-65; other instances are detailed by Chavarría, 2006: 26-27)—but also across Western Europe (Lewit, 2009: 82-83).

3. Materials and methods for the identification of organic residues

To understand the use of the *dolia* at the Roman villa of Pla de l'Horta, a molecular study of organic residues was designed in two complementary analytical phases. The aim was to identify the products contained in these large storage vessels by analysing samples from different parts of the vessels and from different areas of the site. The materials and chromatographic methods used in each phase of the study are detailed below.

3.1. Phase 1: Analysis of the bottoms of the *dolia*

The first phase focused on analysing the bottoms of 16 *dolia* from a warehouse dating back to the 4th century AD. The extractions were performed on 0.1 to 0.5 g of ground pottery spiked with 10 µg of n-tetratriacontane. At the same time, a sample containing only a known amount of solvent and internal standard was analysed in order to document possible contamination in the system during analysis. Lipid extraction was performed using the acidified methanol protocol, adapting the protocol of Correa-Ascencio and Evershed (2014), designed

to recover polar compounds still present in the ceramic matrix, which has been shown to increase the degree of recovery of lipid compounds in ceramic samples.

The ground pottery was extracted three times with a solvent mix of dichloromethane and methanol –DCM:MeOH 1:1– and dried under a nitrogen flux. The samples were then resuspended in DCM and derivatised with 20 µl of N,O-bis(trimethylsilyl) trifluoroacetamide –BSTFA– with 1 % trimethylchlorosilane –TMCS–, dried again and resuspended in isooctane to be submitted to chromatographic analysis. Samples were analysed with a 7820A Agilent Gas Chromatograph –GC– fitted with a Flame Ionisation Detector –FID– to assess the presence/absence of lipidic contents. The injection was done in splitless mode at a temperature of 300 °C and eluted through an HP-1 capillary column –60 m length, 250 µm internal diameter, 0.25 µm film thickness– using hydrogen as the carrier gas. The oven temperature was initially set at 50 °C for 1 minute and then increased at 6 °C min⁻¹ to 320 °C, where it stayed for 20 minutes. From the extract in isooctane solution, 1 µl was injected into an Agilent 7890A GC coupled to an Agilent 5975C Mass Spectrometer. The GC was fitted with a DB-5MS column measuring 30m length × 250 µm internal diameter × 0.25 µm film thickness. The GC injector was operated in splitless mode and helium was used as the carrier gas. The oven temperature was set at 50 °C for 2 minutes and then increased at 15 °C min⁻¹ until it reached 170 °C, then a new ramp at 5 °C min⁻¹ brought the oven to 320 °C and held at that temperature for 6 minutes. The Mass Spectrometer was run in electron impact mode and masses were acquired in full scan mode between 50 to 800 m/z.

- Sampling: Approximately 1 gram of ceramic dust was extracted from the interior of each vessel. To do this, a Dremel-type drill with a tungsten burr was used on a previously cleaned area to avoid contamination.
- Lipid extraction: An extraction protocol with acidified methanol was used. This method was specifically chosen because it has been shown to significantly increase the recovery of lipid

compounds in ceramic samples by releasing polar fatty acids that are strongly adsorbed in the pores of the ceramic matrix (Correa-Asencio and Evershed, 2014). This ensured maximum recovery and identification of the preserved fatty acids.

- **Chromatographic Analysis –GC-FID–:** The extracted samples were initially analysed using Gas Chromatography with Flame Ionisation Detection (GC-FID). This technique acted as a first screening step to document the presence or absence of general lipid content in the vessels.
- **Isotopic Analysis –GC-C-IRMS–:** Subsequently, samples with confirmed lipid presence were analysed using Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry –GC-C-IRMS–. This analysis focused on determining the isotopic values of the two most abundant fatty acids, palmitic (C16:0) and stearic (C18:0), in order to reliably diagnose the origin of the fat (ruminant, non-ruminant, dairy, etc.).

3.2. Phase 2: Analysis of the dolia walls

In the second phase, samples from the central walls of four of the *dolia* in the aforementioned warehouse were reanalysed, along with samples from other containers in the *villa*.

- **Sampling:** Sampling was again carried out using a Dremel-type drill, first to remove the surface layer in contact with the sediment and the manipulator –thus avoiding modern contamination– and then to pulverise the pottery and obtain the powder for analysis (Molina and Rosell-Melé, 2019). The amount of sample used varied between 0.1 and 0.5 g of ceramic powder.
- **Lipid extraction:** In this phase, the extraction was performed three times with a mixture of dichloromethane and methanol solvents –DCM: MeOH 1:1–. An internal standard (n-tetratriacontane) was added to the samples for quality control.
- **Derivatisation:** Prior to chromatographic analysis, the extracts were derivatised with

N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1 % trimethylchlorosilane –TMCS– to make the compounds volatile and suitable for injection into the chromatograph.

- **Chromatographic Analysis –GC-MS–:** The main analysis in this phase was carried out using Gas Chromatography coupled with Mass Spectrometry –GC-MS–. This powerful technique was selected for its ability to identify specific molecular biomarkers based on their mass and unique fragmentation pattern, allowing for the unambiguous identification of compounds such as resins, tars, or markers of specific plants. The objective was to resolve the ambiguities of the first study and obtain a more complete characterisation of the residues.

In both phases, blank samples –containing only solvent and internal standard– were analysed to document and rule out any possible contamination of the system during the analytical process.

Gas chromatography with flame ionisation detection –GC-FID– is a fundamental technique in the analysis of organic residues. Its main function is to document the presence or absence of general lipid content in a sample and to enable the relative quantification of the compounds detected. It acts as a first screening step to determine whether a ceramic sample contains enough lipids to justify more complex and costly analyses.

The main limitation of GC-FID is that, although it identifies and quantifies compounds based on their retention time in the chromatographic column, it does not provide detailed structural information or isotopic data. This deficiency makes it difficult to determine the exact origin of fats (animal vs. vegetable, ruminant vs. non-ruminant) without additional analysis, as many of these compounds are present in a wide variety of natural sources.

Gas chromatography-combustion-isotope ratio mass spectrometry –GC-C-IRMS– is a high-precision technique designed to determine the origin of fats by analysing the ratio of stable carbon isotopes ($^{13}\text{C}/^{12}\text{C}$) in specific fatty acids. In archaeology, the analysis commonly focuses on palmitic

acid (C16:0) and stearic acid (C18:0), which are the most abundant in animal and vegetable fats. The isotopic ratio, expressed as a $\delta^{13}\text{C}$ value, varies between different types of organisms due to their different metabolic pathways. Furthermore, the difference between the values of the two main fatty acids ($\Delta^{13}\text{C} = \delta^{13}\text{C}_{18:0} - \delta^{13}\text{C}_{16:0}$) allows for an even finer distinction. This methodology can reliably differentiate between fats from ruminant and non-ruminant animals and dairy products, based on ranges of values established from modern reference collections (Copley *et al.*, 2003). While absolute $\delta^{13}\text{C}$ values can be altered by factors such as the animal's diet—e.g., consumption of C4 plants—the $\Delta^{13}\text{C}$ difference is less affected and more indicative of the organism's specific metabolic processes, thus providing a more robust classification. Its strength lies in its ability to diagnose the type of fat with high reliability. However, as observed in the case of Pla de l'Horta, it has limitations.

