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# Investigation of historical dart poisons using synchrotron based infrared microscopy and spectroscopy☆

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ABSTRACT

Museum Victoria holds in its Indigenous Collection a number of poison darts and arrows from Southeast Asia and Africa. Synchrotron FTIR microspectroscopy was used to analyse the stained tips of three sets of small wooden darts from Southeast Asia covering three collection periods between 1873 and 1971. As part of an on-going project for the identification of hazardous substances in the collection, we wished to identify if poisons were present on these items, and if present whether they were still active and whether they pose a risk to staff working with the collection. Infrared spectra in the mid-IR region and transmission mode were recorded from small sample areas of particles recovered from each of the darts. The presence of cardiac glycoside, calcium oxalate, plant proteins and carbohydrates in the spectra have enabled us to confirm the presence of and to identify toxins on the darts.



## 1. Introduction

Museum Victoria, Melbourne, Australia, holds in its Indigenous Collection a number of blow pipe poison darts from Southeast Asia (Fig. 1). The focus of this investigation was the stained tips of three sets of small wooden darts in bamboo quivers from Southeast Asia covering three collection periods. Two sets were collected from the Malaysian mainland and added to the collection in 1873 and 1934 and the third set was collected in the state of Sarawak, Borneo and donated to the Museum in 1971, (Fig. 2). Very little information has been recorded with these items and information about the possible poisons was either not available or not recorded when the items were added to the collection and the identity of the residues on these items has therefore remained unknown. Ethnographic information indicates that the toxins used on Malaysian darts are probably from the *Antiaris, Stychnos* or *Strophanthus* plants, the active ingredient being contained in the latex, bark or seeds [1].

Blow pipes with poison darts were used in Southeast Asia for hunting and in some instances for tribal warfare. The main toxin generally used in Malaysian darts is well known and comes from *Antiaris toxicaria* (the Upas or Ipoh tree) [1] which was widely distributed in Malaysia and Southeast Asia during the period in which these darts were produced. Indigenous production of poison darts involved the latex of the tree being collected from scars in the bark and then dehydrated over a low fire for about a week, as overheating caused the antiarin to separate from the sugar component of the cardiac glycoside, rendering the material inactive [2]. The dehydrated thick paste was applied to the end of thin 25–30 cm long darts, which when kept over time becomes dry and hard. Cardiac glycoside poison is known to diffuse through the blood stream rapidly, throughout the whole body of the prey, causing death by heart failure.

The latex of *A. toxicaria* contains a complex mixture of around 30 cardiac glycosides [1,2,4,8] including β-antiarin with α-antiarin, antiosid, malayosid and convellatoxin. The structure of these compounds is based on a steroidal aglycone linked to one or more sugar moieties. The end feature of the aglycone is a five membered lactone ring (Fig. 3). Similar in structure to digoxin, the lactone ring and the OH group at the C14 position are credited with the pharmaceutical activity of these compounds [5]. The αβ-unsaturated five membered ring lactone gives rise to double carbonyl bands in the 1780–1740 $cm^{-1}$ region [6] although work by Jones and Gallagher [7] suggests that the bands could be present in a broader range depending on the associated structure. Other five membered ringed lactone configurations present single carbonyl bands in the 1780–1760 $cm^{-1}$ region [6]. The cardiac glycoside mixture present in the *Antiaris* latex includes structures of both saturated and unsaturated lactone rings with single and double carbonyl bands [3,8].

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**Fig. 1.** (a) X 008904 Malaysia Darts and Bamboo quiver, the base of the quiver contains a large deposit of dried poison; (b) X 041975 Malaysia Darts and Bamboo quiver; (c) X 075938 Sarawak Malaysia Darts and Bamboo quiver, the base of the quiver contains a large deposit of dried poison.

Many of these cardiac glycosides have been studied for their therapeutic values as a heart treatment and in cancer treatment due to their similar structure and properties to digoxin [3,9]. Another major source of dart poison can be the *Strychnos* species including *Strychnos nux-vomica* with the main active component being the alkaloid strychnine. This material is extracted from the roots or stem bark. In some regions the two materials were reportedly mixed to form the lethal paste [4].

The thin wooden darts held in the Museum Victoria collection have a thick coating of poison on the tip with the residue being highly desiccated and with some small particles having accumulated in the bottom of the bamboo quivers. As part of an on-going identification of hazardous substances in the Museum's collection the aims of this study were to answer three questions: were poisons present on these darts; were they still active; and whether they pose a risk to staff working with the collection.

The complex makeup of plant latex incorporating proteins, carbohydrates, lipids, waxes, as well as possible toxins, makes the infrared spectra a complex mixture of strong and overlapping bands. Given the low levels of the toxic materials contained in this complex matrix it is has previously proved difficult to detect them. The excellent signal to noise at high spatial resolution achievable with the synchrotron IR microscope enabled us to examine small sections of the matrix and microscopic particles within the matrix.

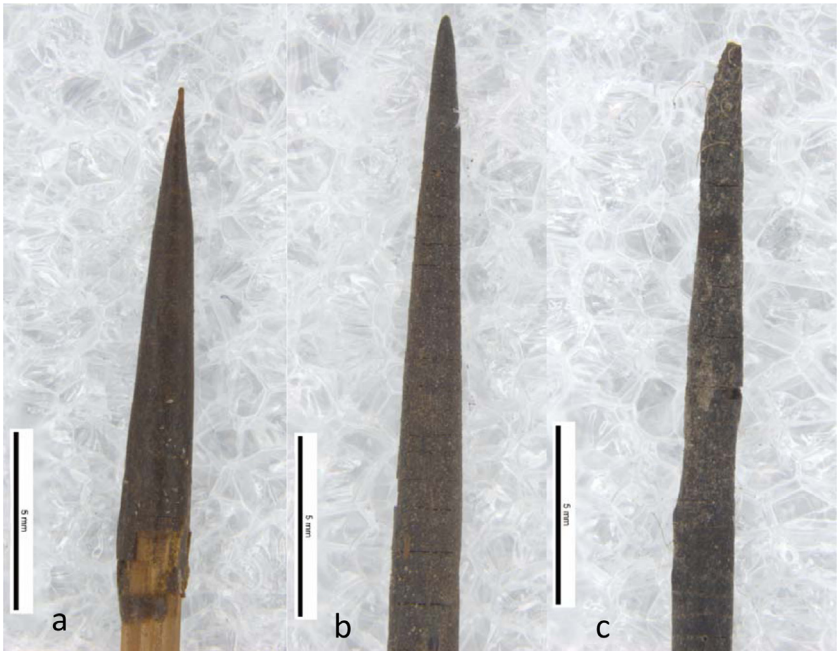


**Fig. 2.** Dart tips showing the desiccated nature of the thick coating of dried poison. (a) X 008904; (b) X 041975; (c) X 075938.