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UV light impact on ellagitannins and wood surface colour of European oak (*Quercus petraea* and *Quercus robur*)

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Abstract

Two European oak species (*Q. petraea* and *Q. robur*) have a high content of phenols which may participate in the alteration of colour upon UV irradiation. To study the photodegradation process of oak surfaces, the two oak species extractives, vescalagin, castalagin, ellagic acid and gallic acid were analysed quantitatively by HPLC before and after UV irradiation. Irradiation time was altered between 3, 24, 72, 96, 120, 144, 192 and 216 h. In parallel, any colour changes of Oak wood surface was followed after 120 h of UV-irradiation by measuring CIELAB parameters (DL*, Da*, Db* and DE*). We observed that 60% of total phenol content of extractives decreased after the maximal exposure time. Our findings also showed that castalagin and gallic acid were destroyed after 216 h and vescalagin and ellagic acid after 72 h. This study proves the photosenibility of oakwood extractives which, supplementary to lignin degradation, would strongly result in the discolouration of oak heartwood.

Keywords: Castalagin; Ellagic acid; Ellagitannins; Gallic acid; European oak; Photodegradation; Vescalagin; Wood colour

1. Introduction

European oak, which covers a surface of more than 4 million ha [1], is an economically significant wood in France. Oak wood is frequently coated with transparent finishes to keep its natural colour [2]. Unfortunately, when exposed to environment conditions (sunlight, water, oxygen, changing temperature, etc.), oak looses its aesthetical appearance. The major effect is the colour change: it gradually turns grey and the surface layers erode [3]. All spectroscopic and chemical analyses show that the deterioration is primarily related to the decomposition of lignins because of their chromophoric groups absorbing especially in the range of UV light [4]. In the course of homolytic scission of intramolecular connections phenoxy free radicals arise. Most of them belong to the guaiacyl type [5]. The reactivity of these radicals is dependent of the quantity of oxygen in the surrounding [6,7]. These radicals undergo transformation into quinoid structures which results in the yellowing of the wood surface [8]. Oak is rich in phenolic extractives reaching up to 10% (wt) of the dried wood [9]. Phenols contribute a lot to natural durability [10] and colour of oaks' heartwood [11]. Interestingly, softwoods show more intense photobleaching and photoyellowing effects than hardwoods [12]. The behaviour of cold water-extracted oak upon UV irradiation was monitored and it was found that the extracted oak clears up more quickly than the unextracted one [12]. Pandey [13] irradiated *Acacia auriculaeformis* by Arc Xenon light with 1000 W for 700 h, and studied the effect of the extractives on decolouration and degradation. Extracted wood displayed a more intense colour change due to UV irradiation than unextracted wood [13]. In our study, this effect was also observed after a long exposure to UV radiation. Delignification detected by FTIR spectroscopy, was manifested by the decrease of the band at 1509 cm^{-1}. Whereas, photodegradation of phenolic compounds, which resulted in the carbonyl groups, was deduced from the increase of the C=O band at 1734 cm^{-1} [13]. A high concentration of phenols and ellagitannins in European oak species does not prevent the wood from colour changes and photodegradation, although ellagitannins are known to be antioxidants [14]. The antioxidant capacity of

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the extractives was demonstrated by Harroudi [15] who illustrated the radical processes in the course of photodegradation. Phenols play an important role in coating performances and no efficient and long-term protection of wood has been yet developed [16].

The origin of wood colour modification after UV exposure still remains a complex issue to be investigated in detail. Due to the frequent photo-discolouration of European oak and the important participation of extractives on wood colouration, this paper purposes to study the behaviour of oak phenolic substances towards UV-light.

2. Materials and methods

2.1. Wood samples

European oak heartwood tablets (*Q. petraea and Q. robur*) were provided by Ets Poreaux (Chalon-en-champagne – France). 5 of these tablets, measuring 150 mm× 75 mm× 6 mm, were prepared, planed and stored away from light in order to measure the surface colour. Other tablets were ground twice in a Retsch rotating-Knife grinder to extract phenolic substances. The final granulometry was inferior to 100 meshs.

2.2. Phenolic compounds

- Vescalagin and castalagin were provided by Dr. Bertrand Charrier (University of Pau, Mont de Marsan site) and by Pr. Stephane Quideau (Bordeaux 1 University).
- Gallic and ellagic acids were purchased from Sigma–Aldrich.

