Journal of Archaeological Science: Reports 15 (2017) 150–160

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Identifying ancient beer brewing through starch analysis: A methodology

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ARTICLE INFO

Keywords:
Ancient beer
Fermentation
Starch granules
Archaeological residues

ABSTRACT

As documented in written and artistic records, the production and consumption of beer played a significant role in the social, political, and economic activities of many ancient societies. However, direct archaeological evidence of beer making has been relatively sporadic. To address this gap, we need a better understanding of the microbotanical residues produced by brewing. Thus, we conducted cereal-based fermentation experiments by following some brewing methods likely used in antiquity. Based on previous publications in food science, we investigated how beer-making processes affect the properties of starch granules by documenting the resulting changes that occur in the starch granules of 17 domesticated and wild plant species. This paper introduces a method for identifying starch residues from cereal-based beer, some mixed with other plant additives, which can be applied to future archaeological research in the Old World.

1. Introduction

Beer, made from cereal grains or other starchy substances, was one of the most widely consumed alcoholic drinks in the ancient world (Geller, 1992; Joffe, 1998; Ghalioungui, 1979). Beer making was an integral part of rituals and competitive feasting (Joffe, 1998; Dietler and Hayden, 2001; Dietler, 2006; Jennings et al., 2005), a social regulatory mechanism in hierarchical societies (Neumann, 1994; Joffe, 1998), and possibly a motivating factor for the original domestication of cereals (Braidwood et al., 1953; Katz and Voigt, 1986). Evidence based on written and artistic sources suggests that brewing beer may have been a ubiquitous tradition in antiquity, but direct archaeological evidence of beer has been relatively sporadic.

While raw materials and brewing methods vary geographically and throughout time, all beer-brewing methods produce the same biochemical transformation—that is, the conversion of starch into ethyl alcohol. This process sometimes left archaeological signatures, in the forms of charred cereal malts (e.g., Stika, 1996; Bouby et al., 2011), distinctive chemical markers (e.g., McGovern et al., 1999, 2004, 2005), and damaged starch granules (e.g., Samuel, 1996b; Wang et al., 2016). Carbonized malt is a rare occurrence in archaeological remains, and chemical analysis often requires multiple independent techniques for a reliable interpretation. Starch granules, in contrast, preserve in diverse archaeological contexts and their analytical techniques have been well established. More importantly, starch granules are susceptible to damage when exposed to different food processing methods. Some methods produce unique changes to the appearance of the granules, thus providing a means for identifying certain cooking methods in the archaeological record (Babot, 2003; Henry et al., 2009). In order to develop a method for identifying ancient beer production, we conducted cereal-based fermentation experiments by following some ancient brewing methods recorded in written sources and ethnographic works (Ling, 1957; Karp, 1987; Huang, 2000; Arthur, 2003; Jennings et al., 2005; McGovern, 2009; Lincoln, 2011; Lyumugabe et al., 2013; Yamamoto, 2016). Using a variety of wild and domesticated plants, we investigated how beer-making processes affect the properties of starch granules. Our results show that beer making produces identifiable changes in several types of plant starches. Here we report the results and propose a method for identifying starch residues from ancient beer brewing based on Old World cereals (Triticeae plants, millets, and rice), some mixed with other plant additives (legumes, *Cyperus* roots, and tubers).

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http://dx.doi.org/10.1016/j.jasrep.2017.07.016
Received 13 March 2017; Received in revised form 21 July 2017; Accepted 23 July 2017
2352-409X/

2. From starch to beer: general principles

Starch is a complex sugar that comes in two main forms, amylopectin and amylose, both of which can be hydrolyzed into fermentable sugars by several enzymes such as α-amylase, β-amylase, and starch phosphorylase (Goyal, 1999; Hornsey, 2003). The transformation from starch to beer is a two-phase conversion. During the first phase, starches are broken down into fermentable sugars, a process known as saccharification. This process can be initiated by the enzymes naturally present in cereal grains during germination, or by exogenous enzymes in human saliva and other natural sources such as honey and various plants. In the second phase—fermentation—yeasts convert sugars into alcohol and carbon dioxide. In modern beer brewing, the first conversion is usually achieved by malting and mashing, during which grains are allowed to germinate in a controlled setting to produce diastase enzymes, and then coarsely ground and mixed with heated water (at temperature below 70 °C) to facilitate enzymatic hydrolysis. The second conversion is fulfilled by adding cultured or wild yeasts as the fermentation agent (Briggs et al., 1981; Hornsey, 1999, 2003; Briggs et al., 2004). While "fermentation" sometimes indicates a specific stage for sugar-alcohol conversion, it also broadly refers to the brewing process as a whole. In the rest of the paper, we use "fermented starch(es)/granule(s)" to describe the resulting starches from going through all brewing stages.

