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Fermented beverages of pre- and proto-historic China

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Chemical analyses of ancient organics absorbed into pottery jars from the early Neolithic village of Jiahu in Henan province in China have revealed that a mixed fermented beverage of rice, honey, and fruit (hawthorn fruit and/or grape) was being produced as early as the seventh millennium before Christ (B.C.). This prehistoric drink paved the way for unique cereal beverages of the proto-historic second millennium B.C., remarkably preserved as liquids inside sealed bronze vessels of the Shang and Western Zhou Dynasties. These findings provide direct evidence for fermented beverages in ancient Chinese culture, which were of considerable social, religious, and medical significance, and help elucidate their earliest descriptions in the Shang Dynasty oracle inscriptions.

archaeological chemistry | Neolithic period | Shang Dynasty | alcohol | saccharification

Throughout history and around the world, human societies at every level of complexity discovered how to make fermented beverages from sugar sources available in their local habitats (1). This nearly universal phenomenon of fermented beverage production is explained by ethanol's combined analgesic, disinfectant, and profound mind-altering effects (2). Moreover, fermentation helps to preserve and enhance the nutritional value of foods and beverages. Because of their perceived pharmacological, nutritional, and sensory benefits, fermented beverages thus have played key roles in the development of human culture and technology, contributing to the advance and intensification of agriculture, horticulture, and food-processing techniques (1, 3). Among all strata of society, they have marked major life events, from birth to death, as well as victories, auspicious events, and harvests, etc. Rulers and "upper class" individuals with leisure and resources particularly were drawn to feasting on a grand scale, which often featured special fermented beverages served in and drunk from special vessels (4). In their most developed form, such celebrations were formalized into secular or religious ceremonies for the society at large.

How does ancient China, one of the primal centers for the rise of human civilization, fit into this picture of fermented beverage production, conspicuous consumption, and celebratory and ritual activities that are so well documented archaeologically, historically, and ethnographically elsewhere? Based on the oracle inscriptions from the late Shang Dynasty [circa (*ca.*) 1200–1046 before Christ (B.C.)], the earliest texts from China, at least three beverages were distinguished (3, 5, 6): *chang* (an herbal wine), *li* (probably a sweet, low-alcoholic rice or millet beverage), and *jiu* (a fully fermented and filtered rice or millet beverage or "wine," with an alcoholic content of probably 10–15% by weight). According to inscriptions (6), the Shang palace administration included officials who made the beverages, which sometimes were inspected by the king. Fermented beverages and other foods were offered as sacrifices to royal ancestors in various forms of bronze vessels, likely accompanied by elite feasting (7). Later documents, incorporating traditions from the Zhou period (*ca.* 1046–221 B.C.), describe another two beverages (5): *luo* (likely made from a fruit) and *lao* (an unfiltered, fermented rice or millet beverage or the unfermented wort).

A much earlier history for fermented beverages in China has long been hypothesized based on the similar shapes and styles of Neolithic pottery vessels to the magnificent Shang Dynasty bronze vessels (8), which were used to present, store, serve, drink, and ritually present fermented beverages during that period. By using a combined chemical, archaeobotanical, and archaeological approach, we present evidence here that ancient Chinese fermented beverage production does indeed extend back nearly nine millennia. Moreover, our analyses of unique liquid samples from tightly lidded bronze vessels, dated to the Shang/Western Zhou Dynasties (*ca.* 1250–1000 B.C.), reveal that refinements in beverage production took place over the ensuing 5,000 years, including the development of a special saccharification (amylolysis) fermentation system (5, 9) in which fungi break down the polysaccharides in rice and millet.

Materials and Methods

Pottery sherds from 16 vessels were extracted and analyzed from domestic contexts at Jiahu (10), an early Neolithic village in Henan province in China, radiocarbon-dated and dendro-calibrated to subperiods III (*ca.* 7000–6600 B.C.), II (*ca.* 6600–6200 B.C.), and I (*ca.* 6200–5500 B.C.). In addition to its repertoire of very early pottery, this site also has yielded the earliest playable musical instruments (11), the earliest domesticated rice in northern China (12), and possibly the earliest Chinese pictographic writing (13). The pottery corpus comprised perforated basins, two-handled, narrow-mouthed storage jars (e.g., Fig. 1*a*), and jars with high, flaring necks and rims, which were well suited for preparing, storing, and serving beverages. The sherds tested were primarily from vessel bases, which absorb more liquid and are where precipitates accumulate.

To assess later developments in the Chinese fermented beverage production, liquid samples of the contents of two late Shang/early Western Zhou Dynasty (*ca.* 1250–1000 B.C.) bronze vessels from Henan province elite burials were extracted and analyzed: a lidded *he* "teapot" (Fig. 1*b*) from the Liu Jiazhuang Tomb at the capital of Anyang (14) and a lidded *you* jar from the Changzikou Tomb in Luyi county (15).

