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MOLECULAR EVIDENCE FOR THE MIXING OF MEAT, FISH AND VEGETABLES IN ANGLO-SAXON COARSEWARE FROM HAMWIC, UK

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ABSTRACT

Absorbed lipid residues from twenty-four 6th to 9th century coarseware potsherds from the major Anglo-Saxon trading centre of Hamwic (Southampton, UK) were analysed by gas chromatography mass spectrometry (GC-MS) in order to reconstruct dietary habits for this particular site. The results show that the vessels were used for preparing ruminant fats, vegetables (mainly cabbage) and marine foods. Beeswax was found once and most likely relates to a sealing function or to honey. Remarkable features were the isomeric mixture of 8- to 16-hydroxyoctadecanoic acid and the co-occurrence of C_{17:1}, C_{19:1} and isoprenoid fatty acids. These features were proposed as biomarkers for ruminant and aquatic food sources, respectively. Furthermore, the carbonyl position distribution in mid-chain ketones was used to identify mixtures of animal and plant derived ketones. Other detected biomarkers included odd-chain fatty acids, vicinal dihydroxy fatty acids, ω-(o-alkylphenyl)alkanoic acids and steroids. The paper highlights the difficulty in interpreting complex lipid signatures which

show a mixture of various foods, as observed in the majority of the samples. This was linked to the preparation of stews or the recycling of vessels.

KEYWORDS

residue analysis, Anglo-Saxon, ceramics, lipid biomarkers, mid-chain ketones, degraded animal fat, brassica leaf wax, fish, marine, beeswax, gas chromatography, mass spectrometry

INTRODUCTION

The characterization of organic residues found in archaeological deposits has developed rapidly in recent decades. Firstly, the continuing development of biomarkers or molecule-species relationships has significantly enlarged the scope of source organisms that can be identified in amorphous organic residues (Colombini et al. 2009; Hansel et al. 2004; Evershed 1993; 2008a; Outram et al. 2009; Regert 2011). Secondly, experimental studies have led to a better understanding of the impact of physical and chemical phenomena on the deposition and transformation of organic residues in ceramic matrices (Charters et al. 1997; Evershed 2008b; Lapp 2012; Romanus et al. 2009; Stern et al. 2000). The knowledge that has resulted from these two fields merges together in the archaeological biomarker concept, which comprises the exploration of many aspects of past human activity (Evershed 2008a). One aspect is the preparation of foodstuffs in ancient ceramic vessels. Owing to the absorption of food residues in the ceramic pores upon repeated vessel use, organic compounds are shielded from diverse degradation mechanisms and can thus be preserved for several thousands of years. Because these residues lack any morphological characteristics, advanced analytical chemical techniques are required for their characterization. The hyphenation of gas chromatography and mass spectrometry (GC-MS) is now the most widely used technique, which allows for separation of complex mixtures and rapid identification (e.g. Craig et al. 2007; Kedrowski et al. 2009; Olsson and Isaksson 2008; Ribechini et al. 2009; Salvini et al. 2008).

The certainty with which natural products can be traced in organic residues inherently relies on the specificity of the biomarkers. This is particularly important when considering the mixing of different commodities, which inevitably complicates the chemical composition of

organic residues. For example, beeswax lipids are sufficiently specific to identify their presence in mixtures (Baeten et al. 2010; Charters et al. 1995; Ribechini et al. 2008, 2011). Marine products which are heated to temperatures over 270 °C also have a characteristic signature owing to the catalytic conversion of (C₁₆–C₂₂) (poly)unsaturated fatty acids to ω-(o-alkylphenyl)alkanoic acids upon heating in ceramic vessels (Craig et al. 2007; Evershed et al. 2008; Hansel et al. 2004; Heron et al. 2010). However, fish that is not extensively heated in ceramic vessels remains problematic to identify based on lipid biomarkers (*cf.* Brown and Heron 2005). Nevertheless, encouraging novel avenues have been recently opened through analysis of protein residues (Dallongeville et al. 2011).

Whilst previous work has been successful in identifying mixtures of different types of animal fats (Evershed et al. 2002; Regert 2011), the intermingling of fats and oils has proven somewhat more problematic owing to the strong similarity in lipid composition between these commodities. Plant oils contain relatively more mono-, di- and triunsaturated C₁₈ fatty acids than animal fats, but these compounds are more prone to oxidation processes and thus are poorly preserved in the archaeological record. Nevertheless, certain oxidation products such as 11,12-dihydroxyeicosanoic acid and 13,14-dihydroxydocosanoic are occasionally found in organic residues and are biomarkers for *Brassicaceae* seed oil (Colombini et al. 2005; Romanus et al. 2008).

The issue of mixing can also be addressed by looking at the steroid composition. Cholesterol and plant sterols are biomarkers for animal fats and vegetal oils, respectively (Evershed 1993; Heron et al. 2010). This diagnostic value remains unchanged upon degradation processes such as reduction, dehydration and oxidation (Baeten et al. 2012; Evershed et al. 1992; Mackenzie et al. 1982; Rontani and Volkman 2005). A disadvantage, however, is that sterols constitute only a minor portion of fats and oils and thus may be undetectable in archaeological residues.