Although there is no consensus on the details of the ancient brewing process, the basic techniques can be reconstructed from historical documents and ethnographic works. Far different from what we would recognize as beer today, early brews were most likely a multi-ingredient concoction, akin to a porridge or thin gruel, and fermented with airborne wild yeasts (McGovern, 2009; Hayden et al., 2012). Cereals were likely mixed with other ingredients such as roots, tubers, fruits, and herbs, which added additional starch and microorganisms. Mashing and fermentation was a continuous process often without a filtration stage to separate the grain fragments from the wort. This brewing tradition is still customary throughout ethnic groups in Africa and Asia. In Africa, sorghum malts are mixed with various plant additives to produce a traditional sorghum beer with a thick consistency (Karp, 1987; Arthur, 2003; Lincoln, 2011; Lyumugabe et al., 2013). In Cambodia, various ethnic groups mix steamed rice with rice husks and starters, producing alcoholic beverages drunk by using a bamboo straw with a filter (Yamamoto, 2016). Similar brewing traditions have been observed in Taiwanese aboriginal groups, who produce fermented beverages made of millet or rice, sometimes mixed with other starchy plants (Ling, 1957). Unfiltered beer often contains a large amount of insoluble materials, which are mainly starches and husks that are not digested during mashing and fermentation, sometimes forming a layer of residues visible on the walls of ancient brewing vessels (Geller, 1992; Maksoud et al., 1994). The residual starches, in particular, tend to show modifications in their structure and shape, which indicates the presence of beer production (Samuel, 1996a, 1996b).

3. Previous research on starch modification from enzymatic digestion and gelatinization

Enzymatic digestion and gelatinization are the two major processes that cause starch modification during beer making. Previous studies in food science have published detailed descriptions on the morphological changes of starches affected by these two processes. Here we briefly review the results related to this paper.

Starch granules are classified as A-, B- and C-types with respect to crystalline structure. A-type starch (e.g., cereals) is more susceptible to enzymatic hydrolysis than B-type starch (e.g., some tubers), and C-type starch (e.g., legumes) is in between (Kimura and Robyt, 1995; Jane, 2003). Different starch crystalline structures lead to different patterns of degradation during enzymatic degradation.

Generally, there are two general patterns of enzymatic attack that produce different microscopic appearances of starch. With B-type starches, enzymes erode the entire granule surface or sections of it (exocorrosion), resulting in a rough and irregular surface, but the granule may remain birefringent throughout until extensively degraded (Gallant et al., 1992; Oates, 1997; Barton and Matthews, 2006). A-type and C-type starches are attacked by a pattern of endocorrosion, whereby enzymes penetrate the granule surface through surface pores and channels with concurrent hydrolysis from the hilum region toward the outside of the granule (Gallant et al., 1992). Previous researches have shown that starches of Triticeae (Dronzek et al., 1972; Evers and McDermott, 1970; Lineback and Ponpipom, 1977; Galliard and Bowler, 1987; Henry et al., 2009; Claver et al., 2010), millets (Lineback and Ponpipom, 1977; Malleshi et al., 1986. Henry et al., 2009), and beans (Revilla and Tárrago, 1986; Sotomayor et al., 1999) exhibit a pattern of endocorrosion. The results of these studies suggest that starch granules of sprouted cereals and legumes follow an "inside-out" digestion pattern.

The changes that occur during gelatinization of starch granules have been well documented using both light microscopy and scanning electron microscopy (e.g., Hill and Dronzek, 1973; Bowler et al., 1980; Vaughan, 1979; Henry et al., 2009; Babot, 2003). Starch granules show different swelling characteristics at different aqueous conditions. Studies by Bowler et al. (1980) and Williams and Bowler (1982) demonstrate a two-stage pattern of starch gelatinization. According to their observation, at low temperature (< 70 °C), starch granules swell in a relatively slow and well-defined pattern, showing either two-dimensional (Triticeae) or three-dimensional expansion (others). After this stage, as temperature is further raised, changes take place rapidly and starch structure appears more complex, showing distortion, random convolutions and disintegration. This observation provides valuable data that help to identify gelatinized starches produced by ancient beer making. Because beer making involves low-temperature heating (< 70 °C), we might be able to distinguish the gelatinized granules produced by brewing from those by higher-temperature cooking based on their morphological differences.

However, to our knowledge, there has been no systematic study on the effect of beer brewing on the morphology of starch granules. In order to better understand how the appearance of starches can be modified during the brewing process, which involves both enzymatic degradation and gelatinization, we conducted a series of experiments to document how different stages of beer making process may cause changes to starch granules. We will compare our results with previous studies in the conclusion.

4. Materials and methods

We chose 17 Old World plants covering A-, B-, and C-type starches, including both wild and domesticated species (Table 1). Prior to the experiments, the native starches of the raw plants were examined to have a baseline against which to compare changes due to beer making (Fig. 2). The experiments employed three brewing methods. Method A applied to all Triticeae plants and millets, during which each plant went through three main stages of malting, mashing, and fermentation, producing single-ingredient brews (Fig. 2 Box a). Method B used barley as the main ingredient and followed the same procedure as Method A, with the only difference that a non-cereal plant was added to each set of barley to produce a mixed beer (Fig. 2 Box b). Method C applied to rice, which was steamed and then mixed with a starter (honey or *jiuqu* fermentation starter) to initiate saccharification and fermentation (Fig. 2 Box c). To compare the damage to starch resulting from beer brewing with the damage from other food processing techniques, we conducted additional cooking experiments on selected plants (Fig. 2 Box d). Detailed information about the experimental procedures is shown in Fig. 1 and Table 2.

After the experiments, a part of each sample was taken by scraping off a portion of solid substances. The extractions were then mounted in