Gas chromatography coupled with mass spectrometry (GC-MS) is one of the most powerful tools in analytical chemistry. The technique first separates the components of a mixture using gas chromatography and then identifies them individually in the mass spectrometer. Identification is based on the molecular mass of the compound and its unique fragmentation pattern, which acts as a molecular 'fingerprint', allowing for unambiguous identification. In the second Pla de l'Horta study, GC-MS played a crucial role in enabling the identification of specific non-lipid biomarkers that had gone unnoticed in the first analysis. The great strength of GC-MS is its ability to identify diagnostic compounds that other techniques cannot specify, such as resins, tars or markers of specific plants.

Once the theoretical foundations of these three methodologies have been reviewed, the next step is to examine how they were applied in practice and what specific results they yielded in the case study of the Roman *villa*.

4. Analysis process

In order to understand this storage space, a molecular study of organic residues was carried out on the walls of different *dolia* in this space. This was done alongside other *dolia*, which in this case are not sets of vessels. Instead, they are isolated specimens located in what has been interpreted as work areas of the *villa*, with the aim of discovering what products the *dolia* contained. Two rounds of studies were carried out: in the first, the bottoms of the 16 *dolia* in the warehouse, dating from the 4th century AD (Fig. 3), were analysed. In the second, samples from the walls of four of the *dolia* in the warehouse were subjected to a new analysis, along with samples from other areas of the *villa*. The two studies are presented below, in order, with the respective methodologies and results.

The first study involved an initial analysis using gas chromatography with a flame ionization detector—GC-FID—in order to document the possible preservation of organic residues. In a second analysis, we used a gas chromatograph coupled in continuous flow to an isotope ratio mass spectrometer—GC-C-IRMS—to characterize the isotopic values of the main fatty acids: palmitic acid (C16:0) and stearic acid (C18:0). The protocol involved extraction with acidified methanol. This extraction method uses a basic solution with acid to release the polar fatty acids that are still inside the ceramic matrix and that other protocols such as solvent extraction—DCM: MeOH—are unable to recover (Correa-Asencio and Evershed, 2014). Therefore, this protocol ensured maximum recovery and identification of the fatty acids preserved within the pieces. Extraction of the sample pulverized with a Dremel-type drill and a tungsten burr on the previously cleaned area. The samples were also analysed by gas chromatography with a flame ionization detector—GC-FID—to document the possible presence of lipid content inside the vessel. Finally, isotopic analysis by GC-C-IRMS was performed to reliably diagnose the origin

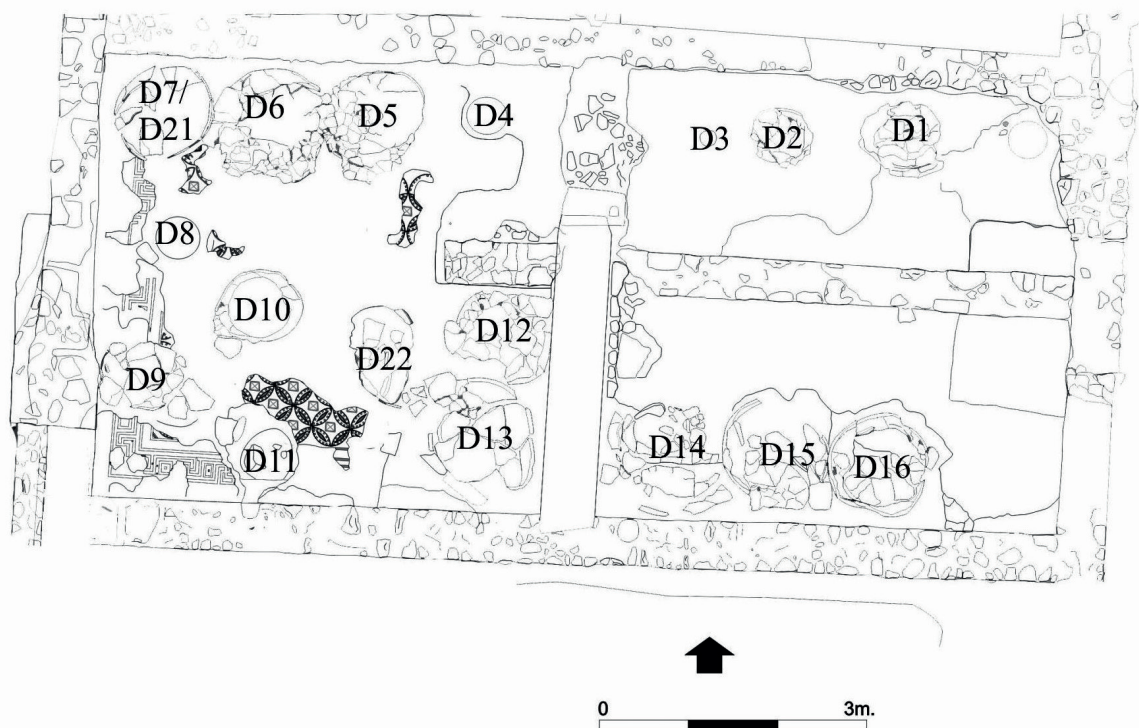


FIG. 3. Plant of the dolia warehouse whit the dolia samples numbers.

of the fat contained in these vessels –ruminant fat, non-ruminant fat, dairy content, among others–.

5. Results of the Analyses at Pla de l'Horta

The result of the first study was as follows: The chromatograms obtained by GC-FID analysis confirm the presence of lipids in 15 of the 16 samples analysed. All chromatograms show a clear profile of long-chain fatty acids, where palmitic acid (C16:0) and stearic acid (C18:0) stand out from the rest of the compounds. The prominent presence of both compounds is explained by their high recurrence in the composition of triacylglycerols (Regert, 2011; Evershed *et al.*, 1997). In three of the pieces analysed, a majority presence of fatty acids is observed, both quantitatively and qualitatively. These are the samples corresponding to *dolia* D3, D7, and D16 (Fig. 4). In all three cases, the chromatograms show a clear profile of long-chain fatty acids

(C14-C18:0), with palmitic acid and stearic acid being the most abundant. Their presence, much greater than that of unsaturated fatty acids (C18:1), suggests that these compounds are of animal origin. The animal content is also supported by the preservation of other compounds such as C17:0 fatty acid, which, together with C15:0 acid, is associated with fats from ruminant species. Specifically, the two fatty acids are formed in the intestines of ruminants because of bacterial activity (Regert, 2011). The presence of both compounds in these samples could be an indicator of their ruminant origin, but as highlighted in Steele's work⁴, the presence of C17:0 in small quantities is also documented in vegetable oils such as olive oil and sesame oil, so it cannot be used as a diagnostic element in isolation. To a lesser extent, the fatty acids C14:0 and C15:0

⁴ Steele, V.: *Organic residue analysis of red lustrous wheelmade ware*. PhD Dissertation presented in the Univ. of Bradford.

