

Overview on natural dyes and their IR-spectra – Part III: Natural dyes based on wooden materials

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ABSTRACT

This paper on wood originated natural dyes is part III of a review series on natural dyes and their infrared spectra (IR spectra). Currently discussed are samples originated from yellow, red and blue wood of different types and supplied by different companies. Further, it is reported on quebracho wood extracts, dragon palm resin and osage yellow as dye materials. Dye materials from different barks are also considered. IR spectra are recorded from cut wooden pieces, wood powder and extracts. The IR spectra are analyzed and discussed in respect to composition of the samples. Reference measurements are done with different wooden samples gained from different sources. Finally, it is aimed to report spectroscopic data for identification of natural dye materials to support material identification and quality control.

Keywords

wood based dyes,
natural dye,
infrared spectroscopy,
hematoxylin,
brasilin,
sandalwood,
dragon palm,
logwood,
quebracho,
osage yellow

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1 Introduction

Natural dyes find nowadays broad application in food industry or in cosmetics [1-3]. A broad overview on a broad range of different natural dyes is given by H. Schweppe almost 30 years ago [4]. A more recent and as well excellent overview is given by Dominique Cardon in 2007 [5]. However, for textile applications natural dyes can be named as nice-product, because of the strong dominance of synthetic dyes in textile industry [6-8]. Nevertheless, natural dyes can support a valuable concept for a complete bio-based production of textile products, which are after end of use also biodegradable [9,10]. The application of natural dyes on natural fibers can be seen as part of a future with eco-friendly perspective using sustainable products [11, 12]. Additional to coloration, further textile functionalization in the area of antimicrobial properties are reported to be realized by application of recipes containing natural dyes [13-16]. Natural dyes are mostly plant based gained often from annual plants with a short life time [17,18]. In

contrast to this, dyeing components can be also produced from specific types of wood [19,20]. This mostly tropical wood containing dye stuffs in different colors as red, yellow or blue. To realize a sustainable approach, it is of course necessary to use for dye production only wood species which are broadly available. In the current overview on natural dyes based on wooden materials, materials from five different wood species and dragon palm resin are presented and investigated by infrared spectroscopy (IR spectroscopy). This overview is part III of a series on natural dyes and their IR spectra. Part I presents natural dyes based on anthraquinone and naphthoquinone structures, while in part II indigo related dye products are presented [21,22]. The IR spectroscopy is an analytic method well established in the organic chemistry and also used to investigate polymer materials [23-25]. This method is also very valuable for investigation and identification of natural and synthetic fiber materials [26-29]. Also, spectroscopy with near infrared light can be used for dye and fiber identification [30,31]. IR spectroscopy can be used to identify organic dye stuffs and discuss their structural characteristics [32]. By this, it is also possible to identify natural dyes in historical textiles [33,34]. A short review on IR-spectra of several prominent natural dyes is given by Priyadharsini et al. [35]. However, these researchers did not discuss wood based natural dyes. For this, the aim of the current paper is to support an overview on different wooden materials and dye based from them. Wood based materials from different suppliers are investigated. Different types of wood are compared to answering the question, if and how they can be distinguished by IR spectroscopy. Here, also a comparison is made to the IR spectra of different types of conventional wood which are not used for dyeing purposes. The investigated wooden materials are from different forms as cut pieces, powder, bark and extracts, if they are all available. The view on the IR spectra of different forms is done to investigate also the influence of the preparation of the wooden materials on the IR spectrum. Additional to conventional wood, also dragon palm resin is considered in the current overview. The dragon palm tree is form botanical point of view different from conventional trees. However, to support a broad overview and a comparison of different materials, also dragon palm resin is discussed. The reported IR spectroscopic data support people working in quality control or researchers who are interested in spectroscopic identification of natural dyes on textile samples from various sources.

2 Materials and Methods

2.1 Investigated wooden materials and dye extracts

Several wooden materials for dyeing purposes are discussed in the actual study. Also dye extracts from wood are part of this overview. The discussed wood materials can be categorized according to the related coloration – blue wood (logwood), yellow wood and red wood (sandal wood and brazil wood). Please, compare photographs in Figure 1.



Fig. 1 Pieces of different wood materials used in current investigations. Photographic images are presented with higher magnification.

The discussed materials are gained from four different suppliers; Kremer Pigmente GmbH (Aichstetten, Germany), Pflanzenfärbershop (Hückelhoven-Baal, Germany), Das Wollschaf (Zweibrücken, Germany) and Carl Roth GmbH (Karlsruhe, Germany). Further, a log wood extract was gained from the initiative PlanAlto (Mexico) and considered for comparative investigations. The discussed and investigated materials are listed together with short information and the related supplier in Table 1. As references the product web pages of the suppliers are given to support further details on dyeing recipes and work safety. The wood materials are gained as cut pieces or powder. Also, dye extracts and bark material with dyeing capability are considered. Reference investigations are done with wood materials without dyeing capability. As reference materials, fresh collected and dried wood is used. Also, wooden materials gained from the company Modulor (Berlin, Germany) are used for reference measurements. As further reference material tannin powder is considered for comparison to quebracho wood extract (Table 1).

Table 1. Investigated wood materials and dye stuffs.

No.	Content	Form	Supplier	References
W1	Yellow wood	Cut pieces	Kremer	[36]
W2	Yellow wood	Cut pieces	Pflanzenfärbershop	[37]
W3	Blue wood / log wood	Small cut pieces	Kremer	[38]
W4	Blue wood / log wood	Small cut pieces	Pflanzenfärbershop	[39]
W5	Blue wood / log wood	Powder	Pflanzenfärbershop	[40]
W6	Blue wood / log wood	Extract	Pflanzenfärbershop	[41]
W7	Blue wood / log wood	Extract	Wollschaf	[42]
W8	Blue wood / log wood	Extract	PlanAlto	[43]
W9	Hematoxylin / C.I.75290	powder	Carl Roth GmbH	[44]
W10	Red wood, Brazil wood	Cut pieces	Kremer	[45]
W11	Red wood, Brazil wood	Extract	Pflanzenfärbershop	[46]
W12	Red wood, Brazil wood	Extract	Kremer	[47]
W13	Red wood, sandal wood	pieces	Pflanzenfärbershop	[48]
W14	Red wood, sandal wood	powder	Kremer	[49]
W15	Quebracho wood	extract	Pflanzenfärbershop	[50]
W16	Tannin	powder	Kremer	[51]
W17	Dragon palm resin	powder	Pflanzenfärbershop	[52]
W18	Dragon palm resin	powder	Kremer	[53]
W19	Osage Yellow	powder	Kremer	[54]
W20	Buckthorn bark, Frangulae Cortex	Dried pieces	Pflanzenfärbershop	[55]
W21	Buckthorn bark, Frangulae Cortex	Dried pieces	Kremer	[56]
W22	Linden bark, Tiliae Cortex	Dried pieces	Pflanzenfärbershop	[57]
W23	Purple willow bark, Salix Purpures	Dried pieces	Pflanzenfärbershop	[58]
W24	Apple tree bark, apple tree grinded	Dried pieces	Kremer	[59]
WR1	Wood from cherry tree	Reference material	German garden – cut in summer 2022	----
WR2	Wood from mulberry tree	Reference material	German garden – cut in summer 2022	----
WR3	Balsa, wood sheet	Reference material	Modulor	[60]
WR4	Birch, airplane plywood	Reference material	Modulor	[60]
WR5	Beech, rotary veneer, press-dried	Reference material	Modulor	[60]
WR6	Wooden boat deck	Reference material	Modulor	[60]

