Supporting Information

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SI Text

Sample Preparation and Extraction

The amphora sherds were first examined macroscopically and under low magnification. Soil adhering to the amphora sherds was then physically removed, followed by light washing with distilled water. Resin-like particles were noted in the interior soil of nos. 4 and 8. The interiors of nos. 4 and 5 had small, darkened areas in places, possibly remnants of ancient residues. Only no. 9 had a black resin-like deposit covering its entire interior surface. No. 7 had a yellowish clump of resin-like material filling the toe of its base, which did not extend up the sides of the interior. Even in the absence of visible residues, the aluminosilicate structure of pottery is ideal for absorbing and retaining ancient organic compounds, especially those with polarity.

The interior surfaces of the sherds were ground down to a depth of 1–3 mm with a Dremel rotary grinder with a tungsten-carbide burr. To remove and discard this interior surface, as some researchers do (1), would have been largely to destroy the samples. It should also be noted that the amphora interiors were less exposed to any ground-water contamination. Samples of ground-down pottery, soil containing resin-like particles (nos. 4 and 8), the resin-like material in no. 7, and the pressing platform sample were pulverized with an agate mortar and pestle.

For the ground-down pottery, our standard chloroform/methanol procedure (2, 3) by either Soxhlet extraction or boiling in borosilicate glassware for 30 min, combining and evaporating to dryness, was used. The latter procedure was sometimes preferable because of the build-up of fine clay particles in the Soxhlet apparatus.

The platform, which had only been cleaned by physical means and water since its excavation, was sampled by chiseling away an ~5 × 5-cm interior area of the limestone, which had a reddish coloration on its surface, to a depth of 2–3 mm, and pulverizing.

The samples weighed about 3–5 g and yielded from <5–400 mg of extract. The highly sensitive Fourier-transform infrared spectrometry (FT-IR), gas chromatography-mass spectrometry (GC-MS), and liquid chromatography-mass spectrometry (LC-MS) analyses required very small amounts of these samples (0.1–0.2 mg). Three extractions of 14 g of the platform sample yielded a total extract of 9 mg for the FT-IR and GC-MS analyses.

FT-IR Databases and Searches

FT-IR spectra were searched for "matches" against large databases of relevant natural products and processed organic materials, synthetic compounds, modern wine samples, and "ancient wine reference samples." The latter were residues from ancient vessels that likely originally contained wine, based on strong archaeological criteria or exterior inscriptions that recorded their contents. All of the samples, except no. 8, provided matches to ancient and modern wine samples, especially those that were resinated, to a high level of probability (90 or above on a scale of 100, according to Thermo Scientific's proprietary OMNIC algorithm).

The primary IR data are not presented here because of limitations of space. Moreover, for the purpose of this paper, the pertinent compounds are much more exactly characterized by gas chromatography-mass spectrometry (GC-MS), ultraHPLC tandem mass spectrometry (LC/MS/MS), HPLC with a linear ion trap-Orbitrap mass spectrometry (Orbitrap LC/MS), and headspace solid phase microextraction (SPME) coupled to GC-MS. Suffice it to say that the higher-polarity tartaric acid, which was extracted by methanol, has a distinctive doublet in the 1,740–1,720 cm^{-1} carbonyl region, with a less intense shoulder at the lower wave number (frequency). Its hydroxyl absorption occurs in the 1,450–1,430 cm^{-1} region. By contrast, the carbonyl of lower-polarity resinous acids, which were extracted by chloroform, has a single intense absorption at 1,720–1,700 cm^{-1}, and its hydroxyl absorption is in the 1,470–1,455 cm^{-1} region. Some researchers claim that resin absorption overlaps with tartaric acid in the 1,740–1,720 cm^{-1} region; their own spectra (figure 4 in ref. 4), however, belie this assertion in showing a significantly lower carbonyl peak (1,710–1,700 cm^{-1}).