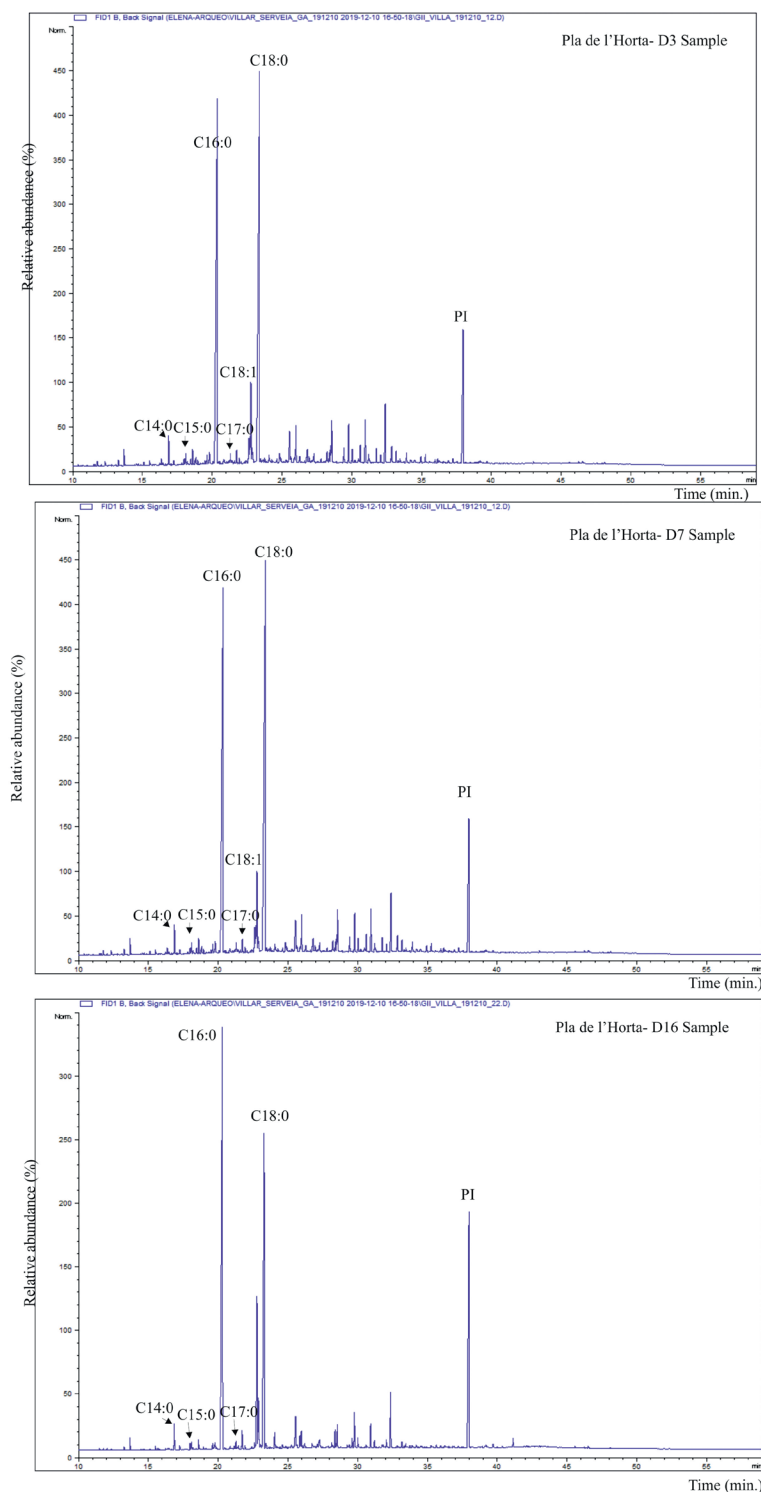


FIG. 4. Chromatograms obtained using GC-FID. Identified peaks: PIP atró internal (C34: n-tetratriacontane); Cx:0 long-chain fatty acids with x number of carbons (samples D3, D7 and D16).

are also documented. On the other hand, the isolated preservation of unsaturated acid C18:1 is usually associated with the presence of fats from non-ruminant species, but it is also documented in plant products such as olive oil (Mirabaud, 2007)⁵. In this sense, isotopic analysis will allow us to confirm whether we are dealing with fat from ruminant animals or even vegetable oils. Samples from pieces D1, D2, D4, D5, D6, D9, D10, D11, D14, and D15 also show long-chain fatty acids and unsaturated C18:1. In addition, some of these samples contain the fatty acids C15:0 and C17:0. However, the amount of these compounds is lower than that of the others.

On the other hand, there is a notable lack of fatty acids in the samples from containers D8, D9 and D12, suggesting that these *dolia* may have been used less intensively than the rest. However, the context in which these containers were found should also be considered, especially *dolia* D12, which is located in a spot that is not easy to access and therefore may have been used less frequently than other examples from the same warehouse. Nevertheless, the lower degree of preservation did not prevent isotopic analysis from being performed on these samples. Sample D13 did not preserve any organic compounds associated with its use. This would indicate that the piece may have contained some non-organic substance, such as water, or some substance that left no chemical evidence on the piece. Even so, a second analysis will be performed to confirm this assertion.

These analyses revealed clear profiles of long-chain fatty acids, such as palmitic acid (C16:0) and stearic acid (C18:0), indicating the presence of fats or oils. The $\delta^{13}\text{C}$ results for many samples fell within intermediate ranges, which could indicate mixtures of different types of fat. Another possible explanation is the influence of the animal's diet, as consumption of C4 plants—such as certain grasses—can alter isotopic values and lead to ambiguity in interpretation.

Isotopic analysis by GC-C-IRMS was performed on all samples except D13, which did not preserve

organic compounds. Isotopic analysis allows for a reliable diagnosis of the type of fat contained in the vessels. This analysis defines the $\delta^{13}\text{C}$ value of the two most common fatty acids among animals: C16:0 and C18:0. The isotopic ratio of carbon isotopes ^{13}C and ^{12}C , expressed as the $\delta^{13}\text{C}$ value, allows the origin of fatty acids to be determined (Regert, 2011). Specifically, the $\delta^{13}\text{C}$ value reflects the differences that occur in the fractionation between C16:0 and C18:0 as a result of the different metabolic pathways followed by both compounds in the adipose tissues of different animal species. Based on this ratio, we can determine whether the fats come from ruminant or non-ruminant animals, or even whether the fat comes from the animal's milk or adipose tissue (Copley *et al.*, 2003; Regert, 2011; Dudd *et al.*, 1998).