Depending on the analytical technique, solvents of varying polarity (methanol, chloroform, and/or hexane) were used to extract the ancient sherds, either by sonication or by twice boiling for 20 min. The two portions were combined, filtered to remove fines, and gently evaporated to dryness. Before extraction, the sherds were washed gently in water to remove adhering soil. The total amount of solid extract obtained from each sherd ranged from ≈5 to 60 mg, depending on the sherd's size and thickness and the amount of absorbed organic material. An unextracted

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Abbreviations: B.C., before Christ; *ca.*, circa; GC-MS, gas chromatography–mass spectrometry; HPLC, high-performance liquid chromatography; FT-IR, Fourier-transform infrared spectrometry.

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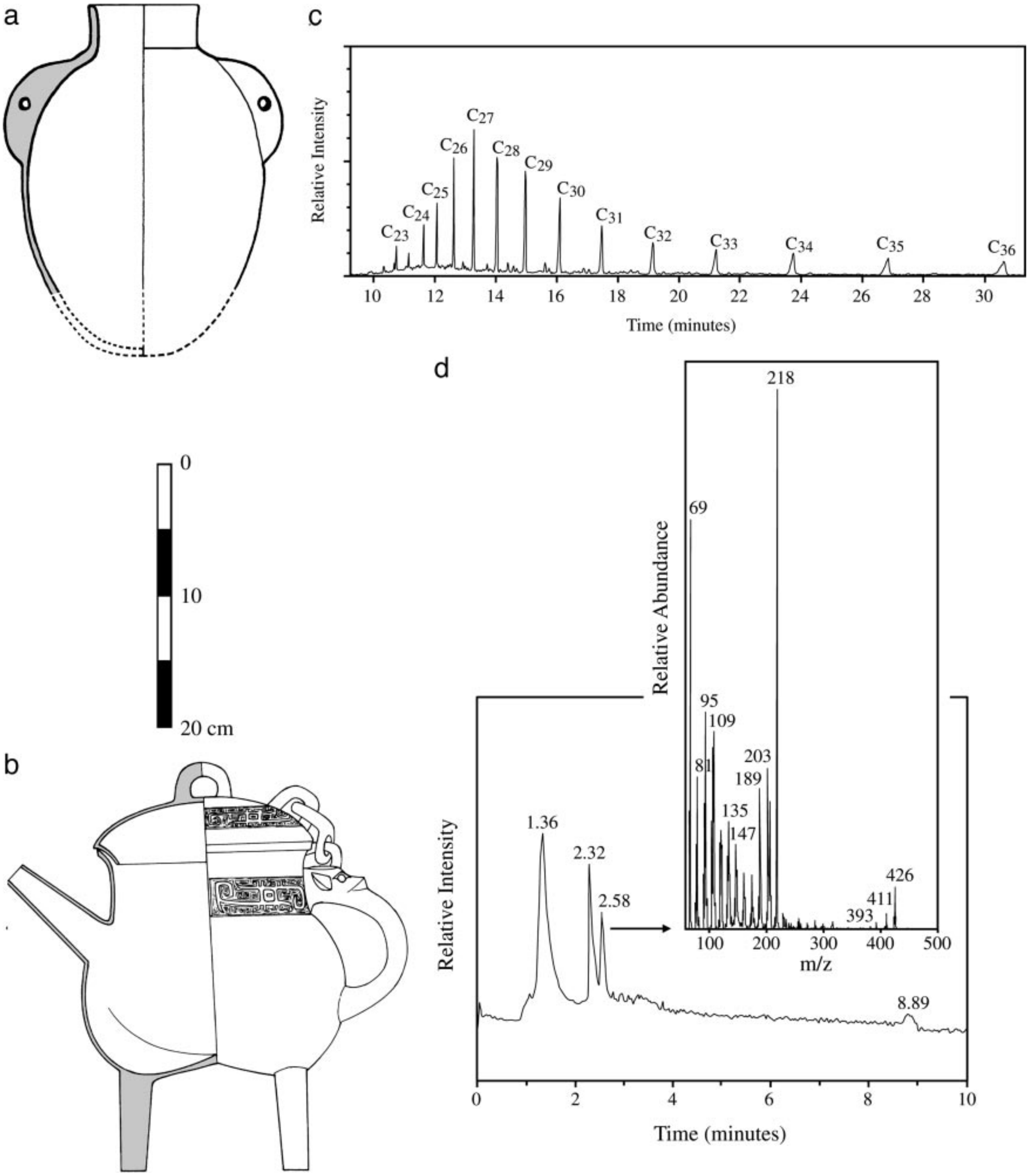