Linear long-chain alkanones, also referred to as mid-chain ketones, represent another class of biomarkers which are particularly useful for identifying fats and plant wax lipids (Evershed et al. 1995; Raven et al. 1997). These compounds either originate from plant epicuticular waxes (Kolattukudy 1980; Walton 1990) or can be produced by pyrolysis of acyl lipids (Evershed et al. 1995; Raven et al. 1997). Discrimination between vegetal and animal derived mid-chain

ketones can be achieved by (i) examining the distribution of their carbon numbers and (ii) the presence of related alkanes or mid-chain alkanols. Additionally, it has been raised that the carbonyl position may also be informative (Raven et al. 1997).

The results presented herein describe the GC-MS characterisation of lipid extracts of 24 potsherds of Anglo-Saxon coarseware from Hamwic (Southampton, UK). This analysis formed part of a wider investigation into the use of pottery in the settlement (Jervis 2011, forthcoming). In order to identify food and non-food commodities, several biomarkers are critically evaluated: (i) fatty acids, (ii) fatty acid degradation products, (iii) sterols and (iv) wax lipids. Particular attention is given to interpretative issues, especially in the case of mixing of both animal and plant derived compounds. Furthermore, we aimed to determine whether the faunal remains provide an accurate reflection of the food eaten in the settlement and to provide information regarding cooking methods, particularly the mixing of foodstuffs, which is not detectable by any other means. Integrated analysis of food remains and the vessels in which they were prepared is rarely undertaken and this study is intended to demonstrate the value of such an approach and to encourage further such analysis in the future, to build a more complete view of domestic life in the early middle ages.

ARCHAEOLOGICAL CONTEXT

Extensive rescue excavations in Southampton, undertaken since the 1940s, have revealed evidence of the extensive, proto-urban, mid-Saxon settlement of Hamwic, founded in the 7th century and occupied for a further 250-300 years (Andrews 1997; Birbeck and Smith 2005; Morton 1992). The settlement was part of a network of trading centres across the North Sea zone and also operated as a centre of craft production (Cowie and Hill 2001). An extremely large (ca. 50000 sherds) ceramic assemblage, comprising both locally produced and imported pottery from 36 sites in Hamwic, has been the subject of four major studies (Hodges 1981; Jervis 2011; Mephram 2005; Timby 1988). The pottery has typically been recovered from deposits of domestic waste, dumped in pits which had been dug for a variety of functions. Three broad ceramic phases have been identified. It has not been possible, however, to securely date these phases due to the absence of long stratigraphic sequences and absolute dating evidence (Timby 1988). The first phase relates to the foundation of the settlement and

is characterised by the Organic-tempered Wares, typical of Anglo-Saxon sites in southern England (Jervis, in press). The second phase is characterised by the presence of Sandy Wares, produced locally, but probably influenced by French and Low Countries pottery which had been imported into the settlement. The final phase is characterised by the presence of Gritty Wares, typically tempered with flint or gravel. In the second and third phase Chalk-tempered Wares also occur. These were probably produced around Winchester to the north and may have entered the settlement as containers (see below). A wide range of imports are present, but these are not the subject of this study.

The analysed sherds are all likely to be from jars, the predominant form amongst the locally produced pottery in the Hamwic assemblage. These were used for a range of functions, but those investigated all exhibit evidence of being used as cooking vessels, in the form of sooty deposits. Analysis of the faunal remains from Hamwic (Bourdillon and Coy 1980; Hamilton-Dyer 2005) has demonstrated cattle to be the predominant food source within the settlement, although the quantity of sheep consumed increases in the later phases of the settlement. Another major component of the diet were marine resources, as evidenced by mussel and oyster shells as well as fish bones (Winder 1980; Wyles 2005). The extent of fish exploitation, however, may be somewhat underestimated at this site because sieving was not undertaken during early excavations (*ibid.*). Previous studies of residues have been small in number. Analysis of contemporary Ipswich Ware has demonstrated that vessels were used as containers and that leafy vegetables were a key component of diet, although they are not typically reflected in the archaeological record in representative quantities (Blinkhorn 1997). Analysis of later Anglo-Saxon (9th-11th centuries) vessels from Raunds and West Cotton have revealed a similar range of biomarkers (Charters et al. 1993, 1995).

EXPERIMENTAL

All solvents and reagents used were of analytical or chromatographic grade. Chloroform, *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) and *n*-heptadecane, used as internal standard, were purchased from Acros Organics, methanol and toluene from Fisher Scientific.

Samples and sample preparation

Twenty four ceramic potsherds from the final two ceramic phases (*cf. supra*) were chosen for analysis (table 1). Vessels were too fragmented to undertake an analysis of the distribution of lipids in different parts of vessels, which can also be informative in regard to cooking practices (Charters et al. 1993, 1997; Evershed 2008b). In order to avoid contamination from soil lipids, the outer surface (ca. 2 mm) of the potsherd fragments was removed with a hand drill (*cf. Stern et al. 2000*). The inner surface was only superficially cleaned. The fragments were then coarsely ground with mortar and pestle and powdered with a ball mill. About 5 grams of the powdered samples were extracted by soxhlet extraction using chloroform : methanol (2:1 v/v). An amount of *n*-heptadecane was added as internal standard prior to extraction. Subsequent to extraction, the lipid extract was derivatised with MSTFA. After removal of excess reagent and solvent, the samples were analyzed by GC-MS. More detailed information can be found in previous publications (Romanus et al. 2008; Baeten et al. 2010).

