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Influence of Thermal Modification and Impregnation with Biocides on Physical Properties of Italian Stone Pine Wood (*Pinus pinea* L.)

Marco De Angelis [1], Miha Humar [2,*], Davor Kržišnik [2], Swati Tamantini [3] and Manuela Romagnoli [3,*]

[1] Institute of Wood Sciences, University of Hamburg, Leuschnerstrasse 91c, 21031 Hamburg, Germany; marco.de.angelis@uni-hamburg.de
[2] Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana, Rožna Dolina Cesta VIII 34, 1000 Ljubljana, Slovenia; davor.krzisnik@bf.uni-lj.si
[3] Department for Innovation in Biological, Agro-Food and Forest Systems, University of Tuscia, 01100 Viterbo, Italy; swati.tamantini@unitus.it
* Correspondence: miha.humar@bf.uni-lj.si (M.H.); mroma@unitus.it (M.R.)

Featured Application: In recent decades, the importance of wood has also been increasing for outdoor intended use. A more sustainable approach has turned the attention from faraway tropical forests to local wood, that is, European species. Unfortunately, most of the species are not durable; thus, in order to utilize them in outdoor conditions, protection must be provided. Stone pine (*Pinus pinea*) is one of the most common tree species in the Mediterranean region, with a great potential in applications with higher added value, instead of being used only for burning or packaging. This investigation explores methods for an improvement of the service life of stone pine sapwood using impregnation and modification techniques.

Abstract: The sudden availability of Italian stone pine *(Pinus pinea* L.) wood due to the infestation of pathogenic fungi and insects highlighted the need to promote its use as a short supply chain resource in Italy and other Mediterranean countries. However, the durability of stone pine sapwood must be enhanced if outdoor use is to be considered. The impregnability of stone pine wood was studied following the standard EN 351-1:2008, using immersion, vacuum, and high-pressure methods with natural waxes and organic solvent-based and copper-amino-based preservative solutions. The efficacy of the impregnation was determined by calculating the kilos of preservative absorbed per cubic meter of wood and by measuring the penetration depth of the preservative. Thermal modifications were carried out using five different maximum temperatures, and their efficacy was determined by measuring the mass loss and color change. Subsequent to thermal treatments, the wood was exposed to a water-vapor-saturated atmosphere, and the increase in mass was calculated for different periods. Stone pine and Scots pine sapwoods showed similar response to the treatments with the exception of soaking impregnation methods where stone pine showed higher uptake, in particular when Silvanolin was used. Our investigation shows that stone pine can be a suitable short supply chain resource in Italy that, when impregnated, could be tested for outdoor use, exactly as is the case with Scots pine.

Keywords: *Pinus pinea* wood; thermal treatments; impregnation; durability; short supply chain

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1. Introduction

The Italian stone pine or umbrella pine (*Pinus pinea* L.) is a noticeable tree species in southern Europe and North America. In Europe, the growth of the stone pine has been promoted since Roman times. Thus, it is widespread from Portugal to Syria and along with some coastal areas of the Black Sea [1]. In the Mediterranean basin, stone pine forests and woodlands cover 700,000 ha [2], including 80,000 ha in Portugal, 470,000 ha in Spain,

40,000 ha in Italy, 50,000 ha in Turkey, and 21,165 ha in Tunisia [3]. Important stands also exist in France, Greece, Lebanon, and Morocco [4,5]. The distribution of the species in Italy is also notable in urban and peri-urban areas. For example, in the city of Rome, *Pinus* is the most common genus, with more than 51,000 trees [6,7]. For centuries, the stone pine has been cultivated for its wooden products, including timber and firewood, as well as for its non-wood products, including edible pine nuts and edible mushrooms, and for allowing pastoralism under its forest canopy [8]. Its wood was used in construction and the naval industry; in particular, its resin was used to seal the hulls of wooden ships [9,10]. Moreover, stone pine stands provide environmental services such as consolidation of coastal areas and protection against erosion [11]; in terms of forest management, the species requires wide spacing. In modern times, the economic importance of stone pine has declined; nowadays, the wood is used for low-value products such as pallets, paper, cellulose, wood chips, and energy. Nevertheless, as with other conifers, Italian stone pine can be used for panel composites and light construction purposes such as insulation boards and wood wool [7]. The tree species suffers from infestations of pathogenic fungi throughout the Mediterranean basin such as *Diplodia* species [2] and *Coleosporium tussilaginis*, *Heterobasidion annosum*, *Melampsora populnea* [7]. Many insects, such as *Matsucoccus josephi* and *Pissodes castane*, are also responsible for the abrupt die-off of the species in recent years. Trees attacked by the above-mentioned pests perish in a short time [12], and this event leads to a sudden availability of stone pine wood, which is generally used as biomass for low-value-added energy production. The COVID-19 pandemic has increasingly highlighted the need to resort to the concept of a short supply chain and to use the resources in a nearby area [13–16]. Stone pine wood can be a valuable resource to consider because the mechanical properties such as bending strength (83 MPa), modulus of elasticity (MOE—13,500 MPa), and compressive strength (41 MPa) are comparable to the values of widely traded pines such as Scots pine (*Pinus sylvestris*) (98 MPa—MOR, 14,000 MPa-MOE, 46 MPa—compressive strength). Moreover, the mechanical properties are higher than spruce, which shows a bending strength of 66 Mpa and a compressive strength of 36 Mpa [17]. However, most of the xylem in the tree trunk is sapwood tissue [18], which is not durable and needs to be protected somehow, especially when used outdoors [19]. The goal of our research was to investigate the effect of impregnation and heat treatments on some physical properties of sapwood and heartwood of Stone pine wood and comparing it with Scots pine sapwood, beech, and spruce. The wood species were impregnated using three different preservative products: Belocid, Silvanolin, and Montan wax 50. Different impregnation methods were applied: soaking, vacuum, and full-cell method. The radial and tangential penetration depth of Silvanolin was studied. Five new sets of samples were heath treated using five different maximum temperatures, and the mass loss was calculated. The heath-treated samples were exposed to a water-vapor-saturated atmosphere and the moisture uptake was measured. After the heat treatments, the color change was measured using the CIE L*a*b* system (Commission Internationale de l'Eclairage). Wood color is an important factor influencing customers' decision making and purchasing decisions [20,21]. The investigations were performed in order to consider the use of Italian stone pine wood for the same application for which Scots pine is used, i.e., considering the use category for outdoor conditions.