Fig. 1. Representative pottery and bronze vessels dating to the Neolithic period and the Shang/Western Zhou Dynasties, showing selective analyses of their contents. (*a*) Typical Neolithic storage jar from Jiahu (no. T109:65, subperiod II, *ca.* 6600–6200 B.C.). (*b*) Lidded *he* ''teapot'' from Anyang (Liu Jiazhuang Tomb, no. M1046:2, *ca.* 1250–1000 B.C.). (*c*) GC-MS analysis of chloroform extract of *a*, showing homologous series of *n*-alkanes. (*d*) HPLC-MS analysis of chloroform extract of *c*, showing the presence of β-amyrin; oleanolic acid was attested at 8.9 min.

aliquot of each liquid sample was retained for direct analysis of volatile compounds. Solids in the latter also were filtered out and analyzed separately.

Five analytical methods [gas chromatography–mass spectrometry (GC-MS), high-performance liquid chromatography–mass spectrometry (HPLC-MS), Fourier-transform infrared spectrometry (FT-IR), stable isotope analysis, and selective Feigl spot tests] were used to identify the chemical constituents of the pottery and liquid extracts as follows.

Briefly, the protocol for the GC-MS analyses was to run 1-μl chloroform extracts on a standard quadrupole instrument, equipped with nonpolar fused silica columns optimized for sterol analyses, in Drexel University (Philadelphia, PA) and the Eastern Regional Research Center of the U.S. Department of Agriculture. The U.S. Department of Agriculture samples were methylated and injected in a split mode; the Drexel samples, whose small sample size precluded derivatization, were injected in a splitless mode. Total-ion scans were followed up by selected-ion monitoring to identify important, low-level components. Retention times and mass spectra were calibrated by normal paraffin and plant sterol standards. Several blank extractions were carried out to simulate the entire extraction process and analyzed for contaminants and other artifacts caused by sample handling and preparation.

Highly volatile compounds in the liquid samples were detected by a modified GC-MS technique, namely, purge-and-trap ther-

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mal desorption. The aqueous samples were sparged with helium gas, and the organic volatiles were trapped on a short adsorbent column attached to a Scientific Instrument Services (SIS, Ringoes, NJ) Short Path Thermal Desorption accessory. The trapped material then was desorbed onto a cryogenically focused head of a nonpolar fused silica GC column and subsequently eluted. Peaks were identified by retention time and mass spectral matches with standards.

Several types of HPLC analyses were run on the pottery and liquid extracts. At the U.S. Department of Agriculture, 100-μl chloroform extracts were run by using a gradient normal-phase set-up with an evaporative light-scattering detector (16). The same extracts were more definitively characterized by an isocratic normal-phase system, interfaced to a mass spectrometer. At the University of Pennsylvania Museum's laboratory, isocratic normal-phase analyses of methanol extracts were carried out on an instrument equipped with a UV detector. An in-house database of several hundred ancient samples and modern reference compounds was searched for the highest probability matches. Our database includes natural products (e.g., tree resins and beeswax), processed organic materials (such as modern wine, honey, grains, etc.), synthetic compounds generally occurring in natural and processed organic materials of interest, and "ancient reference samples" (i.e., residues extracted from inscribed vessels that state they contained a particular beverages, food, spice/herb, resin, etc., and comprised of both intact and degraded components).

In the University of Pennsylvania Museum's laboratory, diffuse-reflectance FT-IR analyses of approximately 1 mg of methanol- or chloroform-extracted pottery or liquid sample, deresolved at 8 cm^{-1} wavenumber, were searched for the best matches against large commercial databases and an in-house corpus of ancient samples and modern reference compounds. Differences between the spectra of the chloroform and methanol extracts attributable to varying solvent selectivities enabled the fine details of complex mixtures to be worked out.

Stable ^{13}C and ^{15}N isotope measurements (17) were made of the filtered solids from the two liquid samples, as well as chloroform and methanol extracts of the Jiahu pottery sherds, at the University of Bradford. This analytical method can readily distinguish between C_3 and C_4 pathway plants mainly by using the carbon isotope values, because C_3 plants tend to have δ^{13}C values of approximately -27‰, whereas C_4-pathway plants have δ^{13}C values of approximately -13‰. Primarily plant-based natural products also can be distinguished from those that are animal-derived, because plants have lower δ^{15}N values.

Feigl chemical spot tests (18), with microgram sensitivity, were used to test methanol extracts for tartaric and oxalic acids in the University of Pennsylvania Museum's laboratory. Samples containing tartaric acid show a dark green fluorescence when irradiated by UV light; malic acid, one of the few cross-interfering compounds, gives a nonfluorescent greenish solution. The samples were tested together with blanks and solutions of the acids at low concentrations.

