Studies in organic archaeometry II[1]. Analysis of the ancient content of a flask excavated in Troia

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Dedicated to Professor Kalevi Pihlaja on his 60th anniversary
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Abstract
Potsherds of a flask excavated in the ruins of a Late Bronze Age house of Troia VI were analyzed for the ancient content. Traces of lipids were found and analyzed by capillary gas chromatography: lauric acid, myristic acid, palmitic acid, stearic acid and oleic acid were identified - a mixture in which palmitic and stearic acid were the major components.

All of these compounds survived predominantly as free fatty acids as well as in form of their salts. Since the form of the flask with a narrow mouth only allowed its use for keeping liquids, it can be assumed that the ancient content was either olive oil or milk; and the presence of lower-chain fatty acids is giving preference to milk.

Keywords: Archaeometry, prehistoric pottery, Late Bronze Age, Troia, capillary gas chromatography, lipids, fatty acids, milk

Introduction

Within the "Troia Project" (head: Prof. Dr. M. Korfmann[2]) carried out by the University of Tübingen pieces of pottery were excavated in 1997[3] within the ruins of a Late Bronze Age house (late Troia VI) destroyed by fire. The potsherds (Figure 1) were parts of a broken "pilgrims' flask", i.e. a flask of oval shape with a handle and narrow mouth (Figure 2: height: ca. 27,5 cm, width: ca. 18 cm, mouth inside: ca. 3,4 cm), obviously destined to contain a liquid.

Figure 1. Parts of the broken flask with yellowish sediment.

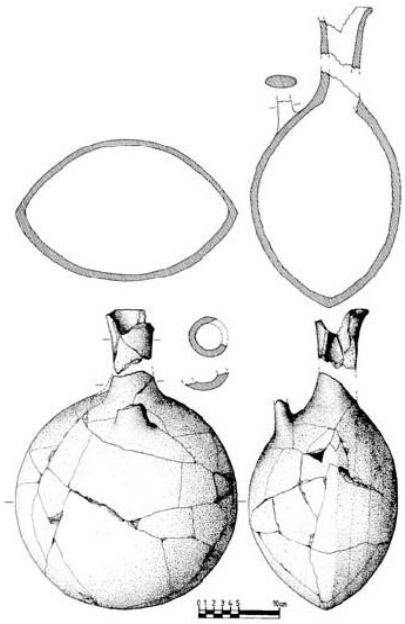

Figure 2. Schematic reconstruction of the "pilgrims' flask".

At the inside of the potsherds a yellowish sediment was found and - although being predominantly inorganic - was analyzed at the Vienna University of Technology for possibly contained lipids.

This work was mainly undertaken in the *Laboratories for Lipid Analysis* (Prof. Dr. L. Puchinger) at the *Institute of Applied Botany, Technical Microscopy and Organic Raw Material Studies,* Vienna University of Technology.

Experimental Section

Preliminary studies

A sample was warmed up with 10% oxalic acid in MeOH at 40°C, then left at room temp. for some days: this solution was analyzed by GC. Results obtained**:** small quantities of palmitic and stearic acid were present.

Sample preparation for capillary gas chromatography (CGC)

1. A sample was extracted with $CHCl_3$/MeOH (2:1) for 30 min in an ultrasound bath.[4, 5]
2. Part of the solution was used to search for *non-acidic substance classes* like steroids, stearyl esters, triglycerides, etc., by CGC for non-polar compounds[6, 7, 8]
3. Part of the same solution was used to study the possible existence of *free fatty acids* by CGC-detection.[4, 9, 10] For this purpose the following procedure[11] was applied: the solvents of the original lipid extract were distilled off to dryness, the residue was dissolved in petrol ether. The free fatty acids present in this solution were neutralized with 14% aqueous KOH (phenolphthalein) and the salts thus obtained were extracted with 50% aqueous EtOH. Upon purification (multiple extractions with petrol ether) the aqueous EtOH phase was acidified (2N

HCl). Finally the free fatty were extracted with petrol ether, the solution was dried (Na_2SO_4) and concentrated. The subsequent methylation was carried out by heating for 15 min with BF_3-etherate under pressure in a closed reaction vessel (ca.90°).

4. One more part of the original $CHCl_3$/MeOH solution was treated with methanolic KOH for 3 hrs at 80°C to hydrolyze *esters still existing* in the sample. Upon acidifying this solution with 85% H_3PO_4 the free fatty acid thus obtained were extracted with n-hexane and methylated by BF_3-etherate as described above to yield the corresponding methylates, which were used for CGC studies of the fatty acid pattern. [9, 10]

Studies in search of polar compounds

By means of the methods described above sterols, stearyl esters and triglycerides (i.e. unhydrolyzed fats) were searched for: although further more detailed studies will be necessary for a precise answer, it was already found out now that some triglycerides (in not yet determined quantity) were still present as well as some not yet identified substances (degradation products, alkanes ?).

