Plant constituents involved in coating practices among traditional African potters

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Abstract. A phytochemical survey of several plant species used in sub-Saharan Africa for the treatment of pottery, as well as some coating experiments carried out with purified extracts of *Bridelia ferruginea* stem bark, indicated that procyanidin fractions play a predominant role in the coating properties of the plant extracts. The analysis by high performance gel permeation chromatography of organic compounds isolated from the vessel walls suggested that products deriving from pyrolysis of procyanidins are detectable both in contemporary and older pottery, and their analysis could be useful for archaeological purposes.
Key words. Pottery technology; archaeology; *Bridelia ferruginea*; procyanidins; Cameroon; sub-Saharan Africa.

Traditional potters of sub-Saharan Africa frequently coat their pots, after firing, with organic mixtures[1]. Similar treatments are also reported in other parts of the world[2]. However, despite its importance, this type of treatment has never been the focus of a detailed study. Ceramologists usually view it as a waterproofing technique aiming at increasing the heating effectiveness[3] and, perhaps, the strength of the pottery[4].

During recent ethnographical fieldwork in southern Cameroon, one of the authors had the opportunity to observe different kinds of post-firing treatments. In the 21 ethnic groups surveyed[5], potters systematically collected fresh stem bark of the following plants: *Bridelia ferruginea* Benth. (Euphorbiaceae), *Bridelia micrantha* Baill. (syn. *Candelabris micrantha* Hochst) (Euphorbiaceae), *Terminalia superba* Engl. et Diels. (Combretaceae) and *Macaranga spinosa* Muell.-Arg. (Euphorbiaceae). The bark was crushed, soaked or boiled in water for several hours, and the aqueous extract either sprinkled on the pots as they came red hot from the fire, or rubbed on after cooling. According to the potters, the purpose was to strengthen, waterproof and color the vessels.

An experimental study showed that these post-firing treatments increased the heating effectiveness of vessels by reducing their permeability. The phenomenon is particularly apparent when potters use coarse clays and fire their pots at relatively low temperatures, as was invariably done in Cameroon[6,7].

No literature has been encountered describing the permeability change of the pots after application of plant extracts, or on the selection of specific plant species for this purpose. Archaeologists interested in reconstructing past technological behavior could gain a better insight into pottery techniques and functions if these treatments could be identified. Other types of organic residues on ancient pottery—for example, fatty acids accumulated and retained in ancient vessels—have already been used to deduce more about the life style at the time[8].

In this paper, we describe the chemical composition and coating properties of some of the plant species used. Since *B. ferruginea* is more frequently used in this regard (either in Cameroon or in other regions of Africa), we devoted the first part of our experimental study to this species. Previous phytochemical investigations have shown the presence of tannins, triterpenes, lipids, steroids and flavonoid glycosides in *B. ferruginea*[9-12]. Interestingly, the plant is used in traditional medicine for the treatment of diarrhoea, dermatological diseases, toothache and gonorrhoea; these uses could be related to the presence of tannins.

Methods and results

In order to identify the constituents responsible for the waterproofing effects, an aqueous decoction of the stem bark of *B. ferruginea* was prepared following traditional techniques (30 g of crushed stem bark in 100 ml water), lyophilized and chromatographed on a Sephadex LH-20 column (60 mm I.D. × 20 cm length), eluted with water, and then with water-acetone 1:1 (v/v). The aqueous acetone fraction was concentrated to remove the organic solvent and further lyophilized; the aqueous fraction was directly lyophilized.

Both fractions were tested for their waterproofing performance in comparison with the crude aqueous extract, using test-vessels; the methodology will be discussed in a forthcoming publication[13]. The results showed that the aqueous acetone fraction was more effective than

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the aqueous one in waterproofing. Preliminary analysis of this fraction by planar chromatography on cellulose and silica gel showed that it contained mainly tannins of the procyanidin group (condensed tannins), visible as red spots on the chromatograms after spraying with the vanillin-hydrochloric acid reagent. The aqueous fraction, on the other hand, contained gallotannins (hydrolyzable tannins) which were detected by planar chromatography using the same adsorbents and Cl_3Fe as spray reagent. It was therefore postulated that the procyanidins in extracts of *B. ferruginea* are important in pottery coating.

The coating efficiency of a concentrated aqueous solution (10%) of the extracted procyanidin fraction was tested by spraying the solution onto borosilicate solid-glass beads heated at 550 °C in a muffle. The coating efficiency of the pyrolysis products from procyanidins was found to be very high. The adherence of the film coating to the beads was strong, and its solubility in water and in most organic solvents very poor. This was not found to be the case with a 10% solution of tannic acid, a polyphenol which is chemically related to the gallotannins. This indicates that not all naturally-occuring polyphenols are equally suitable for pottery coating. At the present state of this study, it cannot be determined whether constituents of the extracts other than procyanidins also contribute to the overall coating effects.