Gas chromatography – mass spectrometry

GC-MS analyses were performed with an Agilent 6890N GC instrument, equipped with a HP5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) and coupled to an Agilent 5973 Network Mass Selective Detector. One µl of lipid extract, dissolved in toluene, was injected in the splitless mode at a temperature of 290 °C. The oven temperature was held at 140 °C for 2 min, increased to 325 °C at 4 °C min⁻¹ followed by an isothermal 5 min hold at 325 °C. Afterwards a second step of 1 °C min⁻¹ to 340 °C was programmed. The mass spectrometer was held at a temperature of 340 °C and operated in scan mode, with spectra being recorded between *m/z* 50 and 700. Peak assignments were made by comparison with relative elution times from literature, a mass spectral library (NIST 2.0) and interpretation of the mass spectra.

RESULTS AND DISCUSSION

The analysed samples are listed together with the lipid yields in table 1. The lipid extracts were primarily composed of acyl lipids, suggesting that the vessels were indeed associated

with food consumption. Free fatty acids such as palmitic and stearic acid are the most abundant lipids, although mono- and diacylglycerols were also retrieved in many cases. A significant amount of diagnostic lipids was retrieved for most of the samples except for BJ1, BJ3, BJ10, BJ16, BJ20, BJ21 and BJ22 (table 1). These samples only contained minute amounts (0 to 20 $\mu\text{g g}^{-1}$) of even numbered ($\text{C}_{14}\text{-C}_{20}$) saturated fatty acids. Therefore, the results of these samples are discarded unless stated otherwise. Apart from acyl lipids, aliphatic hydrocarbons, alkanols, mid-chain ketones, wax esters, vicinal dihydroxy fatty acids, ω -(*o*-alkylphenyl)alkanoic acids and steroids were also detected. The results and the significance of these biomarkers will be discussed in the following sections. An overview of all detected biomarkers is given in table 2.

Fatty acid distributions

Most vessels exhibit a free fatty acid profile with a high stearic acid content. This is generally interpreted as indicative of animal fats. To quantify this predominance of stearic acid, the palmitic : stearic acid (P/S) ratio has been explored in the past by examining the fatty acid composition of extant animal and plant tissues (Eerkens 2005; Kimpe et al. 2002; Romanus et al. 2007; Skibo 1992). Animal fats, particularly those of ruminants, tend to have lower P/S ratios than vegetal oils. 16 samples exhibited a P/S ratio below 1.3 which would be indicative of ruminant animal fats (table 1) (Romanus et al. 2007). Only one sample (BJ18) had a higher value (1.4). The robustness of this ratio, however, has been widely debated because of the complexity of degradation processes and uncertainties with respect to the mixing of different commodities (Colombini et al. 2009; Regert 2011). Furthermore, certain vegetal oils may have relatively low P/S values such as sesame oil (1.9), fenugreek (2.1) grape seed oil (2.1) and walnut oil (2.7) (Dubois et al. 2007). Therefore, P/S ratios should be interpreted with caution.

Furthermore, significant amounts of odd-chain and branched fatty acids, notably pentadecanoic acid ($\text{C}_{15:0}$), heptadecanoic acid ($\text{C}_{17:0}$) and equivalent anteiso- and iso-isomers, are detected in all samples. Additionally, monoacylglycerols (MAG) and diacylglycerols (DAG) with odd carbon numbers were also identified in 13 samples (table 2). While these fatty acids may derive from bacterial or ruminant lipids, it has been shown that the intrusion

of microbial lipids in ceramics is negligible (Dudd et al. 1998; Kimpe 2003). Moreover, we have taken precautions to avoid this type of contamination by removing the outer surface of the sherds (*cf.* Stern et al. 2000). By consequence, it is more likely that they are indicative of ruminant adipose or dairy fats. Isoprenoid fatty acids such as pristanic and phytanic acid were also detected in 8 samples (table 2) and might indicate the presence of marine fats and oils (Hansel et al. 2004). However, they also occur in milk fats (Vlaeminck et al. 2006).

Interestingly, low quantities of two unusual fatty acids, *viz.* heptadecenoic acid (C_{17:1}) and nonadecenoic acid (C_{19:1}), were detected together with pristanic and phytanic acid in samples BJ9 and BJ11 (table 2). While C_{17:1} may occur in milk (Vlaeminck et al. 2006), an extensive literature survey has shown that the simultaneous occurrence of C_{17:1} and C_{19:1} is typical for fish such as carp and catfish (Rasoarahona et al. 2004, 2008) and for sea foods such as limpets, shrimps, cuttlefish, crabs and sponges (Ando and Nozaki 2007; Barnathan et al. 2003; Carballeira and Alicea 2001; Denis et al. 2009; Le Bihan et al. 2007; Kawashima et al. 2008). Concentrations of these monounsaturated fatty acids are comparable to those of isoprenoid fatty acids, namely 0.2-2% of the total fatty acid concentration (*cf.* Ackman and Hooper 1968). The uniqueness of C_{19:1} is furthermore demonstrated by the fact that a commercially available standard of this fatty acid is used as an internal standard for determining the fatty acid composition of a.o. milk fats (e.g. Abdelqader et al. 2009; Petit et al. 2001). Meta-analysis of previous data from our laboratory demonstrated the presence of both C_{17:1} and C_{19:1} in fish remains from contemporary (Quseir al-Qadim, Egyptian Red Sea coast) and archaeological (Hierakonpolis, Naqada II period, 3800-3300 BC) contexts. To our knowledge, these unusual fatty acids have never been reported in an archaeological context. We therefore suggest the co-occurrence of C_{17:1}, C_{19:1} and isoprenoid fatty acids as a novel biomarker for aquatic food sources.

