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Poison, plants and Palaeolithic hunters.
An analytical method to investigate the presence of plant poison on archaeological artefacts.

Borgia V.,[a] Carlin M.G.,[b] Crezzini J.[c]

[a]McDonald Institute for Archaeological Research, University of Cambridge, United Kingdom

[b] Department of Applied Sciences, Northumbria University, Newcastle upon Tyne, United Kingdom (m.carlin@northumbria.ac.uk)

[c] Centro Studi sul Quaternario, Sansepolcro (Arezzo), Italy

ABSTRACT

In this paper we present the development of a method for the detection of toxic substances on ancient arrow points. The aim is to go back in time until the Palaeolithic period in order to determine if poisonous substances were used to enhance the hunting weapons.

The ethnographic documentation demonstrates that hunters of every latitude poisoned their weapons with toxic substances derived from plants and occasionally from animals. This highlights that often the weapons would be rather ineffective if the tips were not poisoned. The fact that toxic substances were available and the benefits arising from their application on throwing weapons, suggests that this practice could be widespread also among prehistoric hunters.

The project reviewed the research of the toxic molecules starting from current information on modern plants and working backwards through the ages with the study of ethnographic and historical weapons. This knowledge was then applied to the archaeological material collected from International museum collections.

Results have shown that using this method it is possible to detect traces of toxic molecules with mass spectrometry (MS) and hyphenated chromatographic techniques even on samples older than one hundred years, which we consider a positive incentive to continue studying plant poisons on ancient hunting tools.

1. Introduction

Within Palaeolithic studies, many questions concerning hunting weapons and the efficiency of the spears/arrows enhanced with stone armatures or bone elements remain unanswered. Recently, use-wear analysis and experimental archaeology have provided new insights into the use and effectiveness of hunting weapons, and now archaeological science methods may help us to further reconstruct the kinds of hunting techniques used during the Palaeolithic period. It may also allow an understanding of the role spears/arrows played in these pursuits (Allchin, 1996; Backwell et al., 2008; Costamagno, 1999; Gaudzinski and Roebroeks, 2000; d'Errico et al., 2012; Keeley, 1996;

Lombard, 2005; Lombard and Pargeter, 2008; Shea, 2006; Stanley et al., 1974).

An aspect of prehistoric hunting weapons that was scarcely taken into account by researchers is concerning the use of poisonous substances on arrows.

During the Palaeolithic age, the improvement of the technique of hunting at a distance, with the invention of the throwing weapons (spearthrower, bow), was a real revolution in hunting strategies brought by Modern Humans.

Killing at a distance requires no more a physical confrontation but the use of a “strategy of deceit”, which is deeply linked to our species. The deceit lies in the phases of the hunt: the silence of the ambush, the attention to every movement and wind direction, the simulation to allow the approach, and finally the launch and the capture of the prey (Brizzi, 2005).

The “coward's weapon”, as the English playwright John Fletcher defined the poisons, is a further deceit that Man uses against the prey, so that it is immediately incapacitated.

The ethnographic documentation teaches us that hunters of every latitude poison their weapons with toxic substances derived from plants and animals (Bisset, 1979, 1981, 1989, 1992a; Bisset and Hylands, 1977; Cassels, 1985; Jones, 2009; Heizer, 1938; Mayor, 2008; Neuwinger, 1996; Noli, 1993; Osborn, 2004; Philippe and Angenot, 2005).

A study on the arrows currently used by the Bushmen (Noli, 1993) has highlighted that these weapons would be often ineffective if the tips were not poisoned. The arrows of many hunters, thrown with bows, penetrate into the prey to a depth that is not enough to kill a large animal.

It is not clear to what extent, but Prehistoric populations were familiar with the environment in which where they lived: they knew the edible plants (therefore the toxic ones) and perhaps also their medicinal use. The fact that toxic substances were available to the Prehistoric hunters and the notable benefits arising from their application for hunting (safety distance of the hunter from the prey, quick killing of big prey), suggests that this practice could have been widespread. In particular, the toxic substances may allow for incapacitation of the animal which means that it is not possible to run far away, irrespective of whether a mortal wound was imposed: this is essential for the recovery of meat and skin in good condition.

Formulation of a poison for hunting is relatively easy and the risk is minimal. In modern hunter-gatherer populations poisons are always made by an expert and the substance is conserved in a protected place: for this reason, the poisoning of other members of the group is unlikely.

Taking into account each of these factors, was developed a method capable of detecting plant poisons on archaeological spears/arrows. The main aim was to establish when poisonous substances began to be used in conjunction with weapons as a way of further improving their hunting success.

2. A brief history on the use of poison in hunting

The use of poisoning arrows in Prehistory is yet to be fully proved, as the only study that we have currently has been widely debated.

The debate relates to a wooden stick 32 cm long found in Border Cave, South Africa and dated about 24,500 BP (d'Errico et al., 2012).

The results from gas chromatography analysis carried out on the stick, absolutely similar to the poison applicators used by Kalahari San, indicated traces of ricinoleic acid (castor oil, Ricinus Communis). The use of this substance as a poison has been questioned (Evans, 2012; d'Errico et al., 2012) as castor oil is only slightly toxic (if not purified) and not commonly used as a poison. Ricin can be extremely lethal only if purified with modern techniques, and for this reason has been listed as a warfare biological weapon and involved in a number of incidents: the homicide of the dissident Bulgarian Georgi Markov in 1978 is the most famous (Carrico, 2009; Fredriksson et al. 2005; Shep et al., 2009). The lethal dose of castor oil is therefore probably too high to be considered as a poisonous substance for arrow points, also considering that poisons are chosen not only for an immediate action on the nervous or cardiovascular system of the animal, but also to slow their escape. Another weak point of the hypothesis of d'Errico and co-authors is the fact that we have not found any ethnographic comparison for the use of castor oil as a poison on arrows (Bradfield et al., 2015). This does not mean that the primary function of the stick analysed by d'Errico et al., was inevitably different: another component, more toxic, of the compound, could have been lost or not identified. The lump of organic material containing Euphorbia tirucalli, found in the same context, seems to be also interesting, as this plant is often mentioned in the ethnographic literature as poisonous (Bisset, 1989).