2. Materials and Methods

2.1. Materials

2.1.1. Wood

Samples of Italian stone pine wood (*Pinus pinea* L.) were cut from the bottom section of three trees growing in the urban area of Rome (Italy) (latitude: 41°53′30″ N longitude: 12°30′40″ E, altitude: 52 m). The wood used for this study was free of growth anomalies and decay. The trees were about 45–50 years old and had a 40–50 cm diameter. Separate samples of heartwood and sapwood were prepared to study their properties individually. Samples from European beech (*Fagus sylvatica* L.), Scots pine (*Pinus sylvestris* L.), and Norway spruce (*Picea abies* L.) served as the control.

2.1.2. Preservatives Solutions

Three preservative solutions were used: Montax 50 (Romonta, Amsdorf, Germany), Silvanolin (Silvaprodukt, Ljubljana, Slovenia), and Belocid (Belinka, Domžale, Slovenia). Montax 50 consisted of a montan wax derived from lignite-containing wax (50–80%), resin (20–40%), and bitumen (10–20%) suspended in an aqueous medium. The dry content of the wax in the treatment solution was about 5%. Silvanolin was a commercial preservative manufactured by Silvaprodukt on the basis of copper hydroxide carbonate, ethanolamine, quaternary ammonium compounds, boric acid, and octanoic acid; the detailed composition of the product can be found in the patent by Humar and Pohleven [22]. Silvanolin was dissolved in an aqueous medium to achieve a copper concentration of 2500 µg/g. Finally, Belocid, produced by the Slovenian company Belinka, consisted of a mixture of organic solvents, biocides (IPBC, propiconazole, permethrin), and alkyd resins. The concentration of biocides was lower than 1%, and the concentration of alkyd resins was between 5 and 10%. These three preservative solutions allow for comprehensive impregnation studies.

2.2. Methods

2.2.1. Impregnation with Preservative Solutions

Seventy-five samples of sapwood and 15 of heartwood were cut with a size of 25 × 25 mm in cross-section and 100 mm in length for the tests of impregnation of the wood with preservatives. The cross-sections of the samples were sealed with a double layer of epoxy resin to allow penetration of the solution only in the radial and tangential directions. An equal number of sapwood samples of Scots pine, Norway spruce, and beech wood were used as controls and prepared in the same manner. Spruce was selected as the control because it is known that the species when dried under 30% moisture content is refractory to impregnation because of the aspirated pits in the tracheid [23–25]. Five samples were used for each treatment and preservation product. Before treatment, the samples were conditioned at 20 ± 2 °C and 65 ± 5% relative humidity, and the mass was determined. The standard EN 351-1:2008 [26] was used to investigate the impregnability of the wood with wood preservatives. Three different impregnation methods were used: (I) vacuum impregnation, (II) full-cell pressure method, and (III) soaking. Three soaking method impregnation durations were applied: 15, 60, and 480 min. As the low permeability of the heartwood was to be expected and due to the limited quantities of heartwood, the stone pine heartwood was treated only with the full-cell method, which is one of the most commercially important methods. The amount of preservative absorbed was measured by gravimetric analysis, taking into account the difference in density. Samples were placed in plastic containers and soaked with the preservative for each treatment. An inert mesh of polyethene terephthalate (PET) with a mesh size of 10 × 10 mm was used to separate the samples. Lead weights were used to prevent the samples from floating. The treatments were carried out at room temperature. A laboratory-scale impregnation chamber (Kambič, Semic, Slovenia) was used for vacuum and full-cell treatment. Vacuum (−0.085 MPa) was applied for 30 min, and then the samples were submerged at atmospheric pressure for 2 h. For the full-cell treatment, the samples were first kept under vacuum (−0.085 MPa) for 20 min, then under high pressure (1 MPa) for 2.5 h, and finally under vacuum (−0.085 MPa) for 30 min. The specimens were left for an additional two hours and immersed at atmospheric pressure to determine as much accurate retention as possible as prescribed from the leaching standard ENV 1250-2:1994 [27]. At the end of each treatment, the samples were carefully wiped to remove the excess preservative and weighed to the nearest 0.01 g. Radial and tangential penetration of Silvanolin was checked by cutting the samples along the midsection and treating them with a 2% potassium ferrocyanide reagent. The presence of Silvanolin was highlighted by the reagent with a dark reddish color. The depth of penetration was measured for each sample at the middle point of each of the four sides of the section. The experiment was carried out in five replicates. Unfortunately, we could not determine the penetration of Montax 50 and Belocid because these preservative solutions are colorless, and no color reagents have been developed to make their penetration visible.