The role of pyrolysis products from procyanidins as waterproofing compounds was further confirmed by the fact that the aqueous extracts prepared from the stem barks of other plants used by potters, *B. micrantha*, *T. superba* and *M. spinosa*, were also found to contain procyanidins. However, semi-quantitative determination by planar chromatography of the procyanidin concentrations were lower than in *B. ferruginea*, which may explain why *B. ferruginea* is more frequently used by potters.

A decoction of roots of *Krameria triandra* Ruiz. et Pacon (Krameriaceae) (Rathania), which are also known to have a high procyanidin content, also displayed good coating performance when aqueous extracts were sprayed on glass beads following the above method. This plant is known for its medicinal properties, but its use in pottery has not been reported.

Since all the evidence indicates a preponderant role for procyanidins in pottery coating, it would be interesting to identify the pyrolysis products derived from their application to vessels. Surface temperature at the time of application is obviously critical in this context. Thermometric measurements carried out in the field showed dramatic variations of the temperatures inside traditional firing structures; these variations were further extended during the cooling, so that vessel temperature before application on the pots is likely to be anywhere in the range 450 °C $\pm$ 150. Different pyrolysis compounds could be produced at different temperatures.

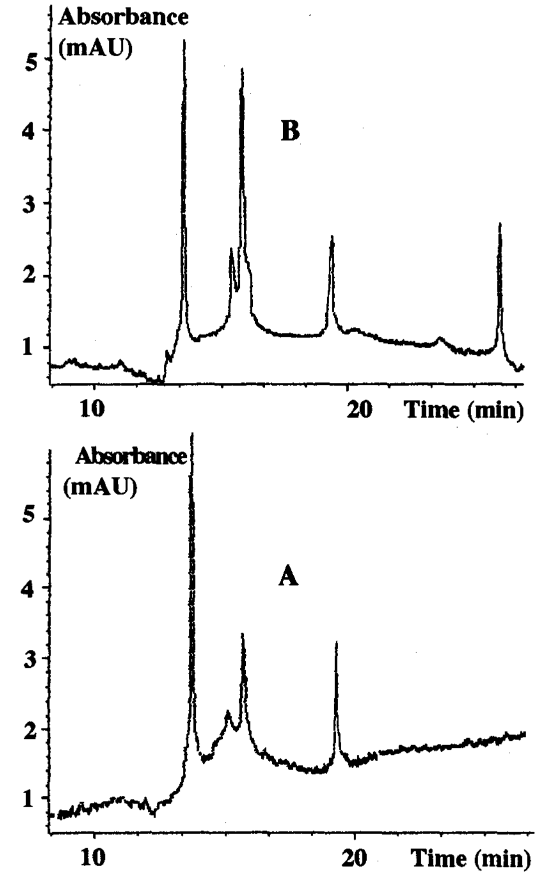

Figure 1. Separation by high performance gel permeation chromatography of acetone-water extracts of walls of Cameroonian vessels. *A*. Contemporary sample, never used before analysis *B*. $\pm$ 50-year-old sample.

The question of whether these pyrolysis products are stable or whether their structure changes during pottery use and storage is important for archaeologists. If some of them are transformed into stable structures, these could be used as tracers for archaeological studies.

Comparative studies by high performance gel permeation chromatography of extracts of old ($\pm$50 years old) and recent vessels from Cameroon were carried out. The samples (crushed fragments from either the inner surface, the external surface or the whole wall of the vessels) were extracted with a 1:1 (v/v) mixture of acetone and water. This mixture was found to be most efficient among all the tested solvents in dissolving the pyrolysis products from procyanidins, and it showed a low solubilising effect on other constituents present in the samples. The acetone-water extract was then filtered on a pre-washed paper filter, then through a column (10 mm I.D. × 3 cm length) filled with Toyopearl HW-40 S; the eluate was evaporated and the residue dissolved in a water-tetrahydrofuran mixture (1:10 v/v). This last solution was used for the high performance gel permeation chromatography analysis. Chromatography was carried out on a TSK-Gel G 3000 PW × 1 column (7.8 mm I.D. × 30 cm length). The column was eluted with a linear gradient of tetrahydrofuran in water (0 to 30% v/v, within 20 min); the detection was carried out using a diode-array detector at 270 nm, a wavelength which afforded the best results for further comparisons. The chromatographic separation showed the diversity of the compounds which were present in these samples. Nevertheless, the results indicated that the method could be helpful for purposes for comparison. For example, the patterns of peaks eluting between 10 and 20 min from a contemporary sample of Cameroonian pottery and a ±50 year-old sample showed very similar features (fig. 1). Preliminary analysis performed with pieces of ±2000 year-old pottery indicated that the proposed method could be useful for the study of coating products used by early potters. However, a systematic study of pottery coating processes is needed to determine the influence of each factor involved, especially in respect to the temperature. Additional research is also required to identify thoroughly the stabilized plant residues accumulated in archeological pottery. The authors are presently studying all these parameters in order to obtain more specific information which could be used for the analysis of very ancient pottery and to avoid misleading interpretations due to interfering substances from the environment.

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