2.2 Analytical methods

The infrared spectra (IR spectra) of investigated dyes and wooden materials are recorded with a FT-IR spectrometer IRTracer-100 from Shimadzu (Japan) using a Specac Golden Gate ATR unit. Photographic images with enhanced magnification shown in Figure 1 are taken by using a Dino-Lite Premier Digital Microscope.

3 Discussion on wood dyes and their IR spectra

3.1 Reference wood materials

Wood as material is built up by a mixture of several components as e.g. cellulose, hemicellulose, lignin etc. The composition of wood the IR spectra taken from different types of wood are broadly discussed in literature [61-63]. However, to support valuable reference data for the IR spectra of wood, IR spectra are taken from several typical wood materials without dyeing purposes (see Figures 2 and 3). Figure 2 shows the IR spectra of two types of fresh cut wood after drying for four months under ambient conditions. One wood sample is taken from a cherry tree and the other one from a mulberry tree in summer 2022 (Germany). The number and position of signals in both IR spectra are mainly similar, even if these are different types of wood (Figure 2).

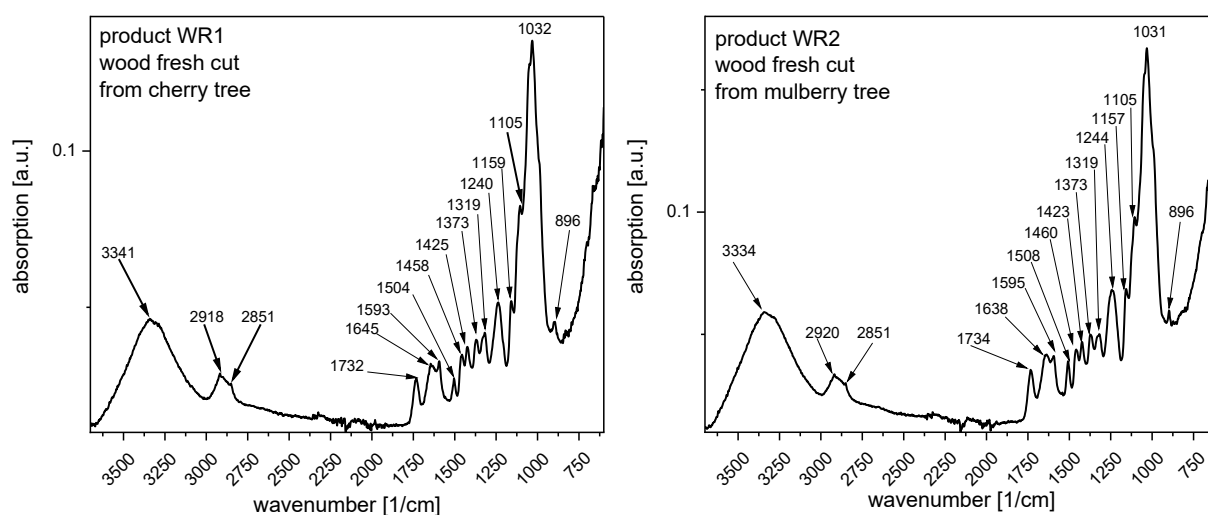


Fig. 2 Comparison of IR spectra of two different types of fresh wood (reference samples WR1 and WR2).

Figure 3 presents IR spectra of different commercially offered types of wood. These spectra are nearly similar to each other, even if they are gained from different wood types. Also, they show a strong similarity to the IR spectra of fresh wood (compare Figures 2 and 3). Only the peak at around 1640 cm^{-1} is for the samples WR3, WR5 and WR6 weaker or only visible as shoulder.

Prominent signals in these IR-spectra can be assigned to the cellulose component in wood. The broad signal around 3333 cm^{-1} is assigned to O-H stretching vibration of hydroxy group and water. The signal around 2900 cm^{-1} is related to C-H stretching vibration of aliphatic units as $-\text{CH}_2-$ and $-\text{CH}_3$ [23,24]. The strongest signal at around 1030 cm^{-1} is related to C-O stretching vibrations of unit present in cellulose and other wood components [61]. All samples exhibit a medium peak around 1734 cm^{-1} which is typical for a C=O stretching vibration of an ester group. However, the mentioned main components of wood like cellulose or lignin do not contain ester groups. It could be estimated that this peak is caused by ester compounds from fatty acids. Fatty acids are found in wood biomass and those compounds are probably a part of energy storage of the tree [64]. The signal around 1640 cm^{-1} can be assigned to C=O stretching vibration of amide groups present in proteins [24]. Especially the fresh cut wood should contain protein. The signal around 1595 cm^{-1} can be assigned to C=O stretching vibration of a ketone group attached to an aromatic ring system and interaction with a hydroxy group by hydrogen bridge bond. By this arrangement the C=O bond is weakened and the related signal is shifted to lower wavenumbers [24].