2.2.2. Heat Treatments

Heat treatment modification was investigated on 75 samples of sapwood and 40 samples of the heartwood of stone pine (*P. pinea*) with a width of 25 mm, a thickness of 15 mm (in crosscut direction), and a length of 50 mm, which were cut according to the EN 113:2006 [28]. As a control, 75 samples of beech (*F. sylvatica*) and sapwood Scots pine (*P. sylvestris*) were used with the same size of stone pine. Fifteen samples of sapwood of stone pine and eight samples of the heartwood of stone pine were used with the relevant controls for each different treatment temperature. All samples were oven-dried (103 ± 2 °C; 24 h) before and after heat treatment and weighed to calculate the mass loss due to thermal modification. The thermal modification processes were performed as prescribed by the commercial Silvapro treatment [29]. Five maximum modification temperatures were applied: 180 °C, 195 °C, 210 °C, 220 °C, and 240 °C. The samples were modified at the target temperature for 3 h. Each different heat treatment, regardless of the maximum temperature, was characterized by seven different heating stages that gradually increased the temperature and kept it constant for the required time. The total heating time was eight and a half hours. The treatments were carried out in a laboratory-scale modification chamber (Kambič, Slovenia) in an atmosphere with reduced oxygen concentration achieved by applying vacuum in the first phase. In the following phases, the atmosphere consisted of superheated steam to avoid the formation of cracks and changes on the wood in the early phases of the treatment. At the end of the treatment, a cooling phase was carried out in the chamber at atmospheric pressure.

The thermally modified wood was characterized by determining the mass loss and hygroscopic properties. The hygroscopicity of the heat-treated wood, i.e., the ability of the material to absorb water from the ambient air, was tested by placing the samples in a glass chamber over distilled water (RH = 98 ± 2%). Seven of fifteen thermally modified samples were used for this test. The mass of the samples was determined after 24, 72, 168, 240, 408, 600, and 720 h until the constant mass was determined. After thermal modification, the color of the samples was determined. Color changes are one of the first and easiest indicators of changes in the wood. Two radial sides of each sample were scanned. The color in the images was evaluated using the CIE L*a*b* system (Commission Internationale de l'Eclairage), where L* represents lightness, varying from 100 (white) to 0 (black); a* (along the *x*-axis) red (+) to green (−), and b* (along the *y*-axis) yellow (+) to blue (−) being the chromaticity coordinates [30,31] using CorelDRAW 8 software (Ottawa, ON, Canada). Scanning was performed with the HP Scanjet G4050. The scanning parameters were set separately for dark, semi-dark, and light samples to obtain the most representative color of the surface. The average color coordinates of the respective plane were calculated directly with the software. It should be noted that the entire sample surface was analyzed. The color change (ΔE) between the control samples and the treated samples were calculated using Equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔL*, Δa*, and Δb* are the differences between the initial and final values of L*, a*, and b*, respectively.

Statistical Analysis

Statistical descriptive parameters (i.e., mean value and standard deviation) are reported for each measurement. Moreover, the significance of the mean differences within the different preservative products and between the different impregnation methods was tested using Tukey's HSD post hoc test (p-value < 0.05). The same was performed on the mass-loss parameter as assessed in each heat treatment. All graphs, diagrams, and analyses were produced using OriginPro 9.1 (OriginLab Corporation, Northampton, MA, USA).

3. Results and Discussions

P. pinea is a valuable and multifunctional species in Italy and other Mediterranean regions [32]. The contribution of the present study is to build possible value chains, especially where there are surpluses in biomass availability for sudden mortality phenomena due to climatic changes and pathogen infestations and to encourage new plantation of the species, which can become a resource in a bioeconomy perspective. The results are discussed by comparing the behavior of sapwood and heartwood of stone pine with control samples of Scots pine, beech, and spruce wood. Some preliminary comments are on wood density values. It is remarkable to evidence as Stone pine (537 $\pm$ 35 kg/m^3) and Scots pine (491 $\pm$ 16 kg/m^3) sapwoods had similar densities, spruce wood density was the lowest (411 $\pm$ 14 kg/m^3), while beech wood (852 $\pm$ 53 kg/m^3) and stone pine heartwood (815 $\pm$ 47 kg/m^3) had the highest density values and were quite similar. Indeed, the measured density of Scots pine and stone pine sapwood was lower than reported in literature, at 550 kg/m^3 and 610 kg/m^3, respectively [17]. The density measured in the specimens of stone pine heartwood deserves a special mention because it is in the upper range of wood density reported in *P. pinea* in Italy [17]. In fact, the most commonly assessed value of density in heartwood is 650 kg/m^3 [33]. The different gravimetric densities of sapwood and heartwood of stone pine can be attributed also to the high resin content of the heartwood [19].

