CHAPTER FOURTEEN
The Archaeology of Alkaloids
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Chemical analysis of ancient residues is one of the most promising techniques in archaeology today. The variety of case studies in this volume is testament to the potential of this developing field of inquiry. That said, I would like to draw attention to a type of evidence that has seen comparatively little attention within the field of residue analysis: alkaloids and other molecules that are not related to subsistence resources, but are of great cultural importance nonetheless. In my conclusions I will identify issues relating to ritual practices and ideology, on which the study of prehistoric alkaloid-use can provide information. Most of my examples are drawn from North American contexts, but this geographic limitation is solely for the sake of brevity. Old World examples of the use of alkaloids abound, and some examples are presented towards the end of this chapter.

Alkaloids can be defined based on the following characteristics: they are organic molecules, generally containing at least one nitrogen atom, which is contained in a heterocyclic ring structure. Additional groups, such as methyl radicals, give each alkaloid its unique chemical properties. Alkaloids are comparatively small for organic compounds, and atomic weights range typically between 100 and 300. Alkaloids are basic in pH, and the resulting bitter taste is likely a primary evolutionary factor as a defense mechanism in the variety of vascular plants and fungi that contain them. Figure 1 depicts the molecular structure of several alkaloid compounds discussed in this chapter.

These molecules are significant to archaeology because they occur widely in wild plants as natural toxins, so any prehistoric population likely had a variety of alkaloid-bearing plants in their local environment. Of the available alkaloids, many are known to have a variety of biological effects on the human body and mind when ingested, and can act as narcotics, stimulants, or hallucinogens. Therefore, alkaloid-bearing plants were widely exploited as medicinal or psychoactive agents by prehistoric cultures worldwide. Many of these compounds are still utilized by modern societies; many more were used in prehistory.

Like foodstuffs, alkaloid-bearing plants could leave organic residues behind containing trace amounts of the active compounds. Some studies have indicated that alkaloids, or characteristic metabolites and decay products, can survive in prehistoric samples in detectable concentrations despite the solubility of some compounds (Raffuf and Morris 1960). This is important as there have been allegations that the study of prehistoric alkaloids is a fruitless endeavor due to the high potential of loss or decay of alkaloid biomarkers in archaeological contexts. I would argue that this is a matter to be evaluated experimentally rather than assumed a priori, and that the limited available experimental results appear promising for archaeological research.

An advantage of the study of alkaloids is that they are relatively easy to deal with in terms of chemical analysis. These small molecules are relatively easy to extract with organic solvents, such as methanol, chloroform, or diethyl-ether, and can be retained in solution for some time pending analysis. In fact, the retention of dissolved alkaloids can be an analytical step as it can produce characteristic decay products in a reasonable amount of time, weeks to months, which would be impractical to derive through natural aging. Dissolved alkaloids can be identified with standard instrumental methods, such as gas chromatography (GC), combined gas chromatography mass spectrometry (GC/MS) or high performance liquid chromatography (HPLC). Because many of these compounds are used in modern contexts, often as legally controlled substances, protocols for their detection and comparative samples are often available from food and drug regulatory agencies. Databases of alkaloid mass spectra are readily available and do not need to be produced *de novo*.

Despite the relative simplicity of the analysis and the high data potential of the topic, there has been comparatively little archaeological research into the ancient uses of alkaloids. Most studies of prehistoric plant use, whether through archaeobotanical approaches or through chemical analysis of organic residues, have focused on subsistence resources. In terms of residue analysis this has most commonly proceeded through the identification of characteristic fatty acids (Evershed et al. 2001). There has been precious little effort expended in analyzing organic residues that may have derived from plants with medicinal or psychoactive uses, which could have played roles in prehistoric ritual practices. This

should not be taken as a criticism of the excellent work on subsistence that has been conducted, but rather as the identification of untapped sources of data than can potentially be used to address archaeological and anthropological questions of great significance.