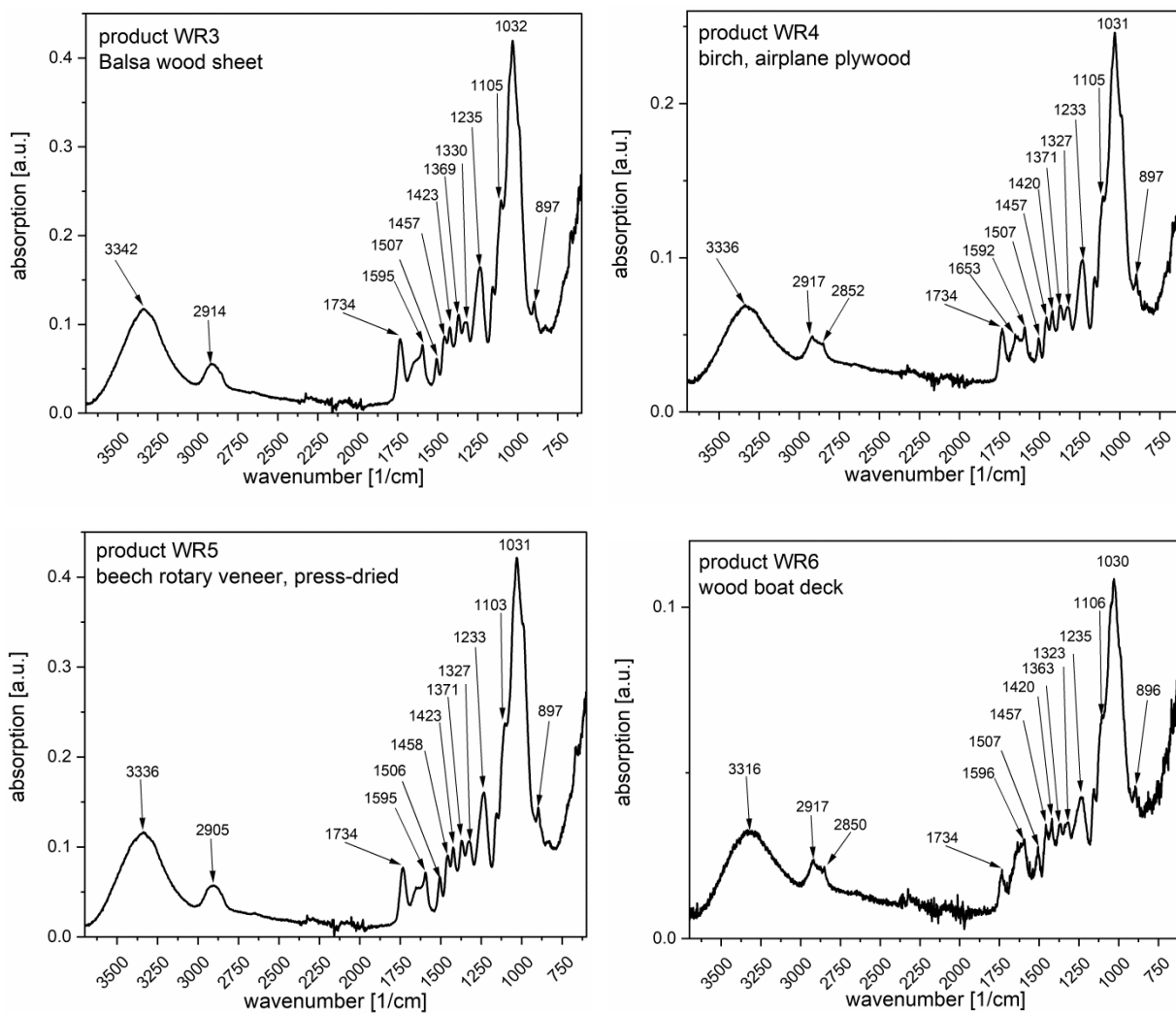


Fig. 3 Comparison of IR spectra of different types of wood (reference samples WR3 to WR6).

3.2 Yellow wood

Yellow wood also named as dyer's mulberry or old fustic (CI Natural Yellow 11). Yellow wood is gained from the heartwood of the tropical tree dyer's mulberry (*Chlorophora tinctorial* or *Maclura tinctoria*) [4,5,36]. One main colored compound of yellow wood is the dye morin. Morin is a dye of flavonoid ground structure (compare Figure 4) [5,65]. In combination with aluminum salts, morin exhibits also fluorescence properties [66].

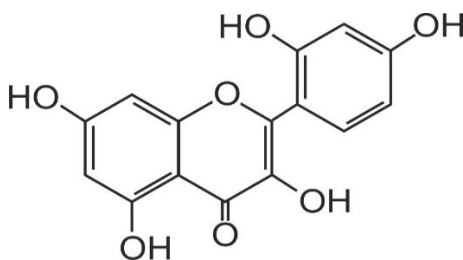


Fig. 4 Chemical structure of Morin dye, as one colored component in yellow wood / old fustic.

The infrared spectra of two samples from yellow wood cut pieces gained from different suppliers are shown in Figure 5. The IR spectra of both yellow wood samples are nearly identical with nine similar peaks in the finger print area of the spectra. The IR spectra of yellow wood are also nearly similar to the spectra of the reference wood materials (Figure 2 and 3). One main difference is that the IR spectra of

yellow wood do not exhibit a signal around 1640 cm^{-1} . Following the arguments above, these yellow wood products contain less content of protein. This fits to a remark in literature that for dyeing purposes the heartwood of old fustic is used [5]. In contrast to wood near to the bark, heartwood should contain lower content of protein. However, the products W1 and W2 exhibit a clear medium signal at 1595 cm^{-1} . This signal can be assigned to the C=O vibration of the ketone group attached to the aromatic ring system of morin. This ketone group is neighbored by two hydroxy groups which may form hydrogen bridge bonds to the ketone group. By this, the C=O bond is weakened at the vibration is shifted to wavenumbers below 1600 cm^{-1} . In summary it can be stated that it is not possible to identify yellow wood by IR spectroscopy and distinguish it clearly from other wood materials. Also, the presence of the dye morin cannot be clearly determined by this spectroscopic method.

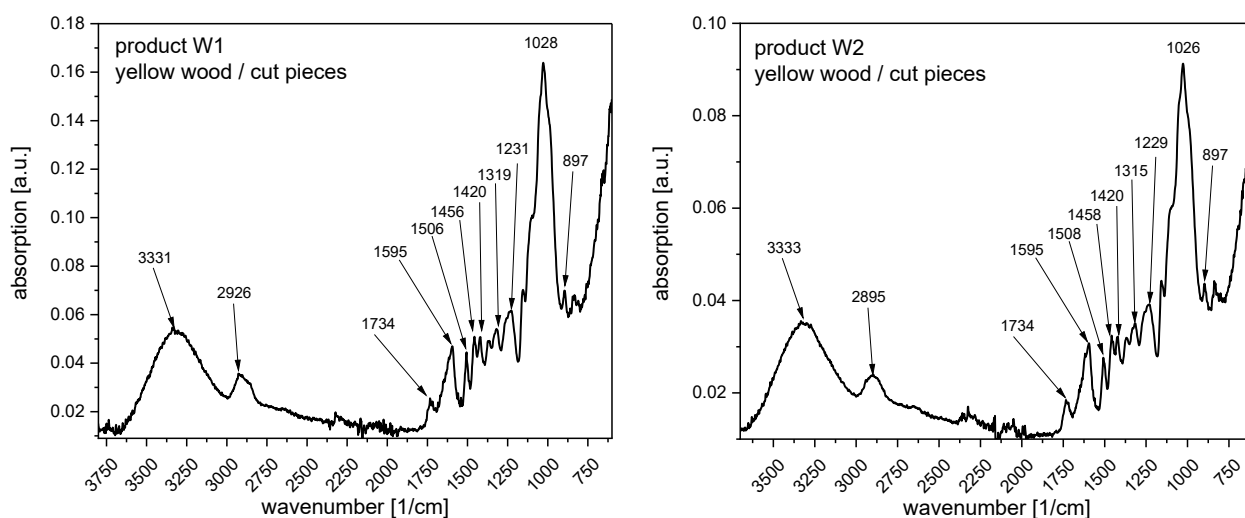


Fig. 5 Comparison of IR spectra of two different samples from yellow wood (sample W1 and W2).