Fatty acid degradation products

The presence of many fatty acid derived products in all samples shows that the lipids have endured extensive degradation indicative of cooking activities. For instance, short chain (C₆-C₁₂) ω-hydroxy fatty acids and α,ω-dicarboxylic acids are typical oxidation products of unsaturated fatty acids (Regert et al. 1998). In view of the relatively low concentration,

however, their significance is rather limited as they could derive from both animal or plant commodities. Furthermore, trace amounts of γ -palmitolactone, γ -stearolactone and equivalent δ -lactones were detected in all samples. These compounds are rarely detected in archaeological contexts (Charrié-Duhaut et al. 2009; Buckley and Evershed 2001). A reasonable explanation for their occurrence in the present lipid extracts would be their formation from saturated fatty acids by free radical hydroxylation at carbon atom C₄ or C₅ and subsequent intramolecular esterification (Nawar et al. 1988; Vajdi et al. 1979).

More diagnostic is the presence of a mixture of hydroxystearic acid (C_{18:0}) isomers in samples BJ9, BJ11 and BJ13 (table 2). From figure 1, it can be deduced that the position of the hydroxyl group ranges from C₈ to C₁₆, with the C₉ and C₁₀ isomers as the most prominent ones. These hydroxy fatty acids must have been formed by acid-catalyzed hydration of a series of octadecenoic acid isomers (C_{18:1} $\Delta^{9,10,11,12,13,14,15,16}$), possibly under the influence of heating and the metal ions in the ceramic fabric. The presence of series of C_{18:1} isomers has been found to be highly diagnostic for ruminant fats owing to the biohydrogenation of dietary fats by micro-organisms in the rumen (Mottram et al. 1999). Furthermore, the predominance of C_{18:1} Δ^9 and Δ^{11} in this isomeric series correlates closely with the distribution of the hydroxy-C_{18:0} isomers observed in the present data set (figure 1). To our knowledge, this is the first time that an isomeric series of hydroxy-C_{18:0} has been identified in lipid residues.

Vicinal dihydroxy fatty acids, occurring as a pair of diastereomers, are another group of degradation products and were detected in 7 samples (table 2). These compounds are formed by free radical or hydroperoxide induced epoxidation of monounsaturated fatty acids and subsequent epoxide ring opening (Hansel and Evershed 2009; Romanus et al. 2008). Information on the original structure of the fatty acids, such as carbon number and position of the double bond, is retained during oxidation. The presence of multiple positional isomers of dihydroxy C_{18:0}, viz. hydroxyl groups on positions [9,10], [10,11], [11,12] and [13,14], in samples BJ9, BJ11 and BJ13 corresponds most probably to a ruminant fat origin, the more because various hydroxy C_{18:0} isomers were observed in these samples (*cf. supra*). The presence of C₁₆ and C₂₀ dihydroxy fatty acids in a few samples and the co-occurrence of isoprenoid fatty acids (table 2), may indicate a contribution of marine commodities (Hansel

and Evershed 2009). Nevertheless, C₁₆ and C₂₀ monounsaturated fatty acids also occur in plant oils.

Another class of thermal degradation products are ω -(o-alkylphenyl)alkanoic acids, which were detected in 6 samples (table 2). These compounds are formed by isomerisation and intramolecular Diels-Alder reactions from polyunsaturated fatty acids at temperature above 270 °C (Hansel et al. 2004). It was recently shown that these compounds can also be formed from mono- and diunsaturated fatty acids such as C_{18:1} and C_{18:2} (Evershed et al. 2008). This implies that C₁₈ ω -(o-alkylphenyl)alkanoic acids could derive from both animal fats and plant oils. By contrast, C₂₀ and C₂₂ ω -(o-alkylphenyl)alkanoic acids are diagnostic for marine lipids owing to the high concentration of polyunsaturated fatty acids such as C_{20:5}, C_{22:5} and C_{22:6} in the latter. In the present assemblage of potsherds, only trace amounts of C₁₈ ω -(o-alkylphenyl)alkanoic acids were identified (table 2). Furthermore, the co-occurrence of C₁₈ ω -(o-alkylphenyl)alkanoic acids, C₁₆-C₂₀ dihydroxy acids and isoprenoid fatty acids in samples BJ7, BJ9 and BJ13 may indicate marine fish oils. However, this hypothesis cannot be confirmed because we were not able to confirm the presence of C₁₆, C₂₀ or C₂₂ ω -(o-alkylphenyl)alkanoic acids even with the mass spectrometer in single ion monitoring mode.

Mid-chain ketones represent another class of fatty acid oxidation products; they were detected in many samples. However, they will be discussed in detail below.

Steroids

Small amounts of sterols, *viz.* cholesterol and sitosterol, and sterol oxidation products, *viz.* cholesta-3,5-dien-7-one, were detected in 8 vessels (table 2). Cholesterol and its oxidation products are typically animal derived sterols, while sitosterol is indicative of plant commodities (Evershed 1993; Heron et al. 2010). While this statement is generally valid, it should be acknowledged that plant oils may contain cholesterol, typically in 1-2% of total sterol concentration (Moreau et al. 2002; Belitz et al. 2004), and similarly that plant sterols may be detected in certain animal species such as shell fish (Copeman and Parrish 2004). This implies that a sterol composition featuring a high phytosterol concentration and small amounts of cholesterol may entirely derive from plant lipids, and vice versa. In the current

sample set, however, cholesterol was never detected together with phytosterols (table 2). In conclusion, the detected steroids merely indicate a single food source, namely an animal fat in case of cholesterol and cholesta-3,5-dien-7-one or a vegetal origin in case of sitosterol.