Another way to evaluate and interpret the isotopic values of C16:0 and C18:0 is based on the isotopic ratio: $\Delta^{13}\text{C} = \delta^{13}\text{C}_{18:0} - \delta^{13}\text{C}_{16:0}$, in relation to the value of $\delta^{13}\text{C}_{16:0}$. Fats derived from dairy products always have a value below -3.3‰ , fat from ruminant species between -3.3‰ and -1‰ , and fat from non-ruminant species between -1‰ and -3‰ (Copley *et al.*, 2003; Regert, 2011)⁶. The type of fat was identified based on these values ($\Delta^{13}\text{C}$ and $\delta^{13}\text{C}$). The type of fat was identified by comparing the results obtained in the *dolia* from the Roman *villa* at Pla de l'Horta with those published in the reference collections obtained from the analysis of contemporary animals and contemporary plant species—olives and olive oil—(Copley *et al.*, 2003; Outram *et al.*, 2009; Regert, 2011; Spangenberg and Ogrinc, 2001; Steele *et al.*, 2010)⁷. As shown in Figs. 5 and 6, the results are usually represented in regions or ellipses that indicate the area of highest probability for each type of fat, areas calculated from the $\delta^{13}\text{C}$ value of the different types of fats.

About the isotopic results, if we look at the $\delta^{13}\text{C}$ values obtained for C16:0 and C18:0, most of the samples fall within an intermediate range between the values defined for ruminant and non-ruminant

⁵ Also cf. Steele, *op. cit.* n. 3.

⁶ Also cf. Steele, *op. cit.* n. 3.

⁷ Also cf. Steele, *op. cit.* n. 3.

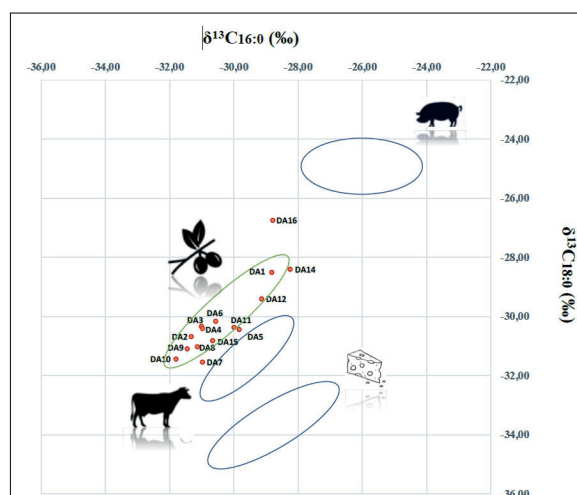


FIG. 5. Graphic representation of the isotopic results obtained for the 16 dolia samples analysed (first study); the ellipses confidence represents the proposed values for each type of animal fat (blue ellipse) and vegetable oil (green ellipse).

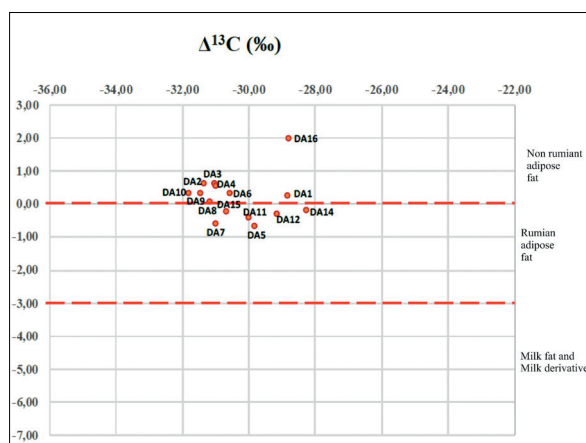


FIG. 6. Distribution of the 16 dolia samples (first study), in relation to the $\Delta^{13}\text{C}$ value for each type of fat.

fats (Fig. 5). This zone has been defined in the work of Copley *et al.* (2003) as the region where samples with a mixture of fats from different sources—ruminant and non-ruminant animal species—are located.

However, when these data are compared with the values obtained for $\Delta^{13}\text{C}$, samples DA3, DA7, DA8, DA11, DA12 and DA14 show fat content from ruminant species (sheep, goats and/or cattle), while

the rest of the samples show values associated with non-ruminant species (Fig. 6).

The inconsistency in the values obtained for $\delta^{13}\text{C}$ of C16:0 and C18:0, which differ from those defined for ruminant species, could be explained by a factor related to the diet of these animal species. It is possible that the animal species, which would later be consumed, received a diet richer in C4 plants than in C3 plants, which alters the value of ^{13}C (Craig *et al.*, 2005). On the other hand, the isotopic values defined for plant species must also be taken into account. The $\delta^{13}\text{C}$ values defined for olive oil and olives in the works of Steele *et al.* (2010) and Spangenberg and Ogrinc (2001) (green ellipse in Fig. 5), fall within this range compared to the samples analysed from the Roman villa of Pla de l'Horta. These results are reinforced when we consider the chromatographic results for all the pieces, which show a very high value of oleic acid (C18:1). This result is usually associated with the presence of vegetable oils such as olive oil (Mirabaud, 2007; Steele, 2008). Thus, based on the isotopic values and the analysis of the chromatograms, it is very likely that these vessels contained olive oil. Furthermore, the isotopic results of the pieces do not correspond to any of the regions defined for the different types of animal fat. However, it cannot be ruled out that at some point during their useful life, the containers may also have contained animal fat. The chromatograms obtained show a clear profile of long-chain fatty acids (C14-C18:0), suggesting the presence of animal fat in these pieces. In this regard, the only sample that appears to have a clearly animal origin is the one associated with piece D16, in which the isotopic values ($\delta^{13}\text{C}$ and $\Delta^{13}\text{C}$) differ from those defined for vegetable oils (Figs. 5 and 6) and align with those defined for fat from non-ruminant species. This interpretation is further strengthened by the fact that this is the piece with the best preservation of fatty acids. It is not possible to specify whether this use was simultaneous or whether the contents differed over time.

For the second study, we selected fragments from four *dolia* belonging to that warehouse, along with other *dolia* samples from other areas of the

villa. All samples corresponded to the walls of the containers, in the central section of the piece.

The sampling is done with a Dremel to first remove the layer of pottery in contact with the ground and the archaeologist, to avoid any plastic or lipidic contamination, and then to grind the pottery into a fine powder (Molina and Rosell-Melé, 2019).