3.3 Blue wood

Logwood as blue colored wood is also named as campeachy wood (*Campechianum Lignum* or *Haematoxylon campechianum L.*) [5,7,67]. This plant is native in Central America and Mexico [5,68]. One component in logwood is hematoxylin $\text{C}_{16}\text{H}_{14}\text{O}_6$ – see also the chemical structure in Figure 6 [69,70]. Hematoxylin belongs to the category of flavonoids and is less colored. After oxidation it is formed into the colored hematein (CI Natural Black 1 and 2) [4,67,71,72]. The dye hematein itself is red colored. However, in combination with iron mordant or aluminum mordant grey or blue coloration are gained [67].

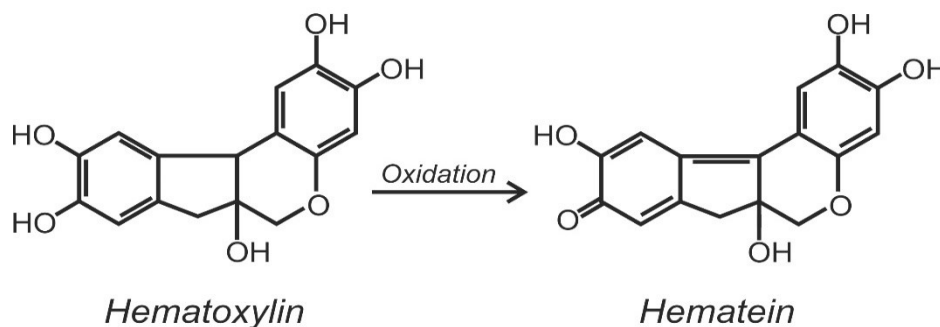


Fig. 6 Chemical structures of colored compounds Hematoxylin and Hematein as components in logwood.

The IR spectra of two logwood cut samples supplied by two different companies are presented in Figure 7. An IR spectrum of a logwood powder is shown in Figure 8. The IR spectra of these samples are nearly identical containing nine typical signals in the fingerprint area of the IR spectra. Main features of the IR spectra of log wood compared to yellow wood are similar, so it is nearly impossible to distinguish these both wood types from each other by IR spectroscopy. For logwood the signal at 778 cm^{-1} is clearer

compared to yellow wood. Further, the signal at 1605 cm^{-1} appears at higher wavenumber compared to the analogous peak for yellow wood appearing at 1595 cm^{-1} . The spectra of logwood pieces presented in Figure 7 exhibit a peak at 2855 cm^{-1} related to C-H stretching vibration. This peak is very weak for the logwood products W3 and W4. For logwood powder W5, instead of the peak at same position a clear shoulder is determined. This different appearance of that signal from wood cut pieces or grinded powder might be explained by the variability in the physical dimensions of the measured materials.

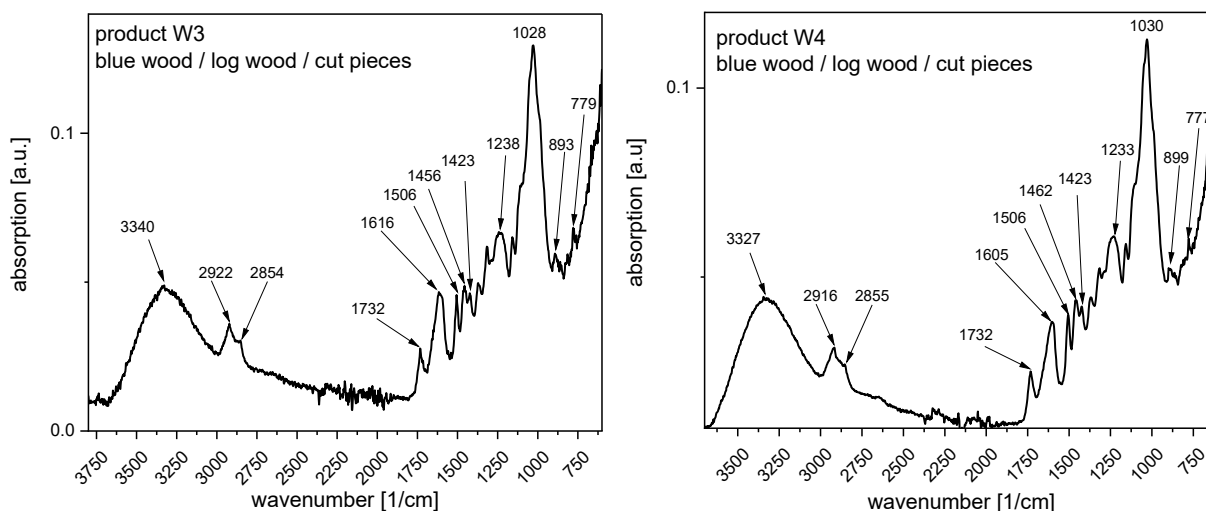


Fig. 7 Comparison of IR spectra of two different samples from blue wood – log wood, cut pieces (samples W3 and W4).

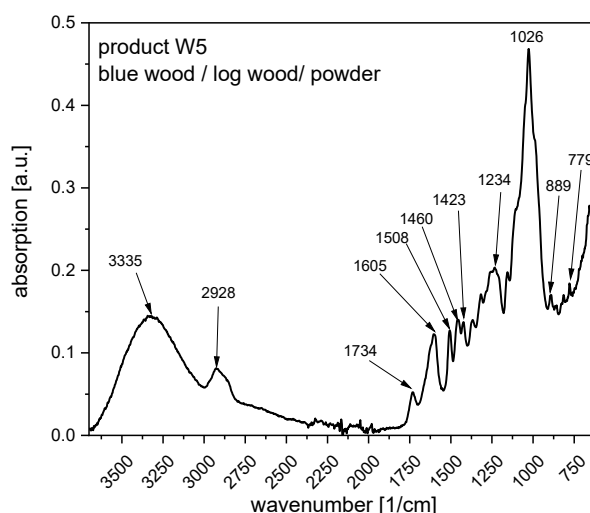


Fig. 8 IR spectra of powder made from blue wood – log wood (sample W5).