Wax lipids

Beeswax Long-chain even numbered alkanols (C₂₂-C₃₂) were detected in all samples except for BJ23 and BJ24. Additionally, odd-chain alkanes (C₂₅-C₃₃) were also detected in a number of samples. These compounds are widespread constituents of plant epicuticular waxes (Kolattukudy 1980; Walton 1990) and beeswax (Tulloch 1971). In only one sample (BJ18) positive evidence for beeswax was found due to the presence of palmitate esters (C₄₀-C₄₂), 15-hydroxypalmitate and a series of (1,ω-1)-alkanediols (C₂₄-C₂₈). This pattern is clearly indicative of beeswax (Aichholz and Lorbeer 1999; Baeten et al. 2010; Garnier et al. 2002). Higher molecular weight palmitate esters (C₄₄-C₅₀) could not be detected with the adopted splitless injection technique. Furthermore, the relative enrichment of higher molecular weight *n*-alkanes (maximum at C₃₁) and *n*-alkanols (maximum at C₃₀) provides evidence for the degraded state of beeswax (Regert et al. 2001). However, other biomarkers point out that beeswax was not the sole commodity in this vessel. The presence of mono- and diacylglycerols indicates an additional acyl lipid source. The presence of odd-chain fatty acyl chains is furthermore indicative of a ruminant fat source (table 2). Beeswax has been found regularly in ceramic vessels (e.g. Heron et al. 1994; Evershed et al. 1997), even together with animal fats (Charters et al. 1995). In this particular case, beeswax may have been applied as a sealant or may be linked to the presence of honey.

Plant epicuticular waxes Evidence for plant epicuticular waxes was found based on the presence of long-chain alkanols and alkanes (*cf. supra*). However, due to widespread occurrence of these molecules among plant waxes, more detailed identifications cannot be made at this point.

Mid-chain ketones, on the other hand, are more diagnostic and were detected in 14 samples (figure 2, table 2). As stated above, these compounds may derive from the heating of fats. Alternatively, they are also major constituents of plant epicuticular waxes. Criteria used to

distinguish the origin of these compounds are (i) carbon number distribution, (ii) simultaneous occurrence of related mid-chain alkanols and alkanes and (iii) the position of the carbonyl group (Evershed et al. 1995; Raven et al. 1997). These criteria are discussed in the following paragraphs. Particular attention will be given to the usefulness of the criteria to identify mixtures of fats and waxes.

A first attempt to determine the origin of the ketones was made by examining the carbon number distribution (table 2). Figure 3a displays the ketone profile of four representative samples. Sample BJ5 exhibits a very broad distribution of mid-chain ketones with a carbon number ranging between 29 and 37. This pattern can be clearly linked with the ketonic decarboxylation reaction of acyl lipids occurring at temperatures exceeding 300 °C (Evershed et al. 1995; Raven et al. 1997). The C₃₃ mid-chain ketone has the highest concentration, followed by C₃₅ and C₃₁ components. While the latter two could result from the condensation of two C₁₈ and two C₁₆ acyl chains, respectively, the C₃₃ ketone is most likely produced by reaction of one C₁₆ and one C₁₈ acyl chain. Bearing this in mind, one can note that in this particular sample the overall abundance of C₁₈ acyl chains is about 1.5 times higher than that of C₁₆ acyl chains, a feature which is typical for animal fats (*cf. supra*). By contrast, only one ketone, namely nonacosanone (C₂₉), was detected in the lipid extract of sample BJ16 (figure 3a). This may be indicative of a *Brassica oleracea* (cabbage) leaf wax origin (Evershed et al. 1991; Kolattukudy 1980). The ketone profiles of samples BJ2 and BJ11 are less straightforward to interpret (figure 3a). Although the broad carbon number distribution is unequivocally indicative of processed animal fat, the C₂₉ ketone seems to exhibit an anomalously high concentration, particularly in sample BJ2. This may indicate that nonacosanone may be partially derived from cabbage leaf wax. Hence, the carbon number distributions are not able to give unequivocal evidence for mixtures of both sources.

The second criterion used to distinguish animal and plant derived ketones, is the simultaneous occurrence of related mid-chain alkanols, indicative of a leaf wax origin (table 2). These alkanols were identified in many samples but not in all the specimens where ketones were detected. In all cases, nonacosan-15-ol was the major mid-chain alkanol and was detected together with small amounts of nonacosan-14-ol, as evidenced by the mass spectrum. While alkanols in cabbage leaf wax indeed have a variable position of the hydroxyl group, only

nonacosan-15-ol is enzymatically oxidised to the corresponding nonacosan-15-one (Kolattukudy 1980). In several samples, the co-occurrence of mid-chain alkanols and a broad distribution of ketones indicate a mixed origin, *viz.* cabbage leaves and a fat source (table 2). While positive identification of alkanols constitutes unambiguous evidence for leaf wax lipids, their absence not necessarily excludes leaf waxes. Indeed, the concentration of alkanols in fresh cabbage leaf waxes is considerably lower than that of ketones (Evershed et al. 1991).