Instruments used

For the analysis of fatty acids: CGC Carlo Erba Vega Series 6000, 30m x 0,32mm fused silica DB-225 (J &W) column (25 µm film thickness). Carrier gas: He (180 kPa); inj. and det. temp.: 260°C; Program: 4min 90°C//10°/min//160°C/5°C/min//220°C//7min 220°C.

For the analysis of non-polar compounds (e.g., unhydrolyzed fats, sterols, etc.):

CGC Carlo Erba Mega Series, 15m x 0,32mm fused-silica DB-5 (J & W) column (25 µm film thickness). Carrier gas: He (150 kPa); inj. and det. temp.: 350°C; on-column injection

Program: 1min 78°C//25°C/min//230°C/14°C/min//342°C//20min 342°C

Results and Discussion

Identified fatty acids

By means of the methods described above two groups of results were obtained:

1) fatty acids originating from free and/or esterified lipids

lauric acid	(C 12:0)	ca. 1 %
myristic acid	(C 14:0)	ca. 6 %
palmitic acid	(C 16:0)	ca. 38 %
stearic acid	(C 18:0)	ca. 48 %
oleic acid	(C 18:1)	ca. 7 %

2) fatty acids originating from [Ca?] salts of free fatty acids

myristic acid	(C 14:0)	ca. 13 %
palmitic acid	(C 16:0)	ca. 44 %
stearic acid	(C 18:0)	ca. 39 %
oleic acid	(C 18:1)	ca. 4 %

(in both cases the approximated %-values are referring to the total quantity of the fatty acid mixture)

Summary of the results and interpretation thereof

Although the sample was only consisting of a crust-like sediment of mainly inorganic character, by means of GC *some fatty acids could be identified*.

The major components were palmitic and stearic acid, while the percentage of oleic acid is rather low.

The substances found were mainly stemming either from free fatty acids or from their respective salts considering that this pottery had only a rather narrow mouth, the conclusion is obvious that its content had been a fatty liquid, i.e. **either olive oil on the one hand or milk or a milk-like liquid (e.g., diluted yoghurt) on the other hand.**

The low percentage of oleic acid as well as the fact that lower-chain fatty acids were present**,**[12, 13] **one can assume with some probability that the ancient content was milk or a milk-like liquid.**

Future studies will have to confirm this interpretation and - hopefully - will find out from which animal the milk was made.

References and Notes

1. Our latest paper in this series: Sauter, F.; Jordis, U.; Graf, A.; Werther, W.; Varmuza, K.; *Studies in OrganiC Archaeometry I ARKIVOC* **2000**, *(v)*, 735.
2. We would like to express our sincere thanks to Prof. Korfmann and his co-workers for confronting us with this interesting topic.
3. For archaeological details c. f.: Korfmann, M.; *Troia - Ausgrabungen 1997 Studia Troica*, 1998, *8*, p 37f.
4. Christie, W. W. *Gas chromatography and lipids;* The Oily Press: 1989, Ch. Extraction of lipids from tissues and other preliminaries to analysis, p 27.
5. Christie, W. W. *Lipid analysis;* Pergamon Press: 1982, Ch. Isolation, separation, identification and structural analysis of lipids, p 17.
6. Christie, W. W. *Gas chromatography and lipids;* The Oily Press: 1989, Ch. High-temperature gas chromatography of triacylglycerols, p 188.
7. Puchinger, L. Phyton (Austria), 1989, *29 (3*), p 233.
8. Christie, W. W. *Gas chromatography and lipids;* The Oily Press: 1989, Determination of lipid profiles by gas chromatography, p 228.
9. Christie, W. W. *Gas chromatography and lipids;* The Oily Press: 1989, Chapter: Gas chromatographic analysis of fatty acid derivatives, p 89.
10. Christie, W. W. *Gas chromatography and lipids;* The Oily Press: 1989, Chapter: The preparation of methyl and other esters of fatty acids, p 66.
11. Schormüller, J. *Handbuch der Lebensmittelchemie*; Springer-Verlag: 1969; Vol. IV, Chapter: Freie Fettsäuren, p 736.
12. *Lexikon der Biochemie und Molekularbiologie;* Herder: Freiburg, Basel, Wien, 1991; Topic: Milch (Vol. 2, p 388), Olivenöl (Vol. 3, p 8).
13. Souci, S. W.; Fachmann, W.; Kraut, H.; *Die Zusammensetzung der Lebensmittel, Nährwerttabellen*. (Wissenschaftliche Verlagsanstalt Stuttgart, 1981); p 6, 10, 16, 184