GC-MS Extractions and Analyses

For the liquid-injection GC-MS analyses, already extracted samples were taken up in a 1:1 mixture of chloroform and methanol, heated for 1 h at 60 °C, centrifuged, the solubles concentrated down, and derivatized by either methylation with Alltech II Me-Prep or by silylation with BSTFA (*N*,*O*-bis(trimethyl-silyl)trifluoroacetamide). The silylated samples were treated with a small amount of formic acid to acidify any tartrate present to tartaric acid. One-microliter samples were injected splitless onto a 30 m × 250 μm × 0.25 μm film thickness HP-5MS column (5% phenyl methyl siloxane) of an Agilent HP 6890 GC, run at a 1.5 mL/min flow rate. An HP 5973 mass selective detector was used with the injector port at 325 °C. The oven temperature was held at 50 °C for 2 min, then programmed to increase at 10 °C/min to 325 °C where it was held for 10.5 min for a total run time of 40 min. The transfer line to the mass spectrometer was at 300 °C. The key silylated tartaric acid ion at *m/z* 219 was detected by selected ion monitoring, which enhances sensitivity. Compound identification was made by retention time and mass spectrum using National Institute of Standards and Technology (NIST) 05.

Some of the GC-MS analyses were overloaded (e.g., peak B in Fig. S3, representing the dominant compound, dehydroabietic acid, in the residue). Despite overloading, the compound eluted at the correct retention time and with the correct masses. If the sample had been diluted to prevent overloading, the terpenoid components present in lower concentrations would not have been detected.

LC/MS/MS Extractions and Analyses

Because previous analyses of the extracted powders had been negative, separate extractions of soil containing resin-like particles (nos. 4 and 8), the resin-like material in no. 7, and the platform sample were carried out at the Alcohol and Tobacco Tax and Trade Bureau (TTB). Approximately 50–75 mg of the soil and resin-like material and 620 mg of the platform were mixed in 5 mL of 1% to 2.8% ammonium hydroxide in water/methanol (80:20, vol/vol), stirred overnight, and ultrasonicated for 1 h. Two milliliters of methylene chloride were added to samples that appeared to be more resinous. Ammonium hydroxide enhances dissolution of tartaric acid in basic solution so that the latter can be detected as the negative ion and its fragments. All aqueous extracts/suspensions were concentrated by evaporating off the methanol and/or reducing the water content, followed by filtration through a 0.45-μm Nylon Acrodisc filter.

It should also be noted that short retention times are typical for ultrahigh performance LC methods and present no problem in separating tartaric acid from other compounds that elute at later retention times. More importantly, our identification techniques relied on multiple factors, including retention times and accurate mass measurements that enable the unambiguous identification of tartaric acid.

Orbitrap LC/MS Extractions and Analyses

Samples of Lattara nos. 4 and 7 were also analyzed by Orbitrap LC/MS using the same extract solutions as for LC/MS/MS. The

LC/MS/MS extract of the platform sample was also purified by solid phase extraction before analysis.

After conditioning with 2 mL of methanol and 2 mL of ultrapure water, ~600 μL of extract was loaded onto a Waters Oasis Max 3-cc cartridge and rinsed with 2 mL of 5% ammonia in water followed by 2 mL of methanol. Tartaric acid (and other organic acids) were then eluted using 2 mL of 5% formic acid in methanol. The eluate was dried in a CentriVap (Labconco), resuspended in 100 μL of 2.8% NH_3 in water, and transferred to an HPLC vial.

A Thermo Scientific Accela High Speed LC coupled to a Thermo Scientific LTQ Orbitrap XL hybrid mass spectrometer was used for the analyses. HPLC separation was achieved with a Phenomenex Luna 5 μm phenyl-hexyl column (1.00 mm × 250 mm) maintained at 40 °C and a flow rate of 100 μL/min. Mobile phase (A) was composed of 10 mM ammonium formate, pH 8.4, and mobile phase (B) was acetonitrile. Mobile phase (B) was ramped from 0% to 85% over 5 min, held constant at 85% until 11 min, then ramped back down to reequilibrate the column. A 10-μL sample injection was used.

The experimental parameters were optimized as follows: spray voltage 2.2 kV, tube lens 85 V, ion transfer capillary voltage of −26 V, ion transfer capillary temperature 275 °C, sheath gas 30 (arbitrary unit, a.u.), and auxiliary gas 5 (a.u.). Both the sheath gas and auxiliary gas were nitrogen. Full scan spectra were acquired over a mass range of *m/z* 50–250. To maintain a sufficient number of data points across chromatographic peaks, a mass resolution setting of 15,000 (at full-width-half-maximum for *m/z* 400) was used, which resulted in a mass resolution of ~27,000 for tartaric acid. Automated gain control (AGC) was set to 5×10^5 ions with a maximum injection time of 1 s. For MS/MS measurements, the AGC was set to 1×10^4 ions with a maximum injection time of 100 ms, and the mass window for precursor ion selection was set to 1.0. Parent mass selection, collision induced dissociation (CID), and fragment mass detection all occurred in the ion trap. For tartaric acid, the collision energy was set to 28%; the compound was monitored for the molecular fragment at *m/z* 87.

