December 2010 *ISSN : 0974 - 7486* *Volume 6 Issue 4*

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 6(4), 2010 [212-223]

Adsorption of pinosylvin onto different species of fresh and stored wood

Ildiko Mohammed-Ziegler[1,2*#], Allan Holmgren[2], Willis Forsling[2], Maine Ranheimer[2]
[1]Hemercy KKT, H-2521 Csolnok, Arany J.u. 28., (HUNGARY)
[2]Lulea University of Technology, Division of Chemistry, SE-97187 Lulea, (SWEDEN)
#Gedeon Richter Plc., H-2510 Dorog (HUNGARY)
E-mail : mohazihu@yahoo.com

Received: 14th May, 2010 ; Accepted: 24th May, 2010

ABSTRACT

The adsorption of pinosylvin- a natural antifungal agent - on wood was studied by Raman microprobe technique. The adsorption properties of twelve different European wood species were compared. The effect of solvents used, heat treatment, and prolonged storage of the samples on pinosylvin adsorption ability was analysed by means of the Raman intensity ratios of characteristic lines. It was found that the surface concentration of pinosylvin increased when the Lewis acidity of the solvent increased. Besides, adsorption of pinosylvin was less efficient on during prolonged storage the surface of wood became more hydrophobic after prolonged sample storage. In case of heat treatment (120°C, 3 h) no remarkable effect on the amount of adsorbed pinosylvin was observed. Simultaneously, the intensity of the fluorescence background increases. Moreover, the possible influence of B.E.T. specific surface area and lignin content (described by the kappa-value) on the amount of adsorbed pinosylvin was investigated. As revealed, B.E.T. specific surface area did not vary significantly between the different wood species, and therefore it has no significant effect on the efficiency of pinosylvin adsorption. However, the surface concentration of pinosylvin seems to increas with the lignin content. The amount of solvent residue in each sample was measured by diffuse reflectance infrared Fourier transform (DRIFT) technique. For a few wood samples (e.g. pine heartwood, ash, and Hungarian oak) UV-Raman scattering was used to characterize the aromatic components of these wood species. The morphology of the samples was investigated with the aid of scanning electron microscopy (SEM) images. Furthermore, the B.E.T. specific surface area was found not to vary significantly between the different wood species, and therefore it has no significant effect on the efficiency of pinosylvin adsorption. However, the surface concentration of pinosylvin seems to increas with the lignin content. DRIFT spectroscopy was found to be useful to detect solvent residue in the wood samples and the evaporation of polar solvents is a rather slow process. However, it was not possible to detect adsorbed pinosylvin by DRIFT measurements, due to the low concentration and the lack of characteristic frequencies differing from other wood constituents.

KEYWORDS

Pinosylvin;
Adsorption;
Raman microscope;
DRIFTS;
SEM.

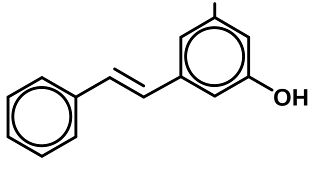
INTRODUCTION

It is known that different kind of trees contain extractives which have fungicidal / fungistatic effect[1-3]. Pinosylvin (see Scheme 1) and its derivatives are natural fungicidal components of the heartwood of some pine trees, e. g. Scots pine (*Pinus sylvestris L.*)[2-4]. Therefore it would be desirable to apply pinosylvin for protection of wood against fungal infections.

In a previous work about the adsorption properties of wood components, pinosylvin and some polyhydroxybenzene derivatives were studied[5]. It was shown that by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements that the hydroxyl bending modes in the adsorbates were affected by adsorption, indicating hydrogen bonding to be responsible for the interaction between the adsorbate and the substrate surface. This experience is in agreement with the results of other authors[8,9], claiming that adsorption to the hydroxyl groups of different wood polymer components explain well their sorption characteristics. To the best of our knowledge only a few publications have appeared in the literature discussing the problems of adsorption on wood or its constituents (e. g.[6-8,10]).

Yellow pine and Scots pine represent two species of the well-known pine trees classified as softwoods and a third species of that type is Douglas fir. Oak and apple woods are popular materials used in the furniture industry. These are classified as hardwoods. Oak, ash and some other hard trees are suitable materials for barrels since the vessels in the heartwood are closed by a special tissue, the so called tylosis[2] and therefore impermeable to liquids.

In this study twelve different species of wood were examined with respect to their sorption properties using pinosylvin as adsorbate. Furthermore, the dependence of the pinosylvin sorption on solvent, prolonged storage of the wood, and heat treatment was investigated.



Scheme 1 : Chemical structure of pinosylvin

EXPERIMENTAL

Sample preparation

Pinosylvin solutions were prepared using acetonitrile, acetone, diethyl ether and chloroform. The concentration was 3.5×10^{-3} mol/l. Since pinosylvin is insoluble in water, only organic solvents could be used for the experiments. The chosen solvents represent various polarity, both protic and aprotic types are tested. After weighing, the different kind of wood slices were placed in separate tight-fitting tubes. Then pinosylvin solutions were added to each sample, maintaining the relation 10^{-2} g of wood in 4 ml of solution. The samples were thoroughly mixed by shaking for 3 days allowing the pinosylvin to adsorb onto the wood structure. Then the wood samples were separated from the solutions and air dried for at least 1 week. The Raman spectra of the samples were recorded without further sample treatment. The heat treated samples were kept at 120°C for 3 hours before the adsorption process.

For the DRIFTS measurements the samples were frozen in liquid nitrogen and ground together with KBr (5 mass-% of wood) in a Retsch Mixer Mill MM 200 using a 10 ml stainless steel jar. Spectra of the powderized samples were recorded.

The kappa-value measurements were carried out according to a standard procedure[29].

Instrumental methods

The Raman microprobe measurements were performed on a Renishaw 2000 Raman microprobe system which includes an Olympus BHSM microscope. The samples were excited by a 20mW diode laser with the excitation wavelength of 782 nm. Data were collected using a 50x objective and a resolution of 4 cm^{-1} in the wave number region between 3100 and 400 cm^{-1}. 256 scans were accumulated to achieve a good signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

The UV-Raman spectra were recorded at the Renishaw laboratory in Gloucestershire, England. The samples were examined using a Renishaw Raman System 1000. UV optimized optic components were used to give high throughput and good signal to noise spectra. Spectra were obtained using a HeCd-laser operating at 325 nm. The spectrometer was equipped with a

UV-enhanced CCD camera and the collection optic was a 40X objective. A laser output of 30 mW was used, which resulted in a maximum incident power at the sample of approximately 4 mW. In order to avoid damage of the sample through heating by the laser beam, the laser power on the sample was reduced to 1 mW and the samples were spun while the spectra were collected.

The DRIFT spectra were recorded by a Perkin Elmer System 2000 FT-IR instrument equipped with a Perkin Elmer Diffuse Reflection Accessory. For each sample 128 scans were accumulated and spectra were calculated relative to a KBr background. The Kubelka-Munk transformation of spectra was performed by the Perkin Elmer Spectrum Lite software.

The B.E.T. specific surface area was measured with a Micrometrics ASAP 2010 instrument. The measurements were carried out by allowing nitrogen to adsorb onto the samples at 150°C and five different pressures were used.

The scanning electron microscopy (SEM) images were acquired with a Cam Scan instrument at 5, 10 or 15 kV with a working distance of 5 mm. The samples were coated with gold to obtain sufficient conductivity.

