International Journal of Engineering Sciences & Research Technology

(A Peer Reviewed Online Journal)
Impact Factor: 5.164

IJESRT

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THOMSON REUTERS

ISSN: 2277-9655
[Deveoglu *, 7(10): October, 2018] Impact Factor: 5.164
IC™ Value: 3.00 CODEN: IJESS7

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

TANNINS AS A CHEMICAL AGENT

Ozan Deveoglu*

* Cankiri Karatekin University, Faculty of Science, Department of Chemistry, Cankiri, Turkey

DOI: 10.5281/zenodo.1462725

ABSTRACT

Plants containing tannin compounds (also called tannic acid) are usually used for mordanting textiles of wool, silk and cotton *etc*. nowadays. The mordant types using in the natural dyeing are rather important. Mordants such as chrome and copper have been usually used for mordanting the textiles. But these mordants are not eco-friendly, toxic and carcinogen chemicals. Whereas, the tannin compounds are non-toxic and eco-friendly. However, these compounds can show antimicrobial, antibacterial, antifungal and antioxidant activities at the same time. Two tannin-rich mordant sources in Turkey are walloon oak (*Quercus ithaburensis* Decaisne) or gall oak (*Quercus infectoria* Olivier). The tannin compounds determined in the natural dyeing, in the present-day textiles or the historical textiles are mostly gallic acid (a trihydroxybenzoic acid), ellagic acid or their derivatives.

KEYWORDS: *Quercus ithaburensis* Decaisne, *Quercus infectoria* Olivier, tannin, mordanting, mordant

I. INTRODUCTION

Walloon oak (*Quercus ithaburensis* Decaisne)

Walloon oak is an oak type defoliating in winter and growing up to fifteen-twenty meters high. Its fruits mature usually in two years. This tree grows in Turkey and Greece - in the Aegean region, especially. The acorn goblet is four and six centimeters in diameter. Its outer part is wrapped with fingernails and in hemispherical form. It has the biggest goblet within oak types. The acorn's fruits are up to three centimeters length, cylindrical, fawn colored and puckery tasty. In Turkey, there are about twenty oak (*Quercus*) types. Their fruits can be gathered under the acorn name without discrimination

Gall oak (*Quercus infectoria* Olivier)

Gall oak shows it's widest distribution in Marmara and Black sea regions. It is a large tree in about twelve meters high and eighty centimeters in diameter. This tree's leaves are not always defoliated in autumn. The defoliation continues up to spring in the warm winter years. The gall oak wasp (Cynips insana (West.) Mayr)'s female in June and July months leaves in the gall oak's buds it's eggs. Around the eggs, shellacs having rich nutrition layer with thin membranes, oily substances, sugar and protein are formed. There is a protective layer also outside of the nutrition layer. These layers in question create gall. The formed gall is round and about two centimeters in diameter. Since this event occurs on this oak at the most, this type is named as gall oak.

II. LITERATURE REVIEW

Walloon oak (*Quercus ithaburensis* Decaisne) (Short History)

The acorn is used as human and animal food since the Paleolithic (50.000 BC years ago). It was also used in dyeing of leather and tanning. It was abundantly used to obtain black colour with iron mordant in Turkish carpets and rugs. But the acorn cups contain tannin compounds as colourants. So, the abrasions in the black-dyed parts of textiles are seen owing to tannins in time.

Gall oak (*Quercus infectoria* Olivier) (Short History)

It is known that gall oaks were used in various areas such as dye, leather working as well as ink making from Sumerians to the present. Gall oak is collected for dyeing and tanning. In Turkey, the collected gall oak is firstly grinded and then is boiled with wool. The obtained colour is a colour between dirty yellow and brown. This type of dyeing is known as "*tetre dyeing*" in public in Turkey. The black colour for the tetre-dyed wool was obtained mordanting with iron mordant. The black dyeing was realized in Turkish carpets and rugs in this way. But, this type of dyeing suffers from spilling and abrasion. Instead of this type of dyeing, black colour was obtained with

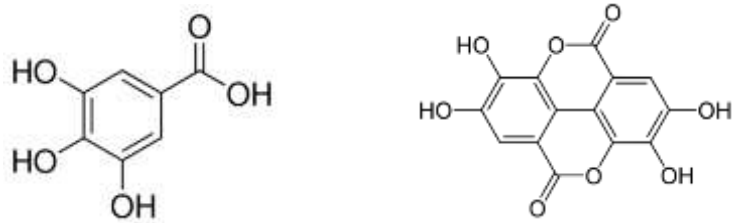
ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

using together madder, indigo and yellow colour giving plants in Iran. In these dyeings, the corrosion is not formed in the black colour for ages [1].

The photos relating to gall oak (*Quercus infectoria* Olivier) and walloon oak (*Quercus ithaburensis* Decaisne) plants are given Figure 1. Also, figure 2 shows the chemical structures of gallic acid and ellagic acid.