The third criterion is the position of the carbonyl functionality. Owing to a high specificity in the biosynthesis of ketones, leaf wax always consists of symmetrical ketones, *e.g.* nonacosan-15-one in *Brassica oleracea* (Kolattukudy 1980). On the other hand, the ketonic decarboxylation of animal fats produces nonacosan-14-one owing to the condensation of C₁₄ and C₁₆ acyl chains, rather than of C₁₅ acyl chains. GC-MS analysis of the lipid extracts facilitates the determination of this carbonyl position by exploring the mass spectral information of the different peaks (*cf.* figure 2). Main fragments result from α -cleavage, γ -cleavage, McLafferty rearrangement and concerted double hydrogen transfer (Vajdi et al. 1981). The masses of these fragments are listed in function of carbon number in table 3. Because the double hydrogen transfer fragments do not exhibit mass overlap with other fragments (*cf.* overlap between α - and γ -cleavage) and are sufficiently abundant, they were considered as the best indicator of the carbonyl position and were used in the remaining part of this paper. By extracting the ions resulting from double hydrogen transfer from the total ion current (TIC) chromatogram and calculating the relative peak areas, the distribution of the carbonyl positions can be determined in function of the ketone carbon number:

$$RE_{i,k} = \frac{E_{i,k} \cdot 100\%}{\sum_i E_{i,k}}$$

$E_{i,k}$ is the peak area (in extracted ion chromatogram) of the ketone with carbon number k , with the ion representing a carbonyl functionality on carbon atom i . For asymmetrical ketones, peak areas of two ions were summed (*cf.* table 3). The distribution of the carbonyl position, represented by the relative peak areas $RE_{i,k}$, is plotted for each ketone carbon number in figure 3b. In case of sample BJ5, the animal origin of the ketones, indicated by the carbon number distribution (*cf. supra*), is supported. The presence of nonacosan-14-one as sole isomer

evidences its formation from C₁₄ and C₁₆ acyl chains deriving from an animal fat (table 3). In contrast, nonacosan-15-one is the only isomer in sample BJ16 which is consistent with a leaf wax source. In samples BJ2 and BJ11, the presence of both nonacosan-14-one and nonacosan-15-one indicates a mixed origin.

Furthermore, it becomes clear from figure 3b that odd-chain fatty acids were also present in the animal fat source in sample BJ2 and BJ5. For example, dotriacontan-15-one (C₃₂), dotriacontan-16-one (C₃₂) and tetratriacontan-17-one (C₃₄) must have been formed by heating a fat that contained small amounts of C₁₅ and C₁₇ acyl chains (table 3). Such odd-chain compounds are typically observed in ruminant fats (both adipose and dairy fat) or in bacterial acyl lipids (*cf. supra*). However, the latter source can be excluded as the fraction of microbial lipids in the thermally processed lipid molecules must have negligible. Moreover, the occurrence of odd-chain acyl signals in the mid-chain ketones provides an even more robust proxy for ruminant fats than free odd-chain fatty acids because post-burial formation of ketones can be excluded (*cf. supra*).

The observation of ketones derived from odd-chain fatty acids, however, can cause some ambiguity as to the origin of nonacosan-15-one. The latter may in principle be formed by condensation of two C₁₅ acyl chains. To test this hypothesis, the original fatty acyl distribution (in the mid-chain ketones) can be reconstituted, assuming that all ketones arise from decarboxylation. Therefore, the relative peak areas $E_{i,k}$, weighed by the relative abundances of the individual ketones, are summed:

$$F_i = \sum_k \left(E_{i,k} \cdot A_k / \sum_k A_k \right) \quad \text{and} \quad RF_i = \frac{F_i \cdot 100\%}{\sum_i F_i}$$

A_k is the peak area (TIC chromatogram) of the ketone with carbon number k . RF_i is the relative abundance of the fatty acyl chain with carbon number i (equals the carbonyl position, *cf.* table 3). For asymmetrical ketones, the peak areas $E_{i,k}$ of the two ions were summed and divided by 2 to calculate the F_i value for both fatty acyl chains (*cf.* table 3). The theoretical fatty acyl distribution can thus be reconstituted by plotting the RF_i values in function of i (figure 3c). This plot allows a straightforward detection of anomalies. For example, samples

BJ2 and BJ11 show unexpectedly high abundances for C₁₅ acyl chains, confirming that the mid-chain ketones cannot exclusively be derived from heated animal fat, but must to some extent derive from cabbage leaf wax. On the other hand, sample BJ5 does not exhibit anomalies in the reconstituted fatty acyl profile, supporting the hypothesis that the odd-chain fatty acyl moieties are indeed all originating from a ruminant fat source. Furthermore, anomalies in the reconstituted fatty acyl profiles can even become clearer when comparing these plots with the free fatty acid distribution in the same lipid extracts (figure 3d). The predominance of C₁₈ over C₁₆ acyl chains in sample BJ2, BJ5 and BJ11 (figure 3c) further confirms a ruminant origin of the animal fat in these samples.

In conclusion, it becomes clear that the carbon number distribution of ketones and the co-occurrence of alkanols do not always allow distinguishing between animal and plant origins, especially in cases of suspected mixing of both sources. Conversely, analysis of the carbonyl position distribution can be particularly helpful for such issues. After applying all of these criteria to the data set, it was found that 5 vessels were exclusively used for processing an animal fat, 2 vessels for preparing cabbage and 7 vessels for the preparation of both foodstuffs (table 2, last column). Mid-chain alkanols were detected in the samples for which positive evidence was found for the preparation of cabbage, except for one sample (BJ8). The latter is most probably due to the fact that mid-chain alkanols are less abundant in leaf wax compared to ketones (*cf. supra*).