Results and Discussion

A minimum requirement for establishing the original contents of an ancient vessel is to identify fingerprint compounds (biomarkers) for specific natural products and ingredients in its extracts. Sometimes unequivocal chemical confirmation, e.g., for Royal Purple dye (19), is achievable. Chemical identification and interpretation, however, often is impeded by environmental and microbial degradation, modern contamination, human processing in antiquity, and the degree to which a region's natural resources have been adequately surveyed for biomarkers. The advantage of using a number of independent chemical techniques, as in this study, is that one's confidence that a particular compound is present increases if the results from each method agree and reinforce one another.

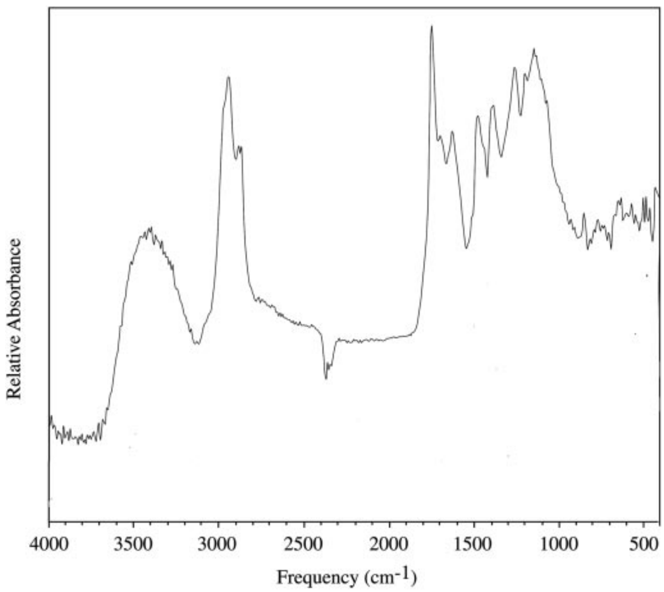

Fig. 2. Diffuse-reflectance FT-IR analysis of storage jar (compare Fig. 1*a*) methanol extract from Jiahu (no. T109:8, subperiod III, *ca.* 6200–5800 B.C.).

Archaeological criteria also must be assessed for their bearing on the original vessel contents. The fabrication and style of a vessel are related to whether it held a liquid, semiliquid, or solid material. Narrow, high-mouthed jars and jugs, for example, were likely used to handle and store liquids. Deep, open vats or bowls, on the other hand, are most convenient for processing more viscous materials or serving solid food. Details of the residue on the interior of a vessel (possibly a precipitate from a liquid), associated archaeobotanical materials, and the archaeological context itself (whether a tomb, residence, workshop, pit, etc.) all can provide clues as to how a vessel was used. Such inferences, based on historical, ethnographic, and modern analogies, are at lower probabilistic levels than the chemical analyses. Yet, they are crucial in developing logically consistent working hypotheses, which are constrained by the limited archaeological record, and in setting the course of future archaeological and chemical research.

An Early Neolithic "Mixed Fermented Beverage." The FT-IR and HPLC results for 13 of the 16 Jiahu extracted pottery sherds, when searched for the closest matches in our databases, showed that they were chemically most similar to one another. This result implies that all these vessels originally contained or were used to process a similar liquid. The three samples that did not match the larger group were extremely small, resulting in less definitive chemical determinations that likely account for their divergency rather than their contents having originally differed.

Besides matching one another, the Jiahu samples yielded good FT-IR and HPLC matches to modern rice and rice wine, resinated and nonresinated grape wine (ancient and modern), modern phytosterol ferulate esters, modern beeswax, modern grape tannins, various tree resins and herbal constituents (ancient and modern), modern diacylglycerols, and modern calcium tartrate. These matches correlate with specific IR absorptions and HPLC retention times and UV absorptions.

Fig. 2 shows an IR spectrum characteristic of the Jiahu group and illustrates how the statistical searches and matches correlate with specific absorptions. The sharp, intense peaks at 2,920 and 2,850 cm^{-1}, as well as the absorption at 730–720 cm^{-1}, are the result of long straight-chain hydrocarbons (e.g., *n*-alkanes). Tartaric acid, the principal organic acid in grape wine and also occurring in other Chinese natural sources (see below), probably accounts largely for

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Table 1. δ^{13}C and δ^{15}N values of ancient Chinese jar extracts and modern reference samples

Sample	Period	δ^{13}C*	δ^{15}N†	C, %	N, %	C:N
Rice (*Oryza sativa*)	Modern	−26.1	5.4	39.8	1.1	41.0
Foxtail millet (*Setaria italica*)	Modern	−10.7	4.1	41.3	2.1	22.8
Broomcorn millet (*Panicum miliaceum*)	Modern	−12.0	2.9	40.9	2.5	19.3
Changzikou Tomb, Luyi county	Shang/Western Zhou	−25.3	4.8	18.7	1.6	13.9
Liu Jiazhuang Tomb, Anyang	Shang/Western Zhou	−15.9	5.3	3.6	0.1	45.1
Jiahu (no. T109:8)	Early Neolithic	−28.6	N/A	90.4	0.1	1,860.1
Jiahu (no. F1/H28/46:16)	Early Neolithic	−21.5	N/A	N/A	N/A	N/A

Because of changes in atmospheric carbon in the last century (the Suess effect), modern isotope values may differ from those in antiquity. Small sample size accounts for some data not being available (N/A).