(a) Gall oak (*Quercus infectoria* Olivier) **(b)** Walloon oak (*Quercus ithaburensis* Decaisne)

Figure 1. The photos of gall oak (*Quercus infectoria* Olivier) **(a)** and walloon oak (*Quercus ithaburensis* Decaisne) **(b)**



(a) **(b)**

Figure 2. The chemical structures of gallic acid **(a)** and ellagic acid **(b)**

Tannins as a chemical agent

The term "tannin" was first applied by the French chemist Armand Seguin to define the chemical compounds responsible for the formation of leather in 1796. Tannins do not express a single compound. They represent a large class of organic compounds [2,3].

In the food industry, tannins can be used in wine, beer and fruit juice. At the same time, these compounds are also used in the dye industry as caustics for cationic dyes (tannin dyes) [4].

Besides, they are also used as coagulants in rubber production [5].

Their acorn cups contain about 25-35 % tannins. The complicated chemistry of tannins has been explained by Schweppe [6].

Walloon oak (acorn cups) was used to obtain black colour in the Ottoman textiles. However, it was used in 13th century Seljuk carpets and 15th-20th century Ottoman textiles [7].

Gall oak extract contains mainly ellagic acid compound. This compound has an affinity for dyeing substrates because of the presence of –OH (auxochrome group) [8].

Galls belonging to *Quercus infectoria* include between 40 to 70 % of tannins [9].

In 2010, Karadag et al. analysed natural dyes in 15-17th centuries Ottoman silk textiles (kaftans, brocades, velvets and skullcaps) by HPLC-DAD. In some historical textile samples, ellagic acid or/and it's derivatives were determined. The samples relating to inventory numbers are as follows: 13/1515 (16th, silk brocade, red),

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

13/1507 (16th, silk brocade, red), 13/1449 (17th, silk velvet, red), 13/1960 (16th, silk brocade, red), 13/1671 (17th, silk brocade, red), 13/1918 (16th, silk velvet, red), 13/1673 (16th, silk brocade, red), 13/1900 (16th, silk velvet, red), 24/1804 (16th, silk skullcap, red), 13/1909 (first half of 17th, silk kaftan, red) and 13/6 (second half of 15th, silk velvet, kaftan, red). Ellagic acid sources were determined to be provided from gall oak (*Quercus infectoria* Olivier) [10].

Karadag and Yurdun analysed natural colourants present in the thirteenth-century Seljuk carpets in the Konya Ethnography Museum in 2010. In the samples belonging to 841 (red), 1033 (violet) and 1034 (red, green and black) inventory numbers, ellagic acid was determined. However, these carpet samples were treated with either gall oak (*Quercus infectoria* Olivier) or walloon oak (*Quercus ithaburensis* Decaisne) [11].

In 2010, Deveoglu et al. produced walloon oak natural pigments by means of Al^{3+}, Fe^{2+} and Sn^{2+} metals. In these pigments, gallic acid or/and ellagic acid was identified by HPLC-DAD [12].

Karapanagiotis et al. determined natural colourants in the some silk textiles obtaining from the Monastery of Simonos Petra (Mount Athos) in 2011. In the some of these textiles, ellagic acid was identified [13].

According to the paper published by Okumura in 2011, the yellow warps in the Cairene and Ottoman court prayer rugs were dyed with tannin dyes extracting oak tree growing in East Mediterranean and Southern west Asia [14].

In 2012, Deveoglu et al. analysed silk fibres dyed with *Rubia tinctorium* L. and *Quercus ithaburensis* Decaisne plants and investigated their colour and fastness properties [15].

In 2013, Yurdun and Dolen analysed some historical textiles. In the yellow coloured part (Inventory number: 690), ellagic acid compound was determined. Its source can be either gall oak or walloon oak. Karadag investigated some historical textiles in Topkapi Palace Museum (Istanbul, Turkey). In the samples belonging to 13/1900 (red) and 13/1671 (red) inventory numbers, ellagic acid was determined in the red coloured parts. Probably, gall oak was used in the red coloured parts [16].

Yildiz et al. produced natural pigments from gall oak (*Quercus infectoria* Olivier) shellacs in 2013. In the natural pigments precipitated by Al(III) and Fe(II), separately, gallic acid and ellagic acid components were determined by HPLC-DAD [17].

In 2013, Deveoglu et al. improved the procedures for dyeing of silk fabric with buckthorn (*Rhamnus petiolaris* Boiss) and walloon oak (*Quercus ithaburensis* Decaisne). Besides, the fastnesss properties and the colour analyses were investigated. Also, the natural dye analyses were performed by HPLC-DAD [18].

In 2015, Yildiz and Karadag analysed natural dyes in two caftans. These caftans belong to Topkapi Palace Museum Collection (Istanbul, Turkey). In the caftan relating to 16th century (Inventory No. 13/739), ellagic acid was identified in the purple coloured part. This tannin compound was provided from either walloon oak or gall oak [19].

