Detection of palm fruit lipids in archaeological pottery from Qasr Ibrim, Egyptian Nubia

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In modern times, the trees of the palm family have been of great economic and social importance to the people in Egypt, as in other parts of the world. There are various species of palm and although different parts of the tree can be used, the fruit are of great value. In antiquity, it is expected that the palm fruit would also have been of great importance to people in the region. The chemical analysis of absorbed residues in archaeological pottery is well established, and through the investigation of ceramic vessels (via gas chromatography, gas chromatography–mass spectrometry and gas chromatography–combustion–isotope ratio mass spectrometry) saturated carboxylic acids in the range C₁₂ to C₁₈ have been detected (with an unusually high abundance of C₁₂) from vessels from the Nubian site of Qasr Ibrim. This is mirrored in the saturated fatty acid distributions detected from the kernels of modern and ancient date palm (*Phoenix dactylifera* L.) and dom palm (*Hyphaena thebaica* (L.) Mart.). Mixing in some of the vessels of the palm fruit with another lipid source is indicated through the $\delta^{13}\text{C}$ values. These results provide the first direct evidence for the exploitation of palm fruit in antiquity and the use of pottery vessels in its processing.

Keywords: archaeological chemistry; palm; Qasr Ibrim; Nubia; gas chromatography; gas chromatography–combustion–isotope ratio mass spectrometry

1. INTRODUCTION

The date (*Phoenix dactylifera* L.) and dom (*Hyphaena thebaica* (L.) Mart.) palms have always played an important part in the economic and social lives of the people of Egypt and Nubia. It has been recorded that different parts of the palm tree have been utilized in various ways, for instance in the manufacture of baskets, ropes, rugs, furniture and fencing, used as fuel or animal feed, or given as collateral for loans or as gifts (Treloar 1884; Beadnell 1909; Adams 1977; Lucas 1989; Gale *et al.* 2000). The fruit of the date palm is comprised of a fleshy pericarp and seed. The pericarp has large amounts of carbohydrates present (ca. 75–80% dry weight), including mainly glucose and fructose (Samarawira 1983), which lends a sweet taste to the fruit. For this reason, in modern times, the date palm has been economically important, with large-scale commercial cultivation occurring in Egypt (e.g. Nixon 1951) and has been described as the ‘tree of life for the Arabs’ (Dahlgren 1944).

Strabo mentions that the palm was found ‘in abundance’ in Nubia (Strabo, book XVII, section 2.2), and although intuitively one might expect the palms to have been of similar social and economic importance to the people of ancient Nubia (an area covering part of modern-day southern Egypt and northern Sudan) as they are today, as of yet, direct evidence for the actual processing of palm fruit in antiquity has not been found (Welsby 1996). In Nubia, the main species that exist include the date and the dom palms. The argun palm (*Medemia argun* Württemb.) is said to have been exported

from southern Nubia to Egypt in antiquity (Täckholm 1958). Although the argun is now believed to be extinct, on rare occasions it is in fact found on archaeological sites from the region, but it may be that these samples have been misidentified.

Research performed over the past decade has shown that during the preparation and cooking of food in unglazed pottery vessels, lipids from animals and plants (e.g. from animal fats and plant oils) are absorbed into the clay matrix of the pot. These can then be chemically extracted, identified and quantified by gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS) and gas chromatography–combustion–isotope ratio mass spectrometry (GC–C–IRMS). By matching the chemical properties (structures, distributions and stable isotope values) of residues to those of contemporary plants and animals, exploitation of a number of important commodities in antiquity, including certain staples, has been achieved (e.g. Evershed *et al.* 1999).

The archaeological site of Qasr Ibrim is located on modern-day Lake Nasser, close to the southern Egyptian border. Before the flooding of the Nile in the 1960s, the site was situated on the top of a cliff-top promontory, and during its occupation (ca. 1000 BC to AD 1800) it is known to have gained economic, religious and administrative importance within Lower Nubia (Horton 1991). Studies of the organic material from the site have proven that there has been very good macroscopic preservation of animal and plant material, such as basketry, papyrus documents, leather, textiles, bones and seeds (e.g. Driskell *et al.* 1989; Rowley-Conwy 1991; Rose & Edwards 1998).

