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**DISCOLOURATION OF DIOXANE LIGNIN ISOLATED
FROM OAK WOOD (*QUERCUS ROBUR* L.) AND SWEET
CHERRY WOOD (*PRUNUS AVIUM* L.) IRRADIATED WITH
VARIOUS LIGHT SOURCES**

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ABSTRACT

Wood colour stability is relevant for the final use of this material. The differences in light-induced discolouration among various wood species were studied on an example of two different species – oak wood and sweet cherry wood. To understand the causes of these differences, experiments were carried out on dioxane lignin isolated from these two species. The investigated specimens were exposed to ultraviolet (UV), ultraviolet/ visible (UV/VIS) and visible (VIS) light. The measurements were carried out by colorimetric method, using CIE Lab system, the values of colour coordinates were recorded before the irradiation and after 100 hours of light exposure. The results indicate that, apart from lignin, other wood components such as extraction substances play role in colour changes in the two investigated wood species.

KEYWORDS: Light-induced discolouration, ultraviolet and visible light, oak, sweet cherry, dioxane lignin.

INTRODUCTION

Wood is a complex material consisting of cellulose, hemicelluloses, lignin and extractives. Due to its easy availability and attractive appearance, it is a very popular material for various products for both indoor and outdoor use. However, unprotected wood can absorb a broad range of electromagnetic radiation (Park et al. 1996). Such irradiation may initiate photochemical

reactions causing discolouration of wood surface. Depending on the wood species, the surface of wood exposed to light may turn darker, lighter, or exhibit a yellowish or reddish hue. These changes result from reactions of polyphenols with lignin and with secondary wood components (Laver and Wang 1996, Hon and Chang 1984, Feist 1983, Kawamura et al. 1996). The chromophore groups present in lignin can absorb UV/VIS radiation which in the presence of oxygen forces wood photo-oxidation; while cellulose and hemicelluloses are much less sensitive to light effects.

CO₂ laser irradiation was found causing chemical modifications in beech and maple wood. Higher irradiation dose (from 18 to 57 J.cm⁻¹) caused predominantly degradation of hemicelluloses. Lignin degraded at a lower irradiation dose, and at a higher energy dosage, it condensed (Kubovský and Kačík 2009, Kačík and Kubovský 2011). Due to its aromatic structure, lignin is able to absorb radiation below 440 nm, with an absorption maximum at 282 nm (Fengel and Wegener 1984, Hon 1981, Schaller and Rogez 2007).

The depth of light penetration into wood depends on the wave length. Visible, i.e. blue light with wave lengths of 430–500 nm, penetrates into Sugi sapwood (*Cryptomeria japonica* D. Don) deeper than violet light with wave length of 380–430 nm, and causes brightening of wood surface without significant changes in the IR spectrum of lignin (Kataoka et al. 2007). Suttie (2006) and MacLeod et al. (1995) demonstrated changes in wood colour varying with the length of light waves reaching the surface. A similar phenomenon, resulting from irradiation with electromagnetic waves of three different ranges, was observed in research on surface discolouration of oak wood and sweet cherry wood (Zborowska et al. 2011). The colour change in oak veneer due to exposure to UV light was $\Delta E^* = 11.2$. The exposure of oak wood surface to visible light caused much less pronounced discolouration ($\Delta E^* = 4.3$). The difference in colour modification in sweet cherry wood between ultraviolet and visible light was much less pronounced as in the case of oak wood (5.9 and 4.0).

The aim of this work was to investigate the causes underlying the differences in intensity of light-induced discolouration between oak wood and sweet cherry wood, through testing the colour change in dioxane lignin isolated from the two studied wood species.

MATERIAL AND METHODS

We tested dioxane lignin isolated from oak wood (*Quercus robur* L.) and from sweet cherry wood (*Prunus avium* L.). For comparison, parallel tests were performed on surfaces of oak and sweet cherry veneers. Dioxane lignin was isolated from a wood fraction with particles sized below 0.2 mm, with using the method suggested by Kačík et al. (1992). The material was extracted twice: With alcohol-benzene mixture (2/1 v/v) – extraction time 6 h and with ethanol – extraction time 6 h. Such prepared material was treated with a mixture of dioxane and water (9/1 v/v) in the presence of 0.2 M HCl. The reaction was carried out in the atmosphere of nitrogen monoxide for 5 h, at a temperature of 80°C ± 2°C. After this time, the content of the container was filtered through a Buchner funnel, and the lignin dissolved in dioxane was precipitated in water.