*Measured relative to the Vienna Peedee belemnite standard.

†Measured relative to air.

the major peak at 1,740 cm^{-1} with a shoulder at 1,720 cm^{-1}. Some contribution from tannins, resins, waxes, and other compounds with carbonyl acid groups, however, cannot be ruled out. These natural products and compounds can be partly distinguished by examining their spectra for greater complexity in the carbonyl region above 1,740 cm^{-1} (most indicative of a tree resin) or in the carbonyl region below 1,720/1,710 cm^{-1} (most indicative of beeswax). The hydroxyl stretch band in the 3,450–3,500 cm^{-1} region is in accord with the tartaric acid interpretation, because tartaric acid contains four hydroxyl groups. Most decisive for tartaric acid is the hydroxyl bending band at 1,435–1,445 cm^{-1}, because other important hydroxyl compounds derived from natural sources and of archaeological interest absorb in the 1,460–1,465 cm^{-1} range. Similarly, a tartrate salt, which is more insoluble than the acid and would be expected to precipitate out of solution, is evidenced by a broad carboxylate absorption between 1,610 and 1,560 cm^{-1}. Other carboxylate peaks (at 1,460 cm^{-1}, 1,390 cm^{-1}, etc.) might be attributable to tartrate or other carbonyl/carboxylate-containing compounds. The presence of tartaric acid/tartrate was further borne out by positive Feigl spot tests for the 13 samples in the Jiahu group.

GC-MS analyses of samples in the Jiahu group also showed the uniform presence of an inclusive series of *n*-alkanes, C_{23}–C_{36} (Fig. 1*c*). Stable isotope analysis (Table 1) gave δ^{13}C values (average −25.1‰) that were consistent with a C_3 plant, such as rice or grape, but not a C_4 plant, such as millet or sorghum. Low δ^{15}N values and a very low proportion of nitrogen rule out an animal source.

The most straightforward interpretation of these data are that the Jiahu vessels contained a consistently processed beverage made from rice, honey, and a fruit. Taking each of these constituents and the combined evidence for their presence in turn, rice is strongly suggested from the IR and HPLC searches and matches. In fact, rice is the only cereal that has been recovered by archaeobotanical methods at Jiahu, and it is predominant in the corpus. To establish beyond doubt that rice was the principal grain in the Jiahu beverage, HPLC-MS and GC-MS analyses were run in search of cycloartenol, the principal alcohol in oryzanol (the phytosterol ferulate ester occurring in rice). The compound was not detected, possibly because of degradation.

Beeswax or a plant epicuticular wax, not represented in our databases but chemically similar to beeswax, was supported by the IR and HPLC matches. $C_{23}H_{48}$, $C_{25}H_{52}$, $C_{27}H_{56}$, and $C_{29}H_{60}$, attested in the homologous *n*-alkane series, are especially characteristic of those in beeswax (20, 21). They serve as biomarkers of honey, because beeswax is virtually impossible to filter out completely when processing honey, and its compounds can be very well preserved. By contrast, the sugars in honey, mainly fructose and glucose, rapidly degrade and are lost. Honey is a unique, concentrated source of simple sugars (60–80% by weight) in temperate climates around the world, and humans discovered and exploited it as a sweetener at an early date. It was very likely locally available in the Jiahu region.

Plant epicuticular wax, which occurs on the surfaces of leaves and fruits of many plants (22), also might account for the *n*-alkanes. If the C_{27} and C_{29} compounds predominate, with lesser amounts of the C_{23}, C_{25}, C_{31}, and C_{33} compounds and even-numbered *n*-alkanes at very low levels, then beeswax is indicated. However, plant epicuticular waxes also have *n*-alkanes within the C_{23}–C_{36} range, with the C_{29} compound usually most prominent. Further complicating the picture, when *n*-alkanes constitute a small percentage of the natural product, then this odd/even preference diminishes (23). This phenomenon is especially pronounced for senescent and fossilized leaves (24) and, presumably, also degraded archaeological samples.