External calibration for negative ion mode in the range of *m/z* 150–2,000 was performed using a mixture of SDS, sodium taurocholate, and Ultramark 1621 in an acetonitrile-methanol-water solution containing 1% acetic acid. A formic acid dimer (*m/z* 112.98563, $[M_2 + Na - 2H]^-$) in the background was used as an internal lock mass, which resulted in a typical mass accuracy of less than 1.0 ppm.

Tartaric acid, malic acid, succinic acid, and citric acid in the sample extracts were identified by (*i*) correlating sample compounds with known standards at the experimentally determined chromatographic retention times, and (*ii*) comparing accurate mass measurements with theoretical exact masses for the organic acids. Elemental compositions were calculated from the deprotonated molecule with introduced limits of carbon (0–30), hydrogen (0–60), nitrogen (0–10), and oxygen (0–15), with a mass tolerance of 2 ppm. Peak areas were obtained by either manual integration or by the ICIS peak algorithm in the Xcalibur software package.

Orbitrap LC/MS has been applied to the study of highly complex samples, including meteorites (5), petroleum (6), humic substances (7), and here to the analysis of archaeological samples, for which it proved to be well-suited.

Soil and Stone Control Samples

Orbitrap LC/MS was also used to assess the background levels of tartaric acid produced by microbial activity. Two soil samples (dated *ca*. 425–400 B.C. and 400–350 B.C.) from the same courtyard where the platform was located (zone 27, sector 9), close to the merchants' room, were sampled and sent in March 2013. Similarly, a limestone fragment, mineralogically comparable to the limestone of the pressing platform, was obtained from the nearby city wall (dated *ca*. 475–400 B.C.). After removing vegetation and foreign materials, the soil and limestone control samples were pulverized with a ceramic mortar and pestle. Heterogeneity effects were minimized by grinding and mixing 650- to 750-mg portions of each sample. A second sample of the ancient platform (no. 2) was also run to assure uniform procedure.

In accordance with the LC/MS/MS extraction method, precisely weighed samples were then stirred overnight in a 2.8% ammonium hydroxide in water/methanol (80:20, vol/vol) solution. Each solution was filtered using a Monoject 1 mL syringe equipped with a Pall Life Sciences Acrodisc 25-mm syringe filter with 0.2-μm Supor membrane. Before the sample solution was filtered, we prewet the syringe filter by filtering ~1 mL of 2.8% NH_4OH:MeOH solution through it. Sample solutions usually required two syringe filters due to build up of solid material on the syringe filter. All sample solutions appeared clear and colorless after filtration. Following the protocol described above, and which we used previously, they were then purified by solid phase extraction with ~100% recovery of tartaric acid based on standards, and analyzed.

It should be noted in Dataset S4 that the ancient pressing platform samples, when averaged, have a tartaric acid amount that is more than four times that of the city wall control sample. The ancient Lattara amphoras exceed the amount of tartaric acid in the soil samples, when averaged, by more than two orders of magnitude (Lattara no. 4) and by about three times (Lattara no. 7). These are significant differences, especially when other considerations are taken into account. Because the control samples were gathered during the rainy season, when microbial activity is more intense, their tartaric acid contents can be expected to be higher than usual. It is also likely that the amount of tartaric acid in the platform has declined following its excavation in 1998 and especially after it was moved to the excavation storehouse (1999–2008) and then to the museum (2008–present). Particularly in the climate-controlled environment of the museum, any tartaric acid produced by microbial activity would be minimized.

SPME Extractions and Analyses

Using fresh powdered samples, the headspace SPME analyses were carried out on an Agilent HP 6890 GC with a 5973 mass selective detector, equipped with an HP-5MS column (30 m × 250 μm × 0.25 μm) and Gerstel MPS2 Multipurpose Autosampler with a divinylbenzene/carboxen/polydimethylsiloxane 50/30 μm fiber. Fifty milligrams of sample were suspended in 1 mL of deionized water, to which 0.5 g of NaCl was added. The fiber was exposed to the headspace of the saline suspension at 70 °C for 10 min, followed by 3 min desorption and splitless injection into the GC-MS at 250 °C. To identify possible carryover compounds or contaminants, blank control samples, consisting of only the aqueous saline solutions, were run between the analyzed samples. The mass spectrometer was operated in the scan mode from 40 to 400 atomic mass units. The oven was heated for 29 min from 50 °C to 250 °C at 7 °C/min, and a constant pressure flow rate of 1.2 mL/min was maintained on the column. The compounds were identified by matching scores of 80 or above to those in the NIST 05 and 08 mass spectral libraries (comprising more than 160,000 compounds).