Integration of all biomarker evidence

The aforementioned lipid biomarkers clearly evidence that the vessels were associated with the consumption of meat, fish, vegetables or a mixture of multiple foods. Furthermore, the presence of many degraded lipids which are only formed upon exposure to high temperatures (e.g. mid-chain ketones, ω -(o-alkylphenyl)alkanoic acids) are consistent with the sooty deposits on all sherds, confirming that the pots were used as cooking vessels. In one case, beeswax was found together with an animal fat. In the following section, all the biomarker evidence will be integrated in order to (i) identify the different types of foods by a multi-biomarker approach and to (ii) fully assess the extent of mixing. The assignment of the various commodities is summarised for each sample in table 1.

Animal fats were identified based on the presence of odd-chain mono- or diacylglycerols, isomers of hydroxy C_{18:0}, cholesterol or cholesta-3,5-dien-7-one, and animal derived mid-chain ketones (evidenced by the distribution of their carbon numbers and carbonyl positions). The P/S ratio was not used as a reliable criterion in view of the apparent mixing of different food commodities. In the majority of the samples, the animal fat was specified as ruminant fat due to the presence of isomeric hydroxy C_{18:0} and odd numbered acyl chains (MAGs, DAGs and ketones). In only three samples, the animal fat could not be specified.

The presence of fish oils could not be proven unambiguously based on conventional fish biomarkers. Nevertheless, strong indications for marine foods were retrieved in three samples based on the presence of isoprenoid fatty acids together with C₁₆-C₂₀ dihydroxy fatty acids and C₁₈ alkylphenyl fatty acids. Moreover, the co-occurrence of two unusual fatty acids (C_{17:1} and C_{19:1}) and isoprenoid fatty acids in two samples was proposed as a new biomarker for aquatic foods.

Evidence for vegetal foods was provided by the presence of sitosterol, long-chain alkanols, long-chain alkanes, mid-chain alkanols and plant derived mid-chain ketones (evidenced by the distribution of their carbonyl positions). In 9 samples, the vegetal commodities could be specified as cabbage based on mid-chain alkanol and ketone biomarkers.

Archaeological implications on vessel use

Previous analyses of food consumption in Hamwic have been limited to traditional studies of faunal and botanical remains. Whilst we have a good idea of the types of foodstuffs consumed, we have little understanding of how they were cooked and consumed.

Furthermore, issues of preservation and recovery mean that some, primarily plant-based, foodstuffs may not be visible, or may be under-represented, in the assemblage. Residue analysis was therefore undertaken to investigate cooking practices, alongside a programme of usewear analysis (Jervis 2011). The vessels from Hamwic were used to process multiple foodstuffs, all of which can be observed in the archaeological record. The predominance of ruminant fats correlates with evidence from faunal remains that cattle and sheep are the most

common domesticates consumed in Hamwic (Bourdillon and Coy 1980). Leafy vegetables are regularly identified in Anglo-Saxon pottery by organic residue analysis (e.g. Evershed et al. 1991) and cabbage, along with a wide variety of wild and domesticated plant foods, were present in botanical remains from Hamwic (Hunter 2005). When combined with zooarchaeological indications of stewing – e.g. the absence of ‘ivory textured’ bone (Bourdillon and Coy 1980) – and sooting patterns on pottery (Jervis 2011), these results suggest that meat was cooked and consumed alongside vegetables in dishes such as stews. The lipid biomarkers therefore provide direct evidence of stewing, the dominant cooking method in the Anglo-Saxon period based upon historical sources. For example, a leechdom instructs the cook to ‘stew for a very long time over embers’ (Cockayne 1851, I lxxxvi). This is an important finding, which could not be directly detected by other means. Stewing is typically believed to be the dominant cooking method in the period but this has rarely been demonstrated archaeologically.

It is highly likely that marine foodstuffs are underrepresented in Hamwic’s archaeological record (*cf. supra*). A range of fish and marine molluscs, particularly oysters, have been recovered from excavations in Hamwic, the majority of which could have been caught in traps (Bourdillon and Coy 1980; Winder 1980). A general perception prevails that fish and marine molluscs were an addition to a diet which largely relied upon domesticated species (Wyles 2005). The current study allows us to test this perception, by considering the occurrence of marine biomarkers in cooking pots. Whilst only a small number of potsherds was studied, a case can tentatively be made in support of this view, as positive evidence for aquatic foods appears in only two samples. More valuable are the insights into the cooking of fish. Historical sources suggest that salt fish would have been boiled, possibly in milk or butter (Hagen 2006). For the first time, this analysis has potentially demonstrated this archaeologically, through the co-occurrence of ruminant and marine fats in the same vessel. In the future, however, this hypothesis should be tested in more detail by assessing the presence of dairy fats through stable carbon isotope ratio analysis of fatty acids.

Usewear analysis has indicated that Chalk-tempered Wares likely entered Hamwic as containers (Jervis 2011). This analysis offered an opportunity to test this hypothesis. The presence of beeswax occurs in a single sherd of a Chalk-tempered Ware vessel, when

considered alongside a general absence of consistent usewear on Chalk-tempered Ware vessels, can be presented as evidence in support of the theory that these vessels entered Hamwic as containers. The beeswax may indeed have been used to seal these vessels, making them suitable for transporting liquids. Alternatively, the beeswax may indicate the presence of honey. This was paid as a food-rent in the period and was used both as a sweetener and a preservative (Blinkhorn 1997). Beeswax has also been identified in contemporary Ipswich Ware vessels, believed to have functioned as containers (Blinkhorn 1997). The ruminant fat present in this vessel may be the result of reuse, a phenomenon which can be observed amongst a number of the Chalk-tempered Ware vessels based on usewear analysis (Jervis 2011).