The main components of the detected residues in Fig. 7 consist of a range of diterpenoids, mainly derivatives of the abietic acid and pimaric acid. This kind of tricyclic diterpenoids are widespread among higher plants and are particularly abundant in conifer resins (Otto *et al.*, 2002). The main components are dehydroabietic acid, dehydrodehydroabietic acid, 7-oxo-dehydroabietic acids and methyldehydroabietate. Dehydroabietic acid is the most abundant component of aged pitch from *Pinus* species. It occurs naturally but can also be a product from the thermal dehydrogenation of abietic and pimaric acid, the principal resin acids of conifers, also found in the samples. The presence of both retene and methyl-dehydroabietate is sometimes considered an indicator of pine pitch produced by the pyrolysis of wood as retene is a product mainly formed when the resin is processed at high temperatures. However, during this chemical process—an oxidative decarboxylation, demethylation and aromatisation reaction—, a series of products such as norabietatriene, tetrahydroretene, or simonellite are usually formed,

but could not be found in our samples. Here the absence of other heat biomarkers or any PAH indicating the production of pine tar suggest the use of fresh pine resin (Dimitrakoudi *et al.*, 2011). Thanks to the technique used in second study, diterpenoids such as dehydroabietic acid were detected, which are characteristic and unambiguous markers of coniferous resins, specifically of the *Pinus* genus.

While diterpenoids were the main residue detected in 8 of the 14 analysed samples, traces of degraded fatty acids—hexadecenoic acid, octadecanoic acid and octadecenoic acid—were also detected in 7 cases (Fig. 7). Traces of fat are not commonly reported in the analysis of ancient pine resins (Hayek *et al.*, 1990; Martínez and Petit, 1998; Petit and Martínez, 1999; Marshall *et al.*, 2008; Pecci *et al.*, 2017) and, when present, they have been interpreted as evidence pointing at the vessel's use (Jerković *et al.*, 2011; Izzo *et al.*, 2013). This is possible as the waterproofing of storage vessels with pitch—pine resin—would not be sufficient to totally preclude traces of the contents to eventually permeate inside the vessel's pores (Pecci *et al.*, 2017). In five cases, the presence of free fatty acids is accompanied by trace amounts of β -sitosterol. This is a compound specific of plant organisms and therefore diagnostic for the type of fats contained by the studied vessels. While the presence of β -sitosterol could not be ascertained in two samples

DETECTED COMPOUNDS	UE 2207-1	UE 2207-2	UE 2207-4	UE 2207-5	D 2	D 22	D 21	2186
Hexadecanoic acid	x		x	x	x	x	x	x
Octadecenoic acid	x		x	x	x	x	x	
Octadecanoic acid	x		x	x	x	x	x	x
Retene	x		x	x	x		x	x
Pimaric acid	x		x	x			x	x
Methyl dehydroabietate								x
Dehydrodehydroabietic acid	x	x	x	x	x	x	x	x
Dehydroabietic acid	x	x	x	x	x	x	x	x
7 oxo-dehydroabietic acid	x	x	x	x	x	x	x	x

FIG. 7. Detailed results of the molecular content extracted from the pottery (second study).

–2207-2, 2136 and 2186– their absence could be due to the existence of a different content but could also be explained by preservation issues. Plant organic matter is especially prone to degradation and, therefore, harder to detect.

Analyses of the preserved residues indicate the existence of 4 types of results:

1. Vessels yielding non-appreciable quantities of lipids combined with modern contaminants: D13, 2191, 2193, 2197-3, 2184.
2. Vessels yielding only strong Pinaceae resin signals: D2.
3. Vessels yielding resins mixed with trace amounts of fats of an unclear origin: 2136, 2186, 2197-2.
4. Vessels yielding resins mixed with trace amounts of plant fats: D21, D22, 2207-1, 2207-4, 2207-5.

Therefore, we can tentatively conclude that the studied assemblage corresponds with a number of 14 of storage vessels containing a wide range of products. Some contained products which are not fatty in nature and, therefore, could not be detected through this study. In 9 cases, the vases were coated with pine resin, a practice that will be discussed later. In five cases the contents of the vases could be securely traced to a plant product. The degradation of the recovered residues and the low specificity of the detected molecules prevent assigning said plant products to any species or family. The detected residues would not be a good match for famous roman products such as garum or animal-based foodstuffs. Alternatively, this signal would not be incompatible with olive oil.

5.1. Identification of Fats and Oils using GC-FID and GC-C-IRMS

The protocol for the first study was designed to maximise the recovery of fatty acids absorbed into the ceramic matrix. To this end, an acidified methanol extraction method was used, which is particularly effective in releasing polar compounds strongly adhered to clay. Samples from 16 *dolia* from the late Roman warehouse were analysed.

The GC-FID results were conclusive and laid the foundation for further analysis. The key findings were:

- Lipid confirmation: lipid residues were detected in 15 of the 16 samples analysed.
- Fatty acid profile: all chromatograms showed a profile dominated by long-chain fatty acids, with a notable abundance of palmitic acid (C16:0) and stearic acid (C18:0).
- Presence of oleic acid: a high presence of oleic acid (C18:1) was observed, an unsaturated fatty acid commonly associated with vegetable oils.

Next, GC-C-IRMS analysis was performed to determine the origin of these fats. The $\delta^{13}\text{C}$ values were ambiguous, placing most samples in an intermediate zone between ruminant and non-ruminant fats, suggesting a possible mixture of contents or the effect of diets rich in C4 plants. However, when analysing the $\Delta^{13}\text{C}$ values, a clearer classification was possible: some samples were grouped with ruminant fats, while most were grouped with non-ruminant fats.

The final interpretation of this first study was cautious but revealing. The combination of high C18:1 content –suggestive of vegetable oil– with the isotopic results yielded a complex picture: the isotopic values of the pieces did not correspond to any of the regions defined for the different types of animal fat. Although previous or simultaneous use of the vessels for animal fats could not be ruled out, the most likely hypothesis was that the main content was vegetable oil, probably olive oil. This study therefore identified the fatty contents but left an ambiguity that required a second analysis to investigate other substances and confirm the origin of the content.

5.2. Detection of Waterproofing Resins using GC-MS

The second study focused on a subset of four samples from the storage *dolia*, applying an extraction protocol with a mixture of solvents (DCM: MeOH) and subsequent derivatisation with BSTFA. This treatment prepares the molecules for analysis

by GC-MS, allowing the detection of a wider range of compounds, including non-lipid ones.

The GC-MS results revealed the presence of a number of key biomarkers that had not been detected previously:

The presence of diterpenoids, such as dehydroabietic acid, serves as an unambiguous molecular marker of conifer resin, specifically from the *Pinus* genus. Additionally, the absence of retene and other heat-derived markers is crucial, as it clearly distinguishes the use of raw resin from pitch. Pitch is produced through high-temperature pyrolysis and leaves a distinct chemical profile, which is not present here. The detection of fatty acids –hexadecanoic and octadecanoic– confirms the presence of traces of stored fat content, already identified in Study 1. Finally, the presence of β -sitosterol, a specific plant sterol, conclusively confirms the plant origin of these fats.