Infrared spectra of dye extracts from log wood are presented in Figure 9 and Figure 10. Presented are spectra recorded from two different extracts gained by two different suppliers (Figure 9) and a logwood extract gained from the initiative PlanAlto (Figure 10) [43]. The IR spectra of both extracts W6 and W7 are almost similar to each other with eight analogous signals in the fingerprint area. However, product W7 exhibits an additional shoulder signal at 1700 cm^{-1} which is probable related to a C=O stretching vibration. Because the molecule of Hematoxylin dye does not contain any C=O bond, this signal is obviously caused by Hematin, which is the product from oxidation of Hematoxylin. One significant difference between the spectra of logwood samples (Figure 7 and 8) and the log wood extract (Figure 9) is the medium signal at 1732 cm^{-1} for the wooden samples. This signal is related to a C=O stretching

vibration of an ester group. The component containing this ester group is obviously not soluble in the extraction process and its related signals are not determined for the logwood extract. In the IR spectra of the extracts also the signal around 2940 cm^{-1} is appeared as weak shoulder and by this less prominent to the related signal observed for the cut wood specimen. This signal is related to C-H stretching vibration from compound containing aliphatic units as $-\text{CH}_2-$ or $-\text{CH}_3$. This signal caused by cellulose or lignin in wood is probable more prominent compared to the signals of extracted components, because the colored components Hematoxylin and Hematein do not exhibit aliphatic units. The IR spectrum of the logwood product W8 is in good agreement to the IR spectra of products W6 and W7 (compare Figure 9 and 10). The prominent difference in the IR spectra of all three logwood products is the signal at 1700 cm^{-1} from product W7. This signal is related to a C=O stretching vibration of a component which is probably not part of the dye. The occurrence of such a signal in only one extract product can be explained by the use of different extraction procedures leading the presence of different by-products in the dye product after extraction. All log wood extracts exhibit a clear signal around 1605 cm^{-1} . This signal is reported in literature for hematein at 1602 cm^{-1} and assigned to the C=O stretching vibration of the keto group of this molecule [73]. For this, the presence of oxidized component hematein in the log wood extracts can be verified.

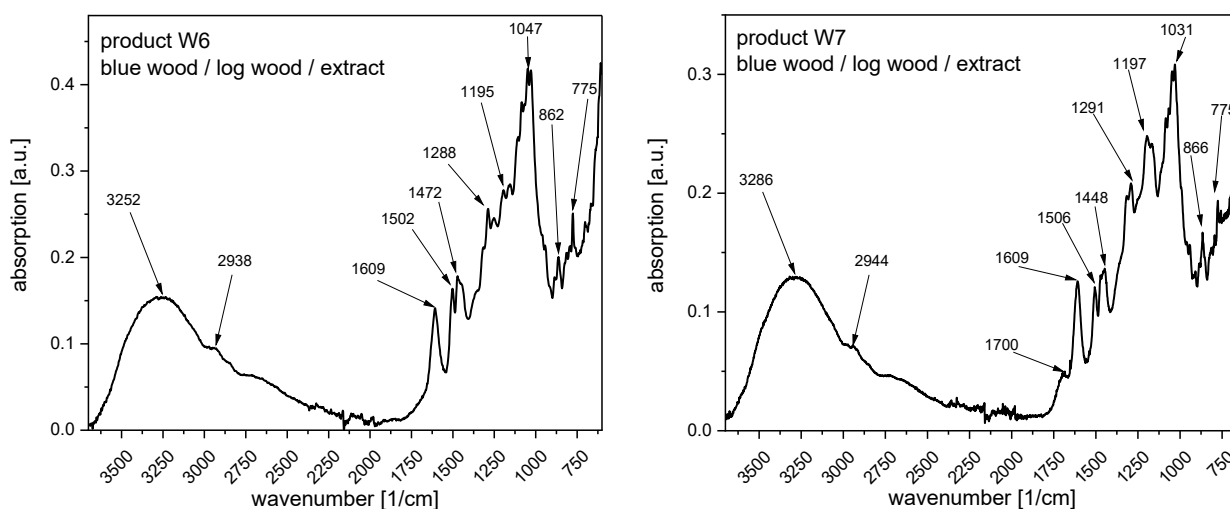


Fig. 9 Comparison of IR spectra of two different extracts from blue wood – log wood (samples W6 and W7).

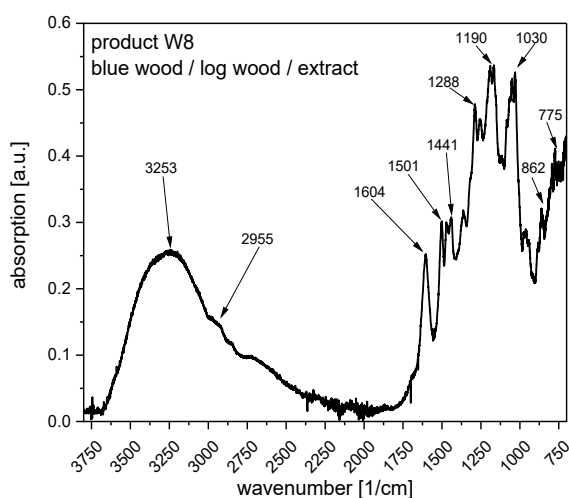


Fig. 10 IR spectrum of an extract from blue wood – log wood (sample W8).

As reference material for the logwood extracts, pure hematoxylin (product W9) is considered. This product W9 is supplied for microscopic use by the chemical supplier Carl Roth and can be assumed to be hematoxylin with certain purity. It is a nearly uncolored yellow powder. The infrared spectrum of product W9 is presented in Figure 11. This infrared spectrum of pure hematoxylin is clearly different from those IR spectra of logwood extracts (compare Figure 11 with Figure 9 and 10). For this it can be stated that the composition of the logwood extracts is clearly different and the extracts contain additional to hematoxylin many other components, which are probably products from different oxidative reactions of hematoxylin. The determined infrared spectrum for hematoxylin (product W9) is quite similar to an IR spectrum reported for hematoxylin in literature, so product W9 can be clearly identified by infrared spectroscopy as hematoxylin [74]. However, an interesting feature of the infrared spectrum of product W9 is the strong signal at 1630 cm^{-1} (Figure 11). A signal in that spectral range should be related to a C=O stretching vibration but the chemical structure of hematoxylin does not exhibit any functional group with a C=O bond. This signal is also reported in literature for hematoxylin. Unfortunately no explanation or assignment is discussed.