Described herein are the results of organic residue analyses of a selection of potsherds, which form part of a

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larger study of vessel use at Qasr Ibrim. These particular sherds were chosen to illustrate our ability, through detailed molecular analyses, to detect the hitherto unrecognized processing in pottery vessels of a regional staple food, namely the palm fruit.

2. MATERIAL AND METHODS

(a) *Samples*

Pottery samples dated to the post-Meroitic period (ca. AD 350–600) were selected from the collection held, on behalf of the Egypt Exploration Society, at the Faculty of Oriental Studies, University of Cambridge. Pots or jars were used, with some of the vessels exhibiting burning on the exterior, indicating the possibility that they were used as ‘cooking’ vessels.

The archaeobotanical evidence points to the presence of date palm and dom palm at Qasr Ibrim and therefore modern and ancient (dated to the same periods as the pottery vessels) reference samples of these two palms were also used.

(b) *Extraction procedure*

Approximately 2 g of pottery sherd were surface-cleaned with an electric hand-drill, and crushed in a mortar and pestle. Twenty micrograms of internal standard (*n*-tetratriacontane) were added to the powdered sherd and then solvent extraction performed (chloroform:methanol; 2:1 v/v; 10 ml, 2 × 15 min sonication) to produce the total lipid extracts (TLEs). An aliquot of the TLE was derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% v/v trimethylchlorosilane (30 µl; 60 min, 70 °C) to produce trimethylsilyl (TMS) esters/ethers of the TLE, which were then evaporated under a stream of nitrogen and dissolved in hexane before GC analysis.

A further aliquot of the TLE was saponified with 0.5 M NaOH/MeOH (2 ml, 70 °C; 60 min), acidified to pH 3 with 3 M HCl, extracted in hexane (3 × 3 ml) and then the solvent evaporated under a steady stream of nitrogen. Methyl ester derivatives of the carboxylic acids were then prepared using boron trifluoride–methanol complex (14% w/v). The reaction was stopped with 1 ml of double-distilled water, the fatty acid methyl esters (FAMES) extracted with chloroform (3 ml × 3 ml), evaporated to dryness and then dissolved in hexane for GC analysis.

(c) *Gas chromatography, gas chromatography–mass spectrometry and gas chromatography–combustion–isotope ratio mass spectrometry*

GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) fitted with a flame ionization detector (FID). For the TLE analysis, a DBI fused silica capillary column was used (15 m × 0.32 mm, 0.1 µm film thickness), the carrier gas was hydrogen and the GC oven temperature programmed from 50 °C, following a 2 min hold after injection, to 350 °C at 10 °C min^{−1} and held at the maximum temperature for 10 min.

The FAMES were analysed on a CP wax 52CB capillary column (50 m × 0.32 mm, 0.2 µm), the carrier gas was hydrogen and the GC oven programmed from 40 °C to 100 °C at 10 °C min^{−1}, then from 100 °C to 240 °C at 4 °C min^{−1} and held at 240 °C for 20 min.

GC–MS analyses were performed on a Carlo Erba 5150 Mega Series GC (Carlo Erba, Milan, Italy) with an on-column injector, linked with a Finnigan MAT 4500 quadrupole mass spectrometer (electron ionization mode, 70 eV) (Finnigan MAT

GmbH, Bremen, Germany). An accelerating voltage of 2 kV was used to scan the *m/z* range 50–600 in a total scan time of 1 s. The GC–C–IRMS analyses were performed with a Finnigan MAT Delta S mass spectrometer, coupled to a Varian GC (Varian Associates, Inc., Walnut Creek, CA, USA) via a Pt/Ni/CuO combustion interface.

3. RESULTS AND DISCUSSION

The investigation proceeded with (i) GC and GC–MS analysis of the TLEs to assess the state of preservation of residues in potsherds compared with modern and ancient date and dom kernels; (ii) GC analyses to provide detailed compositions of the fatty acid components (as FAMES) of the TLEs in order to allow more reliable comparison between residues; and (iii) GC–C–IRMS to determine the $\delta^{13}\text{C}$ values for individual compounds as a means of demonstrating the mixing of commodities in pottery vessels in antiquity.