Further evidence of poisoned arrows are much more recent, as they are dated to the Egyptian predynastic period: the black compound found on the apical part of tips of some arrows originating from the site of Naga ed Der, dated to 2481-2050 BC (Stanley et al., 1974), is now over analysis at the University of Northumbria at Newcastle. A preliminary (rather crude) test carried out by authors of the original article, who injected the mixture into two mice, had proven the presence of a toxic substance, as the compound from the arrows appeared to have a sedative and hypnotic effect on the mice .

The first literary evidence of the use of poisons on arrows dates back to the the Atharva Veda (900 BC), the sacred text of Hinduism, where the use of aconite to poison arrows used in war is mentioned (Nougayrol, 1952; Bisset, 1989).

Another very old testimony is an Assyro- Babilonian tablet found in the Library of Assurbanipal (7th century BC). It says: “Shoot [?] the bow. Let your arrows carry poison!” (Ebeling, 1952; Gelb et al., 1960; Salonen, 1976; Bisset, 1989: p.4).

Poison for arrow is also cited in the Iliad and Odyssey. In Homerus poems, toxic substances seems to be used mainly for warfare, but the tradition of poisoning arrows was at that time already well established (Mayor, 2008).

After all, the same Greek word used to indicate something poisoned, toxic, has the same root of the word for bow, toxon, and both are linked to taxon (hew), that is the tree used to make bows, but also one of the most toxic plants of the Mediterranean vegetation. Aconitum napellus is a toxic plant and acontizo means hurl a javelin. This circle of words is very important and tells us how the connection between notions was strong, and the tradition was already very well “settled” because it had originated a long time before.

It is possible to say that at the time of the Mediterranean Civilization the knowledge of medicinal and toxic plants was already at a very high level and the use of poisoning arrows widespread.

Aconite (Monkshood) was well known by Greeks, even if it is difficult to find information about its use as poison for hunting. A Greek myth tells that aconite was born from the blood of Prometheus. When chained to a rock in the Caucasus, his liver was eaten daily by an eagle: from the blood grew the plant of aconite, the symbol of remorse. Yet, aconite is said by Diodorus Siculus (IV.45.2-3) to have been discovered by Hecate (a goddess with Indo-European origins who is associated with poisonous plant, in particular yew - Haller, 1984; Riddle, 1985).

It is interesting to notice that in all these myths the origins of this plant, at a geographic level, are placed to the East.

In the Gaul and Celtic populations, the tradition of using toxic plants is also documented. They used to call Limeum (Pliny, 27:76) the poison in which they rubbed the points of their arrows to hunt. Limeum was probably extracted from Helleborus, and used for hunting (cutting away the part of the meat affected by venom), but the same drug was used as well as a medicine for cattle.

Konrad Gesner (Conradi Gesneri Medici Tigurini Historiae Animalium, 1604) speaks in his book about a toxic plant, probably aconite, used by Celtic populations for red deer hunting.

The Middle-Age is the period where the interest in poisons becomes obsessive.

Hellebore, Veratrum, monkshood and belladonna where used not anymore for hunting, but to kill wolves (another name of aconite is in fact "wolfsbane") and bears, and especially to poison people.

3.The ethnographic documentation

An extensive ethnographic literature is available for the use of poisonous substances by ancient and modern hunter-gatherers (Bisset 1979, 1981, 1989; Bisset and Hylands 1977; Bisset and Leeuwenberg 1968; Bisset and Mazars, 1984; Cassels 1985; Jones, 2009; Mayor, 2008; Silberbauer, 1981).

Norman Bisset, a former professor of Pharmacognosy at the King's College of London, has been the most important expert of poisons. Born in 1925 in Glasgow (United Kingdom), Bisset was interested in the use of natural substances in the medicine of ethnic groups and he was involved with the launch of the Journal of Ethnopharmacology.

His interest in arrow and dart poisons originated from the study of the Upas tree and Strychnos species in Asia, and he published on all aspects of such plants including history, taxonomy, chemistry and pharmacology; later he became familiar not only with Asian plants, but also with those used in Africa and America. Bisset travelled all around the world to collect information on the making of poisons, and he also learned Chinese in order to read original documents. Most of the knowledge on this fascinating subject is definitely due to him.

Everywhere in the world the preparation of poisons is assigned to a particular figure of the group (the shaman, the group leader etc.) and the preparation mainly occurs secretly, away from the camp, for obvious safety reasons. The variety of plants and animals used in the composition of the poisons is huge, considering that most of the populations studied are using poisonous substances both for hunting and war weapons (Fig. 1).

It is fundamental to underline that although few hunter-gatherer societies remain today, all those that continue to exist are known to use poisons.

Many northern Asian and American populations until few years ago used aconite to kill wolves, tigers and other large animals such as bears and Siberian ibex.

The Ainu of Japan used to hunt big preys with two species of Aconitum: A. ferox and A. japonicum, both very toxic.

“In the spring the Ainu dug, peeled, and dried the roots in the sun, after which they pounded them into a powder between two stones. They then added the gall bladders of three foxes and boiled the mixture in a quart of water until it was reduced by half [...]. At this point, the poison maker added six crushed poisonous spiders and more water and boiled it to a gummy consistency” (Jones, 2009, p.22).