Karadag et. al. analysed some 16-17th century Ottoman silk brocades obtaining from the Topkapi Palace Museum (Istanbul, Turkey) in 2015. According to the analysis results of HPLC, ellagic acid was identified in some historical silk brocades. These are as follows : the samples belonging to 13/1527_1 (ground red), 13/1527_3 (black), 13/1527_4 (orange), 13/1528_1 (ground red), 13/1539_1 (ground red) and 13/1550_1(ground red) inventory numbers. Probably, ellagic acid source plants are either gall oak or walloon oak [20].

In 2015, Torgan et al. dyed silk fabrics with natural indigo, weld (*Reseda luteola* L.) and gall oak (*Quercus infectoria* Olivier). The dyed silk fabrics showed antimicrobial activity [21].

In 2016, Karadag and Torgan identified ellagic acid compound in some samples belonging to 16-17th century Ottoman silk brocades obtaining from Topkapi Palace Museum Collection (Istanbul, Turkey). The source plant

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

of ellagic acid may be gall oak or walloon oak. The inventory numbers are as follows: 13/1005 (red) and 13/1455 (blue and red) [22].

Özer et al. investigated the effect of Turkey Red Oil on colour and fastness properties of sillk fabrics dyed with madder (*Rubia tinctorium* L.) and gall oak (*Quercus infectoria* Olivier) in 2016. Besides, natural dyes were determined in the dyed silk fabrics by HPLC-DAD [23].

Torgan et al. investigated antifungal activity and durability of natural silk fabrics dyed with madder (*Rubia tinctorium* L.) and gallnut (*Quercus infectoria* Olivier) in 2017. Gallnut has perfect antifungal activity for *C. Albicans.* This activity was attributed to gallic acid, ellagic acid and their derivative compounds present in gallnut [24].

Kahraman and Karadag determined natural dyes in some historical silk brocades in 2017. In the samples belonging to 13/360-2 (red) and 13/466-2 (red) inventory numbers obtaining from the Topkapi Palace Museum, ellagic acid was identified. This compound was attributed to the tannin-containing plants (*Quercus*) [25].

In 2017, Al-Sharairi et al. analysed some textile samples belonging to the Museum of Jordanian Heritage by HPLC. This collection dates from the 19th century and has Ottoman costumes. In the sample number 1 (fibres from man cloak; black), tannin (ellagic acid) was determined [26].

In 2018, Karadag et al. dyed silk fabrics with natural dyes extracted from cochineal (*Dactylopius coccus* Costa) and gall oak (*Quercus infectoria* Olivier). Optimum dyeing parameters were determined. The good colour fastness values were obtained with these dye mixtures [27].

Tannin sources belonging to plants can be obtained from roots, stems, bark, leaves and fruits. Besides, tannins include C, H, O, N, P and some inorganic elements in their structures [28].

Tannins composition and concentration differ quite with the species, age and part of the plant [29].

Tannins are water-soluble polyphenolic compounds [30].

Tannins can show important nutraceutical properties. At the same time, they are also used in cosmetics for anti-aging skin care and to struggle hair loss and as astringent [5, 31].

Oak galls contain abundantly tannin compounds. Their main components are gallotannic acid, gallic acid, ellagic acid, starch and sugar [32].

Galls are widely used in tanning, dyeing, mordanting and in the manufacture of ink [33].

Gallic acid is a tanning agent that merged with ferrous sulphate to obtain ink black [34].

Iron gall inks were used as the normal writing material in European and American manuscripts from the 4th to beginning of the 20th century [35].

In Europe, these inks were commonly used from the beginning of the 11th century until the end of the 20th century [36].

These iron gall inks were widely used from the late Middle Ages until the modern times. There are collections of historic iron gall ink documents, manuscripts and artworks on both paper and parchment supports in libraries, archives and cultural institutions present in world [37].

Tannins have an important role in the natural dyeing. These compounds improve the affinity of fibers towards different dyes. The different shades like yellow, brown, grey and black can be obtained with these dyes by means of tannins [38].

III. CONCLUSION

Instead of the chemical mordants, vegetable mordants (tannins) are alternative mordant sources. Some of the chemical mordants can show toxic, allergenic, non-friendly and carcinogen properties. The analysis of the tannin-mordanted textiles with HPLC-DAD shows that if gallic acid or ellagic acid compound was determined, the textile was mordanted with either gall oak or walloon oak. These textiles can be interested in the historical textiles in Turkey. The chemical mordants are an expensive products and cause to environmental pollution. Whereas, vegetable mordants are eco-friendly, non-allergenic, non-toxic, biodegradable compounds. Tannin sources can be easily provided by nature. The tannin source plants can be used both for mordanting and dyeing. Gallic acid and ellagic acid are of important phenolic compounds. These compounds can show biological activities such as antioxidant, antimicrobial and anticancer activity.

Acknowledgment

The author thanks to Prof.Dr.Recep Karadag (Marmara University, Istanbul-Turkey) in providing the plant photos.

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