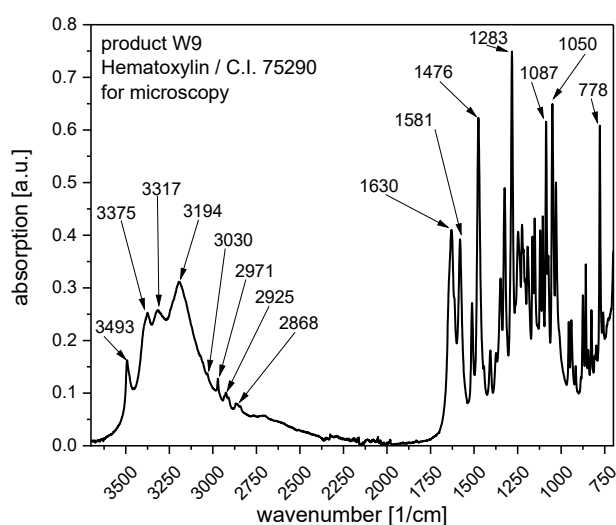


Fig. 11 IR spectrum of hematoxylin (C.I.75290).

3.4 Red wood

In the current overview two different types of red wood are considered – brazilwood and sandalwood [75]. The main colored compound of brazilwood is the dye component brazilin which can be gained from this wood by extraction, e.g. by using water or methanol as solvent [7, 76]. The chemical structure of brazilin is shown in Figure 12. Its structure is quite similar to hematoxylin dye from logwood [5,67,70]. The structural difference between both dyes is an additional hydroxy group at the chromophore of hematoxylin dye acting as auxochromic group. For brazilwood also antibacterial properties are reported [76]. By oxidation of brazilin the colored component brazilein (CI Natural Red 24) is formed (Figure 12) [4,70,78]. It is reported that the further methylation of brazilein improves its color stability against pH changes [79].

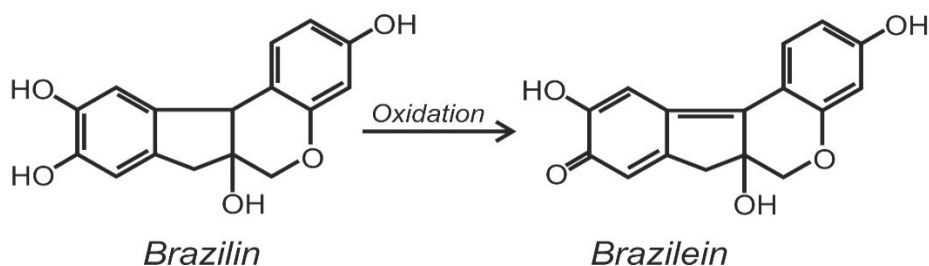


Fig. 12 Chemical structures of the compounds Brazilin and Brazilein as colored components in red Brazil wood.

The infrared spectrum of a brazilwood piece is shown in Figure 13. In contrast to the wood references, the yellow wood and the logwood, for brazilwood a completely different pattern in the fingerprint area of its IR spectrum is determined. For this, brazilwood can be identified and distinguished from other colored wood materials by infrared spectroscopy. Compared to other wooden samples, for brazil wood no signal is determined at 1735 cm^{-1} , only a very small shoulder at 1718 cm^{-1} appears. Lee et al. reported an IR-spectrum of brazilin from a measurement of a dyed silk fabric after subtraction of the infrared spectrum of the silk material [80]. Their reported IR spectrum exhibit a prominent signal at 1609 cm^{-1} , which can be also determined for the actual investigated brazil wood products W10, W11 and W12. This signal could be typical for these products and is probable related to the C=O stretching vibration of the keto group at the aromatic ring system. By this, the presence of the oxidized component brazilin is verified for the investigated brasil wood products.

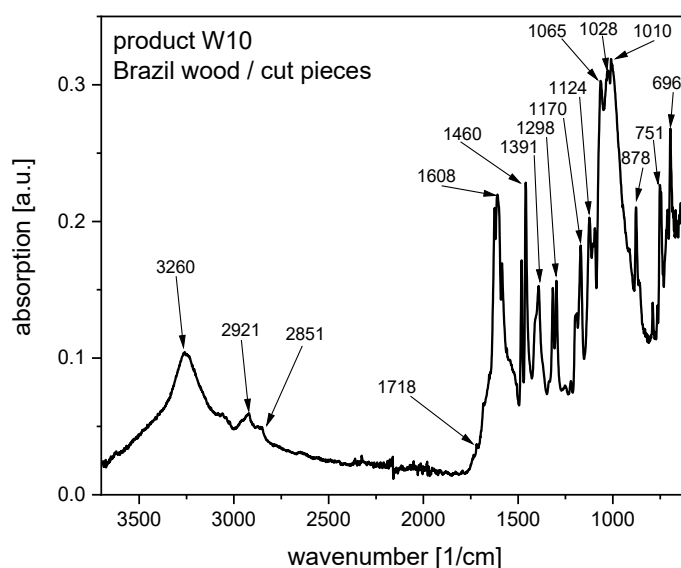


Fig. 13 IR spectrum of Brazil wood – cut pieces (sample W10).

The IR spectra of extracts from Brazil wood are shown in Figure 14. These extracts are gained from two different suppliers and their IR spectra are nearly identical with ten typical signals in the finger print area. A small difference is the weak shoulder at 1715 cm^{-1} determined for product W11. A differentiation of extracts from Brazil wood and the log wood extracts is possible by IR spectroscopy.

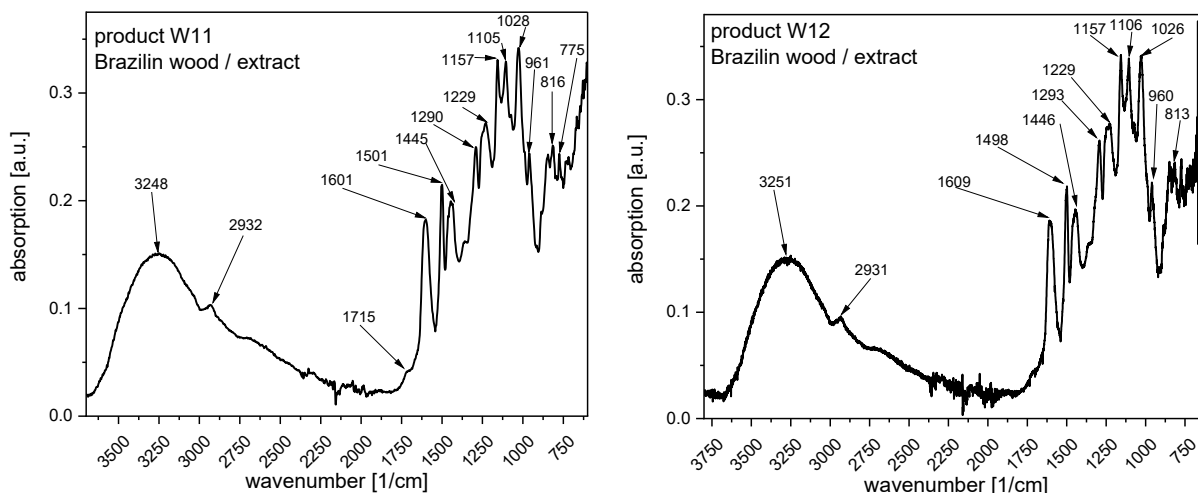


Fig. 14 IR spectra of Brazil wood – extracts (samples W11 and W12).