The inhabitants of the Kodiac Island, instead, simply pounded the dried roots of the plant and then added water. Sea lions and whales were killed with those poisoned spears (Heizer, 1938).

Aconite (Fig. 2-1) is one of the most poisonous plants of the European flora and is widespread particularly in the mountainous areas of the Alps and of Central Europe (Bisset, 1972; Geneviève et al., 2004). It contains alkaloids, at the base of the toxicity of most of the plants derived arrow and dart poisons: aconitine, mesacotine, hypaconitine and jesaconitine (Fig. 5:5).

The alkaloids have effects on the cardiovascular and respiratory systems. Death comes from cardiac and respiratory failure, and 6 mg are sufficient to kill a large mammal in 2 hours.

As other arrow and dart poison, aconite has many pharmacological properties and the plant is still nowadays employed in homeopathy to treat anxiety and neuralgias, or cold and fever (Fig. 2:2). Nevertheless, as the range between a therapeutic and deadly dose is extremely close, the overdose causes many fatalities: from 1999 to 2008 in China seven people died after the ingestion of traditional Chinese medications containing aconite (Liu et al., 2011).

In Southern Asia, darts are traditionally poisoned using Antiaris toxicaria, the Upas (Ipoh) tree, which in Javanese means 'poison'. Many legends are linked with this tree. A Chinese legend says that after being hit with this poison: “Seven up, eight down and nine no life”, that means that the victim takes seven steps uphill, eight steps downhill and a ninth final, fatal step. Indeed Antiaris latex is very toxic, containing a cardiac glycosides (another important class of plant toxins) named antiarine (Brandt et al., 1966; Carter et al., 1997, Dolder et al. 1955; Juslèn et al., 1963, Kopp et al. 1992; Shresta et al., 1992).

South American tribes historically used curare to poison their arrows.

Curare (Fig. 4:2,3), which again means 'poison', is in reality a generic term and has very different regional recipes, including a mix of Strychnos genus plants and Chondrodendron tomentosum or Sciadotenia toxifera. containing curarine and turbocurarine (alkaloids). The potent poison paralyzes the muscles and causes asphyxia: death is reasonably quick, considering that a large mammal can die in only 20 minute. (Bisset, 1992; Bisset and Choudhury, 1974; Bisset and Leeuwenberg, 1968; Bisset et al., 1977; Bratati and Bisset, 1990; Fròes, 1959; Grelier, 1957; Marini-Bettollo et al., 1967; Philippe et al. 2004)

What makes this poisonous compound extremely functional in hunting, apart from the lethal power, is that it has toxic effects only in contact with the blood, but it has no effect if ingested. This makes ingestion of meat very safe.

In Africa, a variety of different plants have been used for poison arrows. In a recent work of Bradfield et al., (2015), all recipes currently used by South African Bushmen hunter-gatherers were collected: the larvae of a leaf beetle called Diamphidia are actually the main component of the mixtures, but also toxic plants, mainly Akokanthera, Adenium, Boophane, Euphorbia, Strophantus (all containing cardiac glycosides, Bally et al., 1951) and Swartzia madagascariensis (containing saponines).

Another important collection of the recipes used to poison arrows is the one related to the American Indians (Jones, 2009). In Table 1 a list of the plants most commonly used by North American Indians to prepare the “poisons” for arrows.

Plant	**Toxicity**
Ranunculus spp.	Toxic. Toxins are degraded by drying.
Eryngium virginianum	No information
Cornus sericea	Not toxic
Potentilla fructicosa	Not toxic

Heracleum maximum	Slightly toxic
Erigeron gandiflorus	Roots are toxic
Cicuta douglasi	Toxic
Aconitum spp.	Very toxic
Yucca angustifolia	Not toxic
Phacelia crenulata	Slightly toxic
Usnea barbata	Irritating
Opuntia polyacantha	Not toxic
Veratrum vivide	Toxic
Rhus toxicodendron	Very irritating
Juniperus communis	Not toxic
Zigadendus venenosus	Toxic
Equisetum telemateia	Not toxic
Euphorbia spp.	Toxic
Artemisia dracunculus	Not toxic
Toxicodendrum sceleratus	Toxic

Table 1 - List of the main plants used by North American Indian tribes (Jones 2009).

The main conclusion that can be drawn from the information in Table 1 is that not all the plants used by these tribes are effectively toxic, or sometimes their degree of toxicity is very low. It must be considered that the aim of adding toxic substances to the arrows is not only to stop the prey on impact , but perhaps also to slow its escape, essentially to weaken it.

This could considerably complicate the search for toxic substances on ancient hunting weapons as "literally hundreds of plants and animals have been recorded as adjuvants" (Bisset 1989, p.15).

In the compound there is often a "primary source" and other substances can be added to thicken the mixture, or even for a magical purpose.

In addition, the American Indians tribes, as many other tribes, used poisons not only for hunting, but also in warfare. In this case, the strategies and substances are much varied. In war, the poisoned arrows have the function to do as much damage as possible to the community of the enemy, also by weakening people with disease and infection (e.g. festering wounds transmitting tetanus - Mayor, 2008).

4. The project - Materials and Methods

This first phase of our project on the use of plant poisons on hunting weapons was to establish an analytical method for the detection of common plants which may have been used on the hunting tools.

