# Fatty Acid Analysis of Archaeological Pottery Vessels Excavated in Tell Mastuma, Syria

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Fatty acids extracted from archaeological pottery vessels (B.C. 900—720 y) excavated at Tell Mastuma, Syria, are characteristic of individual vessels. The molecular-distribution patterns of *n*-fatty acids of these vessels are different from those of the underfloor soil and a human hand, indicating that the fatty acids recovered are proper to the samples. The lamps show a predominance of hexadecanoic and octadecanoic acids with a near absence of other acids in the patterns, suggesting that olive oil was used in the lamps. On the other hand, large pottery jars show a clear presence of nonanoic acid in their patterns. The acid presence is also strikingly noted in carbonized olive, suggesting that olive and/or a chemically olive-related material was stored in the jars. The relative concentration of *cis*-9-octadecenoic acid to octadecanoic acid decreases drastically from modern olive pulp to carbonized olive, and further in the jars and lamps. Apparently, a degradation of the acid had occurred intensely during burial in the soil. A comparison of the molecular-distribution patterns of the jars and lamps to the carbonized olive and olive pulp allows one to conclude that olive and its oil were commonly utilized at the *tell*.

Tell Mastuma is an archaeological site located about 5 km south of the City of Idlib, Syria. The mission by the Ancient Orient Museum, Tokyo, excavated the *tell* over five field seasons from 1980 to 1988, showing that occupation of the *tell* started around B.C. 2400 y in the latter half of the Early Bronze Age, and lasted until around B.C. 700 y in the Iron Age.[1,2] One of the main purposes for the excavation was to investigate whether the prosperity of the *tell* had been related to olive vegetation and its industry, since the vegetation is still widely seen in this region.[1—3] The mission unearthed carbonized olive seeds together with other seeds, as well as stone tools, including turntables, querns, mortars, pestles, and grinding stones, in addition to a number of pottery vessels and their fragments. It seems therefore, likely that olive was utilized for many purposes at the *tell*, especially for the production of olive oil.

It seems that the activity of microbes in soil where those archaeological samples were buried had been low because of the arid climate throughout the history of this region. Therefore, these samples are suitable for analyzing organic compounds; we analyzed some of the samples for fatty acids as remaining and/or chemically altered components of olive and olive oil in order to find an organo chemical clue to ascertain the use of olive and olive oil at the *tell*. A similar type of study was reported in order to detect a trace of olive oil in archaeological amphora fragments by the analysis of fatty acids (mainly several abundant acid).[4] Unfortunately, the ages and excavated places of these samples were not mentioned in the report, because the main purpose was limited to the detection of oil components. In this paper, we report on our results concerning fatty acid analysis, and discuss their characteristic molecular-distribution patterns in relation to the use of those pottery vessels whose excavated sites and ages are clearly known.

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## Experimental

**Materials.** The samples that we analyzed in this study were particularly collected for the purpose of fatty acid analysis during the 1988 field season.[2] They were wrapped up in clean aluminium foil at the excavation sites, and carefully handled so as not to contaminate then by human hands. The names of the samples and their ages are listed in Table 1 together with the weight of the samples used in this analysis. Each sample was a portion of an excavated individual fragment.

**Procedures.** Each sample was pulverized in an agate mortar with a pestle, and extracted by 10 $cm^3$ of 0.5 $mol\,dm^{-3}$ KOH in methanol in a degassed-sealed glass tube at 110 °C for 3 h. After centrifugation of the tube,

Table 1. Archaeological Samples from Tell Mastuma and Their Fatty Acid Concentrations