The dried lignin was pressed into tablets with a diameter of ca 20 mm. The isolated dioxane lignin was light-brown coloured (oak) and dark-brown coloured (sweet cherry). The colour of lignin is due to its reaction with phenolic substances, such as phloroglucinol, in acid environment at high temperatures, resulting in characteristic red-violet tint in lignin groups. The values of colour coordinates (L^* , a^* , b^*) for lignin and veneers are given in Tab. 1.

Tab. 1: Colour coordinates of oak and sweet cherry dioxane lignin and wood surface.

Colour coordinates ¹⁾	Wood species			
	Cherry		Oak	
	Lignin	Wood ²⁾	Lignin	Wood ²⁾
L*	44.92	68.96	60.08	54.43
min	44.02	67.41	49.71	51.27
max	46.06	70.04	60.55	57.31
a*	11.4	10.7	8.8	7.4
min	11.2	9.3	8.7	6.6
max	11.6	12.0	9.0	8.2
b*	15.1	20.8	17.3	14.3
min	14.6	19.1	17.0	13.2
max	15.5	22.1	17.5	15.7

1) mean value from 10 measuring points

2) results concerning wood surface colour change presented in the monograph: Physico-chemical analysis of lignocellulosic materials (2011).

The tested substances were irradiated for 100 hours in a SUNTEST CPS apparatus (xenon lamp), manufactured by Heraeus Company, and in an apparatus ATLAS UVTest™ equipped with UV lamps, manufactured by Atlas Company.

Test parameters:

- xenon lamp: Wave length of light incident onto the surface: 320-800 nm and 400-800 nm (by using an optical filter blocking UV radiation), temperature BST = 38°C, light intensity 550 W.m⁻²,
- UV lamp 340 nm, wave lengths of light incident onto the surface 290-400 nm, temperature = 38°C, light intensity 0.5 W.m⁻².

The colour coordinates of the tested surfaces were recorded before the irradiation and subsequently after 1, 5, 10, 25, 50, 75, and 100 h of irradiation.

The colour parameters in CIE L*a*b* system were recorded with an ELREPHO 2000 spectrophotometer, using a D65 standard illuminant and a 10° standard observer. The sensor head diameter was 12 mm. The measurement of colour coordinates L*, a*, b* and evaluation of colour changes were performed on 10 samples per each light source. The space of CIE L*a*b* system is defined by perpendicular coordinate axes a* and b* and the brightness coordinate axis L* crossing the intersection of a* and b* perpendicular to the a* b* plane. The axis a* expresses colours from green (-a) to red (+a), axis b* from blue (-b) to yellow (+b), and axis L* represents the values from 0 (black) to 100 (white).

Colour change in the CIE Lab system was calculated according to the following formula:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where: ΔE^* – colour change,
 ΔL^* – achromatic coordinate change,
 $\Delta a^*, \Delta b^*$ – chromatic coordinates changes.

RESULTS AND DISCUSSION

Colour and colour stability are important features for products made from wood. The principal manifestation of wood photodegradation is its colour change, a decrease in wood surface colour and brightness. Depending on the species, the wood darkens, fades, grayishes, or acquires yellowish, brownish or orange hue – determined principally by the extractives present in the wood (George et al. 2005). Wood surface change its colour due to varying light exposure (Suttie 2006, Tolvaj and Mitsui 2005). This paper demonstrates that exposure of dioxane lignin to UV/VIS light and to VIS light has also a profound effect on the colour change in lignin.

Fig. 1 illustrates the light-induced colour changes (ΔE) of dioxane lignin isolated from oak wood and sweet cherry wood, and, for comparison, the corresponding colour changes on the wood veneer surface of the two species.