3.1. Vacuum and Full-Cell Method

The results of impregnation of the different wood species are presented in Table 1, where the average uptake of preservative products is reported, with standard deviation expressed in kg/m^3. Indeed, in Table 1, the mean values are reported with upper cases related to the statistical analysis. The mean values with the same upper case are not statistically different so they belong to the same group.

Comparing the vacuum and full-cell methods, it can be observed that the full-cell method resulted in the highest uptake in all wood species (spruce, beech, Scots pine, and stone pine); nevertheless, the heartwood in stone pine proved to be very refractory. In the samples treated with the full-cell method, the heartwood of stone pine showed the lowest uptake of Montax 50 (186.07 $\pm$ 133.45 kg/m^3), followed by Belocid (230.57 $\pm$ 28.97 kg/m^3) and Silvanolin (290.58 $\pm$ 182.06 kg/m^3); the values were revealed to be not statistically different from those of spruce (Montax 50 258.76 $\pm$ 66.27, Belocid 189.33 $\pm$ 104.02, and Silvanolin 391.50 $\pm$ 134.16 kg/m^3). The result is quite remarkable, as spruce is known to be one of the most refractory species due to the presence of aspirated pits in the heartwood and small cells [34]. The low uptake of preservatives in the heartwood of stone pine can be considered irrelevant for practical applications due to the high resin content of this tissue, which provides high wood durability (durability class 2 according to EN 350:2016 [35]), making treatment unnecessary, if not absolutely recommended [19]. The uptake measured using the full-cell method with Belocid was not statistically different between stone pine heartwood (230.57 $\pm$ 28.97 kg/m^3) and beech (275.75 $\pm$ 38.15 kg/m^3). It could be assumed that the organic solvent of Belocid dissolves the mostly lipophilic extractives of the stone pine heartwood, favoring the penetration of the preservative solution [19].

The uptake of Belocid in the sapwood of Scots pine and stone pine with the vacuum method was not statistically different (240.28 $\pm$ 25.55 kg/m^3 in Scots pine and 314.40 $\pm$ 9.97 kg/m^3 in stone pine). The same result was observed with the full-cell method because no statistically significant difference was found between the sapwood of Scots pine (418.09 $\pm$ 7.7 kg/m^3) and of stone pine (393.88 $\pm$ 51.42 kg/m^3).

The uptake of water-based Silvanolin (516.91 $\pm$ 45.74 kg/m^3) was not statistically different from the uptake measured in Scots pine (590.34 $\pm$ 11.99 kg/m^3) in sapwood tissue.

Uptake also depends on the chemical agents used for impregnation; however, as the active ingredients are dissolved in the water or in an organic solvent, this does not significantly affect penetration. Samples impregnated with the full-cell method showed the lowest uptake of the preservative solution when Belocid was tested for almost all wood

species. Looking at Italian stone pine sapwood and comparing the different tested preservative products, the statistically significant lower uptake compared to the one of Scots pine was found in samples treated with Montax 50 and full-cell method (450.53 ± 52.36 kg/m^3 with stone pine sapwood and 565.25 ± 8.55 kg/m^3 with Scots pine sapwood). This clearly shows that the permeability of the two pine species using vacuum and full-cell method was comparable except for the samples treated with Montax 50, which showed a better penetration in Scots pine.

Table 1. Influence of the wood species and impregnation method on the uptake of three preservative solutions and Tukey's significant difference among the mean uptake values for each of the preservative products utilized. Mean values that share the same upper-case letter are not statistically different.

