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## FTIR SPECTROSCOPY FOR THE ANALYSIS OF VEGETABLE TANNED ANCIENT LEATHER

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### Abstract

Tannins classical analysis techniques are empirical, time-consuming and the results depend on the analytical conditions. Physical analysis is much more precise. This study deals about FTIR spectroscopy as a new method to identify vegetable tannins in ancient leather from religious bookbinding.

*Keywords:* ancient leather, FTIR spectroscopy, vegetable tannin, bookbinding

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### 1. Introduction

The leathers used in the past for bookbinding were vegetable tanned, due to their elasticity that allowed easy handling. Chrome tanned leathers that began to be produced later, are scarcely used for bookbinding because they lack elasticity.

In our country, ship and goatskins tanned in oak and spruce fir bark have been used for bookbinding beginning with the XV<sup>th</sup> century. Following the Byzantine bookbinding school, which is the oldest one [1], leather book covers were decorated with painted or imprinted adornments, metallic bindings, jewels or enamels.

The Romanian bookbinding has been a religious art from its very beginning. The adornment is inspired by numerous iconographic sources that can be found in mural painting, religious embroidery and miniatures. The art of book writing and binding prospered in Moldavia and Bucovina's monasteries, such as Neamț, Putna, Bistrița, Humor. Monastic bindings were made up of barks covered with sheep, calf, rabbit or pigskins dyed in different shades of red and black and decorated through embossing. The oldest bookbinding decorates a manuscript from the Tismana Monastery, transcribed on parchment and adorned with frontispieces by Nicodim in 1404-1405 [2].

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Monastery storehouses preserve genuine masterpieces from exquisitely adorned leather; in this respect, the 'D. Stăniloae' Metropolitan Library from Iași is the repository of some rare pieces that are waiting for professional restoration.

Vegetable tannin is a large molecule found in plants, which interacts and transforms animal leather proteins (collagen) into resistant insoluble products. Vegetable tannins may have different chemical structures, but impart some common properties:

- Are miscible with water in any ratio;
- Are insoluble in organic liquids such as: chloroform, ether, gasoline etc.;
- Are polyvalent phenols derivatives;
- Are amorphous substances, very sensitive to oxidation and reduction in the presence of enzymes;
- Are hygroscopic and give birth to polydisperse colloidal solutions.

The scientific investigations are the starting point of the ancient leather restoration. Researches on ancient leather objects have in view the obtaining of specific information and data, which, through subsequent comparative analysis, help in drawing conclusions about [3, 4]:

- The evolution of leather and fur processing technologies;
- The economic and cultural development level of a given geographical area;
- The development of new preservation and restoration methods for leather goods.

Tannins classical analysis techniques are empirical, time-consuming and the results depend on the analytical conditions. Physical analysis is much more precise but has several drawbacks: is destructive, complex and expensive [5].

The aim of this paper is to propose FTIR spectroscopy as a new method to identify vegetable tannins in ancient leather from religious bookbinding.

## **2. Experimental**

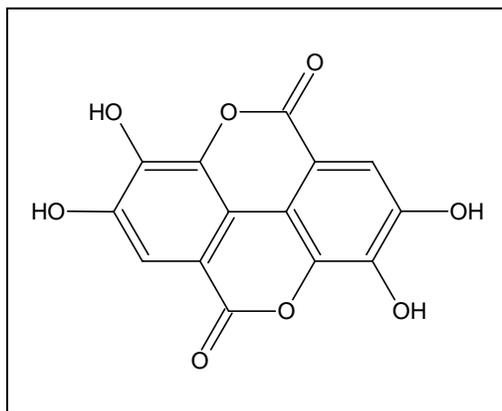
Bookbinding from the beginning of the XX<sup>th</sup> century with no patrimonial value (private collection) have been analysed from the point of view of tannage type. FTIR-spectra in KBr pellets were recorded for the pure oak extract, the hydrolysed extract and the oak-tanned leather extract. The leather extract was obtained in water (at room temperature), the solvent being removed by evaporation. The resulted product was pressed in pellets with KBr (like the oak extract). Similarly it was analysed the water pure oak extract. The used apparatus was a Jasco FTIR 660 plus.

## **3. Results and discussion**

In order to determine the constituents of oak tannin, a series of samples were subjected to IR spectroscopy analysis. FTIR-spectra were recorded for the pure oak tannin (sample 1), and for an aqueous extract of the oak tannin (sample 2). These spectra were compared to the IR-spectra of the oak leather extract (sample 3). The oak tannin extract was examined in order to better compare the

fraction resulting from extraction with those resulted from leather. For the leather extract, that must contain components able to mask certain absorption bands, a spectra deconvolution was imposed.

The IR-spectra of the pure oak and of the oak extract contain bands that can be assigned to the ellagic acid, the main constituent of the oak tannins (Figure 1).