| Sample No. | Sample description | Age | Weight used | Concentration in $\mathrm{nmol\,g^{-1}}$ | | |
|---|---|---|---|---|---|---|
| | | Year | for analysis/g | Total[a)] | $C_{18:0}$ | $C_{18:1}$[b)] |
| 1F | Large pottery jar | B.C. 900—720 | 2.5 | 5.7 | 0.5 | 1.4 |
| 2F | Large pottery jar | B.C. 900—720 | 3.5 | 7.0 | 0.8 | 1.3 |
| 4F | Pottery lamp | B.C. 900—720 | 1.2 | 171 | 66 | 5.3 |
| 5F | Pottery lamp | B.C. 900—720 | 1.3 | 428 | 199 | 12 |
| 6F | Pottery lamp | B.C. 900—720 | 2.5 | 40 | 13 | 2.1 |
| 7F | Pottery lamp | B.C. 900—720 | 1.3 | 1188 | 644 | 152 |
| 12F | Under-floor soil | B.C. 900—720 | 2.9 | 18 | 0.8 | 0.8 |
| 14F | Pottery lamp | B.C. 900—720 | 2.4 | 50 | 12 | 3.1 |
| 15F | Large pottery jar | B.C. 900—720 | 2.5 | 5.1. | 1.2 | 0.4 |
| COF | Carbonized olive | B.C. 2400—2000 | 0.41 | 80 | 8.1 | 47 |
| MOF | Modern olive pulp[c)] | Present | 0.16 | $2.3\times10^5$ | $0.4\times10^5$ | $13\times10^5$ |
| HH | Human hand[d)] | Present | Not applicable | 944 | 82 | 368 |

a) Total concentrations of saturated *n*-fatty acids from $C_8$ to $C_{26}$. b) *cis*-9-Octadecenoic acid. c) A currently growing species of olive was obtained near Tell Matstuma in 1988. d) Glass wool wet with ether which was used to wipe twice a hand of one of the authors'.

the supernatant was recovered. The precipitated residue was extracted three times with 3 $\mathrm{cm^3}$ methanol under sonication; the three methanol solutions were then combined with the supernatant. To the combined supernatant were added 1.5 $\mathrm{cm^3}$ of 6 $\mathrm{mol\,dm^{-3}}$ HCl and 20 $\mathrm{cm^3}$ water, which was extracted four times with 5 $\mathrm{cm^3}$ benzene with shaking. The combined benzene solution was concentrated under reduced pressure and applied to a silica-gel column (Kieselgel 60, Merck Comp., 16 cm×0.6 cm i.d.). The column was eluted successively with 10 $\mathrm{cm^3}$ hexane, 10 $\mathrm{cm^3}$ benzene, and 15 $\mathrm{cm^3}$ methanol. The methanol eluent was concentrated and treated by 1 $\mathrm{cm^3}$ of 15% wt boron trifluoride ($BF_3$) in methanol at 85 °C for 10 min under an $N_2$ atmosphere to make methyl esters of fatty acids. After the addition of 1 $\mathrm{cm^3}$ water, these methyl esters were extracted with hexane and examined by a gas chromatograph (GC), and, when necessary, by a gas chromatograph coupled to a mass spectrometer (GC/MS). The GC was equipped with a OV-1 Bonded fused silica capillary column (OV-1 Bonded, 50 m×0.25 mm i.d.) and with an FID. The MS was scanned every 1.5 s over $m/z$ 32 to 400 in the electron-impact mode at 70 eV or in the chemical-ionization mode at 200 eV with isobutane used as a reacting gas. Identification of the compounds was made by the GC/MS method using standard compounds and an MS library of the National Bureau of Standard, U.S.A. Quantification was performed from peak areas on gas chromatograms compared with those of the standards. Organic solvents were distilled prior to use. The 15% $BF_3$ in methanol was prepared by bubbling $BF_3$ gas into distilled methanol. The aluminium foil was heated at 500 °C for 3 h before use at the excavation site.

## Results and Discussion

A gas chromatogram obtained for a fatty acid analysis of a lamp sample (No. 7F) is shown in Fig. 1. On the chromatogram, 30 fatty acids were identified, corresponding the 30 peaks numbered from 1 to 28. They include 25 saturated fatty acids and five unsaturated ones. Among the saturated ones, eighteen were normal acids from $C_8$ to $C_{26}$, and seven were branched ones from $C_{14}$ to $C_{19}$ (except for $C_{18}$) with two kinds of $C_{15}$ and $C_{17}$. However, no $C_{18}$-branched acid was detected in our analysis, since the branched one has a similar retention time to the unsaturated $C_{18}$ acid (Peak No. 17) on the chromatogram, and was probably covered with the acid, which was much more abundantly present than the branched one. Among the five unsaturated acids, three were of $C_{18}$, and one $C_{16}$ and $C_{20}$. In addition to those fatty acids, four dicarboxylic acids were found on the chromatogram. Identifications of these compounds are shown in the figure caption. Of all 30 fatty acids, the most abundant three acids were hexadecanoic acid ($C_{16:0}$), *cis*-9-octadecenoic acid ($C_{18:1(cis\text{-}9)}$) and octadecanoic acid ($C_{18:0}$).[5)] Gas chromatograms of other archaeological samples were more or less similar to that of the lamp sample, although the relative abundances of individual acids varied among the samples.