Analyses showed that the pottery vessels from the site contain a wide range of lipids that are indicative of degraded plant oils and/or animal fats, and principally include saturated C_{16:0} and C_{18:0} carboxylic acids. However, some of the vessels have an unusual fatty acid distribution, an example of which is shown in figure 1; these vessels contain fatty acids in the range C_{8:0} to C_{18:0} (including branched-chain C_{15:0} and C_{17:0}), with particularly high abundances of C_{12:0}, C_{14:0} and C_{16:0}, and relatively low abundances of C_{18:0} and the other carboxylic acids. Other lipids present, in trace amounts, include a series of odd-chain *n*-alkanes from C₂₇ to C₃₃ and monoacylglycerols (which principally contain C_{18:0}). In some vessels the *n*-alkanes are present displaying a clear unimodal distribution, maximizing at C₂₉, which is indicative of a higher plant origin for the lipids (Kolattukudy 1980).

Analysis of modern date kernels indicates that the majority of the lipids present are in the form of triacylglycerols (TAGs), primarily in the range of C₃₆ to C₅₄, although carbohydrates are also present with traces of free fatty acids. The TAG distribution is very unusual in that the C₄₂ to C₄₈ compounds predominate, whereas with an animal fat or plant oil, one would expect the majority of the TAGs to be more in the C₄₈ to C₅₄ region, due to the presence of abundant C₁₆ and C₁₈ fatty acids (e.g. Evershed *et al.* 1997; Dudd & Evershed 1998).

The TAGs from the date and dom kernel (data not shown) indicate that they are dominated by relatively low-molecular-weight fatty acyl moieties, primarily in the range of C₄₂ to C₄₈. This can be seen in the FAMES of the date kernel after hydrolysis (figure 2). It can clearly be seen that saturated fatty acids in the range C_{12:0} to C_{18:0} are present, as well as unsaturated C_{18:1} and C_{18:2}, with the predominant peaks being C_{12:0} and C_{18:1}. By comparing this distribution with the TLE of an archaeological date kernel (figure 3), the close similarity can be observed. The majority of the TAGs in the archaeological date have been degraded to diacylglycerols (DAGs), monoacylglycerols (MAGs) and to free fatty acids through hydrolysis during burial (Evershed *et al.* 1992). Again, the two most abundant fatty acid components are C_{12:0} and the C_{18:1}. Since all the lipids in the vessels have been degraded to their free fatty acids, either during use or burial, it can be concluded that the seeds offer greater

Figure 1. Partial gas chromatogram of the TLE of an example of a pottery vessel with an unusual fatty acid distribution. $C_{x:0}$ indicates the prominent saturated carboxylic acids, with carbon chain length x ; IS indicates the internal standard (C_{34} n -alkane).

Figure 2. Partial gas chromatogram of the FAMES of a modern date seed. $C_{x:y}$ indicates carboxylic acids with carbon number x and degree of unsaturation y . The elution orders of the saturated and unsaturated fatty acids are reversed compared with figures 1 and 3 due to the use of the polar CP wax 52CB stationary phase in order to resolve the polyunsaturated fatty acids (principally $C_{18:2}$) present in the reference modern date.

protection to the lipids within their structures compared with the absorbed lipids in the potsherds.

Although the seeds confer a high degree of physical and/or chemical protection to the TAGs, preferential degradation of the shorter-chain acyl lipids can be seen, possibly due to the fact that the ester linkages of these moieties are more exposed to hydrolysis due to steric effects, as has been noticed in the degradation of milk fat residues (Dudd & Evershed 1998). Not unexpectedly, the

$C_{18:1}$ present in the seeds, is not found to any large extent in the pottery vessels, hence pointing to a further level of preservation within the seeds, again due to physical and/or chemical protection (e.g. possibly due to the presence of natural antioxidants in the seed). However, the arid environment from which these samples have originated may have some part to play in the survival of the short-chain fatty acids found in the potsherds and archaeological seeds, as these fatty acids are more water soluble than their

Figure 3. Partial gas chromatogram of the TLE of an archaeological date from Qasr Ibrim. C_{xy} indicates carboxylic acids with carbon number x and degree of unsaturation y ; also present are triacylglycerols (TAGs), diacylglycerols (DAGs) and monoacylglycerols (not shown).