The following procedure was developed:

1) To form a database with information (ecology, geographical origin, chemical composition - by mass spectrometry and hyphenated techniques - starches morphology) on the most known toxic plants in order to compare the standards with the archaeological samples;

2) To use ethnographic samples to assess the efficacy of the database in relation to the main research question of whether it is possible to detect the plant alkaloids or cardenolides after thousands of years, taking into consideration the implications of the findings in relation to sample preparation/interpretation of result.

For the first version of the database we focused on the main European toxic plants, well known in literature: Aconitum napellum (monkshood), then Datura Stramonium (Devil's snare), Conium maculatum (Hemlock), Veratrum album (White veratrum), Helleborus (Hellebore) and Taxus (Taxus).

Subsequently, in our collection, we introduced other plants such as Antiaris Toxicaria, Datura quercifolia, Acokanthera and Adenium arabicus.

For each of those plants, information was collected with respect to their main toxic components, and a database on starches is in preparation (Torrence and Barton, 2006. Fig. 2:3,4; Fig. 5: 1-4).

Our main challenge was the one of finding a completely non-invasive method for sampling the ethnographic (and so the archaeological) materials in order to have realistically access to it. Modern analytical techniques enable very detailed chemical information even on very small samples, but the analysis often involves the destruction of the sample itself, and scientific analyses involving destruction of even small parts of the archaeological materials are almost never permitted by the Museums or other institutions where materials are stored.

The sampling method that was employed in this work modifies only partially and temporarily the surface of the specimen.

A cotton swab and approximately 1 mL of distilled water was used simply rubbing the artefacts.

The swabs were then placed in a sealed container and transferred to the laboratory for analysis.

Swabs were treated in the same way as the plant standard as explained in section 3.2 prior to analysis by GC-MS and LC-MS.

Ethnographic samples were collected on 12th March 2014 and 14th June 2014 at the Museum of Archaeology and Anthropology of Cambridge, on 28th January 2015 at the Pitts Rivers Museum of Oxford and on 5th May 2014 at the Museo Etnografico Pigorini of Roma (Italy).

The samples (see Table 3) refers to pots and glass jars with poison for arrows, poisoned arrows and spearheads of various type coming from different parts of the world.

4.1 Analytical instrumentation

Liquid chromatography – mass spectrometry (LC-MS) was carried out on a Dionex™ UltiMate™ 3000 liquid chromatograph hyphenated to a Q-Exactive™ orbitrap mass spectrometer (Thermo Finnigan, Hemel Hempstead, UK). A Kinetix C18 column, 50 mm x 2.1 mm, 2.6 µm particle size fitted with guard column was employed with two mobile phases: mobile phase A was 2 mM ammonium formate at pH 3 and mobile phase B was acetonitrile + 2 mM ammonium formate (at pH 3). A constant flow rate of 350 µL min^{-1} was maintained and a gradient method of 85% mobile phase A for 2 minutes, to 55% A over 8 minutes and equilibrated for 2 minutes at 85% A. The operating conditions of the mass spectrometer were a capillary temperature of 230^{o}C, a spray voltage of 3.5 kV and a m/z range of 100 – 1500.

Gas chromatography-mass spectrometry (GC-MS) was carried out on a Trace™ 1300 gas chromatograph hyphenated to an ISQ™ QD single quadrupole mass spectrometer (both Thermo Finnigan, Hemel Hempsted, UK). The instrumental conditions for the GC-MS are provided in the table below (Table 2). Analyses using both LC-MS and GC-MS were carried out in the Department of Applied Sciences, Northumbria University, Newcastle, UK.

Gas chromatograph conditions	**Mass spectrometer conditions**
Column: DB5-MS (30 m x 0.25 mm, 0.25 µm) **Injection temperature:** 280 ^{o}C **Temperature programme:** 70 – 300 ^{o}C at 20 ^{o}C min^{-1} and held for 10 minutes **Carrier gas:** Helium **Flow rate:** 1 mL min^{-1}	**Transfer line temperature:** 300 ^{o}C **Mass range:** 50-1100 Da (full scan)

Table 2: Instrumental conditions for the GC-MS

4.2 Materials and reagents

Organic solvents (ethanol, ethyl acetate) were purchased from Fisher Scientific (Loughborough). Derivatising reagent MSTFA + 1%TCMS was purchased from Sigma Aldrich (Poole, Dorset). A plant standard of Aconitum nappellum was donated by Cambridge University Botanic Garden, and Helleborus niger, Atropa belladonna, Datura stramonium, Veratum album, Taxus and Conium maculatum were all kindly donated by Trevor Jones, head gardener of Alnwick Gardens. Reference samples of Datura quercifolia, Adenium arabicum and Akocanthera spectabilis were purchased in seed form from Sunshine Seeds.

4.3 Preparation of plant standards

Plant based standards of Helleborus niger, Atropa belladonna and Datura stramonium were provided in leaf format. The leaf was dried in a cupboard for two weeks at room temperature. The leaves were then pulverised and between 50 – 100 mg of the material was transferred to a sample vial. Samples of Veratum album, Conium maculatum and Aconitium were provided as dried roots of plant; these were also pulverised and between 50 – 100 mg of the dried material was transferred to a sample vial.

A sample of curare was provided from the Pitt Rivers Museum in Oxford and was in the form of a swab from an ethnographic pot; a portion of the swab was directly transferred to a sample vial (Fig. 4:2). A reference sample of Antiaris toxicaria was provided from Huw Barton (Leicester University): this was in the form of a dried resin (Fig. 5:1-4). The resin was pulverised and approximately 50 mg was transferred to a sample vial. To all of reference samples, 2 mL of ethanol was added and sealed vials were placed in the ultrasonic bath for 30 minutes. 1 mL of the supernatant was transferred to a Reacti-vial™ and dried down under nitrogen at 70°C. To the dried residue, 100 µL of ethyl acetate and 20 µL of MSTFA + 1% TMCS derivatising reagent was added and the samples derivatised at 70°C for 1 hour. The other 1mL of supernatant was also dried down under nitrogen at 70°C and re-constituted in 200 µL of mobile phase A.