Preservative Solution	Wood Species	Treatment Method				
		Soaking			Vacuum	Full-Cell
		Immersion Time, min				
		15	60	480		
		Solution Uptake kg/m^3, (St.dev)				
Belocid	Scots pine	44.58 ^{AG} (7.52)	58.18 ^{ADG} (8.94)	59.89 ^{ADG} (10.4)	240.28 ^{BF} (25.55)	418.09 ^{C} (7.7)
	Spruce	8.38 ^{A} (2.15)	9.17 ^{A} (1.44)	12.71 ^{A} (2.96)	31.97 ^{AG} (18.59)	189.33 ^{BE} (104.02)
	Beech	22.71 ^{AG} (7.39)	23.02 ^{AG} (2.54)	32.57 ^{AG} (7.77)	126.01 ^{DEH} (34.4)	275.75 ^{F} (38.15)
	Stone pine sapwood	81.22 ^{ADG} (58.01)	76.94 ^{ADG} (21.16)	95.98 ^{GH} (21.8)	314.40 ^{F} (9.97)	393.88 ^{C} (51.42)
	Stone pine heartwood	/	/	/	/	230.57 ^{BF} (28.97)
Silvanolin	Scots pine	35.58 ^{A} (3.24)	47.82 ^{A} (3.19)	84.21 ^{A} (7.58)	370.87 ^{BD} (29.55)	590.34 ^{C} (11.99)
	Spruce	13.62 ^{A} (1.93)	25.16 ^{A} (5.45)	50.45 ^{A} (8.36)	109.42 ^{A} (59.4)	391.50 ^{BE} (134.16)
	Beech	26.40 ^{A} (5.05)	44.11 ^{A} (5.11)	94.01 ^{A} (22.82)	281.86 ^{BD} (81.19)	565.92 ^{C} (30.31)
	Stone pine sapwood	52.63 ^{A} (39.83)	33.50 ^{A} (7.17)	254.60 ^{DF} (116.31)	395.94 ^{BE} (30.74)	516.9 ^{CE} (45.74)
	Stone pine heartwood	/	/	/	/	290.58 ^{BF} (182.06)
Montax 50	Scots pine	39.06 ^{A} (4.91)	55.20 ^{AF} (6.62)	93.02 ^{AEF} (9.2)	358.82 ^{B} (36.55)	565.25 ^{C} (8.55)
	Spruce	14.91 ^{A} (2.29)	23.62 ^{A} (3.75)	46.96 ^{AF} (8.4)	47.93 ^{AF} (7.31)	258.76 ^{D} (66.27)
	Beech	13.62 ^{A} (1.93)	31.24 ^{A} (3.88)	70.36 ^{AF} (4.5)	175.73 ^{DEG} (61.38)	504.29 ^{CI} (32.04)
	Stone pine sapwood	51.67 ^{AH} (29.97)	128.36 ^{FGH} (10.46)	95.34 ^{AG} (39.06)	403.17 ^{BJ} (19.57)	450.53 ^{IJ} (52.36)
	Stone pine heartwood	/	/	/	/	186.07 ^{DEG} (133.45)

3.2. The Soaking Method

The results for the soaking method are presented in Table 1. The soaking method did not produce a statistically significant difference between the values in almost all wood species soaked for 15, 60, and 480 min and in each biocide. The exception is stone pine sapwood, which showed as a rule a higher uptake compared to the other species. It can be assumed that the higher uptake of stone pine sapwood, when the soaking method is used, is a consequence of its porous structure, as already supposed when water is used as

solvent [19]. Moreover, considering the sole Belocid, stone pine sapwood soaked for 480 min showed values of uptake not different from the statistical point of view, from beech treated with the vacuum method. Stone pine sapwood soaked for 480 min in Silvanolin showed an uptake evidently higher (254.60 ± 116.31 kg/m^3) and not statistically different from that of Scots pine and beech treated with the vacuum method (respectively, 370.87 ± 29.55 and 281.86 ± 81.19 kg/m^3). Of note, the result showed a very high variability in uptake (cf. standard deviation) that might have been responsible for a lack in statistical difference in the obtained values. It can be assumed that the higher uptake may have been due to a high sensitivity to the ethanolamine component of Silvanolin of stone pine wood. Ethanolamine is a wood-swelling agent that allows for better penetration of copper-based wood preservatives [31,32].

Figure 1 shows the radial and tangential penetration of Silvanolin in the different wood species and the applied impregnation method. In general, the penetration depth increased with a longer immersion time. It is expected that the vacuum and the empty-cell method lead to a better penetration, which is comparable with the results of the Silvanolin uptake presented before. The higher the uptake, the higher the penetration. Therefore, the highest uptake and penetration were found in the samples impregnated with the full-cell method. This was because the Silvanolin penetrates the entire sapwood cross-section of stone pine. Such a pronounced penetration was only found in the sapwood of stone pine in the case of full-cell and vacuum treatment. However, the sapwood of Scots pine was only fully penetrated in the full-cell method. For the different immersion times, the penetration depth in the sapwood of stone pine increased after 480 min of immersion (3.70 mm) compared to 60 min of immersion (1.30 mm). In beech, spruce, and Scots pine, the penetration depths of Silvanolin after 480 min of immersion were 0.88 mm, 0.85 mm, and 1.30 mm, respectively. On the other hand, comparable penetration was achieved on the sapwood of stone pine after 60 min. The penetration data are consistent with the uptake data, and the results prove that stone pine sapwood is very permeable and copper-ethanolamine systems such as Silvanolin are an excellent choice for treatment.