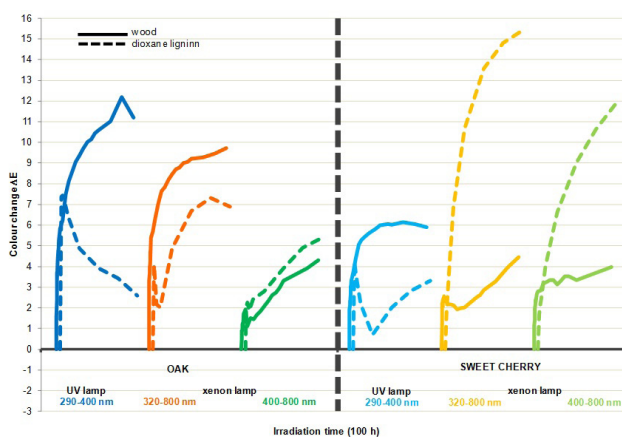


Fig. 1: Light-induced colour change of dioxane lignin isolated from oak wood and sweet cherry wood and of wood surface of the two species b).

The light-induced colour change (ΔE^*) of lignin isolated from oak wood and irradiated with ultraviolet light (UV: 290–400 nm) and xenon lamp light encompassing the radiation range of UV-VIS (320–800 nm) was less pronounced compared to the colour change of oak veneer wood (Fig. 3). The light within visible range (400–800 nm) caused discolouration of dioxane lignin similar to ΔE^* of oak wood surface. The analysis of the effect of UV light (290–400 nm) revealed a fast growth in ΔE^* value in the initial period of irradiation. After having reached the maximum of the magnitude order of 7 units, the growth started to decelerate. The analysis of colour change of lignin isolated from sweet cherry wood indicated that in the initial period of irradiation with the UV lamp, the value of ΔE^* increased rapidly, then decreased, and rose again. On the other hand, in sweet cherry dioxane lignin, UV/VIS and visible light (320–800 nm and 400–800 nm) caused a general increase in ΔE^* with time. Moreover, in the case of lignin isolated from sweet cherry wood, it was also holds that the value of its colour change was much higher compared to ΔE^* of wood veneer surface. The values of colour change of dioxane lignin isolated from oak and sweet cherry wood exposed to the same light showed differences. For example, after 100 h of irradiation (320–800 nm), the colour change of oak lignin was around 7 units; while ΔE of sweet

cherry lignin was 15 units.

These differences result from intensity and directions of changes of colour coordinates ΔL^* , Δa^* and Δb^* (Figs. 2–4). Analysing the change in the brightness (ΔL^*) of dioxane lignin isolated from oak wood and irradiated with three light sources and the lignin isolated from cherry wood and exposed to UV radiation, just in the first phase of irradiation, darkening of the tested surfaces was observed, followed by brightening over the following periods (Fig. 2). In the sweet cherry lignin irradiated with xenon lamp (wave lengths 320–800 nm and 400–800 nm) only brightening was observed.

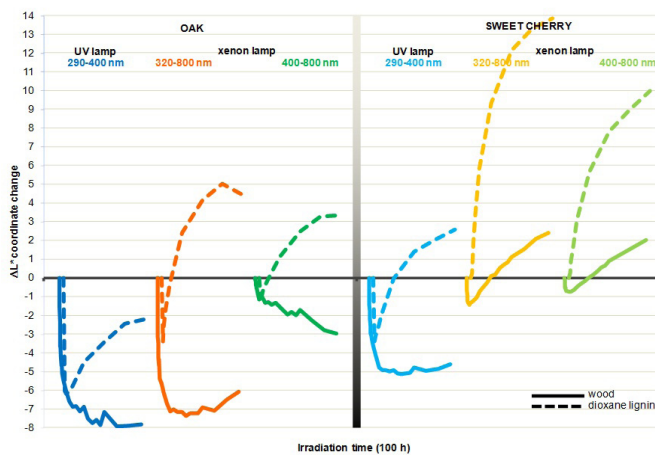


Fig. 2: Light-induced change in brightness coordinate (ΔL^*) of dioxane lignin isolated from oak wood and sweet cherry wood and of wood surface of the two species h).