2.3. Colour measurement

The five tablets were exposed to UV light in Q-pannel QUV at 60 °C of temperature. Wood surface colour changes were measured both without UV irradiation, and after 2, 4, 24, 48 and 120 h UV exposure using MICROFLASH 200d (Datacolour) spectrocolorimeter. CIELAB L*, a*, b* and DE* parameters were measured at five locations on each tablet and average value was calculated. L*, a* and b* values were used to calculate the overall colour changes DE* using the following equation: $DE = (DL^2 + Da^2 + Db^2)^{1/2}$, where DL*, Da* and Db* are the difference between the initial and the final values (before and after UV irradiation) of L*, a* and b*, respectively.

2.4. Extraction

A 250 mg of oak sawdust was extracted with 25 ml of bi-distilled water for 4 h under agitation at room temperature. The solutions collected were filtered through Buchner-funnel porosity 4 (these extracts had a yellow colour).

2.5. Measurement of total phenols

Total phenols content in tannin extract and castalagin solution was measured by using the Folin-Ciocalteu method [17]. The measurements of total phenols were taken both without UV irradiation and after 3, 24, 72, 96, 120, 144, 192 and 216 h of exposure to UV light in Q-pannel QUV.

2.6. HPLC analysis

HPLC: waters system; UV detector with diode slide. Column: C18 Spherisorb ODS2®, 4.6 mm × 250 mm. Detection: at 254 nm; injection volume: 10 μl; flow-rate: 0.75 ml min^{-1}; gradient: H_2O/H_3PO_4 99.9/0.1 (v/v); MeOH 100 v. Separation of castalagin and gallic acid was obtained by using a gradient from 0 to 5% of MeOH for 40 min then to 20% for 10 min. As for oak extract, vescalagin and ellagic acid the gradient was: 0–5% of MeOH for 40 min then increased until 100%. After that, 100% of H_2O/H_3PO_4 took place for 10 min. HPLC analyses were performed without and with UV irradiation after different times.

2.7. Phenols photodegradation

Aqueous solutions of castalagin, vesacalgin and gallic acid were prepared at the concentrations, respectively of 2, 1.5 and 0.4 mg ml^{-1}. Ellagic acid was dissolved in MeOH to have a concentration of 0.25 mg ml^{-1}. Vescalagin and ellagic acid solutions were analysed by HPLC after 2, 24, 48 and 72 h of UV irradiation, whereas castalagin and gallic acid solutions were analysed after 3, 24, 72, 96, 120, 144, 192 and 216 h. As for oak extract, HPLC analysis was done after 2, 4, 24, 48 and 120 h of UV irradiation.

3. Results and discussion

3.1. Colour changes

Fig. 1 presents the evolution of the colour parameters DL*, Da*, Db* and DE* under UV-irradiation. After 120 h of UV-irradiation, we noticed modification of DL*, Da*, Db* and DE* values. Macroscopically, this modification is interpreted by alteration of the initial wood surface colour which is darker than the original. Temisa et al. [18] exposed samples of scots pine sapwood and alder sapwood to UV irradiation and found that

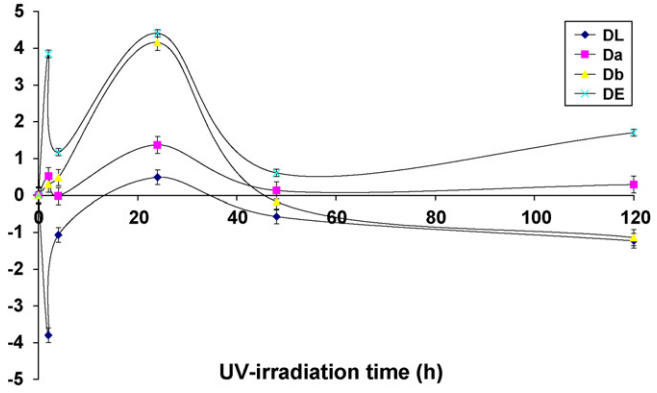

Fig. 1. Evolution of oak heartwood colour after 120 h of UV-irradiation. Colour changes are represented by the parameters DL*, Da*, Db* and DE*. Each value represents the average of 25 measurements.

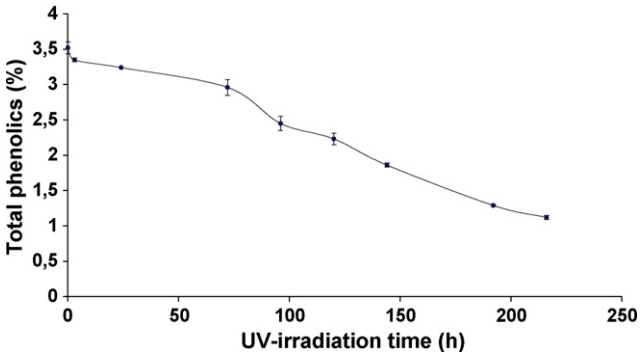

Fig. 2. Evolution of total phenols content in UV irradiated oak extracts. Extracts were obtained after 4 h of extraction of oak wood sawdust in bidistilled water. Each value represents the average of two measurements.

during the weathering of untreated samples' wood surfaces became darker. Kandey [19] correlated changes in wood colour to chemical changes in wood during photodegradation.