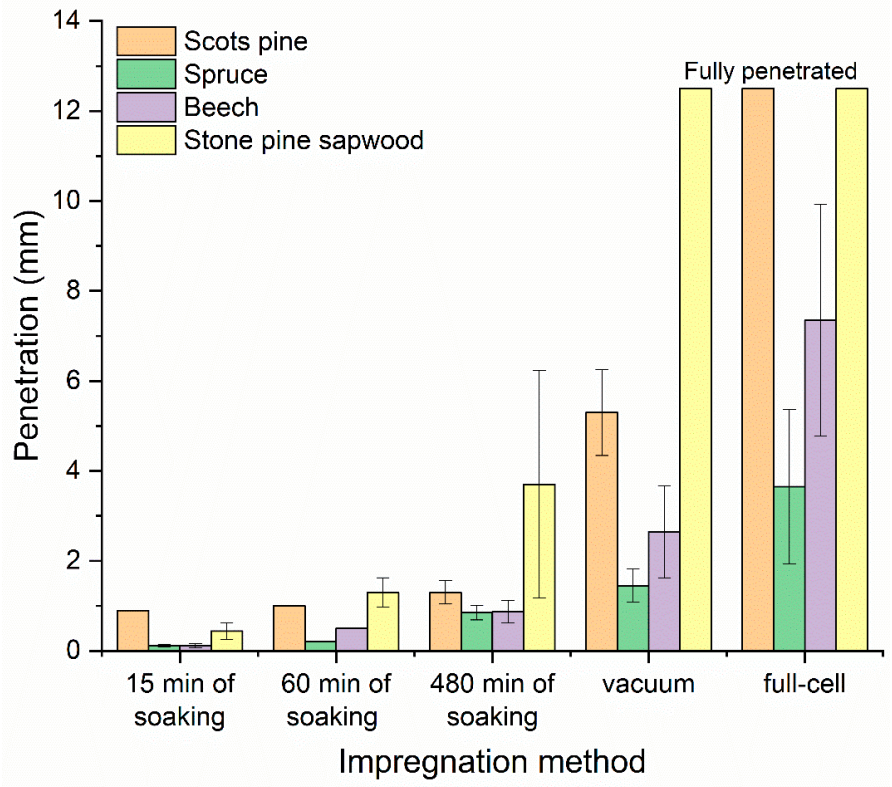


Figure 1. Radial and tangential penetration of Silvanolin preservative solution for the different impregnation methods.

3.3. The Thermal Modification

The effectiveness of thermal modification of stone pine wood was evaluated by mass loss, which is considered a reliable index for predicting the increased decay resistance of wood and a predictor of mechanical resistance [36]. Thermal modification causes first holocellulose and then lignin degradation. Holocellulose is the primary nutritional substrate for various rot fungi and is responsible for the hygroscopic behavior of wood [37]. As a result of degradation, we observed a decrease in the oxygen/carbon (O/C) ratio in wood caused by the formation of carbonaceous materials [38]. At the highest temperature, the degradation of lignin compounds is also involved [39]. Figure 2 shows the different colors of wood species for untreated wood and for each treatment temperature (180, 195, 210, 220, and 240 °C). All wood species became darker and browner with increasing temperature. Even at lower treatment temperatures, Stone pine's heartwood showed significant stains caused by the resin exudates (column D in Figure 2). Darker woods of tropical species were always considered prestigious and luxurious goods. However, due to the decreased availability of tropical species, as well as to the restrictions introduced in their trade, heat-treated wood can be considered a valuable alternative to be appreciated by the consumers [40,41].



Figure 2. Thermally modified samples: Scots pine (**A**), beech (**B**), stone pine sapwood (**C**), stone pine heartwood (**D**).

As an example, it is possible to state that as the temperature rises, there is a pronounced decrease in the L* component (Figure 3). Comparing Figures 2 and 3, it is evident that the greater the darkening, the lower the L* coordinate value. The decreasing rate of the L* coordinate in stone pine sapwood was comparable to the control species, while in stone pine heartwood, the abrupt decrease in L* was more evident already at the lower temperature.

Table 2 shows the percentage of mass loss for each wood species and each maximum treatment temperature. The sapwood and heartwood of stone pine were compared with beech and Scots pine wood. The higher the treatment temperature, the higher the percentage of mass loss. At 180 °C, the heartwood of stone pine showed a mass loss of 9.67 ± 2.84%, the highest among the wood species considered. There were no previous studies on the thermal modification of stone pine heartwood. It is known that the final performances depend on the heating protocol. However, Elaieb, et al. [37] showed that Maritime pine and Aleppo pine release terpenoids during heating, such as hexanal, beta-pinene, camphene, nonanal, isobornyl acetate, caryophyllene, humulene, and caryophyllene oxide, which were identified as predominant compounds. Due to the high resin content in pine wood, it is assumed that the behavior is similar to the results obtained by Elaieb, et al. [37],

and the higher decrease in mass is to be attributed to the volatilization of the resin. In the case of stone pine, no comparison can be made with our investigation as there are no previous studies, only Corsican pine (*Pinus nigra* subsp. *laricio* (Poir.) Maire) wood was studied in Italy [42]. In the case of beech wood, other authors using a different thermal modification treatment observed a lower mass loss than in our study [43], and it is not possible to establish a reliable comparison. Under the most severe heating conditions (above 200 °C), hemicellulose decomposition with acetic acid production and the presence of initial lignin degradation products such as vanillin and guaiacylacetone can be assumed in pines, which are also present in other Mediterranean pines [37]. These compounds have also been detected in Corsican Pine by Py-GC/MS [44]. Up to 220 °C, the sapwood of stone pine showed comparable values for mass loss as that of Scots pine. At a temperature of 240 °C, the sapwood of stone pine showed a higher mass loss (19.56 ± 2.30%) than that of Scots pine (15.75 ± 1.57%).