5. Results

Location	Catalogue number	Description	Provenance	Results
MAA Cambridge	1926.429	Pot with aconite	Asia: China	X
MAA Cambridge	E 1903.437	Spatula with poison wrapped in a palm spathe	Asia: Malaysia	-
MAA Cambridge	Z 14739	Spatula with poison	Asia: Malaysia	-
MAA Cambridge	E 1903.435	Wooden dart with poison	Asia: Malaysia	-
MAA Cambridge	1903-430	Iron arrow single barbed	Asia: Malaysia	X
MAA Cambridge	1894.28	Wooden dart with poison	Asia: Borneo	X
MAA Cambridge	Z 10669	Bone spearhead with poison	Asia: Samoa	X

MAA Cambridge	1995.87	Iron arrow with poison	Asia: China	?
MAA Cambridge	Z 363933	Poisoned spatula	Asia: China	?
Pitt Rivers Oxford	1994.10.18	Glass jar containing curare	South America: Guyana	X
Pitt Rivers Oxford	1914.4.11	Poisoned arrow	Asia: China Zhejiang Province Ningbo	X
Pitt Rivers Oxford	1900.78.49.3	Poisoned arrow	Asia: Japan, Hokkaido	X
Pitt Rivers Oxford	1900.78.49.4	Poisoned arrow	Asia: Japan, Hokkaido	X
Pitt Rivers Oxford	1927.19.2.23	Poisoned arrow	Africa: S.Africa Kalahari	-
Pitt Rivers Oxford	1927.19.2.22	Poisoned arrow	Africa: S. Africa, Kalahari	X
Pitt Rivers Oxford	1927.19.2.26	Poisoned arrow	Africa: S. Africa Kalahari	X
Pigorini Roma	N 346	Brush for curare	South America	-
Pigorini Roma	N 347	Poisoned arrow	South America (Yandamana tribe)	-
Pigorini Roma	N 349	Pot of curare	South America	X
Pigorini Roma	N 350	Poisoned dart	South America (Maku tribe)	-

Table 3 – Samples submitted for analysis. Abbreviations: MAA = Museum of Archaeology and Anthropology, Cambridge; Pitt Rivers = Pitt Rivers Museum, University of Oxford; Pigorini = Museo Etnografico Pigorini, Roma (Italy).

Within the samples from the Museum of Anthropology and Archaeology of Cambridge, the presence of aconitine has been confirmed in the Chinese pot with aconite (Fig. 2: 5-6).

The aconite was identified by the presence of aconitine in the extract (see Figure 5:5).
The arrow with single barbed in iron (1903-430, Fig. 3: 4) from Malaysia, the wooden dart of Borneo (1894.28, Fig.3: 2) and the bone spearhead of Samoa (Z10669, Fig.3: 4-5) all appear to have compounds that may be indicative of the presence of *Antiaris toxicaria*.
The iron arrow from China (1995.87, Fig. 3:6) and the spatula (Z363933) appear to have compounds indicative of the presence of a *Strychnos* species but further standards are required to provide a more definitive answer.
Of the samples submitted from the Pitt Rivers Museum, Oxford, the arrows from South Africa (1927.19.2.22 and 1927.19.2.26, Fig. 4: 4) show the presence of a mixture of compounds similar to the *Acokanthera* family of plants. Artefacts from Japan and China (1900.78.493, 1900.78.494 and 190014.411, Fig. 4:5) appear to have compounds indicative of the presence of aconite.
Of the samples submitted and analysed from the Museo Pigorini, Rome, only one of the samples (N349) provided results, showing the presence of the expected curare or a curare-type mixture. Other plant compounds and other extraneous material have masked the chromatograms which has made it difficult to positively identify curare compounds.

It should be noted in the initial interpretation of the data from GC-MS and LC-MS analyses that there is little information on the treatment of the artefacts from their origin until their appearance in the museum collections. This can affect the interpretation as it is not possible to establish if the presence of the compounds is due to external contamination from other artefacts collected at the same time or being stored in museums. More development of analytical methodologies is required to provide more definitive interpretation of the analytical findings.
However, the initial results appear promising and will be used for further work on the analysis of archaeological artefacts.

5. Conclusions

This first, experimental part of our work was focused on the development of a method for the identification and the analysis of poisonous substances on ancient hunting weapons.
The non-invasive method of sampling that we have employed, consisting of lightly rubbing the ethnographic/archaeological material with a cotton bud imbued with distilled water, has provided positive results, as it was possible to identify toxic components present on some of the artefacts, even after many years.
Our research is clearly complicated by the huge variety of poisonous species and by the chance that symbolic or magical factors may take part in the making of the mixtures, thus making the identification of single components difficult.

Nevertheless, there are factors that assist us:

1) In the majority of the ethnographic arrows that we had the opportunity to examine, a dark residue (the poison) was visible to the naked eye and covered most of the arrowheads (Fig. 4: 4-5); this means that the quantity of poison applied is not infinitesimal, and we have much sample to work with to try to identify plant poisons, even after a long time;

2) the toxic plants used for arrow poison have a regional nature, and particular periods (such as an ice age), or geographical places, can restrict the range of possibilities;

3) the preparation of a poison for arrows is part of a passed-down tradition linked to a territory, not susceptible to sudden changes. In Europe (Fig.1), for example, the traditions linked to toxic plants for hunting/warfare seems to be rather limited, and this is could be helpful for the research on prehistoric hunting techniques.