Chemicals and materials

Pinosylvin (>99%) was obtained from Umeå, Department of Forest Genetics and Plant Physiology, SLU. Acetone (pro analysi) was from BDH AnalaR. Acetonitrile (Uvasol®, >99.5%), diethyleter (SeccoSolv®, >99.5%), chloroform (pro analysi) and potassium bromide (pro analysi) were purchased from Merck.

The following wood samples, that can be read more about in Ref[40], were examined with respect to adsorption properties: (a) samples stored for 8 years (from England): Yellow pine (*Pinus ponderosa*), apple wood (*Malus sylvestris*), Hornbeam (*Carpinus betulus L.),* Douglas fir (*Psendotsuga menziesii* [*Mirbel*] *Franco*), lime *(Tilia platyphyllos Scop.*, large-leafed lime) and Hungarian oak (Q*uercus frainetto Ten.*, from Hungary). (b) Fresh wood samples (from Southern Sweden) represented by English oak *(Quercus robur L.*), Norway maple *(Acer platonoides L.*), common hazel (*Corylus avellana L.*), common ash (*Fraximus excelsior L.*), common alder *(Alnus glutinosa L. Gaertn.*) and Scots pine *(Pinus sylvestris L.*, from Northern Sweden). These types of fresh wood samples have also been the subject of other investigations[16-18,41,42].

All of the used wood samples represent typical European species. Pine is the most popular raw material among wood types. It is used in the architecture, to produce windows and doors, and to prepare furnitures or to tile floor and wall. Oak wood is hard, and it is used for architecture, windows and doors, for boats, and indoor for furnitures or to tile floor and wall. Ash, maple, apple and alder are popular typically in the furniture industry. Lime is used mainly for carving.

RESULTS AND DISCUSSION

In the Raman spectrum of wood lignin exhibits a characteristic stretching vibration at 1604±2 cm^{-1} (Figure 1, see e.g. Refs[11,12]). The observed minor deviation from this frequency (±2 cm^{-1}) is due to the structural differences between the various wood types. Another Raman line occurs at 1664±2 cm^{-1}. This line was assigned to the overlapping signals of hexenuronic acid[13], the stretching mode of conjugated α,β double bonds in lignin[11,14], and glucuromannan (a hemicellulose component)[15]. This assignment is supported by the fact that the intensity of the peak at 1664 cm^{-1} relative to the intensity at 1604 cm^{-1} increases after heat treatment since uronic acids are the products of oxidative degradation of polysaccharides[2].

Pure pinosylvin has two intensive peaks at 1635 and 1597 cm^{-1}, assigned to ν(C-C) stretching vibra-

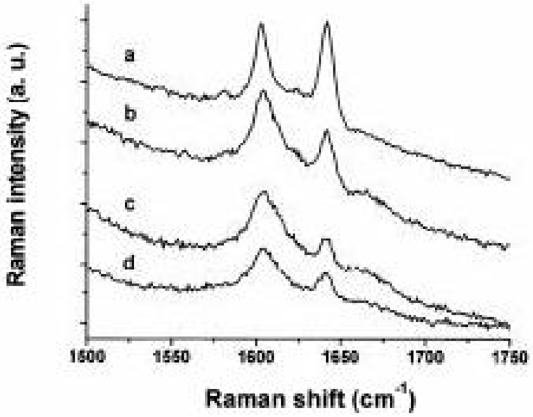


Figure 1 : Raman spectra of fresh Swedish oak samples after treatment with different pinosylvin solutions (a) chloroform (off set for clarity); (b) diethyl ether; (c) acetone; (d) acetonitrile (off set for clarity)

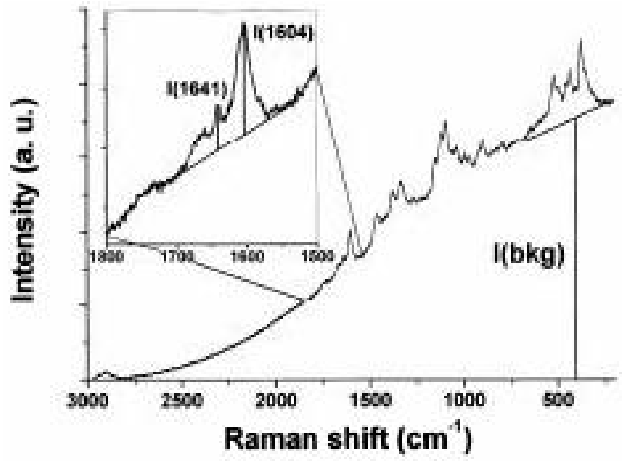


Figure 2 : Definition of the reading of I(1604), I(1641) and I(bkg) intensities illustrated on the Raman spectrum of hornbeam treated with acetone solution of pinosylvin

TABLE 1 : Ratio of the background intensity expressed as R(%)=I(1604)*100/I(bkg) for the treated air dried wood samples stored for 8 years

Solvent	Yellow pine	Apple wood	Hornbeam	Douglas fir	Lime	Hungarian oak
Untreat.	3.25	6.66	10.58	3.56	3.54	7.85
CH_3CN	2.99	8.71	5.42	4.08	2.69	16.47
Acetone	10.20	5.88	6.18	4.68	20.79	27.19
Ether	2.36	6.12	12.92	4.18	9.01	17.18
Chlorof.	2.17	6.52	6.65	2.11	3.03	13.98
Ext.an[a]	3.16	21.03	4.47	7.58	8.21	15.63
Ext.ac[b]	3.30	16.69	7.52	7.28	8.67	13.41

[a] **"Ext. an" means extraction with acetonitrile, blank experiment;**
[b] **"Ext. ac" means extraction with acetone, blank experiment**

TABLE 2 : Ratio of the background intensity expressed as R(%)=I(1604)*100/I(bkg) for the treated samples stored for 8 years, treated with pinosylvin after heat treatment

Solvent	Yellow pine	Apple wood	Hornbeam	Douglas fir	Lime	Hungarian oak
CH_3CN	2.55	5.30	9.12	5.25	5.97	20.58
Acetone	2.86	7.38	8.00	3.22	6.57	11.62
Ether	4.67	9.05	5.04	5.82	2.55	13.10
$CHCl_3$	1.77	3.72	8.56	2.93	8.58	22.41

TABLE 3 : Ratio of the background intensity expressed as R(%) = I(1604)*100/I(bkg) for the treated fresh (wet) wood samples

Solvent	English oak	Norway maple	Hazel	Ash	Alder
CH_3CN	5.67	3.31	15.48	6.55	10.53
Acetone	8.64	6.64	7.18	19.91	20.27
Ether	7.62	6.07	9.88	29.17	34.54
$CHCl_3$	8.53	6.07	3.60	32.01	12.60

TABLE 4 : Ratio of the background intensity expressed as R(%)=I(1604)*100/I(bkg) for the treated, air dried wood samples, without long storage

Solvent	English oak	Norway maple	Hazel	Ash	Alder	Scots pine sapwood
Untreat.	7.80	3.09	6.20	22.02	48.77	2.32
CH_3CN	26.52	10.10	27.16	11.68	29.34	1.09
Acetone	68.13	16.98	37.94	15.15	38.97	1.72
Ether	69.10	8.69	4.83	13.18	30.34	3.35
$CHCl_3$	26.43	8.37	2.92	7.69	12.39	5.22

TABLE 5 : Intensity ratios for the treated wood samples, treated with pinosylvin after heat treatment, without long storage

Solvent	English oak	Norway maple	Hazel	Ash	Alder	Scots pine sapwood
CH_3CN	12.70	5.36	5.79	12.77	35.46	2.89
Acetone	21.53	11.52	6.20	12.13	30.15	3.40
Ether	18.56	11.52	7.68	27.12	6.28	3.98
$CHCl_3$	3.39	4.54	13.70	10.82	18.61	9.85

tions of the aromatic rings[12,16-18]. These two lines shift to around 1641 and 1604 cm^{-1}, respectively, when pinosylvin is adsorbed in the wood structure[5,19]. The intensity of the lignin peak at 1664 cm^{-1} is close to the stretching mode of the double bond of pinosylvin and is rather weak making it hard to detect at high fluorescence intensity. This fluorescence is probably due to emission caused by small amounts of elements like iron. In case of pure pinosylvin no fluorescence was detected.