This method is of great utility in biomolecular archaeological studies. It requires only milligram quantities of valuable archaeological samples, and analyses can be performed rapidly, at lower detection limits, in an aqueous saline solution without prior extraction in an organic solvent.

Tartaric Acid as the Principal Grape Biomarker in the Near East and Mediterranean

Barnard et al. (8) recently claimed that malvidin is a better biomarker than tartaric acid/tartrate for identifying the Eurasian grape and its products in the Near East and Mediterranean regions, including Italy. However, a recent, very thorough bioinformatics search confirms the long-established and general

reliability of Singleton's data (9), namely, that the concentration of tartaric acid in grape (4,000 mg/L) is twenty times that of malvidin (200 mg/L), as a conservative estimate. Natural sources for malvidin, as might be expected for a pigment, are also much more broadly distributed than plants with tartaric acid. They include pomegranate (*Punica granatum*), carrot (*Daucus carota*), apple (*Malus domestica*), whortleberry/bilberry (*Vaccinium myrtillus*), red clover (*Trifolium pratense*), and crocus (*Crocus sativa*).

Ref. 8 also incorrectly states that Middle Eastern hawthorn fruit has high amounts of tartaric acid. Although the tartaric acid concentrations in two Chinese hawthorn species (*Crataegus pinnatifida* and *C. cuneata*) do exceed those of grape (10), the chemistries of different species of the same genus in different regions of the world can vary enormously. Unless trade relations can be established by archaeological evidence between diverse regions at the time under consideration, other plants with high tartaric acid—e.g., tamarind from the Indian subcontinent, hawthorn fruit and star fruit from east Asia, or yellow plum from the New World—are irrelevant. For the period of this paper, *ca.* 525–400 B.C. in southern France and Etruria, no archaeobotanical evidence exists for these nonnative plants.

Pomegranate is the only close contender to grape in having relatively large amounts of both tartaric acid and malvidin. Aarabi et al. (11) state that pomegranate has about 600 mg/L of tartaric acid. However, this fruit is also irrelevant for this discussion because archaeobotanical remains of pomegranate at Lattara are nonexistent.

Thus, if tartaric acid/tartrate is present in an ancient sample, especially together with other organic acids (including succinic, malic and citric, as unambiguously identified by Orbitrap LC/MS here; also see ref. 12) and alcohols, esters, aldehydes, and terpenoid compounds characteristic of modern grape (as identified by SPME here), then the probability increases for a grape product.

Methodological Approach to Identifying an Ancient Grape Product as Wine

Assuming that tartaric acid/tartrate has been identified in an ancient vessel, then several other archaeological and enological factors must be assessed, to determine whether the intended product was wine and not another grape product. A syrup, produced by heating grape juice and concentrating it down, was unlikely for the Lattara amphoras because its viscosity would have left a uniform coating of residue on the inside of the vessel, which was absent. Minimally, then, the amphoras and pressing platform had contained or had come in contact with grape juice. However, any grape juice would not have remained nonalcoholic for long in a warm climate, such as central Italy, given the slow pressing methods used in antiquity. Grape juice naturally ferments to wine in several days, because yeast (*Saccharomyces cerevisiae*) is always present on some grape skins. These microorganisms thrive in grape juice, which is an ideal medium of water and nutrients for their multiplication, and convert the sugars in the juice into alcohol and carbon dioxide. Because of the evident precautions that were taken to protect the liquid from oxygen (stoppering the mouths of the amphoras and adding a tree resin that has antioxidant properties), the intended beverage was then almost certainly wine, not vinegar.