Based on these findings, the samples could be classified. Pine resin residues were detected in 9 of the 14 samples analysed, and in 5 of those cases, they were found alongside vegetable fats confirmed by the presence of β -sitosterol. This allowed four

groups to be defined: vessels with no detectable lipids, vessels containing only resin, vessels with resin and traces of fats of uncertain origin, and vessels containing both resin and vegetable fats. These results not only corroborated the use of *dolia* for storing plant products but also revealed an additional technical practice: waterproofing with pine resin. The next step is to integrate these chemical results with other lines of archaeological evidence to construct a comprehensive interpretation.

6. Anthracological studies on Pla de l'Horta

Various anthracological studies were conducted to ascertain the specific species utilized as fuel within the *villa* of Pla de l'Horta. A total of 1914 charcoal fragments were analyzed from stratigraphic units related to various ovens and furnaces for heating or *praeefurnia* in both the residential and productive sectors of the *villa* (Costa and Vivó, 2024), revealing diverse taxa as fuel, primarily representatives of deciduous vegetation from sub-Mediterranean forests such as maple (*Acer* sp.) and deciduous oak (*Quercus*

sp. *deciduosa*). Additionally, species from Mediterranean forests, including tree strawberry (*Arbutus unedo*), heather (*Erica* sp.), holm oak/kermes oak (*Quercus* sp. *sclerophyllous*), and Aleppo pine (*Pinus halepensis*), were employed (Fig. 8). These species often compose mixed forests in low Mediterranean regions, particularly in shaded areas and depressions. Shrub layer species like rhamnaceae, rosaceae, prunus, and junipers could also have existed within these forests. Moreover, alder represented the riverbank vegetation along watercourses. Overall, the collection of plant-based fuel likely occurred in mixed forests of pine, holm oak, and oak existing

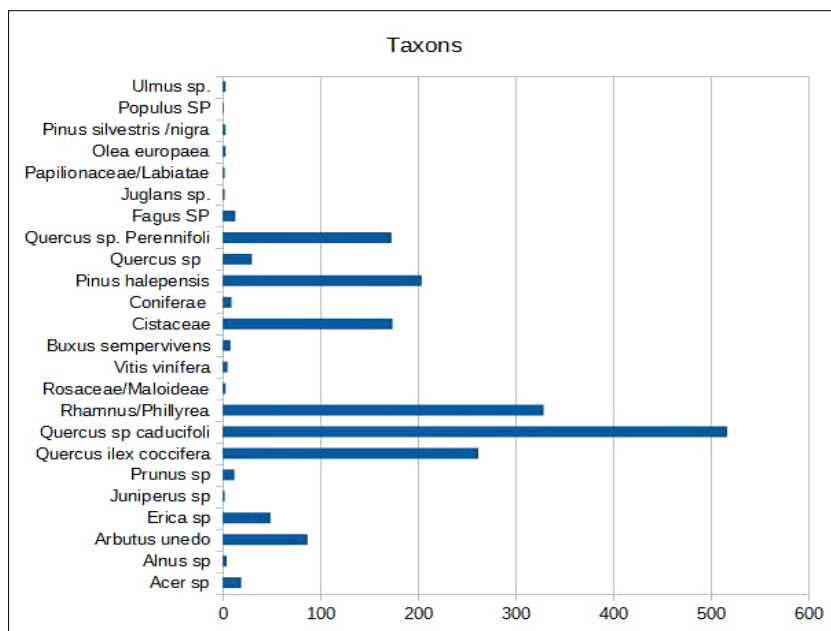


FIG. 8. Representation of the taxa of trees identified in the Roman villa of Pla de l'Horta; total number of samples.

near the settlement. Notably, remnants from pruning the *villa's* primary crop, grapevines and olive tree, were also utilized (Costa and Vivó, 2024)⁸. The latter strata correlate with a hypocaust-heated room and a large oven, dating back to the 1st century AD (Costa and Palahí, 2019b). Presence of shrub taxa, such as tree strawberry, heather, and rhamnaceae, suggests that the forest environment might have been relatively open, as these are heliophytes favoring degraded land. Additionally, grapevine and olive tree remains imply its cultivation within the settlement, albeit not abundant, potentially due to the use of prunings in fires and ovens. Other taxa discovered on-site, such as rosaceae and prunus, might have been cultivated, encompassing apple, pear, peaches, cherries, and almonds. However, wood anatomy analysis cannot confirm their cultivation at Pla de l'Horta, as no fruit remains have been found. Notably, these subfamily representatives often grow wild in the Mediterranean. In contrast, grapevine seed and wood remains and olive tree remains, indicate its local cultivation and periodic management through pruning. The most represented taxa in terms of remains are: *Quercus* sp. *deciduous* –517 fragments–, *Rhamnus/Phillyrea* –329 fragments–, *Quercus ilex coccifera* –262 fragments–, *Pinus halepensis* –204 fragments–, *Cistaceae* –174 fragments–, *Quercus* sp. *sclerophyllous* –173 fragments–. These taxa reflect the choice of forest resources employed as fuel in the settlement (Costa and Vivó, 2024). Noteworthy is the use of Aleppo pine in productive areas, *Quercus* in the large ovens associated with *praefurnia*, and the utilization of the strawberry tree for fires linked to kitchen areas (Costa *et al.*, 2023; Costa and Vivó, 2024).

7. Discussion

Archaeological pottery may contain organic residues that can be found under three main forms:

⁸ ALSO Barberá, A.: *Informe del rentat de sediment i l'anàlisi carpològica de les mostres del jaciment de Pla de l'Horta (Sarrià de Ter)*. Servei d'Anàlisis Arqueològiques, Univ. Autònoma de Barcelona, Juny 2025.

actual contents preserved *in situ* as vessel fills, surface residues that are visible on the exterior or interior of vessels and absorbed residues that are invisible to the naked eye. The final category is by far the most commonly occurring in pottery (Evershed, 2008b: 26).

The first study (GC-C-IRMS) presented a puzzle: a strong indication of vegetable oil, which was nevertheless accompanied by isotopic markers that did not clearly fit any known animal fat profile, leaving open the possibility of mixtures or sequential uses. GC-MS, in the second study, systematically resolved this ambiguity. The detection of β -sitosterol definitively confirmed the vegetable origin of the content, while the identification of diterpenoids revealed a technological practice completely invisible to the first methodology: waterproofing with pine resin. This practice, in turn, is directly related to the maintenance strategy for the *dolia*, complementing structural repairs (lead staples) with sealing to ensure waterproofing and repair minor cracks.

The results of the anthracological study of the site provide an independent and complementary line of evidence. Analysis of the charcoal recovered from large layers near a small room with intensely reddened soil in the productive sector of the *villa* revealed a very specific selection of wood: 94 % of the remains corresponded to Aleppo pine (*Pinus halepensis*). This data contrasts sharply with the charcoal found in the baths' furnaces –*praefurnium*–, where oak wood (*Quercus*), known for its higher calorific value, was preferred (Costa and Vivó, 2024: 112-113).