3.2. Total phenols measurement

Fig. 2 presents the evolution of total phenols content under UV irradiation. We had more than 68% of total phenols degradation after 216 h of UV irradiation. Total phenols analysis was also correlated with oak ellagitannins as stated by Guilley et al. [20].

3.3. Oak extract HPLC analysis

Following HPLC analysis, we identified vescalagin, castalagin, gallic and ellagic acids in the extract oak. Their retention times were, respectively, around 7, 10, 30 and 70 min (Fig. 3). The 24-h UV irradiation chromatogram of the oak extract indicated a slight decrease of the peak intensities of vescalagin and castalagin. In the 48-h one, the decrease of vescalagin was more important than castalagin. As for gallic acid, its peak intensity rose considerably. Besides, many new peaks appeared corresponding to other phenolic compounds, among which, gallic and ellagic acids resulted in tannins photo-degradation. As it was described by Bearnais-Barbry et al. [21], the phenolic compounds may have been generated by radical mechanisms similar to those of lignin photo-degradation. After 120 h of UV irradiation, vescalagin and castalagin peaks disappeared. Gallic acid peak became weak when ellagic acid was not detected. Indeed, we deduce that UV light induces the degradation of phenolic compounds present in oak extract especially castalagin, vescalagin, gallic and ellagic acids. Oxygen, higher temperature and pH are also found to increase the rate of Oak ellagitannins degradation [22].

Fig. 4 presents the evolution of their peak area ratios under UV light. Beyond 48 h of UV irradiation, we observed a progressive decrease of the following ratios: vescalagin/gallic acid, castalagin/gallic acid, vescalagin/ellagic acid and castalagin/ellagic acid. However, there was an increase in castalagin/vescalagin. These results by HPLC analysis could be explained 'by the fact that ellagic and gallic acid result in castalagin or vescalagin photodegradation. Zhentian's works

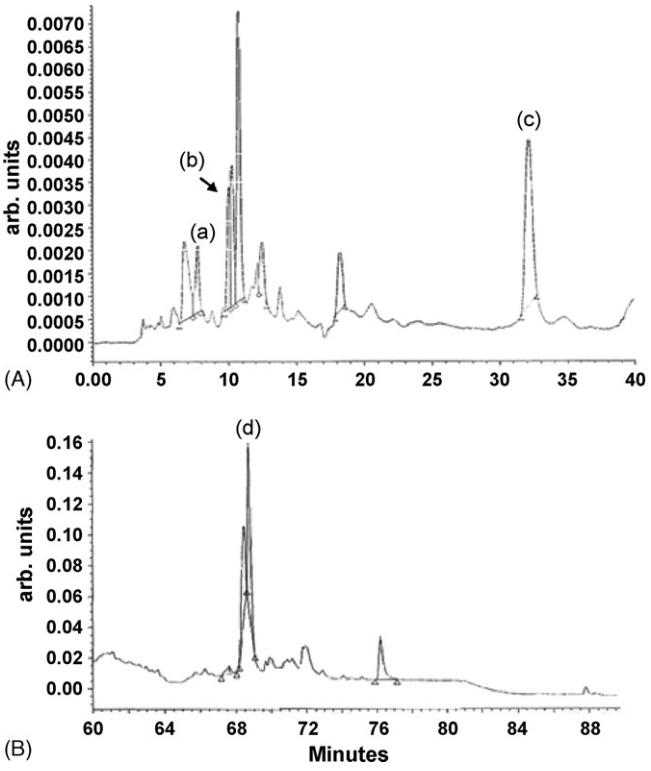

Fig. 3. HPLC chromatogram of non-irradiated oak extract and identification of the four following phenols: (a) vescalagin, (b) castalagin, (c) gallic acid (d) ellagic acid. Detection at 280 nm.

[22] showed that ellagic acid was a product of castalagin and vescalagin degradation.