The fluorescence of the samples also affects the intensity of the 1641 cm^{-1} line. At a high fluorescence background the absorption intensity at 1641 cm^{-1} tends to be lower. Because of that the intensity ratio I(1641)/I(1604), which we have used as a semi-quantitive measure of pinosylvin adsorption (for explanation see Figure 2), will be slightly underestimated. As a measure of the relative influence of the fluorescence background the ratio I(1604)*100/I(bkg) is shown in TABLES 1-5 (see also Figure 2). A higher value of this ratio implies a lower value of I(1641)/I(1604) i.e. a larger underestimation of the amount of adsorbed pinosylvin. Notice that the figures in TABLES 1-5 are given in %.

To measure the surface concentration of pinosylvin exactly is also difficult because pinosylvin is not evenly distributed on the surface of the wood sample. It has been shown that pinosylvin tends to be attached to the lignin rather than to cellulose fibers[5]. Moreover, the intensity of the aforementioned lines changes with the measurement parameters, e. g. focusing, intensity of the exciting beam, etc. Additionally, the penetration of the exciting laser beam depends on the wavelength of the beam. Therefore, the intensity ratio I(1641)/I(1604) seems to be a convenient way to obtain information about the relative amount of adsorbed pinosylvin.

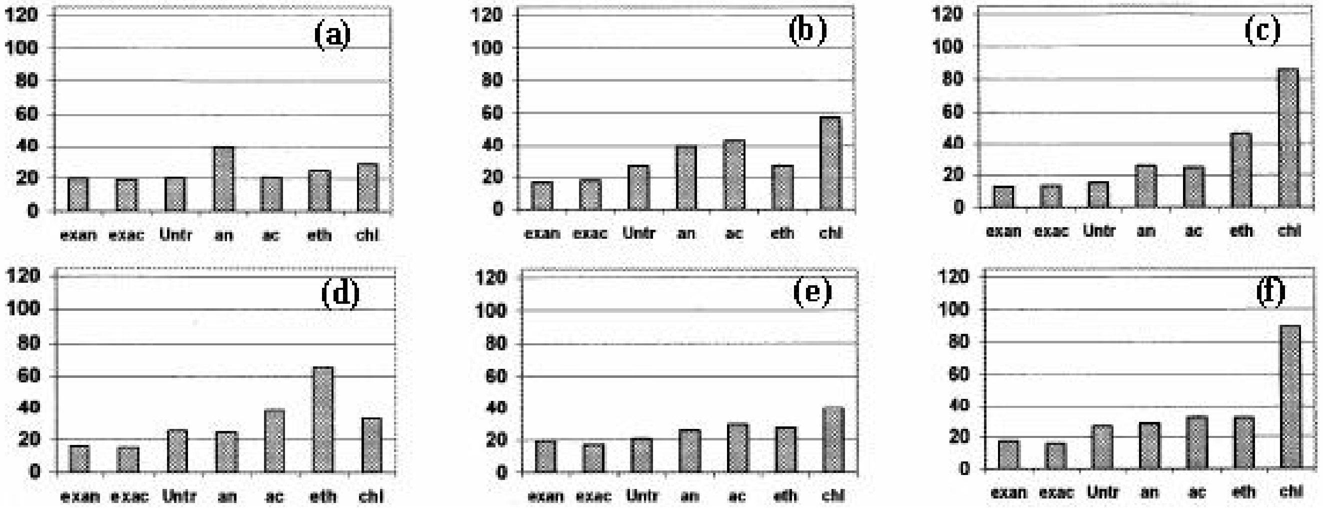


Figure 3 : I(1641)/I(1604) intensity ratios for the treated, air dried wood samples stored for 8 years; (a) Yellow pine; (b) Apple wood; (c) Hornbeam; (d) Douglas fir; (e) Lime; (f) Hungarian oak. Abbreviations: exan = extracted with acetonitrile, blank experiment; exac = extracted with acetone, blank experiment; Untr = untreated wood sample; an = acetonitrile; ac = acetone; eth = ether; chl = chloroform

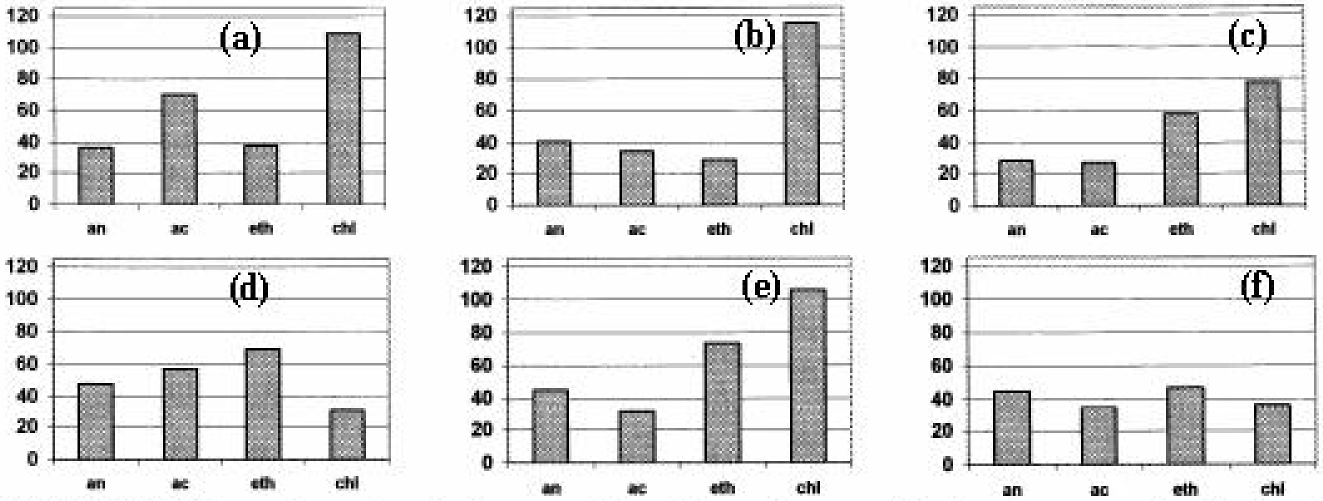


Figure 4 : I(1641)/I(1604) intensity ratios for the treated wood samples stored for 8 years, treated with pinosylvin after heat treatment; (a) Yellow pine; (b) Apple wood; (c) Hornbeam; (d) Douglas fir; (e) Lime; (d) Hungarian oak. Abbreviations: an = acetonitrile; ac = acetone; eth = ether; chl = chloroform

It has to be noted that every wood type has its characteristic extractive content and composition. Besides, the content and composition of the extractives in a given wood type may vary within specimens depending on the circumstences under which the tree grow (composition of soil, alteration of temperature, quantity of rain, etc.)[2,3]. Thus, the effect of extractives and the dissolution of extractives during the treatment was tested, as shown in figure 3. As can be seen, the observed ratios remained unchanged after extraction with pure acetone or acetonitrile in the case of yellow pine and lime. However, in the case of apple wood, hornbeam; douglas fir; and Hungarian oak, the ratios became somewhat lower.