The investigation of the use of poisons in ancient periods is rather an innovative field of research, that adds to our understanding not only of the hunting techniques and rituals, but also of how the plant world was known and exploited by ancient/prehistoric populations, opening new insights on ethnopharmacology (Biagi and Speroni, 1988; Lewis and Lewis, 1977; Semwal et al., 2014).

After all, the principal sources of arrow poisons contain the same molecules that are at the base of the modern medicine treatments. As Paracelsus (1493-1541), the founder of the toxicology, said "sola dosis facit venenum": the dose makes the poison.

This work continues by enriching the database of plant poisons and analysing archaeological artefacts.

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TABLES:

Table 1: List of the main plants used by North American Indian tribes (Jones 2009).

Table 2: Instrumental conditions for the GC-MS.

Table 3: Samples submitted for analysis. Abbreviations: MAA = Museum of Archaeology and Anthropology, Cambridge; Pitt Rivers = Pitt Rivers Museum, University of Oxford; Pigorini = Museo Etnografico Pigorini, Roma (Italy).

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Fig. 1: Map of the principal arrow and dart poison (Bisset, 1989). 1- Aconitum, 2- Veratrum, 3- Acokanthera, 4- Strophanthus, Physostigma, Erythrophloeum, 5- Mansonia, 6- Strychnos, Erythrophloeum, Strophantus, 7- Diamphidia, Urginea, Adenium, Boophone, 8- Aconitum, 9 – Aconitum, Dasyatis, Daphne, Cynanchum, Juglans, 10- Aconitum, Croton, 11- Strychnos, Alstonia, Abrus, 13- Antiaris, Strychnos, Lophopetalum, Beaumontia, Strophantus, 14- Microbial, 15- Microbial, 16- Excoecaria? 17- Palythoa toxica, 18- Aconitum, 19- Rattlesnake, Yucca, 20- Hippomane, Hura, Colliguaja, Euphorbia, Sapium, Sebastiania, Schoenobiblus, 21- Phyllobates, Naucleopsis, 22- Naucleopsis, 23- Chondrodendron/Curarea, 24- Chondrodendron/Curarea, Strychnos, 25- Strychnos, 26- Strychnos.

Fig. 2: 1- Aconitum napellus (monkshood); 2 – Label of a homoeopathic medicine containing aconite; 3 – Starches of Aconitum napellus (roots) photographed at SEM (Photo V.Borgia); 4 – Starches in the sample of the item 1926.429; 5,6 – MAA item n.1926.429, aconite pot from China, enveloped in a newspaper dated 13th July 1926.

Fig. 3: Museum of Archaeology and Anthropology, Cambridge. 1- item n. 1903.437, Spatula covered with poison, from Malaysia; 2 – item n. 1894.28, Quiver with darts from Borneo; 3 – item n. 1903.430, Single barbed iron arrow from Malaysia; 4,5 – item n. Z10669, spearhead from Samoa with label 'Care has been poisoned'; 6- item n. 1995.87, Spatula for poison and iron arrowheads for crossbow, China. (Photo R. Hand, Copyright Museum of Archaeology and Anthropology, Cambridge)

Fig. 4: Pitt Rivers Museum, Oxford. 1- item n. 1914.27.1, bottle of poison, China 1914. Label says: 'Aconite for poisoning the arrows of crossbow tiger traps'; 2 – item n. 1994.10.18, glass jar with curare (collected in 1949-1950), Guyana, South America; 3 – item n.1923.88.372 pot containing

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Fig. 5: Sample of dart poison form Borneo made with Antiaris toxicaria donated by Huw Barton, University of Leicester: 1 – resin, 2- tissue (bark?), 3, 4 – starches (Photo H. Barton), 5- LC-MS data identifying aconitine where (a.) is the total ion chromatogram (TIC) for the full extraction and showing the signal for all ions between m/z 150-2000, (b.) the extracted chromatogram for m/z 646 showing a peak for aconitine and (c.) associated mass spectrum of the aconitine peak from (b.).