Ancient Medicinal Wines and Fermented Beverages

Chemical analysis opens up a new perspective on early Etruscan pharmacology, even preceding written texts, by providing contemporaneous data on the botanicals added to wine. For the wine imported into Lattara, rosemary and/or basil are the most likely additives. Botanically laced wine, especially with rosemary, is also attested chemically at about the same time or somewhat later for funerary rites in northern Etruria and as the principal cargo of ships that foundered in the Adriatic, Ionian, and Aegean Seas. Rosemary was a popular food and beverage flavorant in Roman and Byzantine times, which might account for its avid consumption as a wine additive in Byzantine Nubia (2). Moreover, it contains numerous antioxidant compounds (e.g., rosmarinic acid and carnosol), which have potentially wide-ranging medicinal benefits (13).

Adding a tree resin to wine, to protect against wine disease as well as for medicinal purposes and covering up off-tastes and off-aromas, was a popular and widespread practice throughout the ancient world (14). Later literary references in Pliny the Elder, Strabo, Cato, and others make it abundantly clear that Etruscan wine was often mixed with both fresh pine resin and processed pitch to make *vinum picatum* (Latin, "pitched wine") (15), which left resinous splotches on sidewalls and accumulations on the bases of bronze wine cauldrons at sites throughout Etruscan and Ligurian Italy and Celtic Gaul as early as the fifth century B.C. (16). A metal such as bronze did not need to be sealed with tar, as became more customary for pottery amphoras and other containers in later periods. Resinated wines were still being made in the Middle Ages, according to the extensive agricultural and medical compilations based on classical writings, collectively known as the *Geoponica* (e.g., ref. 17).

Other researchers have begun to report botanical and chemical evidence for herbal concoctions in alcoholic beverages. Far in advance of the Etruscan evidence, native rosemary and mint, together with thyme, were added to a fermented emmer wheat and barley beverage at Genó, near Barcelona in Spain, around 3000 B.C. (18). Mugwort (*Artemisia vulgaris* in the wormwood family), also detected in some of the early Spanish brews, was hypothesized to have been an additive, together with carrot, in a dark, sour barley beer (19) at the settlement of Hochdorf, located next to the tumulus burial for the Celtic prince who was honored in death by a cauldron filled with mead. Wild rosemary continued to be an ingredient in gruit, the principal bittering agent in early medieval European beer, along with bog myrtle, yarrow, and other herbs (20).

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Fig. S1. Two analyzed Lattara samples, according to their representative archaeological types: no. 4 (*Upper*), an Etruscan amphora, and 8 (*Lower*), a Massaliote amphora (photograph and drawings by B.P.L.).

Fig. S2. Remains of the foundations of the Etruscan merchants' quarters in zone 27 of Lattara, dated *ca*. 525–474 B.C. Amphora nos. 4, 5, and 7 came from the concentration of amphoras in room 15 (*Inset*). Photographs courtesy of Michel Py, copyright l'Unité de Fouilles et de Recherches Archéologiques de Lattes.