Given their small sample size and age, the most plausible explanation for the Jiahu samples' C_{23}–C_{36} range of *n*-alkanes is that they derive from epicuticular wax and/or beeswax. This result is consistent with the 730–720 cm^{-1} infrared absorption band caused by straight-chain hydrocarbons (25), accentuated in the chloroform extracts. Contamination from petroleum contaminants, possibly derived from groundwater percolation of pesticides or herbicides or laboratory-introduced, was ruled out by running blanks and because the boiling ranges of *n*-alkanes in modern products have different ranges of *n*-alkanes than those observed for the ancient series.

Grape possibly accounts for the tartaric acid/tartrate, because grape seeds of a presumed wild type constitute the primary ancient fruit remains found at Jiahu. With upwards of 40–50 native wild grape species (26), China accounts for more than half of the species in the world. At least 17 wild species grow in Henan province today, and wine is made from fruit containing up to 19% sugar by weight (e.g., *Vitis amurensis* and *Vitis quinquangularis* Rehd. = *Vitis pentagona* Diels and Gilg).

A large amount of tartaric acid/tartrate in an ancient sample is a strong indicator of a grape product in some parts of the world (e.g., the Middle East; ref. 1), but other sources need to be considered for China. Moreover, the scholarly consensus has been that grape wine was first made from the domesticated Eurasian grape (*Vitis vinifera vinfera*), which was introduced into China from Central Asia during the second century B.C. (5), some six millennia later than the Neolithic period at Jiahu. References to native grapes occur as early as the Zhou period (27) but are enigmatic. These texts do indicate, however, that grapes were appreciated for their sweetness and used in beverage-making.

An especially strong candidate for the source of the tartaric acid/tartrate in the Jiahu samples, instead of grape, is the Chinese hawthorn (*Crataegus pinnatifida* and *Crataegus cuneata*; Chinese herbal name *Shan Zha*). This fruit contains four times the amount of tartaric acid in grape (28), and the modern distribution of hawthorn encompasses northern China (29). A high sugar content implies that it could harbor yeast, like grape. When we first entertained the possibility that hawthorn tree fruit might explain the tartaric acid/tartrate evidence, this species was notably absent in the archaeobotanical corpus of ancient China. In 2002, Z. Zhao

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and his colleague, Zhaocheng Kong, first identified seeds of this fruit from early Neolithic levels at Jiahu, thus strengthening the case for its use in the mixed beverage (Z. Zhao and Z. Kong, unpublished data).

Tartaric acid occurs in two other fruits, although in much lesser amounts (30 mg/liter) than in grape (4 g/liter) or hawthorn tree fruit (16 g/liter), namely, longyan (*Euphoria longyan*; *Long Yan*; ref. 30) and Asiatic cornelian cherry (*Cornus officialis*; *Shan Chu Yu*; ref. 31). The fruits of these trees, which are concentrated in southern China today, are moderately sweet and somewhat acidic. They probably grew farther north in Neolithic times when temperatures were likely milder than today.

Other possible sources of tartaric acid/tartrate cannot be ruled out but yield even lesser amounts (0.1–2 mg/liter) of tartaric acid/tartrate. The leaves of some plants (e.g., *Pelargonium* in the geranium family) have raphides of tartaric acid and calcium oxalate (32), which might be dispersed into a liquid by steeping. Saccharification of rice, which was the traditional method of Chinese beverage-makers since at least the Han Dynasty [*ca.* 202 B.C.–*anno Domini* (A.D.) 220], also produces tartaric acid, depending on the mold used (refs. 5 and 33–35, and see below).

The available chemical, archaeobotanical, and archaeological evidence for the Jiahu jars and basins converge to support the hypothesis that they were used to prepare, store, and serve a mixed fermented beverage of rice, honey, and a fruit. Direct chemical evidence of alcohol is lacking, because this compound is volatile and susceptible to microbial attack. Fermentation of the mixed ingredients, however, can be inferred, because the "wine yeast" (*Saccharomyces cerevisiae*) occurs in honey and on the skins of sugar-rich fruits. Once the juice has been exuded from the fruit or the honey diluted down, yeast begin consuming the monosaccharides and multiplying, within a day or two in warmer climates.

Aromatic Wines of the Shang and Western Zhou Dynasties. Analyses of proto-historic liquid samples from tightly lidded bronze vessels, dated to the late Shang/early Western Zhou Dynasties, showed that they constituted somewhat different beverages than the mixed fermented drink of early Neolithic Jiahu. Numerous bronze vessels, variously dated to the Erlitou (*ca.* 1900–1500 B.C.), Shang (*ca.* 1600–1046 B.C.), and Western Zhou periods (*ca.* 1046–722 B.C.), have been excavated at major urban centers along the Yellow River or its tributaries in Hebei, Henan, and Shanxi provinces of northern China, including Erlitou, Zhengzhou, Taixi, Tianhu, Anyang, and other sites (8). Most often, they have been recovered from the elite burials of high-ranking individuals. The shapes of many of the bronze vessels [ornate tripod vessels (*jue* and *jia*), stemmed goblets (*gu*), vats (*zun*), and jars (*hu*, *lei*, and *you*)] imply that they were used to prepare, store, serve, drink, and ceremonially present fermented beverages, which is supported by textual evidence. Besides serving as burial goods to sustain the dead in the afterlife, the vessels and their contents also can be related to funerary ceremonies in which intermediaries communicated with the deceased ancestor and gods in an altered state of consciousness after imbibing a fermented beverage (36).