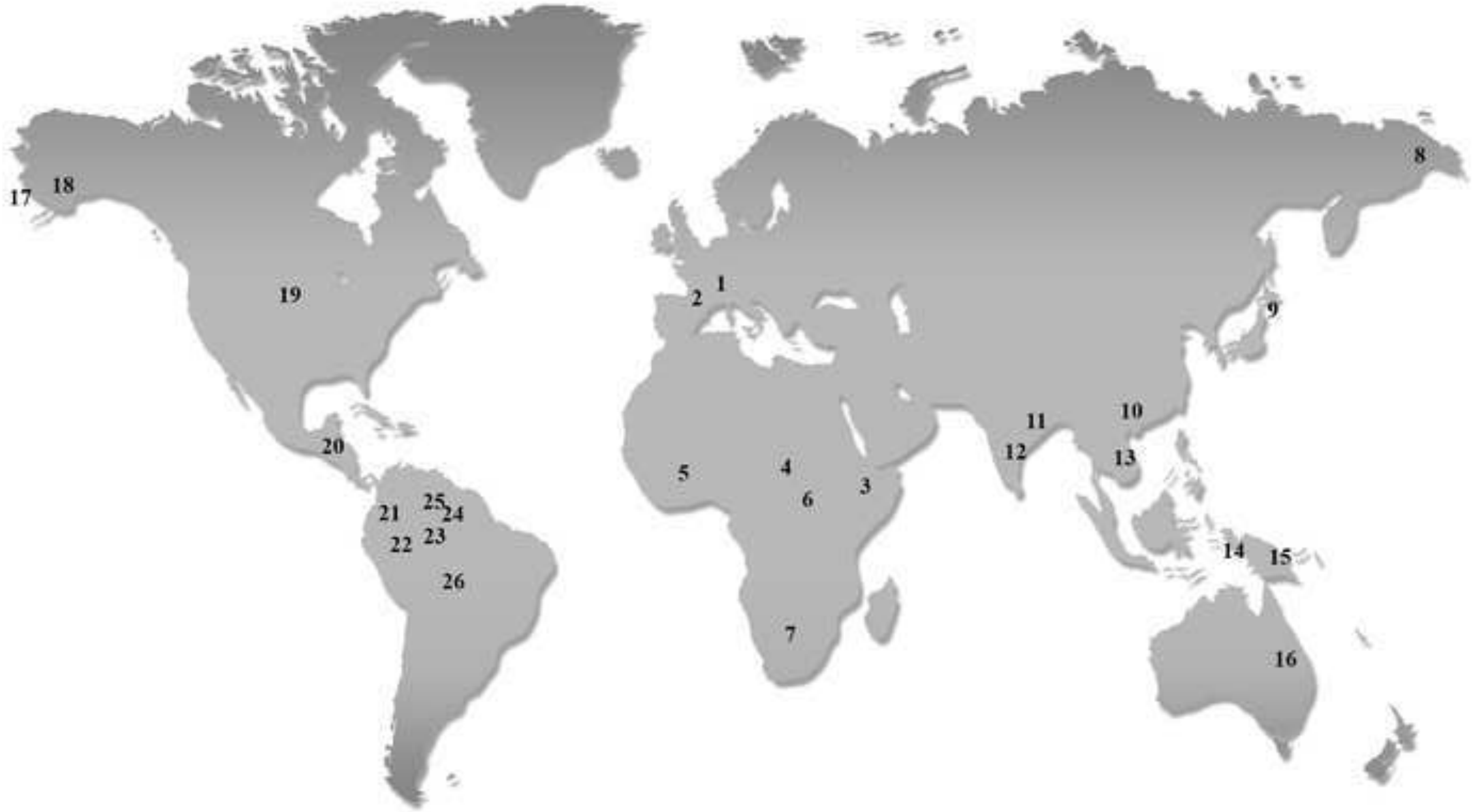
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Figure

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Homeopathic Medicine

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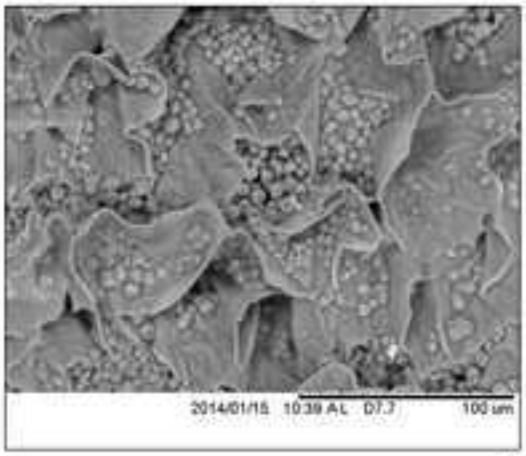

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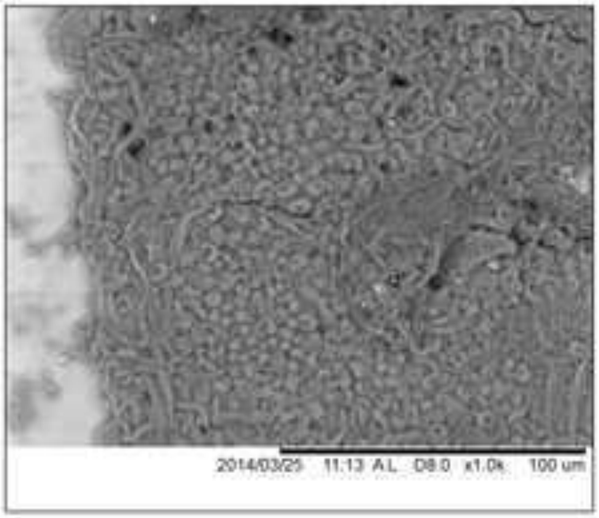

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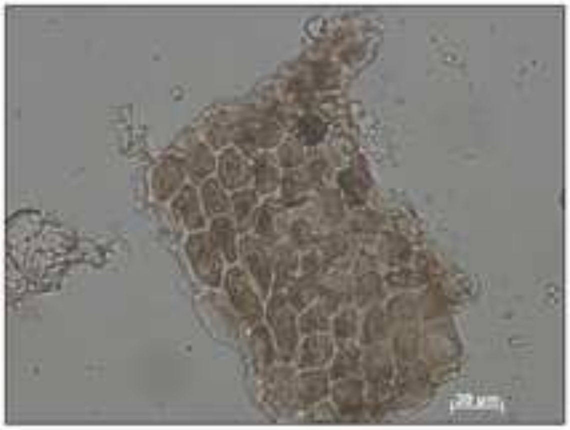