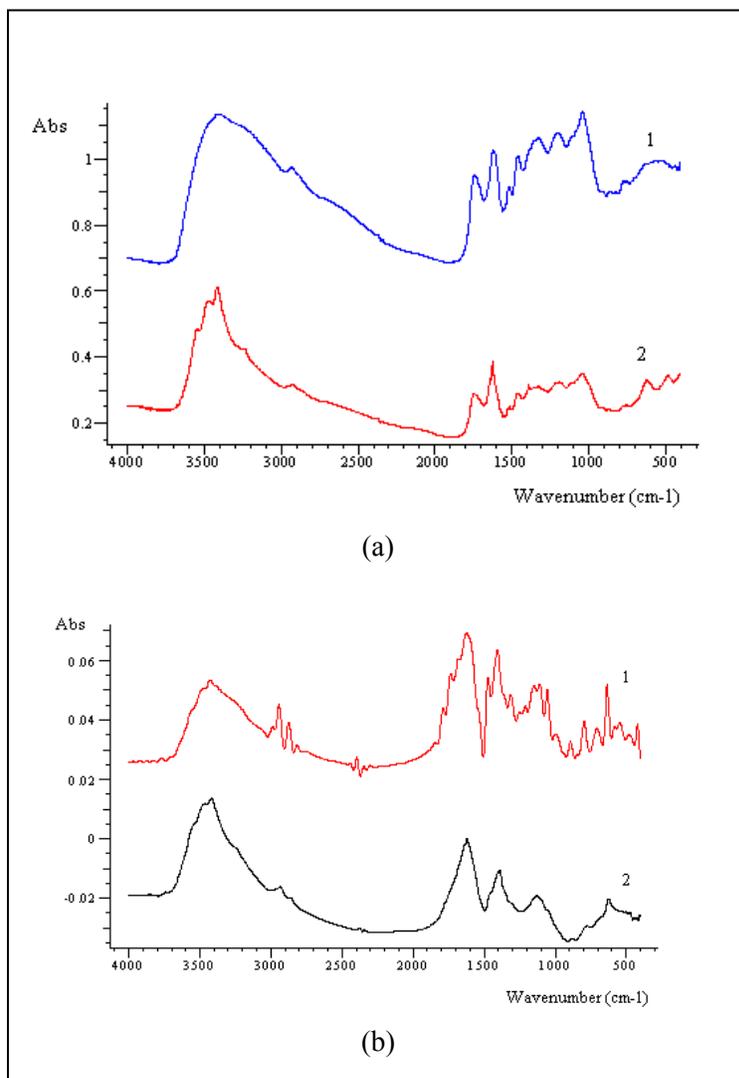


**Figure 1.** Ellagic acid structure.

The main absorption bands belong to the valence vibrations corresponding to OH, C=O, C-O-C groups, to CH bonds and to aromatic rings vibrations as well [6, 7]. In Figure 2, IR-spectra for the pure oak tannin and the tannin extract (a) and for the leather extract (b) are comparatively presented.

Spectra examination reveals that the valence vibration corresponding to the hydroxyl groups  $\nu_{OH}$ , appears in the 3400-3550  $\text{cm}^{-1}$  band, with a maximum at 3414  $\text{cm}^{-1}$  for the oak tannin extract and at 3413  $\text{cm}^{-1}$  for the leather extract, respectively. The distortion band outside the  $\delta_{OH}$  plan appears at 1383  $\text{cm}^{-1}$  for both the tannin and the leather extract. On the other hand, the valence vibration  $\nu_{\eta-OH}$  appears to be slightly shifted at 1196  $\text{cm}^{-1}$  for the leather extract, comparing to 1182  $\text{cm}^{-1}$  for the tannin extract. This could be due to the involvement of the hydroxyl group in bonds with other constituents.

The ketonic group valence vibration  $\nu_{C=O}$  is located at 1735  $\text{cm}^{-1}$  in the pure oak spectra, and at 1720  $\text{cm}^{-1}$  for the leather extract spectra (probably due to the participation in other bonds). The  $\equiv C-H$  group vibrations  $\nu_{C-H}$  are centred at 2928  $\text{cm}^{-1}$  for the oak tannin and at 2926  $\text{cm}^{-1}$  for the leather extract. The symmetrical and asymmetrical  $\nu_{C-O}$  valence vibration appears at 1326  $\text{cm}^{-1}$  and at 1037  $\text{cm}^{-1}$  respectively for the oak tannin and at 1322  $\text{cm}^{-1}$  and 1040  $\text{cm}^{-1}$  respectively, for the tannin extract. The vibrations assigned to aromatic rings are located between 1617  $\text{cm}^{-1}$  and 1451  $\text{cm}^{-1}$  [8].



**Figure 1.** IR-spectra for: (a) sample 1 and 2; (b) sample 3 – normal and deconvoluted.

#### 4. Conclusions

It can be asserted that the IR spectra of the leather extract contains, in addition to a series of bands that are common to those found for the oak extract, a series of other band that can be assigned to other leather extract constituents and superpose to the first bands, forming thus a series of broader band, which can be assessed only after the deconvolution of the initial spectra

In order to confirm the presence of the ellagic acid in the leather extract, which ascertains the oak tannage, further investigations, such mass spectroscopy or other advanced methods, must be carried out.

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