Moreover, the morphology of the tree has to be considered. The use of 50X magnification objective results in the measurement being carried out on an area of about 2μm × 2μm and the difference in the chemical composition between spots might be significant. Therefore in this study only average values of intensity ratios from three different spots are presented (Figures 3-7).

The characteristic Raman bands of lignin and pinosylvin are either located close to each other or overlapping (Figures 1 and 2). The ratios I(1641)/I(1604) and I(1604)*100/I(bkg) can vary between certain values. The lowest value is obtained by the intensities of lignin peaks of untreated wood. Since the concentration and the composition of lignin depend on the type of wood as well as on environmental influences, data for each sample are presented separately. In the case of untreated Scots pine heartwood the ratio I(1641)/I(1604)=89.2 and the I(1604)*100/I(bkg) ratio is 3.63% (The intensity of the background fluorescence is taken at 405 cm^{-1}). The corresponding ratios for pure pinosylvin are 164 (the maximum value of I(1641)/I(1604)) and 0.16%, respectively.

In general, the highest pinosylvin concentration of the samples is obtained after the treatment with chloroform solution. Solutions of acetonitrile and diethyl ether both result in about the same degree of pinosylvin adsorption. The weakest adsorption was observed after treatment with the acetone solution.

The polarity of the solvents might be responsible for the different adsorption properties. Solvent polarity can be quantified in many different ways. For further considerations the permittivity and Reichard's E_T^N values of the solvents are presented in TABLE 6[20,21]. The data indicate that the pinosylvin adsorption does not increase with the polarity of the solvent. However, the solvents used have different hydrogen bonding abilities[21,22]. In TABLE 6, the Dago-Wayland E and C parameters are also presented, where the E parameter measures the strength of electrostatic bonding and the C parameter measures the strength of covalent bonding. From these data it is clear that aceton, acetonitrile and diethyl ether are Lewis bases, but chloroform is a Lewis acid. This indicates that the formation of hydrogen bonds plays an important role in the adsorption process. This experience is also in agreement with our earlier results obtained from IR data[5].

TABLE 6 : The polarity of the applied solvents quantified by the permittivity, Reichard's E_T^N polarity scale and Drago's E and C parameters

Solvent	Permittivity at 20°C[21]	E_T^N[22]	E[22,23]	C[22,23]
Acetonitrile	37.5	0.460	0.886	1.34
Acetone	20.7 (25°C)	0.355	0.937	2.33
Diethyl ether	4.335	0.117	0.936	3.25
Chloroform	4.806	0.259	3.02	0.17
Water	78.54	1.000	1.64	0.57

Shen et al. investigated the Lewis acid-base properties of pine wood by contact angle[23], X-ray photoelectron spectroscopy[24] and FT-Raman spectroscopy measurements[25]. It was found that the surface of pine is more basic than acidic, although the bulk wood is largely acidic (pH≈4.18). The reason is that some functional groups at the surface of the wood react under air

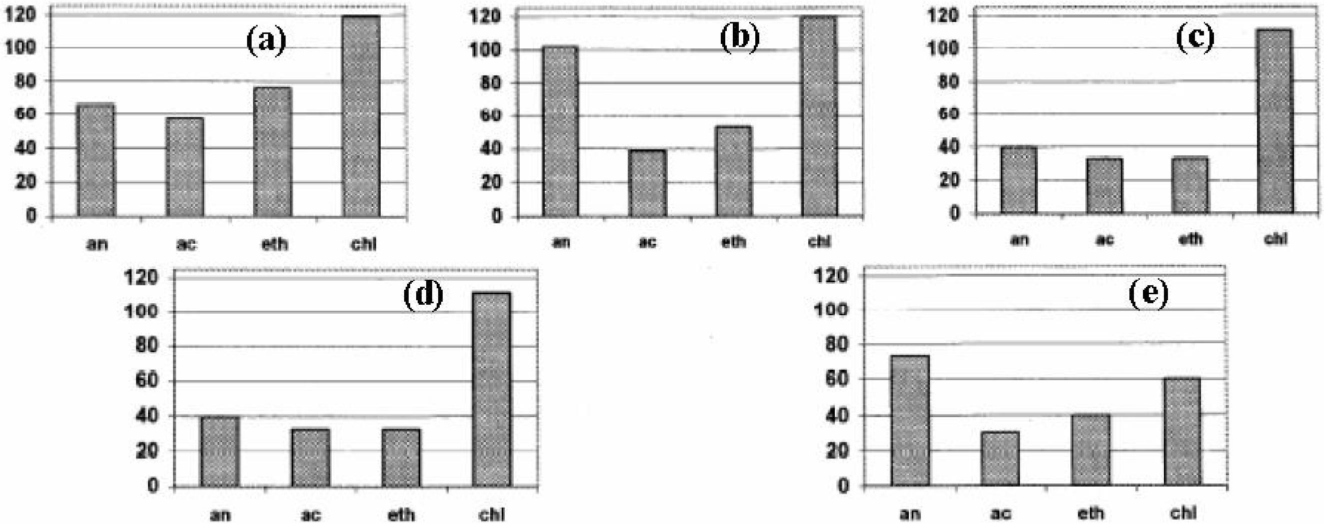


Figure 5 : I(1641)/I(1604) intensity ratios for the treated fresh (wet) wood samples: (a) English oak; (b) Norway maple; (c) Hazel; (d) Ash; (e) Alder. Abbreviations: an = acetonitrile; ac = acetone; eth = ether; chl = chloroform

conditions (oxidizing of some functional groups). The basic character is favorable for the adsorption of pinosylvin since its phenolic hydroxyl groups exhibit acidic properties.

As known from the literature, prolonged wood storage has a remarkable effect on the composition of extractives. The content of lipophilic compounds decreases and the composition changes. The most remarkable effect is the formation of fatty acids from glycerides. Both autooxidative and enzymatic processes take place; oxygen attacks unsaturated sites and generates free radicals. These reactions are substantially faster when the wood is stored in the form of chips instead of logs[2].

TABLE 7 : B.E.T. specific surface area, kappa-value and dry content of the samples

Wood	B. E. T. (N_2)[m^2/g]	K-value	Dry content [(w/w) %]
Yellow pine	0.62	◊	◊
Apple	0.42	◊	◊
Horn beam	0.24	◊	◊
Douglas fir	0.79	◊	◊
Lime	0.47	◊	◊
Hungarian oak	0.29	15.87	95.27^{a})
English oak	0.19	10.32	71.62^{b})/ 95.11^{a})
Norway maple	0.24	12.99	77.21^{b})/ 95.82^{a})
Hazel	0.86	22.9	69.10^{b})/ 96.00^{a})
Ash	0.53	17.79	82.35^{b})/ 95.32^{a})
Alder	0.98	20.14	67.69^{b})/ 95.18^{a})
Scots pine sapw.	0.53	6.07	95.22^{a})
Scots pine heart.	0.56	6.44	94.93^{a})

◊ These values could not be evaluated because of the lack of sufficient amount of sample; [a]When the samples were air dried; [b]When the samples were freshly cut.