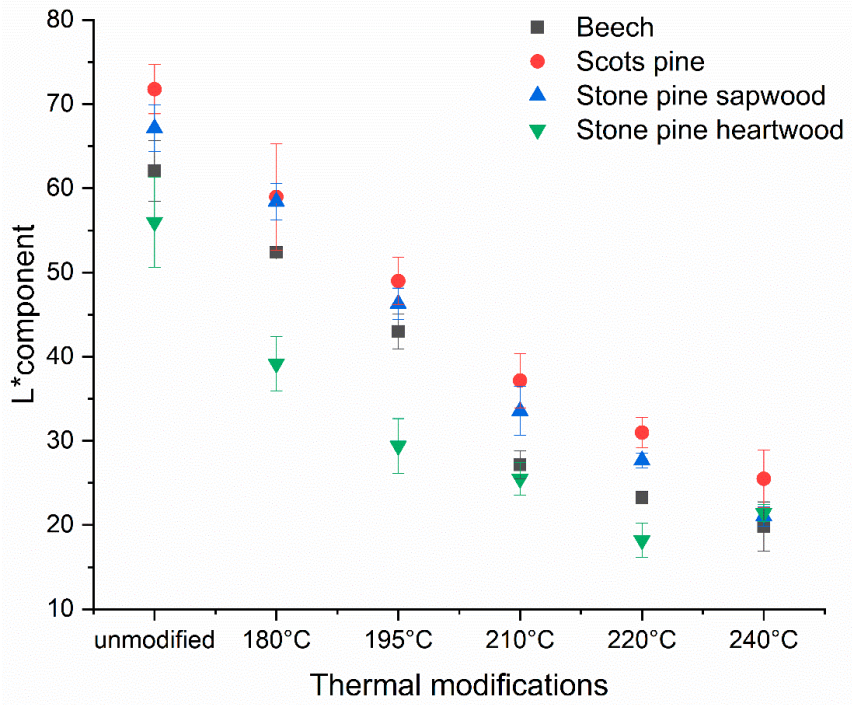


Figure 3. Correlation between thermal modification temperature and color change, considering only the L* coordinate for each species.

Table 2. Wood mass loss for the different temperatures and different wood species, and Tukey's significant difference among the mean values. Mean values that share the same letter are not statistically different.

Maximum Treatment Temperature	Wood Species and Mass Loss in %, (St.dev)			
	Beech	Scots Pine	Stone Pine Sapwood	Stone Pine Heartwood
180 °C	1.35 ^{A} (0.08)	1.33 ^{A} (0.10)	1.34 ^{A} (0.20)	9.67 ^{BE} (2.84)
195 °C	3.37 ^{A} (0.38)	2.95 ^{A} (0.20)	2.99 ^{A} (0.38)	15.03 ^{C} (3.99)
210 °C	10.73 ^{BG} (1.27)	5.74 ^{D} (0.51)	6.73 ^{DF} (0.77)	16.70 ^{C} (1.40)
220 °C	11.47 ^{B} (0.74)	8.67 ^{EF} (0.51)	9.06 ^{EG} (0.50)	20.60 ^{H} (6.42)
240 °C	26.27 ^{I} (1.93)	15.75 ^{C} (1.57)	19.56 ^{H} (2.30)	24.86 ^{I} (0.97)

Further details emerged from the analysis of the mass increase of the thermally modified samples when continuously exposed to an atmosphere of high (98 ± 2%) relative humidity (Figure 4A–E). As described in detail in the literature [36,45], the hygroscopicity of all wood species decreased continuously with the increase of the maximum treatment temperature. The heartwood of the stone pine showed the lowest hygroscopicity, except for the modification at 210 °C, where it showed the same hygroscopicity of beech wood. The resin exudations, discontinuously covering the stone pine heartwood with a mostly water-repellent layer (Figure 2), explain its lower hygroscopicity. The results are consistent with the high hydrophobic behavior of stone pine heartwood found by De Angelis, et al. [19]. Remarkably, the sorption behavior of stone pine sapwood was comparable to that of Scots pine, except for the treatments at 180 and 195 °C, where their sorption curve did not exactly coincide. The curves overlapped perfectly at the treatment temperatures of 210, 220, and 240 °C.