Table 1. *Comparison of the composition and stable isotope values of fatty acids in vessels and seeds*

(The relative abundances of fatty acids (C_{12} – C_{18}) in modern date seeds are normalized values from Devshony *et al.* (1992). The compound-specific $\delta^{13}\text{C}$ values for archaeological date seeds have been corrected for the contribution of carbon from the derivatizing TMS group and expressed as being relative to the v-PDB standard (*Bellemnitella americana*), $\delta^{13}\text{C} = 1000[(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}]$, where R is $^{13}\text{C}/^{12}\text{C}$ in per mill (‰).)

sample identity	$C_{12:0}$		$C_{14:0}$		$C_{16:0}$		$C_{18:0}$	
	%	$\delta^{13}\text{C}$	%	$\delta^{13}\text{C}$	%	$\delta^{13}\text{C}$	%	$\delta^{13}\text{C}$
date kernel	49.8	–32.3	24.9	–31.2	21.9	–31.3	3.4	–31.4
vessel 1	49.2	–33.1	33.0	–29.7	15.8	–28.2	2.0	–28.2
vessel 2	57.8	–31.6	23.2	–30.8	15.5	–29.7	3.4	–28.3
vessel 3	77.2	–33.2	12.9	–32.1	9.0	–28.0	1.0	–28.0
vessel 4	29.0	–32.7	29.5	–31.5	34.1	–29.3	7.3	–29.5
vessel 5	35.7	–32.0	25.1	–31.8	32.0	–27.0	7.1	–27.0

longer-chain counterparts (Larsson 1986, p. 353), and would not be expected to survive in wetter conditions.

Comparison of the fatty acid composition of the pottery vessels and the FAMES of the palm kernels is in itself conclusive evidence for the presence of palm fruit lipids in the vessels due to its unique lipid distribution. However, the use of compound-specific stable isotope analysis provides further confirmation of the presence of palm fruit lipids as well as evidence for the mixing of these lipids with another oil or fat, as seen in table 1.

The relative abundances of the selected saturated fatty acids in vessels 1 and 2 match well with the reference date seeds, as do the compound-specific stable isotope data ($\delta^{13}\text{C}$) for the individual fatty acids. With vessel 3, the relative abundance of $C_{12:0}$ is significantly greater than

the reference samples, although the other fatty acids are present in approximately the same proportions. However, because the $\delta^{13}\text{C}$ values for all the compounds compare favourably with the date (a C_3 plant), it can be stated that the palm fruit lipids, and possibly only palm fruit lipids are present in these three vessels. In the case of vessels 4 and 5, the relative abundances of $C_{12:0}$ are notably lower, and those for $C_{16:0}$ and $C_{18:0}$ are significantly higher than the reference date seeds. This could point to a preferential loss of $C_{12:0}$ during burial, or addition of the $C_{16:0}$ and $C_{18:0}$ components from another source. This mixing of lipids (e.g. with another C_3 plant lipid or animal fat) cannot be ruled out in vessel 4; however, for vessel 5, the less depleted stable isotope values for the $C_{16:0}$ and $C_{18:0}$ point to the possibility of some mixing of the lipids within the vessel during use.

In summary, palm kernels have a unique lipid distribution, and the characteristic short-chain fatty acids ($C_{12:0}$ and $C_{14:0}$) have been detected, we believe for the first time in archaeological pottery vessels. This has been accomplished through the analysis of absorbed lipid extracts in potsherds from the arid Nubian site of Qasr Ibrim. Furthermore, the stable isotope values have pointed to the possibility of mixing of the date lipids with another oil or fat. Thus, the range of commodities that can be identified through chemical analysis, as described in this paper, has been extended, thereby providing a new method for assessing the importance in antiquity of the date/dom fruit both at Qasr Ibrim and on a regional level.