Although the results for our long-term stored samples are not directly comparable with those of fresh ones (since their origins are not identical), the aforementioned phenomenon may explain the tendency of higher pinosylvin surface concentration in the case of air dried wood without long-term storage, particularly after treatment with chloroform solution (Figures 3 and 7). In the case of fresh wood the efficiency of the adsorption process does not show any pronounced tendency. The diagrams given in figures 5 and 6 vary unsystematically between different wood species.

During the pinosylvin treatment extraction is expected to occur. In Figure 3 data is shown representing the effect of acetonitrile and acetone on the intensity ratios. Due to extraction the intensity ratios are slightly lower, whereas the background does not change or slightly increase in intensity (TABLES 3-4).

From our experiments it was observed that the background intensity of the Raman spectra increases slightly with the time i.e. no bleaching effect. This might be due to oxidation of Fe(II) to Fe(III) caused by the laser heating on the probed spot of the sample. The background is also higher at higher lignin contents of the sample. This might be due to the fact that lignin and lignoids are aromatic compounds, which could specificially adsorb iron-containing species or other inorganic compounds.

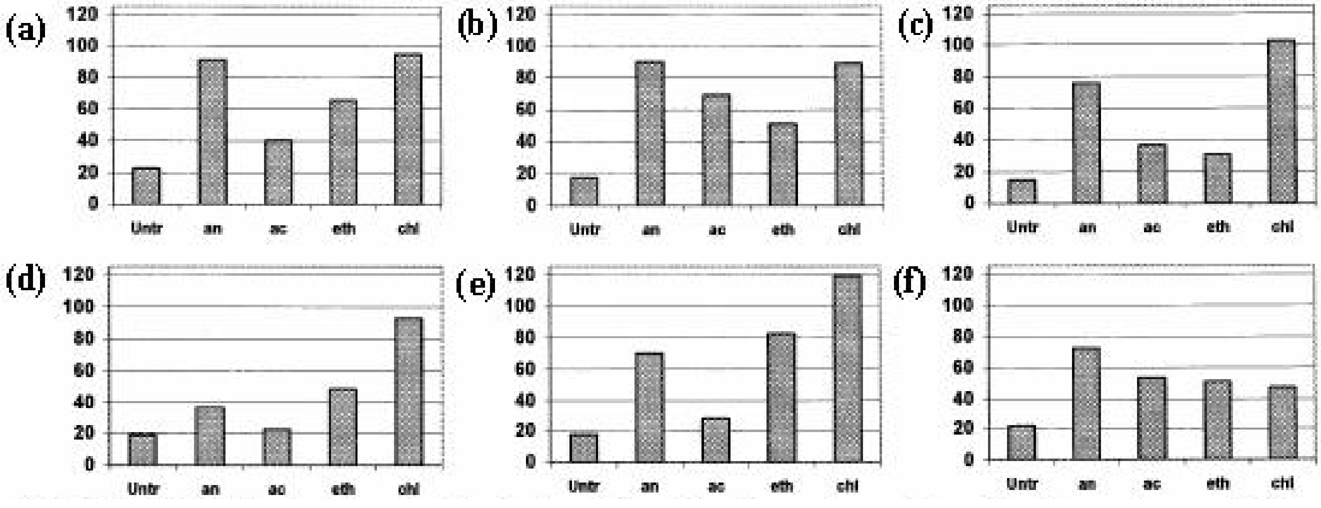


Figure 6 : I(1641)/I(1604) intensity ratios for the treated, air dried wood samples without long storage; (a) English oak; (b) Norway maple; (c) Hazel; (d) Ash; (e) Alder (f) Scots pine sapwood. Abbreviations: Untr = untreated wood sample; an = acetonitrile; ac = acetone; eth = ether; chl = chloroform

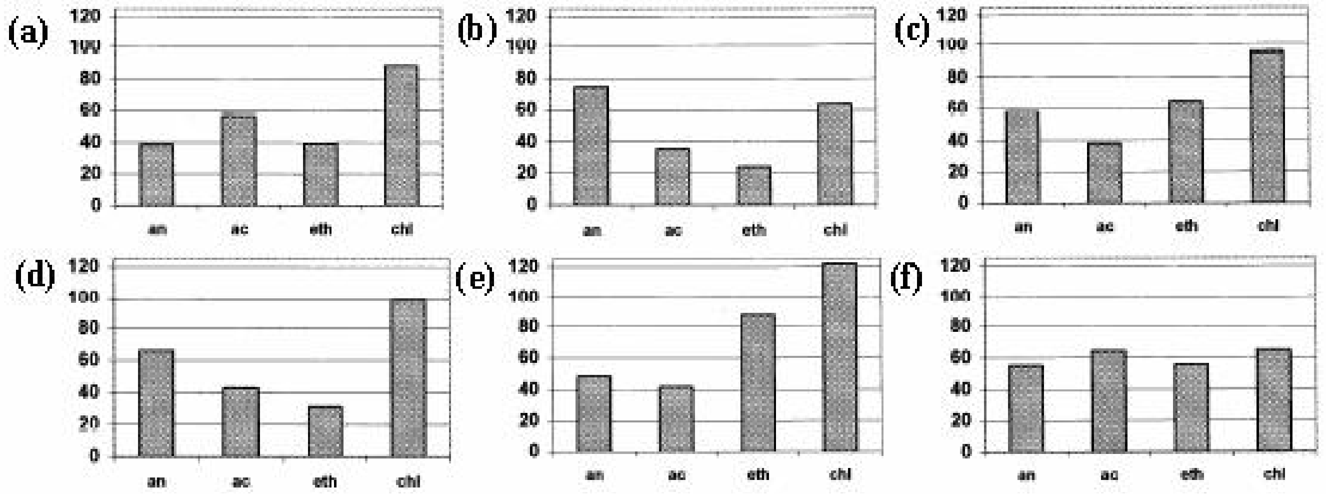


Figure 7 : I(1641)/I(1604) intensity ratios for the treated samples, treated with pinosylvin after heat treatment, without long storage; (a) English oak; (b) Norway maple; (c) Hazel; (d) Ash; (e) Alder (f) Scots pine sapwood. Abbreviations: an = acetonitrile; ac = acetone; eth = ether; chl = chloroform

Furthermore, the background intensity also increases after heat treatment, particularly when the lignin content is relatively high. Simultaneously, the amount of adsorbed pinosylvin increases. The latter observation is probably due to the decomposition of the aromatic components at elevated temperature giving an increased number of adsorbtion sites for pinosylvin. Decomposition of lignin at higher temperatures is supported by other authours, e.g. Canas et al.[26]. They found that in oak and chestnut wood the heat treatment influenced the total content of low molecular weight extractable compounds and that this is due to three factors: 1) cell structure fragmentation and reorganization of the lignocellulose network occur and result in an increase in wood permeability; 2) as a result of the degradation of some wood constituents (such as tannins, lignins, hemicelluloses, cellulose, etc.), the availability of some soluble compounds increases; 3) during heat treatment some specific compound formed, e.g. 5-(hydronxymethyl)furfural or 5-methylfurfural.