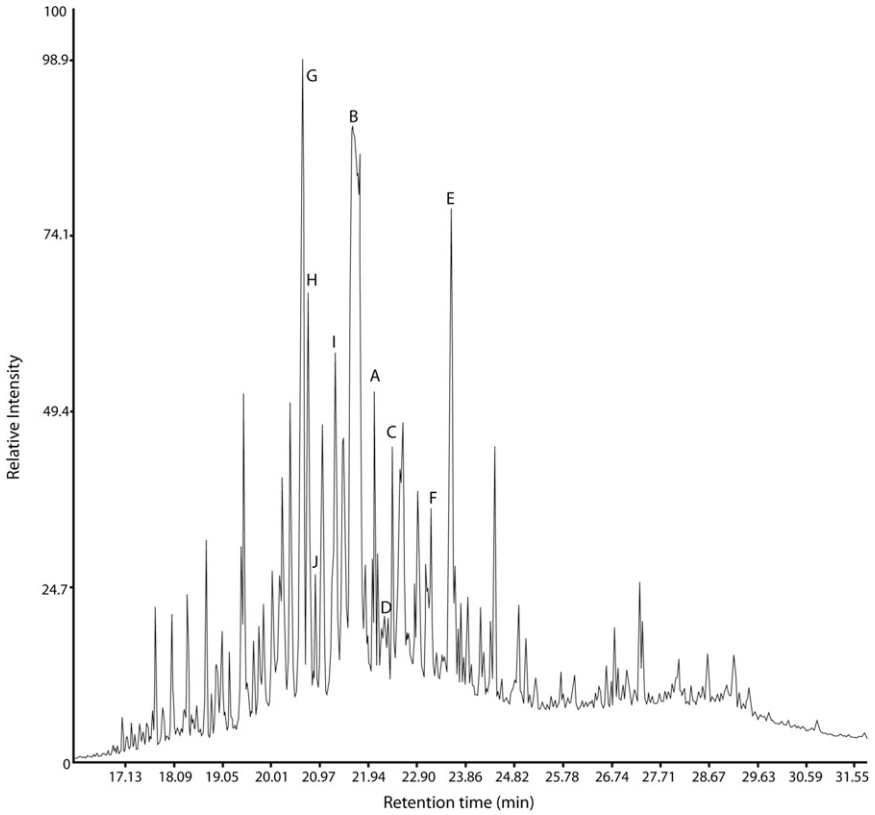

Fig. S3. GC-MS chromatogram for Lattara no. 4, an Etruscan amphora. A, abietic acid; B, dehydroabietic acid; C, tetradehydroabietic acid; D, hexadehydroabietic acid; E, 7-oxo-dehydroabietic acid; F, 15-hydroxy-dehydroabietic acid; G, retene; H, pimaric acid; I, isopimaric acid; J, sandaracopimaric acid.

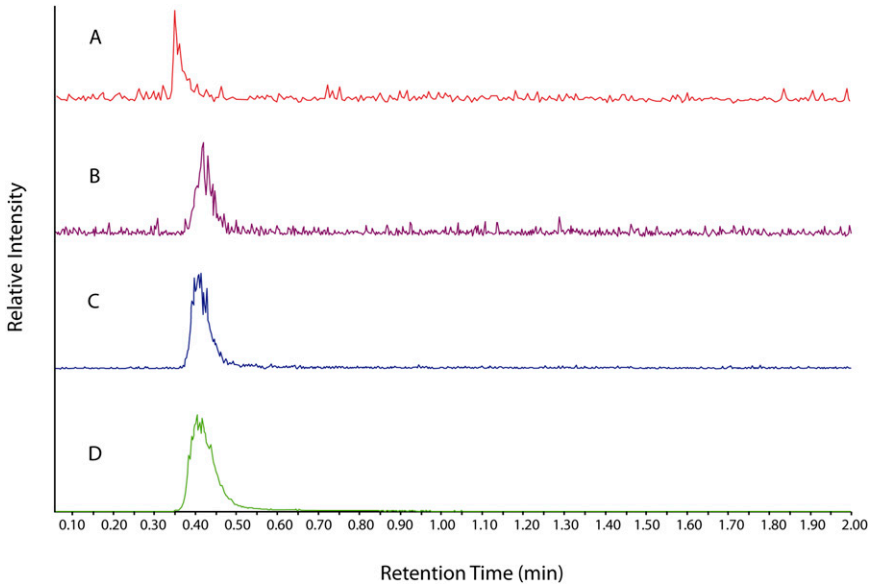

Fig. S4. Multiple reaction monitoring LC/MS/MS traces of L-tartaric acid corresponding to *m/z* 149→87 molecular ion fragmentation for an Etruscan amphora, Lattara no. 4 (*A*) and a Massaliote amphora, Lattara no. 8 (*B*), compared with standard solutions of L-tartaric acid and calcium tartrate (*C* and *D*, respectively). The 4-s earlier retention time for sample no. 4 is due to a slightly different extraction procedure.