The values of change in the chromatic coordinate Δa^* suggest that, due to UV light irradiation, the surfaces of the two analysed lignins acquired more red-colouring in the initial phase of irradiation (Fig. 3). However, longer exposure to light induced changes in the lignin structure, which caused their reddish hue to fade ($-\Delta a^*$). The light of xenon lamp (320–800 nm and 400–800 nm) applied on surface of oak and sweet cherry lignins caused fading of reddish colouring in the both species. The analysis of chromatic coordinate Δb^* changes suggests that the surface of both tested lignins, irrespective of the type of light used (290–400 nm, 320–800 nm and 400–800 nm), became somewhat less yellow in the initial phase of irradiation (Fig. 4); and then the tested surfaces acquired more and more yellow component. However, it should be stressed that oak lignin as well as sweet cherry lignin irradiated with xenon lamp (with a share of visible light) were characterised by higher values of $+\Delta b^*$ compared to the change in coordinate Δb^* for surfaces irradiated solely with ultraviolet light.

The differences in course and intensity of the changes in colour coordinates between wood and dioxane lignin suggest that wood colour change is a complex process driven by the colour change of lignin as well as of the other wood components, such as extractives (Laver and Wang 1996). However, there is lack of documented literature describing colour changes in lignin isolated from wood, especially dioxane lignin. Most of the literature describing the influence of light on lignin colour change concerns wooden elements.

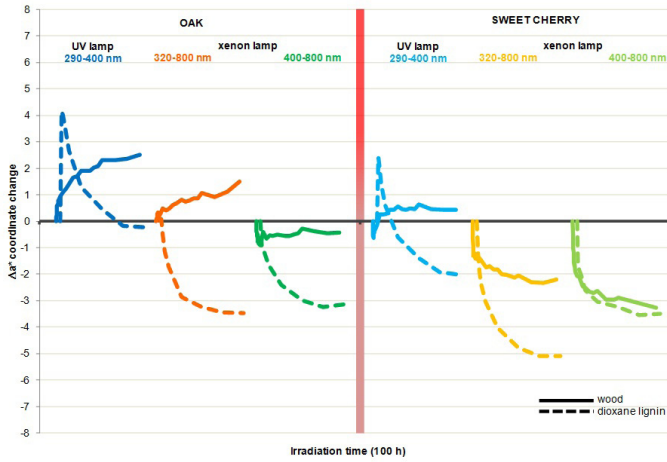


Fig. 3: Light-induced change in chromatic coordinate Δa^* of dioxane lignin isolated from oak wood and sweet cherry wood and of wood surface of the two species *b*).

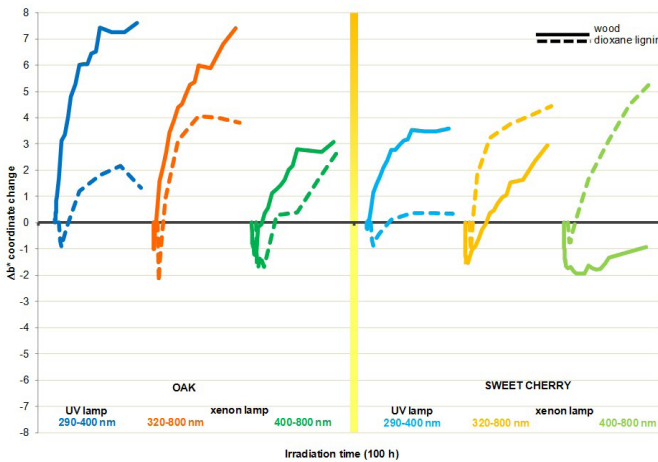


Fig. 4: Light induced change in chromatic coordinate Δb^* of dioxane lignin isolated from oak wood and sweet cherry wood and of wood surface of the two species *b*).

The works dealing with analyses of lignin specimens have mainly been focused on structural changes investigated spectroscopically in an infrared or a UV spectrum (Schaller and Rogez 2007, Jahan and Mun 2009).

CONCLUSIONS

Summarising, we may conclude that that the course of the changes in the colour coordinates Δa^* , and Δb^* in the dioxane lignin isolated from oak wood and the course of the changes of these coordinates in the lignin isolated from sweet cherry are very similar (after 100 h of irradiation with a xenon lamp, the difference between the two species was 2 units).

It seems that the most explanation for the differences in intensity of colour changes (ΔE^*) between the two species gives the component ΔL^* (after 100 h irradiation with xenon lamp 6–7 units). Depending of the wood species and the light source (UV, UV/VIS, VIS), ΔL^* coordinate was positive or negative.

Such facts as that under irradiation oak wood darkens and lignin brightens suggest that, apart from lignin, also extraction substances are active in colour change of wood.

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