

# Natural dyes in green walnut shells for textile materials dyeing

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## Abstract

The purpose of this study was to obtain and characterize a natural dye from green walnut shells. By thin layer chromatography a single brown spot was obtained and attributed to naphthoquinones. Naphthoquinones presence was also proved by the UV/VIS and the IR spectra.

**Keywords:** natural dyes, green walnut shells, chemical composition, UV-VIS, IR, thin layer chromatography.

## Introduction

During the last years an increased interest was noted for the use of natural dyes in textile dyeing process. Particularly are concerned natural vegetable dyes. The main advantage of using them is the fact that their source is renewable, biodegradable and reduces environmental impact on the environment. Still the use of natural dyes involves some disadvantages such as requirement of large amounts of plant material, limited success in dyeing synthetic materials, need for the use of mordents, poor light stability (Taylor, 1986). However, especially in case of natural fibers, replacing synthetic dyes with natural ones represent a not too distant perspective.

The worldwide use of walnut green leaves and shells for natural dyeing of textiles has ancient roots. Recent studies brought them in the attention of specialist since it was found to have, besides coloring properties, good insecticidal effect - thus helping to the fiber protection (Wang et al., 2009). Regarding their chemical composition we found few researches performed leading to the identification of several targeted compounds like juglanins, methyl palmitate, ellagic, gallic and caffeic acids and some volatiles (such as pinocarvone, pinocarveol, myrtenal, myrtenol, caryophyllene epoxide, verbenol, verbenone, terpinolene) (Wang et al., 2009; Chen et al., 2008; Buttery et al., 2000; Segundo et al., 1998).

The purpose of this study was to gather as many information on the chemical composition of the walnut green shells extract by using a series of qualitative analysis such as Borntrager reaction, thin layer chromatography, UV-VIS spectroscopy and infrared spectroscopy thus completing the information already available.

### **Material and methods**

Benzene, ethanol, potassium hydroxide (p.a.), glacial acetic acid and ammonia solution (25%) were purchased from Reactivul București.

For this study it has been used green nut shells harvested in June when it seems to be richest in active principles (Segundo et al., 1998). A quantity of 400 g of these shells was crushed in a mortar and then was subjected to an extraction with hot benzene in a Soxhlet apparatus until exhaustion. The benzene extract was filtered and then evaporated to dryness under a water bath. After cooling a crystalline precipitate was obtained. The precipitate was purified by recrystallization with ethanol. Further the obtained substance was dried and weighed. 18 g of dried extract were obtained.

#### *Borntrager reaction*

Borntrager reaction (Auterhoff et al., 1968) consist in extract treatment with a hot solution of 5 % KOH followed by acidification with acetic acid and dissolution in benzene, when a clearly phase is separated; the clear phase is afterwards treated with ammonia solution.

#### *Thin layer chromatography (TLC)*

For separation of the components from the obtained extract, 0.5 g was diluted with 1 ml benzene; methanol-chloroform 1:1 was used as mobile phase on 250  $\mu\text{m}$  silica gel plate; eight spots were put at the starting line.

#### *Ultraviolet and visible spectroscopy (UV-VIS)*

UV-VIS absorption spectra were obtained using a SPECORD 200 spectrophotometer (Analytic Jena).

#### *Infrared spectroscopy (IR)*

The IR spectra were recorded in 4000-400  $\text{cm}^{-1}$  by filling the extract under a form of thin film of KBr spectral pellets.

### **Results and discussion**

The natural quinine pigments, supposed to be involved in the overall brown color of the walnut extract, range in color from pale yellow to almost black and there are over 1200

known structures. They contain the same basic chromophore, benzochinone. Those present as glycosides may be slightly water-soluble – but for the rest is more likely to be lipid-soluble and would be extracted from a crude plant extract together with carotenoids and chlorophylls (Tamas et al., 1971).

#### *Borntrager reaction*

For confirming that a pigment is quinone type, simple color reactions are still very useful. The extracted sample prepared under the conditions showed above, lead to the apparition of characteristic red color (Segundo et al., 1998; Auterhoff et al., 1968).

#### *Thin layer chromatography (TLC)*

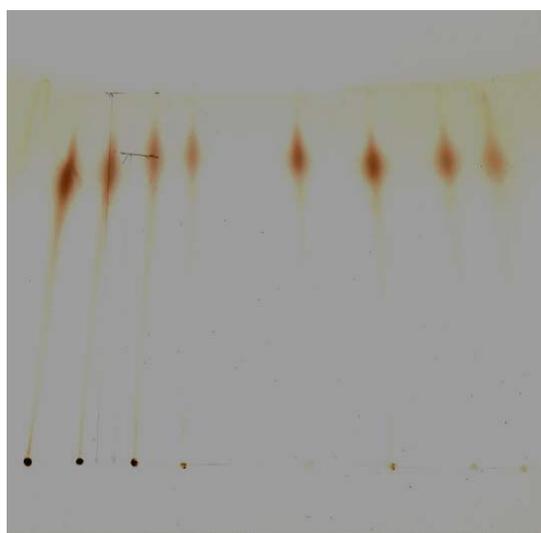
TLC on silica gel is a general procedure for separating quinones. Simple benzoquinones or naphthaquinones are very soluble and can be easily separated in pure benzene, pure chloroform or pure petroleum but complex solvent mixtures are required for those highly hydroxylated. Since they are colored, there is no difficulty to be detected in visible light (Harborne, 1998).