A first round of analysis –Study 1– focused on a set of 16 ceramic containers known as *dolia*, aiming to identify absorbed fatty acids within the ceramic matrix. This identification was pivotal in discerning the preserved lipid types through isotopic analysis – $\delta^{13}\text{C}$ – of these fatty acids. The majority of the findings from these pieces confirmed the presence of biomarkers associated with vegetable oil (Fig. 5). Considering the context of these materials, it is pertinent to relate this to the *dolia's* use as containers for olive oil. Of the prototypical Mediterranean products, vegetal oil can readily be distinguished by analysis of lipid traces (Romanus *et al.*, 2009: 900; Condamin *et al.*, 1976). Additionally, the results

indicated a minor presence of biomarkers linked to animal fat. This suggests that, at some point in the life cycle of these containers, prior to their exclusive use for olive oil, they were utilized for preserving animal-derived products. Qualitative and quantitative analysis confirmed the higher preservation levels of fatty acids in three of the containers, suggesting a potentially more frequent usage compared to the others. In their final phase of use, this set of *dolia* primarily served as storage for significant quantities of olive oil. The second round of analysis confirmed the presence of plant fats in two of the vessels of the warehouse, compatible with olive oil.

In the productive sector of the Roman *villa*, large layers with a very generous amount of charcoal have been located near a small room, where the floor exhibits an unusually intense reddening and a thickness surpassing 80 cm (Fig. 9) (Costa and Vivó, 2024: 112-113). The main characteristic of the set of charcoal associated with the combustion facility is the preponderance of *Pinus halepensis*—94 % of the identified taxa— over a few fragments—7 out of 142— of deciduous *Quercus* sp. and *coniferae*, which are almost irrelevant as fuel in this industrial area. This specific case shows a very particular selection of a forest resource, in contrast to the availability of tree species in the area. This generates a hypothesis supported by data obtained after analysing the *dolia*: the extraction and use for maintenance tasks of natural pine resin in a Roman-era productive space seems to be a reality. In addition, the use of pinewood for combustion, after the resin extraction, for other activities not identified yet is another key finding. Numerous anthracological studies carried out in Roman *villae* throughout the Iberian Peninsula offer valuable insights into vegetation and wood utilization. Euba and Allué's investigation of the Roman *villa* of Moro, in Torredembarra, Catalonia, uncovered the prevalent use of olive, pine, and typical Mediterranean shrub species as significant sources of wood for heating the *villa*'s thermal complex (Euba and Allué, 2003). Similarly, Noguera and Antolinos' anthracological analysis of the surroundings of the Roman *villa* of Los Cipreses, in Jumilla, Murcia, underscored

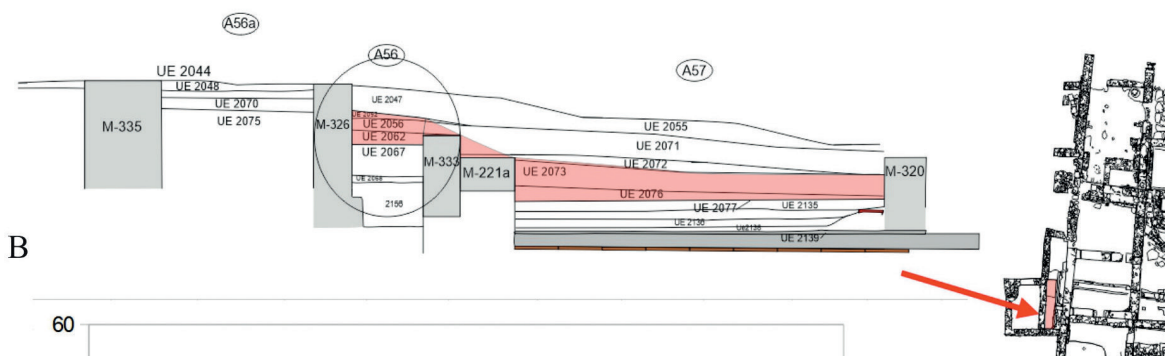
the cultivation of grapevines and olives as primary crops, alongside barley, figs, and other plants on the farm (Noguera and Antolinos, 2009), providing insights into agricultural practices during the Roman period. Piqué's studies (Piqué *et al.*, 2012) delving into wood utilization as fuel in the Roman city of Lleida and various sites in Valles Occidental identified taxa such as Aleppo pine, *Quercus* sp., *Erica* sp., and *Arbutus unedo*. The findings suggested a decline in wood variety over time, potentially linked to forest mass depletion due to high demand (Piqué *et al.*, 2012). Notably, an increase in supra-Mediterranean vegetation from the 2nd century AD indicates a pursuit of resources at higher altitudes, reflecting human impact on lowlands (Piqué *et al.*, 2012).

Additionally, in industrial sites like ceramic production kilns, certain taxa like *Pinus halepensis* and *Quercus* sp. were predominantly used as fuel, reflecting a preference for specific species in production processes (Piqué *et al.*, 2012: 69-70). Similarly, the study by Chabal, Figueiral, and Pelletier (2017) on the Roman *villa* des Prés-Bas in Loupian highlighted the use of oak species, strawberry tree, fruit tree prunings, and scarce conifers as significant fuel sources (Chabal *et al.*, 2017: 87-88). The preference for hardwoods like holm oak, white oak, and elm is attributed to their dense wood, sustaining fire for extended periods (Chabal *et al.*, 2017: 88). The MPCV project detected palaeoecological evidence in the Bosc dels Estanyols of a deforestation process through tree felling and the relationship between pine clearance and pitch production (Orengo *et al.*, 2013: 807). Pitch production, like other activities, was, at least during the Roman period, integrated into supra-regional economic networks, contributing highly necessary and specialized products (Orengo *et al.*, 2013: 813).

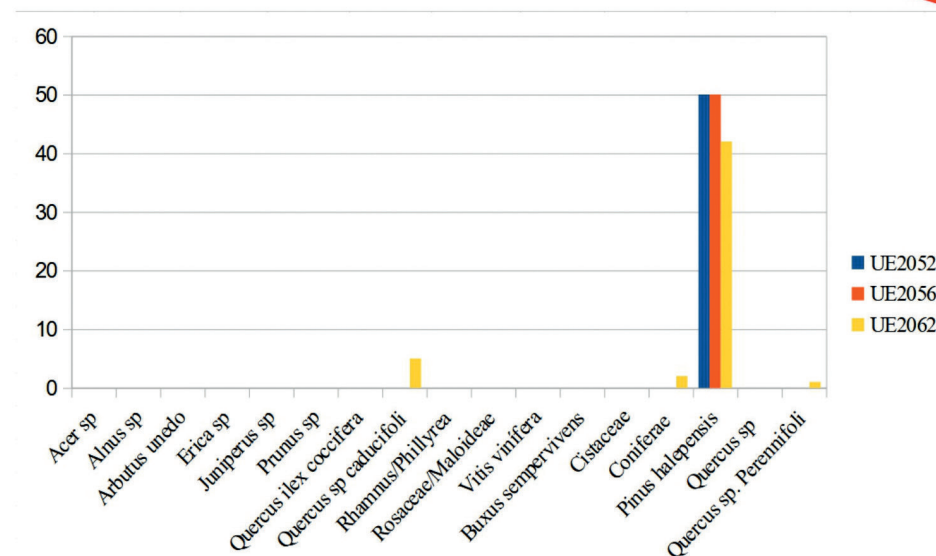
The case of Pla de l'Horta shows us evidence of systematic choice of wood for different purposes. *Quercus* sp. *deciduous* and *Quercus ilex coccifera* are the preferred taxa for ovens linked to the thermal space of the *villa* and other heat chambers, *Rhamnus phillyrea* and *Cistaceae* for small ovens like kitchens and *Pinus halepensis* as the pre-eminent wood in the productive space, linked to a certain