Kotilainen et al.[27] studied the changes of chemical composition of Norway spruce (Picea abies) due to heat treatment under different condition (different temperatures, in air or nitrogen atmosphere). In agreement with Fengel and Wegener[28] and many others (e.g.[2,27]). It was found that hemicelluloses are the most heat sensitive components in wood.

The adsorption efficiency varies significantly with the wood species. To achieve a deeper understanding of the factors contributing to this efficiency some other important properties of the wood samples were determined, such as the B. E. T. specific surface area and the kappa–value (see TABLE 7).

The B. E. T. specific surface area is rather low and do not vary significantly between wood species. The low values contributed to a somewhat higher error in

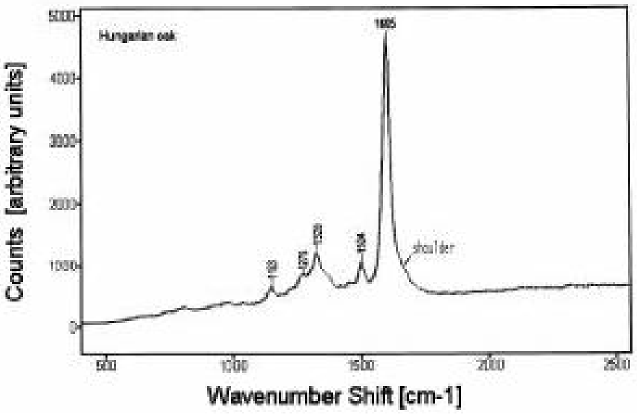


Figure 8 : UV-Raman spectrum of Hungarian oak wood

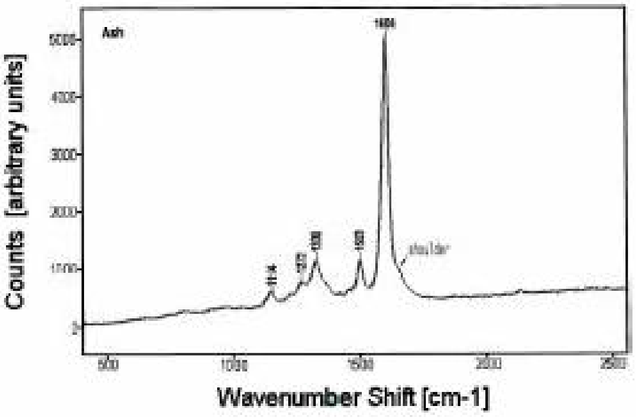


Figure 9 : UV-Raman spectrum of ash wood

the surface area measurements than normal (correlation coefficients ranged between 0.988 and 0.998 in the samples). Moreover, at low specific surface area the measured value depends on the geometry of the sample pieces, which may increase the error of the measurement. Our data indicate, however, that the specific surface area does not directly correlate with the surface concentration of adsorbed pinosylvin.

The kappa-values of the samples are also shown in TABLE 7. The kappa-value of paper, pulp or wood samples is considered as a measure of the lignin content[29]. It must be emphasized that there is no unambiguous function between the kappa-value and the lignin content. The kappa-value depends on the type of the sample and the species of the wood samples since it is based on the measurement of permanganate consumption of the sample[29,30]. Therefore the measurement of lignin content of different plants is also a topic within wood research[30,31]. In spite of these difficulties the kappa-values determined give at least an approximate value of the lignin content of the samples. Although a higher kappa-value did imply a larger amount of adsorbed pinosylvin when chloroform was used as solvent (Figures 3-7) this tendency was less clear than expected. For the other solvents used no such correlation was observed. It rather seems that the choice of solvent is a more important factor. To elucidate the influence of lignin content on the adsorption properties of wood other more exact methods to determine lignin content should be available.

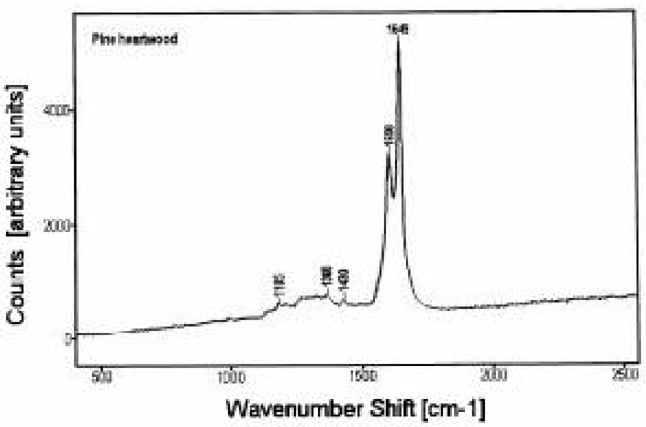


Figure 10 : UV-Raman spectrum of scots pine heartwood

TABLE 8 : UV-Raman spectral data of unstored wood samples

	Lignin band		"HexA band"		Relative intensity= I(HexA)/ I(lignin)
	Location [cm^{-1}]	Intensity [a.u.]	Location [cm^{-1}]	Intensity [a.u.]	
Hungarian oak	1604	4054	1659	392	0.097
English oak	1603	3536	1660	214	0.061
Norway maple	1603	2482	1662	126	0.051
Hazel	1604	1923	1655	118	0.061
Ash	1602	4469	1660	177	0.040
Alder	1604	1709	1653	198	0.116
Scots pine heartwood	1607	2381	1649	4334	1.820

As it was reported[13], the use of the UV-Raman technique serves as an excellent opportunity to measure the lignin content of wood, because of the low fluorescence intensity and the high sensitivity for aromatic signals which is remarkably higher than in Vis-Raman measurements due to the λ^4 dependence of scattered light[13,32]. In consequence of this, the lignin signals are more intensive around 1604 cm^{-1} and the shoulder at 1645 cm^{-1} is clearly visible in the UV-Raman spectra (see Figures 8-9.). As an exception, a strong band occurs at 1649 cm^{-1} in the case of pine wood (Figure 10). As illustrated in figures 8 and 9, the line shape of the UV-Raman spectra of various wood types studied do not differ significantly from each other. However, the shoulder occurring on the aromatic vibration line corresponding to lignin (see Ref.[13]) is assigned to 4-deoxy-4-hexenuronic acid (HexA) as summariezed in TABLE 8. As can be seen from the data, only alder and Scots pine heartwood are characterized by a remarkably higher I(HexA)/I(lignin) ratio. It is probably due to the fact that alder is a dark wood type that means the presence of chromoforic units of higher concentration than in the other onbserved specieses, i.e. higher lignin content. The higher lignin content is also reflected in a higher value of the kappa-number. Scots pine heartwood has not a significantly higher K-number than e.g. sapwood, although it is known to have a high extractive content (see e.g.[2,3,5]) including unsaturated compounds similar to HexA. It is also notable that the aforementioned peak becomes a shoulder in all UV-Raman spectra with exception of the pine heartwood (Figure 10). In the latter case it occurs as a sharp, intense signal exceeding the intensity of the lignin signal at 1608 cm^{-1}. This is also due to the high resin content of the pine heartwood. (It is important to notice that "resin" is often used as a collective name for the lipophilic extractives, mainly diterpenoids (phenolic substances are not included)[2]. Many of them contain double bonds in rings, similar to those of hexeneuronic acids.)