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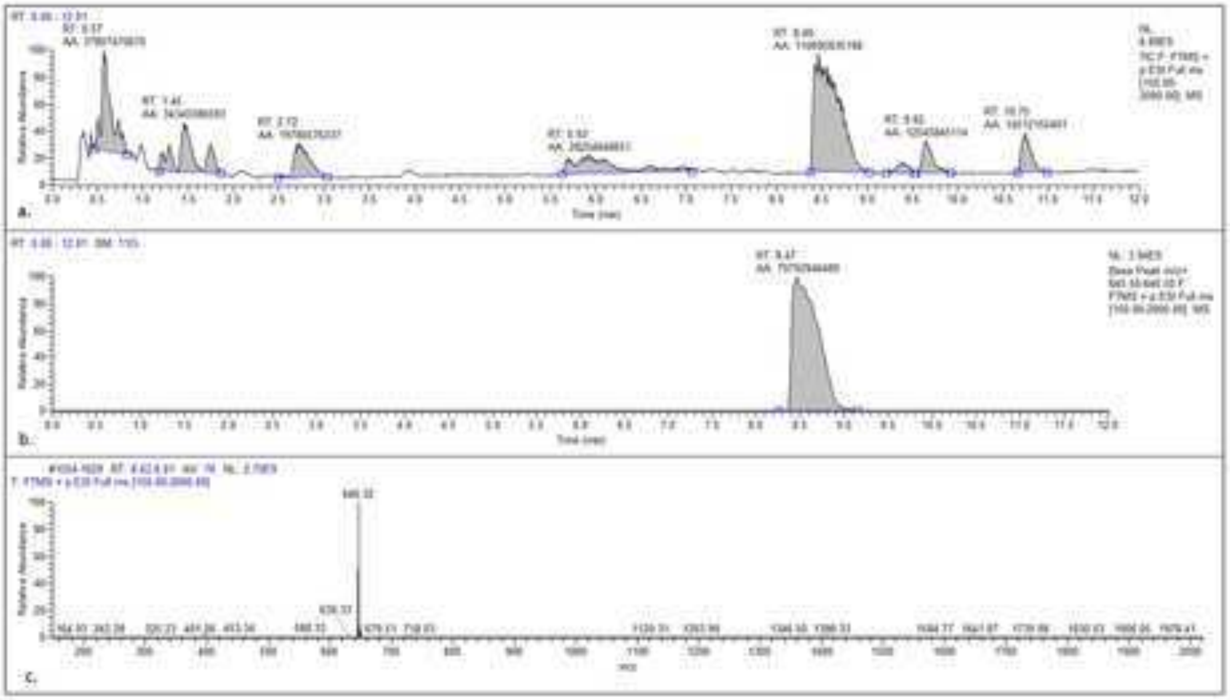

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Plant	Toxicity
Ranunculus spp.	Toxic. Toxins are degraded by drying.
Eryngium virginianum	No information
Cornus sericea	Not toxic
Potentilla fructicosa	Not toxic
Heracleum maximum	Slightly toxic
Erigeron gandiflorus	Roots are toxic
Cicuta douglasi	Toxic
Aconitum spp.	Very toxic
Yucca angustifolia	Not toxic
Phacelia crenulata	Slightly toxic
Usnea barbata	Irritating
Opuntia polyacantha	Not toxic
Veratrum vivide	Toxic
Rhus toxicodendron	Very irritating
Juniperus communis	Not toxic
Zigadendus venenosus	Toxic
Equisetum telemateia	Not toxic
Euphorbia spp.	Toxic
Artemisia dracunculus	Not toxic
Toxicodendrum sceleratus	Toxic

Table 1: list of the main plants used by North American Indian tribes (Jones 2009).

Gas chromatograph conditions	Mass spectrometer conditions
Column: DB5-MS (30 m x 0.25 mm, 0.25 µm) **Injection temperature:** 280 ^{o}C **Temperature programme:** 70 – 300 ^{o}C at 20 ^{o}C min^{-1} and held for 10 minutes **Carrier gas:** Helium **Flow rate:** 1 mL min^{-1}	**Transfer line temperature:** 300 ^{o}C **Mass range:** 50-1100 Da (full scan)

Table 2: Instrumental conditions for the GC-MS

Location	Catalogue number	Description	Provenance	Results
MAA Cambridge	1926.429	Pot with aconite	Asia: China	X
MAA Cambridge	E 1903.437	Spatula with poison wrapped in a palm spathe	Asia: Malaysia	-
MAA Cambridge	Z 14739	Spatula with poison	Asia: Malaysia	-
MAA Cambridge	E 1903.435	Wooden dart with poison	Asia: Malaysia	-
MAA Cambridge	1903-430	Iron arrow single barbed	Asia: Malaysia	X
MAA Cambridge	1894.28	Wooden dart with poison	Asia: Borneo	X
MAA Cambridge	Z 10669	Bone spearhead with poison	Asia: Samoa	X
MAA Cambridge	1995.87	Iron arrow with poison	Asia: China	?
MAA Cambridge	Z 363933	Poisoned spatula	Asia: China	?
Pitt Rivers Oxford	1994.10.18	Glass jar containing curare	South America: Guyana	X
Pitt Rivers Oxford	1914.4.11	Poisoned arrow	Asia: China Zhejiang Province Ningbo	X
Pitt Rivers Oxford	1900.78.49.3	Poisoned arrow	Asia: Japan, Hokkaido	X
Pitt Rivers Oxford	1900.78.49.4	Poisoned arrow	Asia: Japan, Hokkaido	X
Pitt Rivers Oxford	1927.19.2.23	Poisoned arrow	Africa: S.Africa Kalahari	-
Pitt Rivers Oxford	1927.19.2.22	Poisoned arrow	Africa: S. Africa, Kalahari	X
Pitt Rivers Oxford	1927.19.2.26	Poisoned arrow	Africa: S. Africa Kalahari	X
Pigorini Roma	N 346	Brush for curare	South America	-

Pigorini Roma	N 347	Poisoned arrow	South America (Yandamana tribe)	-
Pigorini Roma	N 349	Pot of curare	South America	X
Pigorini Roma	N 350	Poisoned dart	South America (Maku tribe)	-

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