The main dye component of red sandalwood is the dye santalin (CI Natural Red 22) [4 67,81]. Here between the two types santalin A and santalin B is distinguished (compare Figure 15). Further, the dye component santarubin is described with nearly the same molecular structure but appearance of further methoxy groups as auxochromes [67,82]. Santalin belongs to the group of condensed biflavonoids [67] An innovative approach for extraction of santalin from red sandal wood by using a microwave process is described recently by Barkaat et al. [81]. These investigators use extracted santalin for the dyeing of mordanted silk fabrics [81].

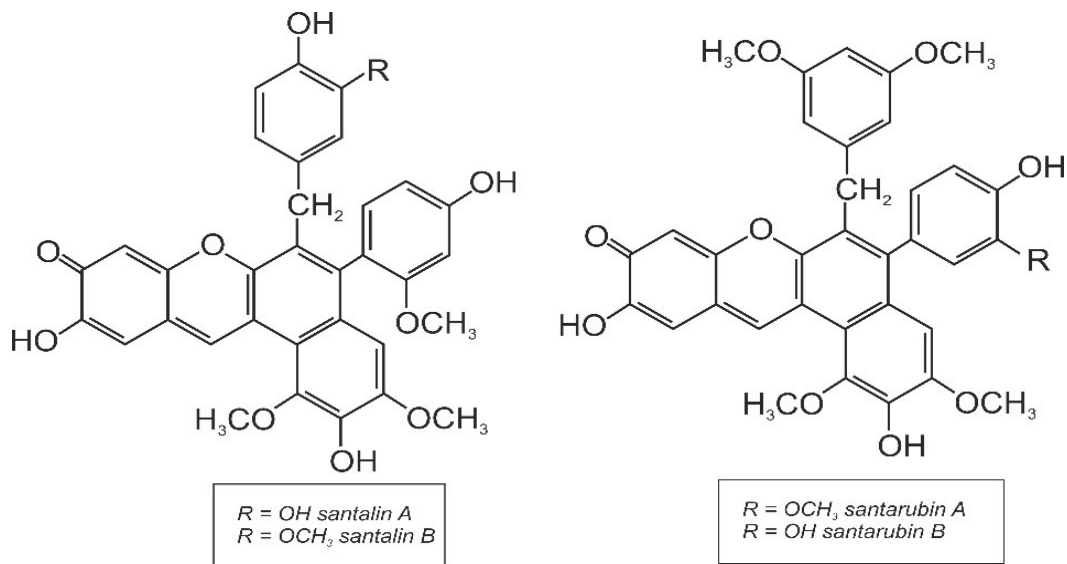


Fig. 15 Chemical structure of different dye species santalin (left) and santarubin (right) as colored components in red sandalwood.

IR spectra of sandalwood pieces and powder from two different suppliers are presented in Figures 16 and 17. Both spectra exhibit nearly the same pattern to each other. A good similarity to other IR spectra of wooden samples is also given. Due to the similarity, it is nearly not possible to distinguish sandalwood from other wood samples by using IR spectroscopy. The spectra from cut pieces sandalwood and sandalwood powder differ with the weak signal at 1620 cm^{-1} which is determined for the sandalwood powder. This peak at 1620 cm^{-1} is weak for sandalwood powder W14. For sandalwood cut pieces W13, instead of the peak at same position a shoulder is determined. The different appearance of this signal might be attributed to the different physical dimensions of both samples.

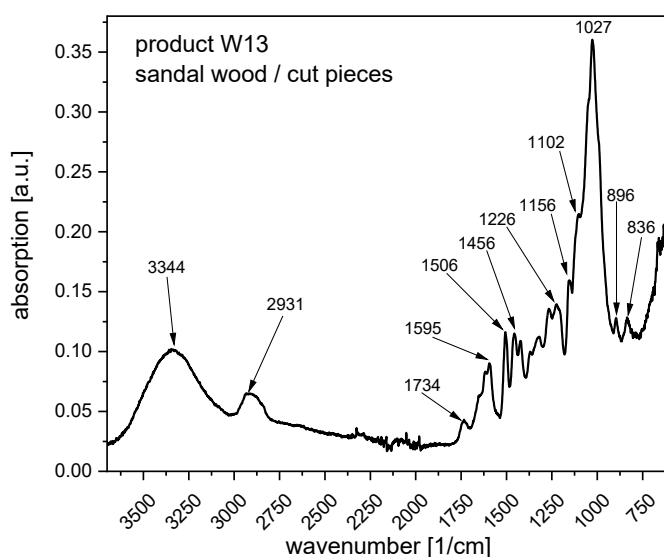


Fig. 16 IR spectrum of sandalwood – cut pieces (sample W13).

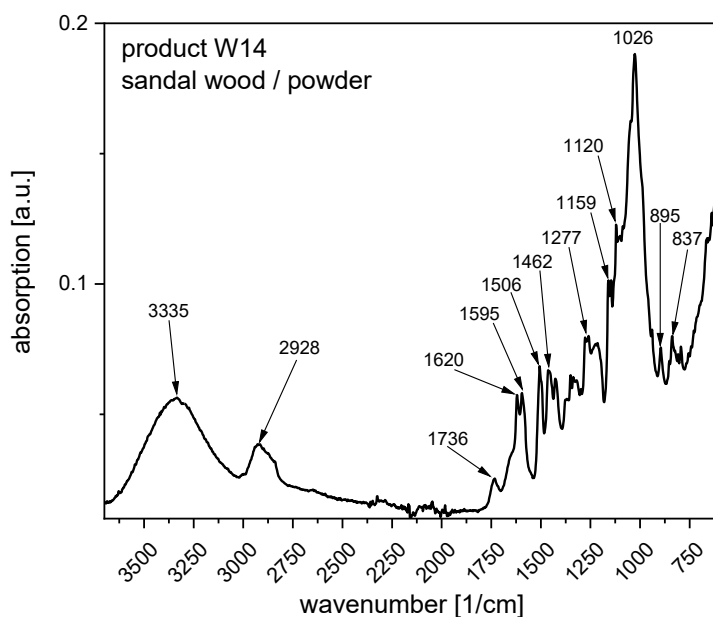


Fig. 17 IR spectrum of sandal wood – powder (sample W14).

3.5 Quebracho wood

Quebracho wood is related to different plants as *Schinopsis quebracho-colorado*, *Schinopsis lorentzii* or *Schinopsis balansae* [4]. However, also other wood types are commonly summarized under the term “Quebracho”. As colored components from quebracho wood different chemical compounds are identified containing a flavonoid unit – as shown in Figure 18 [5,7,83-85].