The measurement of the amount of lignin has failed in this study probably because wood samples have relatively high lignin content, whilst the UV/Raman intensity increases linearly with the lignin content in a lower lignin concentration range. Thus, UV-Raman measurements can be succesfully used for the evaluation of residual lignin in pulps characterized by a K-number below ca. 10[13], with the exception of raw wood. Several methods have been developed for the determination of 4-deoxy-4-hexenuronic acid (HexA) in pulp, such as high performance anion-exchange chromatography, UV-spectroscopy, colourimetry[33] and capillary zone electrophoresis[34]. HexAs do not exist in native wood but are formed from polysaccharides via oxidation reaction, particularly under alkaline conditions (e.g. pulping). Therefore the abbreviation "HexA" does not mean unambiguously hexenuronic acid (however, in heat treated samples hexenuronic acid likely to appear). As far as we know Raman spectroscopy features of HexAs have not been reported yet. However, as it was mentioned at the beginning of Results and Discussion, Agarwal and Ralph[15] showed that a peak located at 1664 cm^{-1} occurs in the Raman spectrum of glucuromannan (which is a hemicellulose constituent) and black spruce (*Picea mariana*) lignin produced by two different methods (enzymatic treatment and milling).

The FTIR technique has also been successfully applied for the characterization of aromatic extracts in plants[35-38] and for the approximation of pH in wood[39]. However, it is clear from this study that the DRIFT spectroscopy technique was very useful in order to detect the residual solvent after the wood samples had been treated with the pinosylvin solutions. However, from an inspection of the DRIFT spectra it is not possible to distinguish between adsorbed pinosylvin and other wood constituents. Raman scattering is far better in that respect because of the very characteristic pinosylvin line at 1641 cm^{-1}.

The evaporation of the solvent from the structure of wood is a rather slow process. After three weeks of drying in air strong solvent peaks could be detected in the case of polar solvents viz. at 1700 cm^{-1} (acetone), at 1636 cm^{-1} (acetonitrile) and at about 752 cm^{-1} for chloroform (see figure 11). After three months no solvent peaks or just solvent traces could be detected by the DRIFTS technique.

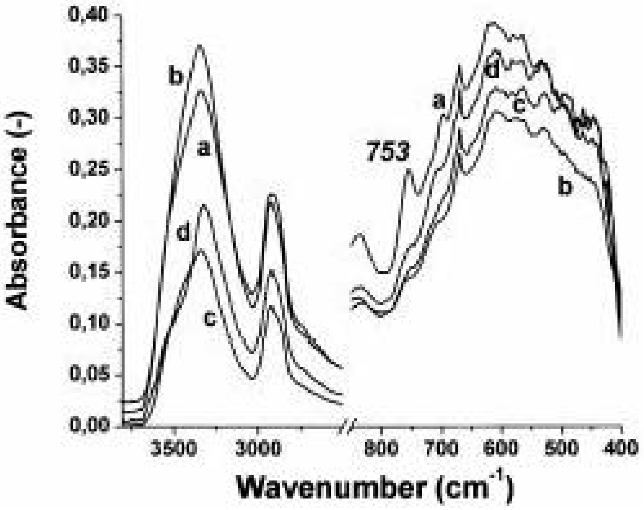


Figure 11 : Kubelka-Munk transformed DRIFTS spectra of fresh alder treated with different pinosylvin solutions (the fingerprint region and the region from 2500 cm^{-1} to 4000 cm^{-1} are shown) (a) chloroform solution; (b) aceton solution; (c) diethyl ether solution; (d) acetonitrile solution; the peak at 753 cm^{-1} originates from chloroform residue

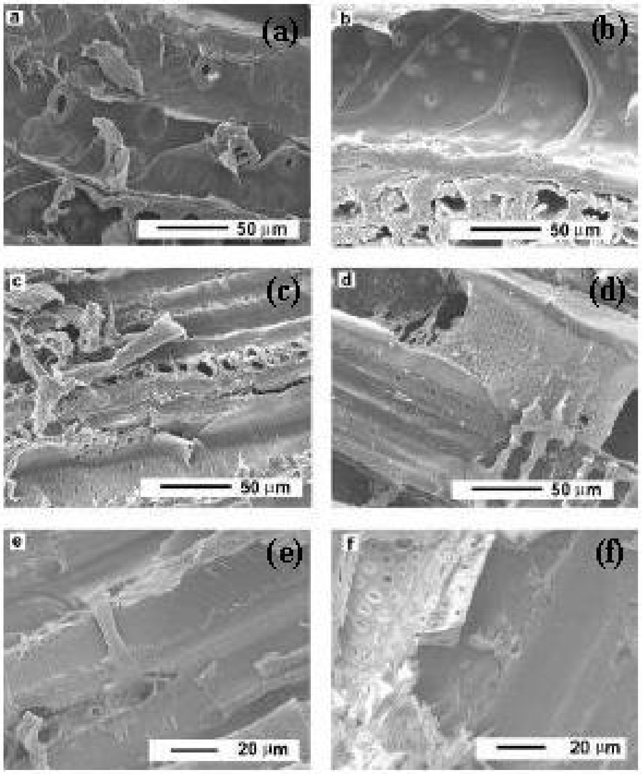


Figure 12 : SEM images of some wood samples (radial view) (a) yellow pine; (b) apple wood; (c) hornbeam; (d) alder; (e) Scots pine sapwood; (f) Hungarian oak

SEM images were acquired to compare the morphology of the different wood samples, since the morphological characteristic of the wood sample was expected to influence the amount of pinosylvin adsorbed. Six images about the radial view of samples are presented in figure 12. Yellow pine and apple wood have looser structure than the other samples. The pore size of the channels of yellow pine is about 5μm, those of Scots pine, alder, English oak, apple wood and lime are 1-2 μm. Hungarian oak, hornbeam and maple exhibit an intermediate pore size, 2-3 μm. The porous size does not reach 1 μm in ash and hazel. The English oak and lime have more dense and rigid structures than the others. Our investigation points to that, in general, a loose structure is favourable for the adsorption due to the more efficient penetration. However, deviations from these general trends are also observed in some cases.

CONCLUSIONS

Effects of solvent used, prolonged wood storage and heat treatment (120°C, 3 h) on adsorption of pinosylvin on twelve different kinds of wood were studied by Vis-Raman microprobe technique. A semi-quantitative approach was introduced by using the characteristic Raman peak ratios.

It was found that the Lewis acid-base properties of the solvent influenced the amount of adsorbed pinosylvin on wood significantly. The surface concentration of pinosylvin increased when the Lewis acidity of the solvent increased. Due to chemical and biochemical reactions during prolonged storage the surface of wood became more hydrophobic and therefore the adsorption of pinosylvin was less efficient. The chemical changes caused by heat treatment (120°C, 3 h) have no large effect on the amount of adsorbed pinosylvin, although the decomposition of hemicelluloses occurs. Simultaneously, the intensity of the fluorescence background increases.

Furthermore, the B.E.T. specific surface area was found not to vary significantly between the different wood species, and therefore it has no significant effect on the efficiency of pinosylvin adsorption. However, the surface concentration of pinosylvin seems to increas with the lignin content, in general. DRIFT spectroscopy was found to be useful to detect solvent residue in the wood samples and the evaporation of polar solvents is a rather slow process. However, it was not possible to detect adsorbed pinosylvin by DRIFT measurements, due to the low concentration and the lack of characteristic frequencies differing from other wood constituents.