3.4. Phenols HPLC analysis

It is difficult to obtain pure vescalagin, hence we detected, beyond vescalagin, traces of gallic and ellagic acids during HPLC analysis. The vescalagin peak intensity decreased when the UV irradiation time increased, then the peak disappeared after 72 h of UV irradiation. The gallic and ellagic acids' peak intensities rose then reduced beyond 48 h of UV irradiation. This increase corroborates Charrier's [23] works that during oak heartwood kiln drying, the concentration of ellagic and

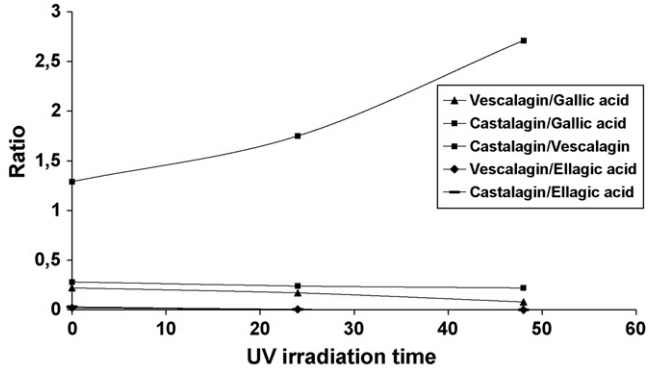

Fig. 4. Evolution of the peak area ratios of the phenolic compounds (vescalagin, castalagin, gallic and ellagic acids) identified in oak extract under UV irradiation.

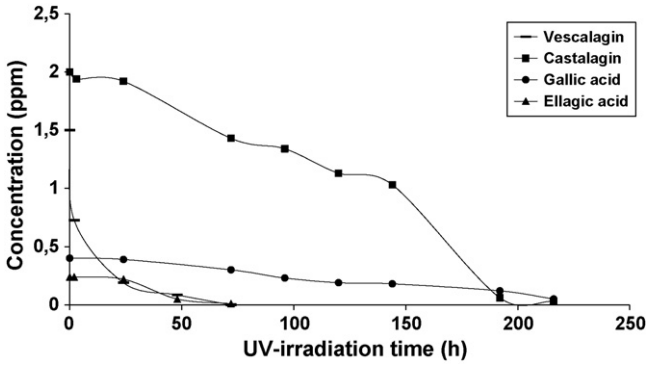

Fig. 5. Kinetic of the photodegradation of vescalagin, castalagin, gallic acid (water solutions) and ellagic acid (methanol solution).

gallic acids increases. After 2 h of castalagin UV exposure, we detected many unknown peaks resulted in castalagin degradation. Among these new products, we found ellagic acid. However, no gallic acid was detected. Charrier et al. [23] exposed aqueous solutions of vescalgin and castalagin to different temperatures (25–55 °C) and found similar results illustrating that ellagic acid results in vescalagin and castalagin degradation. However, gallic acid involved in oak extract might have been due to other tannins photodegradation which is not within the scope of this study. As for gallic and ellagic acids' peak intensities, they decreased with the UV irradiation time. Gallic acid was not detected during the UV irradiation of ellagic acid. Thus, we can say that ellagic acid photodegradation does not produce gallic acid. These behaviours explain that mechanisms of ellagic acid photodegradation are similar as thermal treatment [18]. Fig. 5 illustrates the evolution of vescalagin, castalagin, gallic and ellagic acids' concentrations, which showed varying degrees of photo-sensibility, under UV light effect. After 72 h of UV irradiation, we observed 100% degradation of vescalagin and 95.8% of ellagic acid. As for castalagin and gallic acid, the degradations were, respectively, 98.5 and 87.5% after 216 h. We notice that gallic acid is much more stable than ellagic acid after UV light exposure. We can also conclude that vescalagin is less stable against UV than castalagin. This better stability of castalagin versus vescalagin has previously been observed and documented by Zhentian, Masson and Quideau [22,24,25].

Interestingly, the colour of both oak extracts and ellagitannin aqueous solutions (castalagin and vescalagin) became increasingly yellow during UV irradiation. As reported by Charrier et al. [18] and Zhentian [22], this yellowing is associated with the degradation of vescalagin and castalagin and thus, the discoloration of oak heartwood.

4. Conclusion

This study has focused on the behaviour of ellagitannins exposed to UV light and its impact on wood colour surface changes. The results indicate that castalagin and gallic acid are destroyed after 216 h of UV irradiation whereas, vescalagin and ellagic acid after only 72 h. These original results show clearly the sensibility of oakwood extractives and the different behavioural reactions of vescalagin and castalagin. Supplementary to lignin degradation, ellagitannins in oak woods would strongly result in the discoloration of oak heartwood.

However, complementary studies may be conducted to identify the chemical process of product degradations. A better understanding of these mechanisms should allow improvement of coating system durability for outside uses of phenolic-rich wood.

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