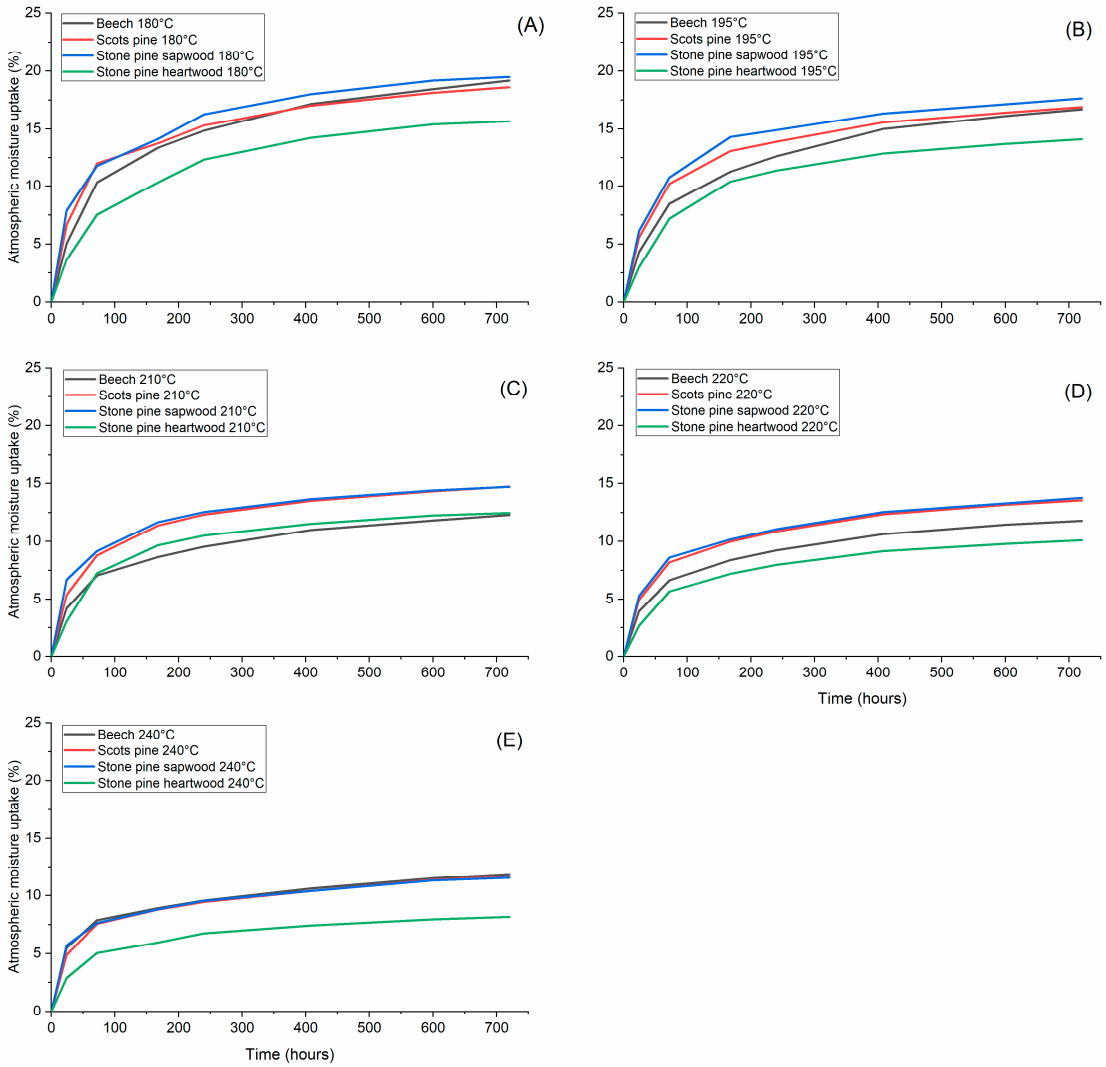


Figure 4. Relationship between maximum heat treatment temperatures and water absorption from ambient air for samples placed above water in a glass chamber (RH = 98% ± 2%): 180 °C (**A**), 195 °C (**B**), 210 °C (**C**), 220 °C (**D**), 240 °C (**E**).

The comparison between the physical parameters after heat treatments makes the sapwood of stone pine an interesting material that has no specific disadvantages compared to the sapwood of Scots pine.

4. Conclusions

Our investigation showed that the stone pine in Italy is to be regarded as a species of short supply chain, one that has interesting end uses, especially when there is a rapid and considerable availability of wood due to sudden extreme climatic events and pests. Considering the physical predisposition to the impregnation treatments of the sapwood, which is evident already with the soaking methods and in particular with Silvanolin, stone pine sapwood is an eligible candidate as a species for outdoor use. The heartwood of stone pine is not suitable for biocide treatment, as biocides' uptake does not reach recommended levels, even with the full-cell pressure process.

As far as a treatment to increase durability is concerned, the sapwood of Italian stone pine can be compared to the sapwood of Scots pine. When treated by soaking, stone pine achieves a higher uptake with a longer immersion time and a similar behavior as the Scots pine at 60 min. The lower uptake occurred with a solution based on organic solvents, while a solution based on copper-ethanolamine showed a good impregnation efficacy.

Heat-treated stone pine wood becomes less hygroscopic, and the decrease in hygroscopicity is more pronounced with increasing temperature. The heat-treated sapwood of Scots pine and stone pine showed comparable hygroscopicity. Heat-treated stone pine heartwood showed resin exudations, which might not be appreciated by the customers. However, treatment of the heartwood of stone pine both by heat or impregnation is of less importance for outdoor end use, and the resin can form a shell that prevents the penetration of pathogens and increases hydrophobicity of the material. The favorable market acceptance of darker wood products, such as the stone pine sapwood, is an alternative to the use of tropical species that are traded for their appreciated color. This favors the use of alternative and higher-value purposes. In conclusion, even if by physical response to treatments, stone pine sapwood is comparable to Scots pine sapwood, further investigations are needed to compare durability and mechanical performances after impregnation and heath treatments to obtain a complete result.

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