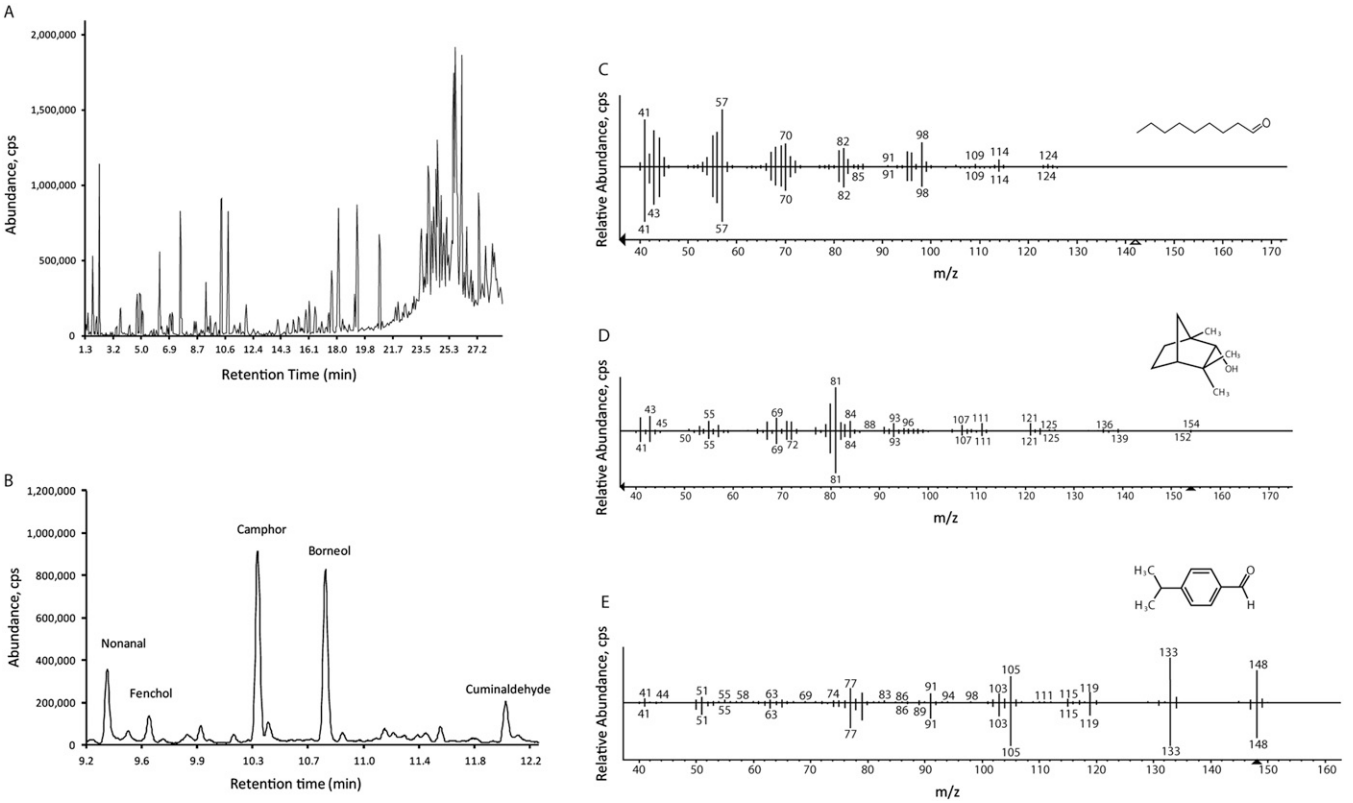

Fig. S5. SPME total ion chromatogram (*A*) of Lattara sample no. 4, with the chromatogram expanded in the 9.2–12.2 min range (*B*) and showing the experimental electron ionization (70 eV) mass spectra of nonanal (*C*), fenchol (*D*), and cuminaldehyde (*E*). The *Upper* traces of *C*–*E* are the experimental mass spectra; the *Lower* traces are NIST 08 database matches. Representative mass spectra of camphor and borneol are published in ref. 2.

Fig. S6. Black-figured vase by the Amasis Painter of sixth century B.C. Athens, recovered from the Etruscan site of Vulci, shows a busy winemaking scene in the vineyard. A hairy satyr merrily stomps away inside an open basket, filled with grapes, from which yellowish juice runs out through the spout of a flat basin, shaped like the Lattara wine pressing platform, into a large jar or *pithos* buried up to its shoulders in the floor. Note the grapevine, supported on poles and trained vertically and horizontally—this trellis method is useful in opening the grapes up to greater airflow and more sunlight for ripening and easy care and harvesting. The yellowish juice points to a white wine and grape, rare in the pre-Roman ancient world. This ceramic masterpiece is the earliest depiction in the Greek world that shows a sequence of vinicultural activities (picking, treading, fermentation) and highlights the close connection of winemaking to music, dance, religion, and celebration. Photograph courtesy of the Martin von Wagner Museum, University of Würzburg. Photograph by P. Neckermann (redrawn and adapted by B.P.L.).

Dataset S1. Description and primary chemical compounds/families of analyzed amphora and pressing platform samples from Lattara

Dataset S1

Dataset S2. Pine tree resin compounds identified by GC-MS for amphora and platform samples from Lattara

Dataset S2

Dataset S3. Chemical compounds identified by SPME for Etruscan amphora nos. 4 and 5 from Lattara

Dataset S3

Dataset S4. Orbitrap LC/MS data for soil and limestone control samples, ancient amphoras, and pressing platform from Lattara

Dataset S4