A



B



C

FIG. 9. A) General view of the combustion zone; B) section of the area where are found the strata whit charcoal from Aleppo pine; C) graphic representation of preponderance of Aleppo pine (*Pinus halepensis*) found in this area.

activity that is not yet clearly defined (Costa *et al.*, 2023; Costa and Vivó, 2024).

The residue analyses of our case of study have revealed the application of pine resin in 9 of the samples, 3 of them, from the late Roman warehouse (Costa *et al.*, 2024: 107-108). Dehydroabietic acid, identified in this sample study, stands out as the most abundant component of aged tar from pinus species, confirming data from anthracological studies conducted at the site (Costa and Vivó, 2024: 107-112) (Fig. 10). It occurs naturally but can also be a product from the thermal dehydrogenation of abietic and pimaric acid, the principal resin acids of conifers, also found in the samples. The presence of both retene and methyl-dehydroabietate can be considered an indicator of pine pitch produced by the pyrolysis of wood as retene is a product mainly formed when the resin is processed at high temperatures. In our case study, the absence of other heat biomarkers or any PAH indicating the production of pine tar (Dimitrakoudi *et al.*, 2011) suggest the use of fresh pine resin. At this point, we can observe a systematic choice of pinewood, obtained in the forest near the property of the *villa*, for two uses: first,

the acquisition of resin –an activity probably done in the same forest–. After the resin was extracted, pine wood was used as fuel for other activities not related to resin production.

8. Conclusions

Consistent with several classical sources, archaeological evidence and scientific publications, this investigation reaffirms the utilization of plant-based resin for producing pitch, employed in conditioning ceramic vessels, as demonstrated by the different evidences found in the Roman *villa* of Pla de l'Horta. An initial analysis aimed to identify absorbed fatty acids within these containers' walls and bases. The outcomes confirmed the presence of biomarkers associated with olive oil, alongside a minor presence of markers associated with prior animal fat use. Probably, apart from one *dolia* –D16–, the rest of the vessels were mainly used to store vegetable oil, possibly olive oil. However, at some point in their useful life, they may also have contained substances of animal origin, from both ruminant

SAMPLE NAME	SAMPLE WEIGHT (g)	TOTAL LIPID EXTRACT $\mu\text{L/g}$	FREE FATTY ACIDS	ABIETIC ACID DERIVATIVES	PIMARIC ACID DERIVATIVES	INTERPRETATION
PH21 UE 2207-1	0.35	41,58	yes	yes	yes	pine resin
PH21 UE 2207-2	0.23	58,04	no	yes	no	pine resin
PH21 UE 2207-3	0.30	0	-	-	-	absence of residues
PH21 UE 2207-4	0.28	29,16	yes	yes	yes	pine resin
PH21 UE 2207-5	0.24	29,47	yes	yes	yes	pine resin
PH14 D2	0.23	10,22	yes	yes	no	traces of pine resin
PH14 D13	0.23	0	-	-	-	absence of residues
PH14 D21	0.16	55,88	yes	yes	yes	pine resin
PH14 D22	0.35	2,08	yes	yes	no	pine resin
PH19 UE 2136	0.44	20	yes	yes	-	pine resin
PH21 UE 2184	0.29	0	-	-	-	absence of residues
PH21 UE 2186	0.18	455,02	yes	yes	yes	pine resin
PH21 UE 2191	0.63	0	-	-	-	absence of residues
PH21 UE 2193	0.46	0	-	-	-	absence of residues

FIG. 10. Main results from the total lipidic content extracted from the pottery and interpretation (second study).

and non-ruminant species. In addition, the Pla de l'Horta study also detected the presence of β -sitosterol, a plant sterol that helped to independently confirm the plant nature of the fats stored in the *dolia*, resolving some of the ambiguity generated by the isotopic analyses. A subsequent study substantiated these findings, uncovering traces of pine resin.

The case study of the Roman *villa* at Pla de l'Horta demonstrates in an exemplary manner how the integrated application of different analytical techniques can reveal economic and technological practices of the past in great detail. The main findings confirm that the *dolia* in the late Roman warehouse were used to store a plant product, most likely olive oil, and that they were systematically waterproofed with fresh pine resin obtained from the forests near the *villa*. A comparison of the methodologies used allows the following key conclusions to be drawn about their application in waste archaeology:

1. GC-FID: GC-FID is confirmed as an indispensable and cost-effective screening step for verifying lipid preservation, although its inability to provide structural data limits it to a purely qualitative initial role.
2. GC-C-IRMS: This offers a robust diagnosis for determining the origin of fats. However, this case study demonstrates that its results can be ambiguous in the face of complex mixtures or dietary factors, requiring cautious interpretation that recognises its limitations.
3. GC-MS: GC-MS proves to be the decisive technique, indispensable not only for the unequivocal identification of diagnostic biomarkers –resins, sterols– that resolve ambiguities, but also for revealing entire technological practices that are invisible to methods focused exclusively on lipids.

Ultimately, this work highlights the importance of adopting an integrated or 'multi-proxy' methodological approach in waste archaeology. True strength lies not in a single technique, but in the strategic combination of different chemical analyses and their contextualisation with archaeological and palaeoenvironmental data, such as anthracology.

The detection of pine resin has been interpreted as a method for waterproofing the interior of the *dolia*. Given the paramount importance of preserving the integrity and impermeability of these containers throughout their lifespan, as evidenced by the lead staple repairs previously mentioned, it is plausible to consider the use of pine resin to waterproof and mend small cracks in the *dolia*'s walls. Its application could serve as a solution to minor ruptures or fissures that, at certain points, might compromise the *dolia*'s seal. Since these ruptures could be subtle, they could not be repaired using the known lead staples as a preliminary step before filling the containers, hence the utilization of pine resin (Costa *et al.*, 2024). As Romanus's study showed, when a pitch layer was applied, it significantly impeded oil permeation through the ceramic matrix. This suggests that using a pitch barrier is recommended to prevent oil losses during storage (Romanus *et al.*, 2009: 908).

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