The fragrant aroma of the liquids inside the tightly lidded jars and vats, when their lids were first removed after some 3,000 years, suggests that they indeed represent Shang/Western Zhou fermented beverages. The Changzikou Tomb vessels, one of which is reported on here, exemplify this phenomenon: of more than 90 bronze vessels in the tomb, 52 lidded examples were still a quarter- to half-full of liquid (15). Most recently (early 2003), an excavation of an upper-class tomb in Xi'an yielded a lidded vessel holding 26 liters of what was described as a liquid with a "delicious aroma and light flavor" (G.C., unpublished data). What accounts for such amazing preservation of liquids, which would be anticipated to have evaporated and disappeared? Chinese bronze-making technology assured that the lids were tightly fitted to the mouths of vessels. Then, over time, the lids corroded and cut off further exchange with the outside atmosphere, hermetically sealing off any liquid remaining inside the vessels.

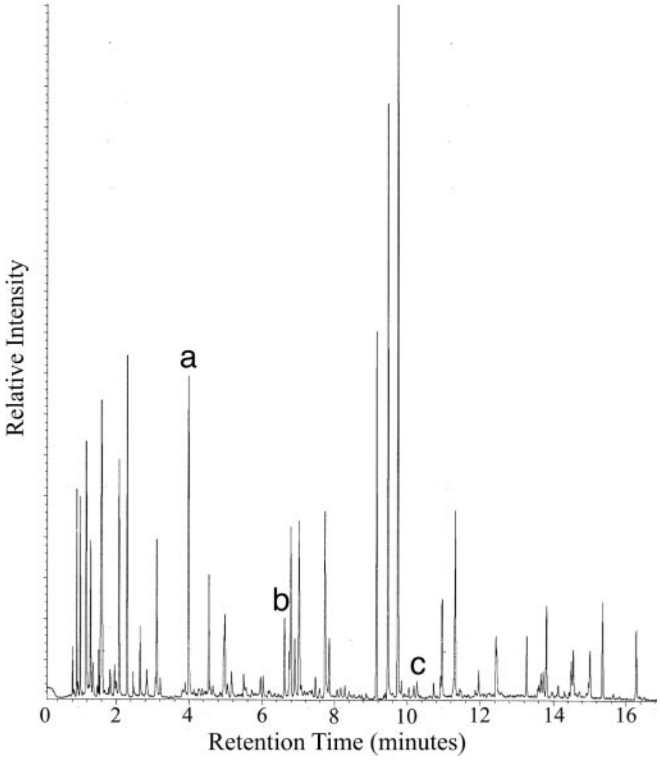

Fig. 3. Thermal desorption GC-MS analysis of lidded *you* jar from the Changzikou Tomb in Luyi county, Henan province, dated *ca.* 1250–1000 B.C. Peaks a, b, and c are caused by benzaldehyde, camphor, and α-cedrene. Possible wine-derived propanoic acid derivatives account for the two most intense peaks near 10 min. Other peaks correlate with ubiquitous environmental contaminants, especially phthalates.

Previous attempts to identify the compounds responsible for the aromas of the liquids contained in the Shang/Western Zhou lidded bronze vessels, as well as other basic ingredients, have been largely inconclusive or are unpublished. Positive evidence for yeast cells was obtained from an 8.5-kg solid white residue inside a *weng* jar at Taixi (37), probably the lees of a fermented beverage. Habitation contexts at Taixi also yielded specific pottery forms, including a funnel and a deep vat with a pointed and recessed bottom ("general's helmet"), which were likely used in beverage-making (3, 5). Several jars at this site also contained peach, plum, and Chinese date (jujube) pits, as well as seeds of sweet clover, jasmine, and hemp, suggesting that an herbal fruit drink was prepared.

Our analyses of the liquids inside lidded jars from Anyang and the Changzikou Tomb can be summarized briefly. Beeswax and epicuticular wax compounds were absent, implying the absence of honey or a plant additive. Tartaric acid and its salts were present at a very low level only in the Changzikou Tomb, consistent with mold saccharification of rice. Although the Changzikou Tomb sample gave a δ^{13}C value of $-25.3‰$ in accord with a C_3 plant such as rice (Table 1), the stable isotope determination for the Anyang liquid ($-15.9‰$) indicated that a C_4 plant was used as a principal ingredient. Millet, which is well represented in the Anyang archaeobotanical corpus, is the most likely candidate.