The total concentrations of saturated *n*-fatty acids from $C_8$ to $C_{26}$ are shown in Table 1 together with the concentrations of $C_{18:0}$ and $C_{18:1(cis\text{-}9)}$ acid. The total concentrations differ from several to over one thousand $\mathrm{nmol\,g^{-1}}$ among the samples. The difference in concentration among samples is probably due to the nature of the samples themselves, because they are portions of excavated fragments which do not represent the whole portions of the vessels. Nevertheless, these totals are quite useful to indicate the values proper to the samples (discussed in the following paragraph). The $C_{18:0}$ concentrations to the total ($C_{18:0}$ ratio) are larger in samples having larger total concentrations than in the smaller ones. These larger ratios were clearly observed in samples No. 5F (ratio of 0.46) and No. 7F (ratio of 0.54). On the other hand, the $C_{18:1(cis\text{-}9)}$ concentrations to the total ($C_{18:1(cis\text{-}9)}$ ratio) were generally small, and roughly similar in all of the archaeological samples (0.03—0.25), except for carbonized olive (No. COF, ratio of 0.59). Furthermore, the sample of modern olive pulp shows a small $C_{18:0}$ ratio of 0.17, and a

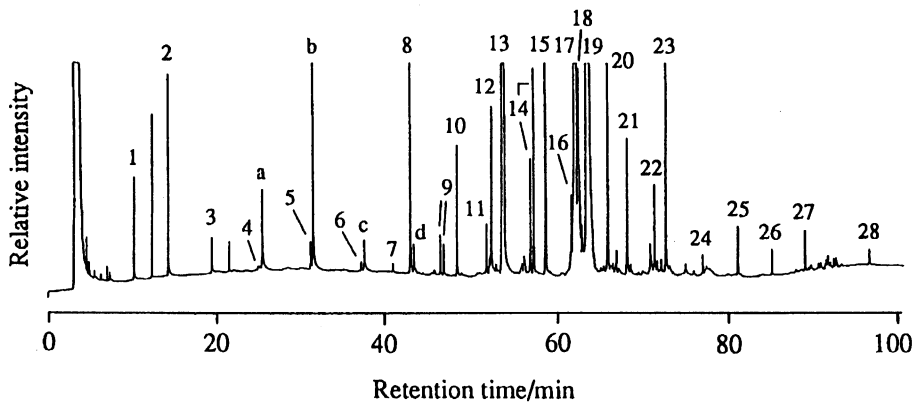


Fig. 1. A gas chromatogram of fatty acids in an archaeological pottery lamp sample (No. 7F) in Tell Mastuma. Peaks are 1 $C_{8:0}$, 2 $C_{9:0}$. 3 $C_{10:0}$, 4 $C_{11:0}$, 5 $C_{12:0}$, 6 $C_{13:0}$, 7 $C_{14:0(br)}$, 8 $C_{14:0}$, 9 $C_{15:0(br)}$, 10 $C_{15:0}$, 11 $C_{16:0(br)}$, 12 $C_{16:1(cis\text{-}9)}$, 13 $C_{16:0}$, 14 $C_{17:0(br)}$, 15 $C_{17:0}$, 16 $C_{18:2(cis\text{-}9,\text{-}12)}$, 17 $C_{18:1(cis\text{-}9)}$, 18 $C_{18:1(trans\text{-}9)}$, 19 $C_{18:0}$, 20 $C_{19:0(br)}$, 21 $C_{19:0}$, 22 $C_{20:1}$, 23 $C_{20:0}$, 24 $C_{21:0}$, 25 $C_{22:0}$, 26 $C_{23:0}$, 27 $C_{24:0}$, and 28 $C_{26:0}$, and a $C_{8:0(di)}$, b $C_{9:0(di)}$, c $C_{10:0(di)}$, and d $C_{11:0(di)}$, where $M$ is the number of carbon atoms and $N$ is the number of double bonds in the abbreviation $C_{M:N}$. In the parentheses, L specifies the position of the double bond in *cis*- or *trans*-L, *br* represents branch, and di indicates a dicarboxylic acid.