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REFERENCES

- Adams, W. Y. 1977 *Nubia—corridor to Africa*, London: Allen Lane.
- Beadnell, H. J. L. 1909 *An Egyptian oasis: an account of the oasis of Kharga in the Libyan desert, with special reference to its history, physical geography and water supply*. London: J. Murray.
- Dahlgren, B. E. 1944 Economic products of palms. *Tropical Woods* **78**, 10–35.
- Devshony, S., Eteshola, E. & Shani, A. 1992 Characteristics and some potential applications of date palm (*Phoenix dactylifera* L.) seeds and seed oil. *J. Am. Oil Chem. Soc.* **69**, 595–597.
- Driskell, B. N., Adams, N. K. & French, P. G. 1989 A newly discovered temple at Qasr Ibrim—preliminary report. *Archéologie du Nil Moyen* **3**, 11–31.
- Dudd, S. N. & Evershed, R. P. 1998 Direct demonstration of milk as an element of archaeological economies. *Science* **282**, 1478–1480.
- Evershed, R. P., Heron, C., Charters, S. & Goad, L. J. 1992 The survival of food residues: new methods of analysis, interpretation and application. *Proc. Br. Acad.* **77**, 187–208.
- Evershed, R. P., Mottram, H. R., Dudd, S. N., Charters, S., Stott, A. W., Lawrence, A. W., Gibson, A. M., Conner, A., Blinkhorn, P. W. & Reeves, V. 1997 New criteria for the identification of animal fats in archaeological pottery. *Naturwissenschaften* **84**, 402–406.
- Evershed, R. P., Dudd, S. N., Charters, S., Mottram, H., Stott, A. W., Raven, A., Van Bergen, P. F. & Bland, H. 1999 Lipids as carriers of anthropogenic signals from prehistory. *Phil. Trans. R. Soc. Lond. B* **354**, 19–31.
- Gale, R., Gasson, P., Hepper, N. & Killen, G. 2000 Wood. In *Ancient Egyptian materials and technology* (ed. P. T. Nicholson & I. Shaw), pp. 537–576. Cambridge University Press.
- Horton, M. 1991 Africa in Egypt: new evidence from Qasr Ibrim. In *Egypt and Africa* (ed. W. V. Davies), pp. 264–277. London: British Museum Press.
- Kolattukudy, P. E. 1980 Cutin, suberin and waxes. In *The biochemistry of plants: a comprehensive treatise. IV. Structure and function* (ed. P. K. Stumpf), pp. 571–645. London: Academic Press.
- Larsson, K. 1986 Physical properties—structures and physical characteristics. In *The lipid handbook* (ed. F. D. Gunstone, J. L. Harwood & F. B. Padley), pp. 334–371. London: Chapman & Hall.
- Lucas, A. 1989 *Ancient Egyptian materials and industries*. London: Edward Arnold.
- Nixon, R. W. 1951 The date palm—‘tree of life’ in the sub-tropical deserts. *Econ. Bot.* **5**, 274–301.
- Rose, P. & Edwards, D. N. 1998 Excavations at Qasr Ibrim—Qasr Ibrim 1998. *Sudan and Nubia* **2**, 61–73.
- Rowley-Conwy, P. 1991 Sorghum from Qasr Ibrim, Egyptian Nubia, c. 800 BC–AD 1811: a preliminary study. In *New light on early farming—recent developments in palaeoethnobotany* (ed. J. M. Renfrew), pp. 191–212. Edinburgh University Press.
- Samarawira, I. 1983 Date palm, potential source for refined sugar. *Econ. Bot.* **37**, 181–186.
- Strabo *The geography* (translated H. L. Jones, 1982). Cambridge, MA: Harvard University Press.
- Täckholm, V. 1958 *Flora of Egypt*, vol. 2. Cairo University Press.
- Treloar, W. P. 1884 *The prince of palms*. London: Low, Marston, Searle & Rivington.
- Welsby, D. A. 1996 *The Kingdom of Kush—the Napatan and Meroitic Empires*. London: British Museum Press.