ACKNOWLEDGMENTS

The authors express their gratitude to Dr. Annette Zimmermann and Dr. Ian C. Wilcock (Renishaw plc) for performing the UV-Raman measurements and to Mrs. Olga Radetzky-Szekeres for helpful discussions. Special thanks to Mrs. Magdalena Lassinantti for her help acquiring SEM images and to Dr. Lubomira Toscheva for her assistance carrying out B. E. T. specific surface area measurements. I. M.-Z. is grateful for the financial support from the Swedish Institute and the Varga Jozsef Foundation (Budapest University of Technology and Economics).

REFERENCES

[1] M.Aoyama, S.Doi; Mokuzai Gakkaisi, **38(1)**, 101-105 **(1992)**.
[2] E.Sjostrom; 'Wood Chemistry-Fundamentals and Applications', 2nd edition, Academic Press, San Diego, **(1993)**.
[3] G.Svensson; 'Naturliga Forsvarssubstanser i tra-Litteraturstudie 1988', Trätek Institutet för Träteknisk Forskning, Stockholm, **(1988)**.
[4] C.C.Celimene, J.A.Micales, L.Ferge, R.A.Young; Holzforschung, **53**, 491-497 **(1999)**.
[5] I.Mohammed-Ziegler, A.Holmgren, W.Forsling, M.Lindberg, M.Ranheimer; Vibrat.Spectrosc., **36**, 65-72 **(2004)**.
[6] J.F.Manville, J.R.Nault; Appl.Spectrosc., **51(5)**, 721-724 **(1997)**.
[7] F.W.Weaver, N.L.Owen; Appl.Spectrosc., **49(2)**, 171-176 **(1995)**.
[8] A.-M.Olsson, L.Salmen; Carbohydride Res., **339**, 813-818 **(2004)**.
[9] J.Berthold, J.Desbrieres, M.Rinaudo, L.Salmen; Polymer, **35**, 5729-5736 **(1994)**.
[10] J.Ludvík, P.Zuman; Microchem.J., **64**, 15-20 **(2000)**.
[11] M.Kihara, M.Takayama, H.Wariishi, H.Tanaka; Spectrochimica Acta A., **58**, 2213-2221 **(2002)**.
[12] F.Billes, I.Mohammed-Ziegler, A.Holmgren, H.Mikosch; J.Phys.Chem.A., **106(26)**, 6032-6041 **(2002)**.

[13] M.Halttunen, J.Vyorykka, B.Hortling, T.Tamminen, D.Batchelder, A.Zimmermann, T.Vuorinen; Holzforschung, **55(6)**, 631-638 **(2001)**.

[14] A.T.Martinez, G.Almendros, F.J.Gonzalez-Vila, R.Frud; Solid State Nuclear Magnetic Resonance, **15**, 41-48 **(1999)**.

[15] U.P.Agarwal, S.A.Ralph; Appl.Spectrosc., **51(11)**, 1648-1655 **(1997)**.

[16] I.Mohammed-Ziegler; Adsorption of Pinosylvin onto the Structure of Wood - Mechanism and Adsorption Parameters, Licentiate Thesis, Lulea University of Technology, Lulea, Sweden, **(2000)**.

[17] I.Mohammed-Ziegler, A.Holmgren, M.Lindberg, W.Forsling; DRIFT and Raman Microscopic Study of the Adsorption of Pinosylvin onto Paper and Wood, Colloquium Spectroscopicum Internationale XXXI, Ankara, Turkey, September, 5-10, 285 **(1999)**.

[18] I.Mohammed-Ziegler, A.Holmgren, W.Forsling; Paper presented at Adsorption and Nanostructures-From Theory to Application- 3rd International Conference of the Kolloid-Gesellschaft, Budapest, Hungary, September 25-28, P37 **(2000)**.

[19] A.Holmgren, B.Bergström, R.Gref, A.Ericsson; J.Wood Chem.Technol., **19(1,2)**, 139-150 **(1999)**.

[20] D.R.Lide (Ed.); 'CRC Handbook of Chemistry and Physics', 71st Ed., CRC Press; Boca Raton, **(1990)**.

[21] C.Reichardt; 'Solvents and Solvent Effects in Organic Chemistry', 2nd Ed., WCH; Weinheim, **(1990)**.

[22] G.Wulfsberg; 'Principles of Descriptive Inorganic Chemistry', University Science Books, Mill Valley; California, **(1991)**.

[23] Q.Shen, J.Nylund, J.B.Rosenholm; Holzforschung, **52**, 521-529 **(1998)**.

[24] Q.Shen, P.Mikkola, J.B.Rosenholm; Colloids Surf.A., **145**, 235-241 **(1998)**.

[25] Q.Shen, H.Rahiala, J.B.Rosenholm; J.Coll.Interface Sci., **206**, 558-568 **(1998)**.

[26] S.Canas, M.C.Leandro, M.I.Spranger, A.P.Belchior; J.Agric.Food Chem., **47**, 5023-5030 **(1999)**.

[27] R.Kotilainen, R.Alen, V.Arpiaien; Paperi Ja Puu-Paper and Timber, **81(5)**, 384-388 **(1999)**.

[28] I.Fengel, G.Wegener; 'Wood.Chemistry: Ultrastructure, Reactions', de Gruyter; Berlin, **(1989)**.

[29] Scandinavian Pulp, Paper and Board Testing Committee, Kappatal, Svensk Oversattning SCAN-C 1:77 Patent, **(1977)**.

[30] A.Ibrahim, P.B.Oldham, T.E.Conners, T.P.Schultz; Microchem.J., **56**, 393-402 **(1997)**.

[31] C.P.Pappas, A.Tarantilis, M.Polissiou; Appl.Spectrosc., **52(11)**, 1399-1402 **(1998)**.

[32] G.Keresztury, in J.M.Chalmers, P.R.Griffiths (eds); 'Theory in Handbook of Vibrational Spectroscopy', John Wiley and Sons Ltd., Chirchester, **1**, 71-87 **(2002)**.

[33] M.Tenkanen, G.Gellerstedt, T.Vuorinen, A.Teleman, M.Perttula, J.Li, J.Buchert; J.Pulp.Paper Sci., **25(9)**, 306-311 **(1999)**.

[34] A.Rydlund, O.Dahlman; J.High Resol.Chromatography, **20**, 72-76 **(1997)**.

[35] E.-M.A.Ajuong, M.C.Breese; Holz als Roh-und Werkstoff, **56**, 139-142 **(1998)**.

[36] H.Schulz, U.H.Engelhardt, A.Wegent, H.-H.Drews, S.Lapczynski; J.Agric.Food Chem., **47**, 5064-5067 **(1999)**.

[37] J.Rodriguez, O.Faix, H.Pereira; Holzforschung, **52(1)**, 46-50 **(1998)**.

[38] J.C.Silva, B.H.Nielsen, J.Rodriguez, H.Pereira, H.Wellendorf; Holzforschung, **53(6)**, 597-602 **(1998)**.

[39] I.Pappas, P.Rodis, P.A.Tarantilis, M.Polissiou; Appl.Spectrosc., **53(7)**, 805-809 **(1999)**.

[40] A.Mitchell; 'A Field Guide to the Trees of Britain and Northern Europe', Collins, London, **(1974)**.

[41] I.Mohammed-Ziegler, A.Oszlanczi, B.Somfai, Z.Horvolgyi, I.Paszli, A.Holmgren, W.Forsling; J.Adhesion.Sci.Technol., **18(6)**, 687-713 **(2004)**.

[42] I.Mohammed-Ziegler, Gy.Marosi, Sz.Matko, Z.Horvolgyi, A.Toth; Polym.Adv.Technol., **14**, 790-795 **(2003)**.