A picture of the obtained thin layer chromatogram is presented in Figure 1. The dye was quickly released from the starting line leading to a single strong brown spot. The compound type can be identified by mean of retardation factor value,  $R_f$ .

$$R_f = h_A / h_s \quad (1)$$

where  $h_A$  was the average distance from the start to the middle of the spots and  $h_s$  the distance from the start line to the solvent end line.

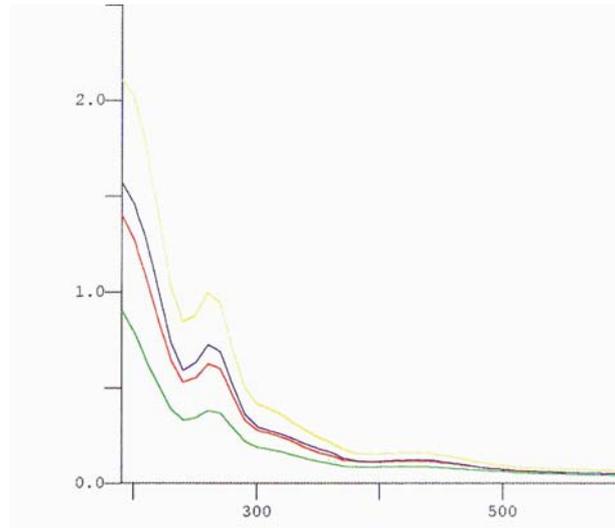
Thus calculated  $R_f$  was found to be 0.81 comparable with literature data for naphthoquinones (Kichner, 1977; Tamas et al., 1971).



**Figure 1.** Thin-layer chromatogram

### *Ultraviolet and visible spectroscopy (UV-VIS)*

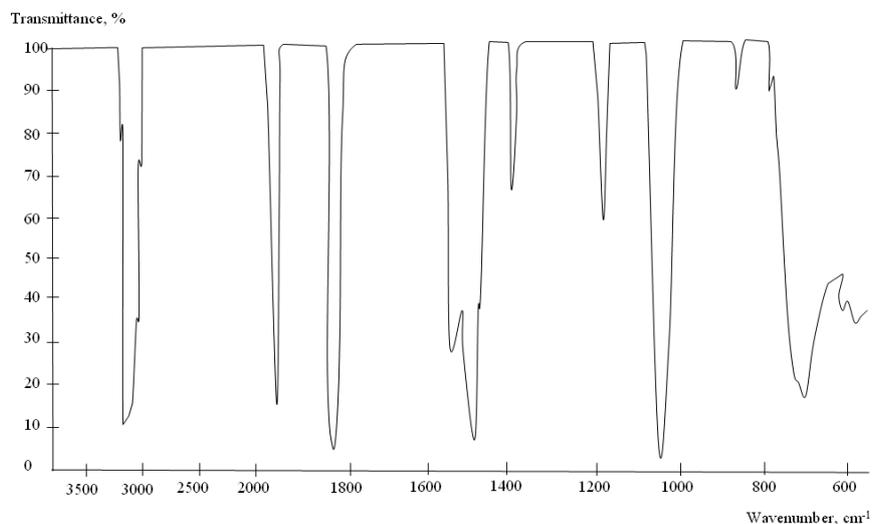
The resulting spectra from UV-VIS analysis of the dye at different concentrations (30  $\mu\text{g/ml}$ ; 15  $\mu\text{g/ml}$ ; 7,5  $\mu\text{g/ml}$ ; 3,8  $\mu\text{g/ml}$  ) are shown in Figure 2. Three peaks appears around  $\lambda = 260 \text{ nm}$ ,  $\lambda = 340 \text{ nm}$  and  $\lambda = 430 \text{ nm}$  wavelengths, which complies with naphthoquinones spectra characterized with strong signals between 240-290 nm, respectively with an average signal around 335 nm and in region of 400-510 nm (Medeleanu et al., 1998).



**Figure 2.** UV-VIS spectrum of the extract of green nut shells

### *Infrared spectroscopy (IR)*

Unlike the UV-VIS spectroscopy which is more useful for quantitative analysis, the IR spectroscopy gives more information about the structural groups present in the green nut shells extract.



**Figure 3.** IR spectra of the green walnut shells extract

It is noted that the IR spectrum of the extract (Figure 3) contains several bands common to naphthoquinones namely (Balaban et al., 1983; Avram et al. 1966):

- (i) the band from  $3200\text{ cm}^{-1}$  indicates the presence of hydroxyl groups and C-H;
- (ii) the band from  $1860\text{ cm}^{-1}$  indicates the presence of C=O groups;
- (iii) the band from  $1550\text{ cm}^{-1}$  indicates the presence of aromatic (CHar) and saturated (C-C) structures existing in naphthoquinone as a derivative of naphthalene;
- (iv) the band from  $1090\text{ cm}^{-1}$  indicates the presence of C-O groups;
- (v) the band from  $700\text{ cm}^{-1}$  indicates the presence of C-H groups. These results are in accordance with other literature studies that found juglone (a naphthoquinone) to be one of the compounds responsible for the brown color (Segundo et al., 1998).

## Conclusions

The purpose of this study was to find the compounds responsible for the brown color of the green walnut shells extract. All analytical techniques used (Borntrager reaction, thin layer chromatography, UV-VIS and IR spectroscopy) pointed to naphthoquinones derivatives. The results are completing and reinforcing the information already available in the literature data. Further studies regarding the dyeing of natural and synthetic textile materials using this dye will follow.

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