CONCLUSION

The present paper describes the GC-MS characterisation of lipid extracts of Anglo-Saxon coarseware from Hamwic (Southampton, UK). From a methodological perspective, the results allowed us to gain new insights on interpretative issues regarding the use of biomarkers to identify food commodities in lipid extracts:

- (i) A mixture of hydroxyoctadecanoic acid isomers with the hydroxyl group attached to carbon C₈ to C₁₆ was detected in 3 vessels. These compounds are degradation products of octadecenoic acid isomers (C_{18:1} $\Delta^{9,10,11,12,13,14,15,16}$), a biomarker for ruminant fats. By extension, the products may equally be considered as biomarker for ruminant fat.
- (ii) When C_{17:1} and C_{19:1} fatty acids are detected together, they are indicative of fish and sea foods. They may be added to the known biomarkers for marine foods, *viz.* C₁₆-C₂₂ ω -(*o*-alkylphenyl)alkanoic acids, C₁₆-C₂₂ dihydroxy fatty acids and isoprenoid fatty acids. An advantage of the proposed biomarkers is that they do not need to be formed upon extensive heating and consequently may be used to trace fermented fish sauces such as *garum*.
- (iii) We have demonstrated the use of the carbonyl position distribution in mid-chain ketones by facile mass spectral deconvolution techniques to identify the biogenic origin

of the ketones. More specifically, the carbonyl position of nocosanone was found to be diagnostic for cabbage leaf wax (nonacosan-15-one), animal fats (nonacosan-14-one) or a mixture of both. Other conventional criteria such as a broad carbon number distribution and the co-occurrence of mid-chain alkanols were only effective to identify an animal and plant origin, respectively, but not a mixture of both sources.

- (iv) We have demonstrated that it is necessary to consider multiple biomarkers to assign lipid signatures to food sources, particularly when the mixing of various sources is suspected. The general pattern for the present pottery assemblage is the predominance of ruminant fats and vegetables, mainly cabbage. Furthermore, indications were found for a minor contribution of aquatic foods.

From an archaeological perspective, this study has offered new insights into the domestic lives of the occupants of Hamwic. For too long artefactual and environmental (*viz.* animal bones, macrobotanical remains, pollen) analyses have been artificially separated by archaeological practice and this divide can only be bridged through the adoption of integrated methodologies (see Mellor 1995; Irving 2011). Furthermore, these studies have been relegated to answering questions of economy, such as trade and provisioning strategies, a process which, within medieval archaeology can be related to the continued primacy of historical sources in defining research agendas (see Austin 1990, 13). The current study demonstrates the value of integrating the study of foodstuffs with that of the vessels in which they were stored, processed and cooked and has offered some valuable insights into cuisine in Hamwic, which goes beyond the simple identification of foodstuffs and cooking vessels. Although only a small set of samples was studied, this analysis has provided fresh information on cooking practices, as opposed to the simple reconstruction of diet, and has supplemented petrological and usewear analysis in the identification of non-local vessels which primarily functioned as containers. Further studies of Anglo-Saxon pottery must be undertaken to contextualise these findings, but they have the potential to inform, for example, wider debates about the level of differentiation between urban and rural lifestyles in the period. These studies have great potential, especially in the promotion of a more fully integrated archaeology, in which the linkages between objects and foodstuffs in the past can be directly related to one another. Such studies can only enrich our understanding of the past and help us to overcome the

divisions between the study of environmental and artefactual remains which is inherent in archaeological practice.

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FIGURE CAPTIONS

Figure 1. Overlay of extracted ion chromatograms (m/z 303, 315, 331, 345, 359, 373, 387, 401 and 415) showing the presence of 9 positional isomers of hydroxyoctadecanoic acid in sample BJ9 (TMS derivatives). The summed chromatograms of m/z 204 and 217 are present in all hydroxy fatty acids (*cf.* Rontani and Aubert 2004).

Figure 2. Partial TIC-chromatogram of the lipid extract of sample BJ5 showing mid-chain ketones, abbreviated by their carbon number. The inset shows the mass spectrum of hentriacontanone.

Figure 3. (a) Concentration (in $\mu\text{g g}^{-1}$ potsherd) of mid-chain ketones in lipid extracts, (b) Distribution of carbonyl position of mid-chain ketones in function of carbon number (black = 14, grey-black pattern = 15, light grey = 16, dark grey = 17, grey-white pattern = 18, white = 19), (c) reconstituted fatty acyl distribution based on carbonyl position of mid-chain ketones, (d) fatty acid distribution in lipid extracts.

TABLE CAPTIONS

Table 1. Summary of analyzed samples, lipid yields (soxhlet extraction) and assigned food commodities based on multiple biomarkers (see text).

Table 2. Summary of identified biomarkers in the 24 samples detected by GC-MS. Individual compounds are abbreviated by their carbon number. Other abbreviations are as follows: pr = pristanic acid, ph = phytanic acid, mar = marine biomarkers $\text{C}_{17:1}$ and $\text{C}_{19:1}$ (see text), ch = cholesterol, chon = cholesta-3,5-dien-7-one, st = sitosterol, f = fat, w = plant wax, b = beeswax.

Table 3. Summary of possible mass fragments of mid-chain ketones, listed by carbon number (CN).