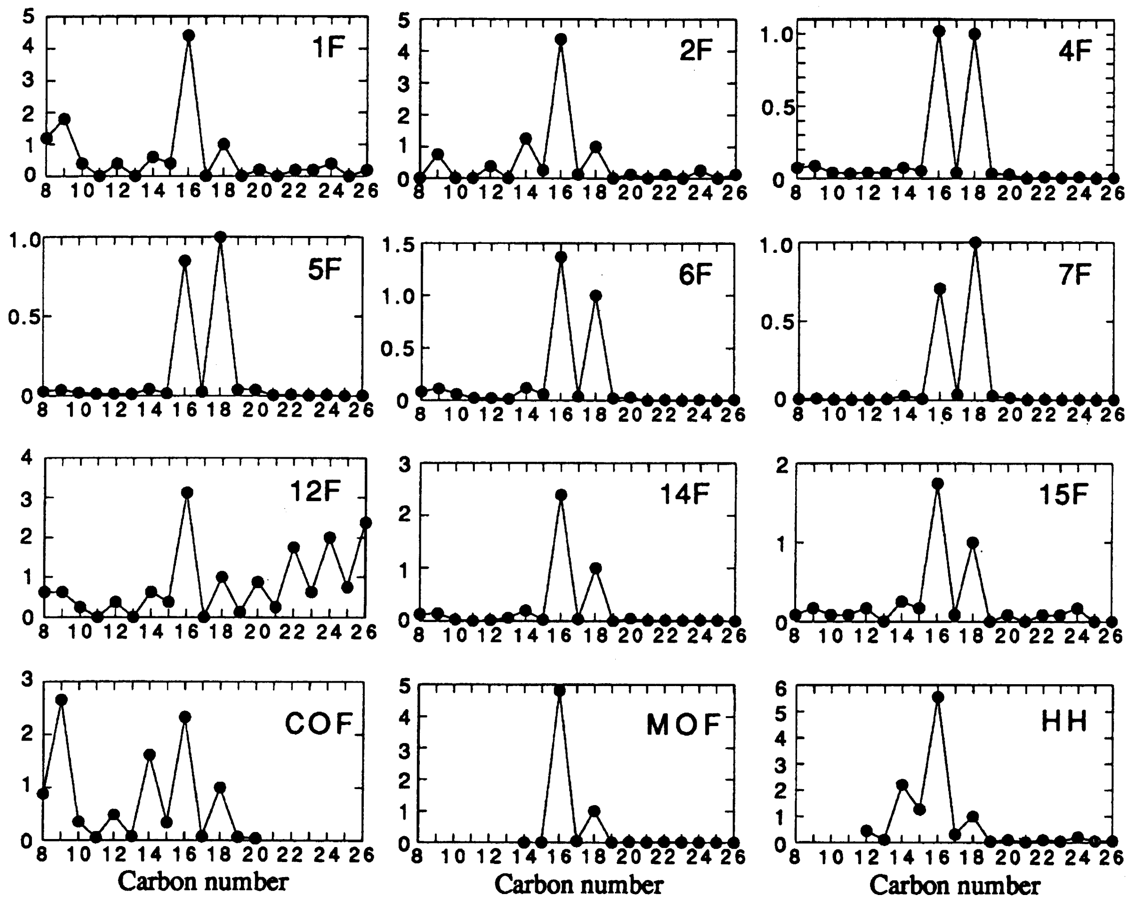


Fig. 2. Molecular distribution patterns of $n$-fatty acids in the archaeological samples from Tell Mastuma. Sample numbers are same as those appeared in Table 1. The concentrations of $C_{18}$ acid are normalized to one.

very large $C_{18:1(cis\text{-}9)}$ ratio of 5.7. The $C_{18:1(cis\text{-}9)}$ ratio change is drastic from modern olive pulp to carbonized olive, and farther to jar and lamp samples compared to the $C_{18:0}$ ratio change. Apparently, the $C_{18:1(cis\text{-}9)}$ acid disappeared much faster than did the $C_{18:0}$ acid from these archaeological samples, probably due to its instability during its burial history. This much faster disappearance of the $C_{18:1(cis\text{-}9)}$ acid than the $C_{18:0}$

acid was also reported even in archaeological samples from the sixteenth century.[6)]