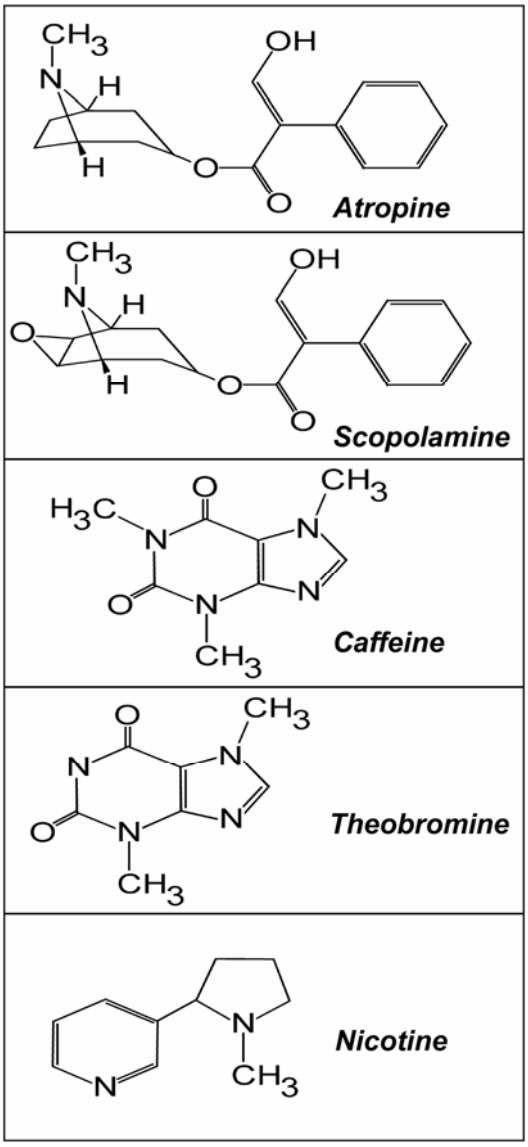

Figure 1: Structures of the alkaloid compounds discussed in this chapter.

In this chapter I will not primarily present analytical results, but offer suggestions for further lines of inquiry instead. It is my hope that colleagues with similar interests will follow up on the potential research questions that I will present, or develop new ones. I will illustrate my argument with a short discussion of one applied study in alkaloid residue analysis that I have conducted, the results of which have previously been published (Rafferty 2002; 2006).

Examples of Alkaloid Archaeology

I will first describe in brief several alkaloids that were often used in prehistoric times, focusing on their context of use and their prehistoric significance. This is intended as a means of illustrating what can be learned from studying the archaeology of alkaloids. I will conclude with a discussion of the implications for archaeology in general and some suggestions for future investigations.

Probably the most ubiquitous of alkaloids used by both modern and ancient human cultures is caffeine (trimethylxanthine). Caffeine is found in several well-known tropical plants, such as *Caffea arabica* (coffee) and *Theobroma cacao* (cacao, the basic ingredient in chocolate). It is soluble in water, as well as ethanol, acetone, chloroform and diethyl ether. By binding to receptor sites for the neurotransmitter adenosine, caffeine acts as a neurostimulant, increasing neuronal activity and stimulating the secretion of epinephrine by the pituitary gland. Caffeine also has the effect of increasing dopamine production and thereby stimulating the pleasure center in the brain.

Of the tropical caffeine-bearing plants, cacao has had the greatest cultural importance in the prehistory of the Americas. Wild cacao is native to South America, and was a cultivated garden crop in prehistoric Mesoamerica. Recent analyses of the early use of cacao have pointed to possible use of the plant by the early Pre-Classic Olmec, perhaps as early as 1,500 BCE (Coe and Coe 2000). This early date is based on linguistic evidence, 'cacao' being a word derived from the Olmec language. The earliest physical evidence of cacao in Mesoamerica dates to the Middle Pre-Classic Period Maya, some thousand years later. HPLC analysis of ceramic vessels from the Mayan site of Colha, dating between 600 BCE and 250 CE, identified both caffeine and the related alkaloid theobromine (which is present in cacao in a much higher concentration then caffeine and thus makes a superior biomarker). It is likely that these vessels were used in the preparation of a cacao-based beverage (Hurst et al. 1989; 2002). The vessels were found primarily in elite burials raising the possibility that the practice of drinking cacao beverages was socially restricted within Mayan society.

While this work is groundbreaking, pushing the known history of cacao back by 1,000 years, there is much we don't know about cacao use in Mesoamerica, and further residue analysis can provide additional information. Was the use of cacao widespread within prehistoric society, or restricted to certain classes or social contexts? Ethnohistoric evidence indicates that cacao was limited to elite consumption during the time of the Spanish conquest (Emboden 1979, 137).