Thermal desorption GC-MS (Fig. 3) revealed that two aromatic compounds, camphor and α-cedrene, were present in the Changzikou Tomb liquid, in addition to benzaldehyde, acetic acid, and short-chain alcohols characteristic of rice and grape wines. Based on a thorough search of the chemical literature of Chinese herbs and other natural products, these compounds might have originated

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from specific tree resins (e.g., China fir, *Cunninghamia lanceolate* Hook.; ref. 38), flowers (e.g., chrysanthemum spp.), or aromatic herbs, such as *Artemesia argyi* in the wormwood genus used to prepare saccharification mold (5, 39). A single open vat, filled with leaves of *Osmanthus fragrans* and holding a ladle, also was found in the tomb (15). Possibly, the beverage in the lidded containers of the tomb was steeped in the leaves, which have a floral aroma like the flowers that are used today in flavoring teas and beverages, and then transferred to the vessels. On the other hand, the absence of any wax compounds argues against this hypothesis.

According to HPLC-MS (Fig. 1*d*) and standard GC-MS analyses, heavier aromatic compounds were present in the Anyang liquid: the triterpenoid β-amyrin and its analogue, oleanolic acid. These compounds are widespread in the Burseraceae (elemi) family of fragrant trees, although other sources (e.g., chrysanthemum) cannot be excluded.

FT-IR and HPLC matches of the Changzikou Tomb and Anyang liquids to samples in our databases provided additional indicators of the original natural products. Both samples were chemically most similar to modern and ancient resinated wine samples, as would be expected if they were fermented beverages flavored with plant-derived compounds. Modern yeast also provided a good FT-IR match for the Changzikou Tomb liquid.

The combined archaeochemical, archaeobotanical, and archaeological evidence for the Changzikou Tomb and Anyang liquids point to their being fermented and filtered rice or millet "wines," either *jiu* or *chang*, its herbal equivalent, according to the Shang Dynasty oracle inscriptions.

Both *jiu* and *chang* were likely made by mold saccharification, a uniquely Chinese contribution to beverage-making (5, 9, 39). In brief, amylolysis fermentation, which remains the traditional method for making fermented beverages in modern China, exploits the fungi of the genera *Aspergillus*, *Rhizopus*, *Monascus*, and others, depending on environmental availability, to break down the carbohydrates of rice and other grains into simple, fermentable sugars. A thick mold mycelium was grown historically on a variety of steamed cereals, pulses, and other materials in making the saccharification-fermentation agent (*qu*). Rice, as an early domesticate and one of the principal cereals of prehistoric China, presumably was an early substrate. Yeast enters the process adventitiously, either brought in by insects or settling on to the large and small cakes of *qu* from the rafters of old buildings. As many as 100 special herbs, including *A. argyi* (above), are used today to make *qu*, and some have been shown to increase the yeast activity by as much as 7-fold (40).

Before such a complicated system as amylolysis fermentation was developed and widely adopted by the ancient Chinese beverage-maker, the grain probably was saccharified by mastication and/or malting. Because cereals lack yeast, the initiation of fermentation would have required a high-sugar fruit and/or honey, as attested by the Jiahu mixed fermented beverage.

Complex urban life eventually led to more specialized beverages and the amylolysis fermentation system, which became the standard method for making rice and millet wine. This changeover likely occurred between the late Neolithic period (mid-third millennium B.C.) and the Shang Dynasty (41). By saccharifying rice and other grains with specialized fungi, the beverage-makers of proto-historic urban China had less need for the sugars or yeast provided by honey or fruit. Although the prehistoric mixed fermented beverage fell into abeyance, this well made beverage was the forerunner of later technical developments. It is probably not coincidental that what some scholars believe to be the earliest Chinese fermented beverage (*luo*) was fruit-based (5). The *weng* jars with fruit remains from the middle Shang site of Taixi (above) would then represent a continuation of a tradition reaching back into the Neolithic period. Even today in many parts of China, a popular drink (*shouzhou mi jiu*) has suspended fruit bits in rice wine.

For nearly 40 years, scholars have relied on the stylistic similarities of the bronze vessels and their earlier pottery counterparts to argue for the existence of a prehistoric fermented beverage, first attested textually in the proto-historic Shang Dynasty. The ancient chemical evidence now enables the later beverages to be traced back as far as 7000 B.C. and reveals how Chinese beverage-making developed over the millennia. Our results also illustrate how both religious ceremonies and activities of everyday life in which these vessels were used, and still important in modern Chinese culture, likely have their basis in prehistory.

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