The molecular-distribution patterns of the *n*-fatty acids in the samples are shown in Fig. 2, where the concentration of $C_{18}$ acid in each sample is normalized to one. The jar and lamp samples clearly show different patterns from that of the under-floor soil sample, which indicates that the contamination of the *n*-fatty acids during their burial history in the soil was not significant to these excavated samples. The soil sample shows an even carbon-number predominance above $C_{20}$ acids, which were probably remnants of pre-burial wax components in higher land plants.[7)] Furthermore, since the patterns of the archaeological samples are different from that of the human hand sample in addition to the low concentration of the $C_{18:1(cis\text{-}9)}$ acid, the contamination during sample handling was insignificant. Therefore, those fatty acid data listed in Table 1 and shown in Fig. 2 are proper to the samples, and the acids are probably remnants of the initial fatty acids present in the samples before their burial and those chemically derived from the initials during the burial history.

An apparent feature in the molecular-distribution patterns of all five lamp samples is a near absence of other carbon numbered *n*-fatty acids than $C_{16}$ and $C_{18}$. The four lamp samples (Nos. 4F, 5F, 6F, and 7F) show that the concentrations of $C_{16:0}$ to that of $C_{18:0}$ are 1.0, 0.85, 1.4, and 0.70, respectively, which fall within a narrow range, although the other lamp sample (No. 14F) shows a higher value (2.4). In this respect, a jar sample (No. 15F) shows a concentration of 1.8 which falls near to the narrow range, and has a similar pattern to those of the lamp samples. It seems from one of the main roles of lamps that the fatty acids in the five lamps as well as the jar are remnants of olive oil stored in samples used at the *tell*.

The molecular-distribution pattern of the carbonized olive sample (No. COF) may be explained by a degradation of the initial fatty acids in olive during its burial history. The sample shows a $C_9$ fatty acid predominance in the pattern. During the burial history, the $C_9$ acid might have been converted from $C_{18:1(cis\text{-}9)}$ acid which was probably by far the most abundant acid in olive before burial, as can be seen in the modern olive pulp sample (No. MOF). It is reported that the $C_9$ acid, in addition to the $C_{18:0}$ acid, was notably formed from the $C_{18:1(cis\text{-}9)}$ acid in a heating experiment in the presence of a clay mineral.[8)] A clear presence of the $C_9$ acid is also noted in two jar samples (Nos. 1F and 2F), suggesting that the source of the $C_9$ acid was also the $C_{18:1(cis\text{-}9)}$ acid initially present in the jars.[9)] If so, and this is very likely, the jars might have been used to store olive or its chemically related material. On the other hand, the $C_9$ acid predominance is scarcely observed in the lamp samples, for which there is no present proper explanation. Nonetheless, it should be noted that the analysis of the bulk sample of a complete lamp shows a predominance that is nearly similar to that of the carbonized olive sample, though the lamp is dated to A.D. 100 to 600 y in the *tell*. This is not to mention that the sample included repeatedly heated portions due to oil burning.

The samples used in this study were excavated fragments of pottery vessels which had been buried in soil nearly 2700 y or longer, and the organic material analyzed were fatty acid molecules which were recovered from the fragments. Since these fatty acids are remnants and/or chemically derived ones from organic material used in these vessels, they represent only a minor portion of the initial fatty acids. In addition, many other sources for fatty acids than olive can not be excluded, since the acids occur widely in animal fats and plant waxes.[10)] It is therefore difficult to present any firm evidence of fatty acids to conclude that olive and/or olive oil were stored in the pottery lamps and jars used at the *tell*. However, it is allowed to conclude that the results of a fatty acid analysis in those pottery vessels together with the results of carbonized olive and modern olive pulp in this study support the interpretation involving the utilization of olive and olive oil, which has been proposed based on the finding of the several kinds of stone tools in the *tell*.[1—3)]

## References

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5) In our recovery test, known amounts of these three acids were mixed with 2.5 g sea sand pre-ignited to remove organic contaminants and were subjected to the same analytical procedures as the archaeological samples. The test showed the recoveries of 82% for 6.3 nmol $C_{16:0}$, 80% for 6.3 nmol $C_{18:0}$, and 80% for 7.9 nmol $C_{18:1(cis\text{-}9)}$.

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8) A Shimoyama, K. Hayakawa, and K. Hårada, *Geochem. J.*, **27**, 59 (1993).

9) In fact, a jar sample whose age is about B.C. 1600 y in the *tell* and therefore, older than the samples 1F and 2F by 800 to 900 y shows a striking $C_9$ acid predominance similar to the carbonized olive sample.

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