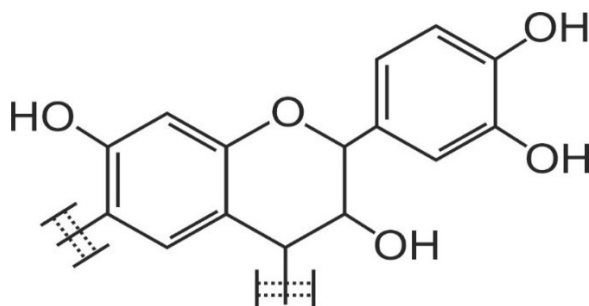


Fig. 18 Chemical structure of the main flavonoid unit of colored component in quebracho wood.

The IR spectrum of a dye extract gained from quebracho wood is presented in Figure 19. The signal at 3230 cm^{-1} is related to O-H stretching vibrations of hydroxy groups. The weak signal at 2940 cm^{-1} is assigned to C-H stretching vibrations from aliphatic units. The prominent signal appearing at 1604 cm^{-1} can be assigned to C=O stretching vibration of a ketone group weakened by hydrogen bridge bond to a hydroxy group. However, the main flavonoid unit shown in Figure 18 does not exhibit C=O units. For this, this determined signal is related to other components in the extract or products as result of oxidation processes. Compared to the other wood extracts, the spectrum of quebracho extract exhibit a strong signal at 1516 cm^{-1} , which may be used for spectroscopic identification of the extract and distinguish it from other wood extract products.

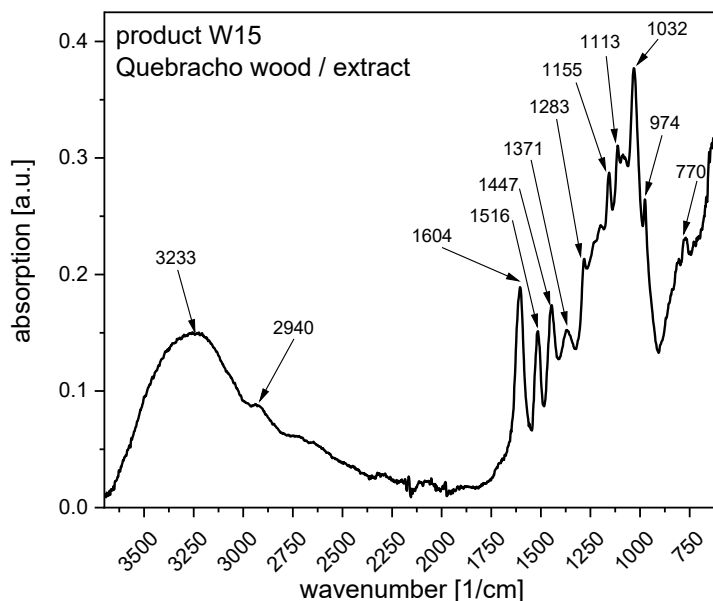


Fig. 19 IR spectrum of Quebracho wood – extract (sample W15).

In literature it is reported that quebracho wood is rich in tannins [7]. However, ester from tannins should lead to an IR signal around 1730 cm^{-1} , due to C=O stretching vibrations [86, 87]. As reference an IR spectrum for a tannin product W16 is recorded and presented in figure 20. The strong peak detected in the spectrum from this tannin sample can be assigned to C=O stretching vibration from an ester group. The IR spectrum of the quebracho wood extract (Figure 18) does not exhibit such a C=O (ester group) related tannin signal. Probable the tannin in quebracho wood is not solved during the used extraction process. Nevertheless, remarkable is that the IR spectra from both products W15 and W16 exhibit a clear signal around 1606 cm^{-1} which could be related to C=O stretching vibrations of keto groups.

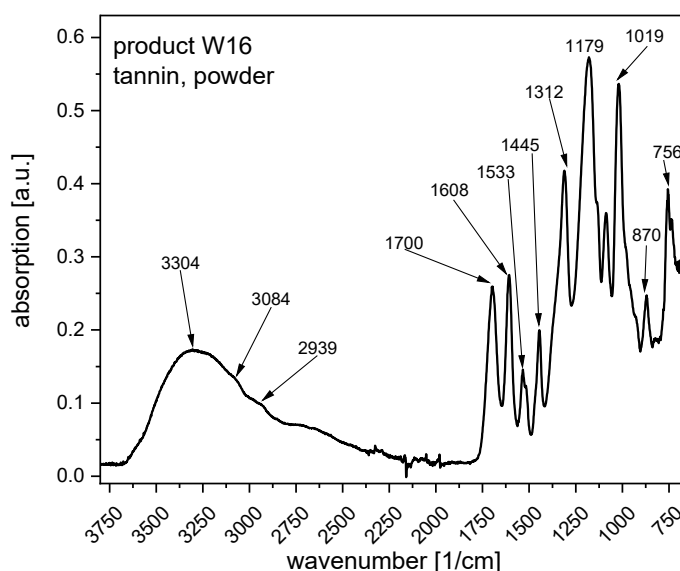


Fig. 20 IR spectrum of a tannin product (sample W16).

3.6 Dragon palm resin

From botanical point of view, palm trees are not conventional trees. Also, the resin from dragon palm (Calamus draco) is exactly spoken not conventionally wood based. Nevertheless, in the actual overview

also the dragon palm resin is considered as plant based red colored material. The dragon palm resin is also named as dragon's blood or CI Natural Red 31 [4,7,88]. Additional to dyeing application also therapeutic uses and antimicrobial properties are reported [89,90]. One main colored component in the red dragon palm resin is the red dye dracorubine (compare Figure 21) [91,92]. Additional to dracorubine also other colored components from the same category occur in dragon palm resin, as dracorhodin, dracoflavylium and 7,4-dihydroxy-flavylium (compare chemical structures in Figure 22) [93].

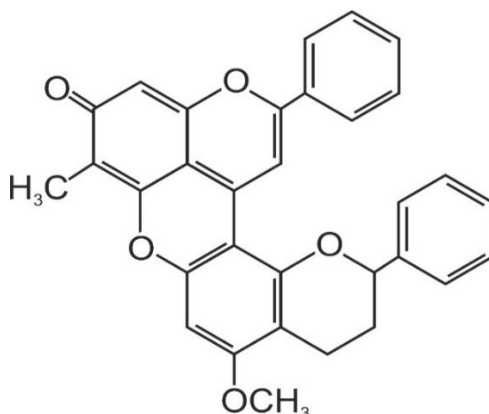


Fig. 21 Chemical structure of the dye dracorubine as one colored component in red dragon palm resin.

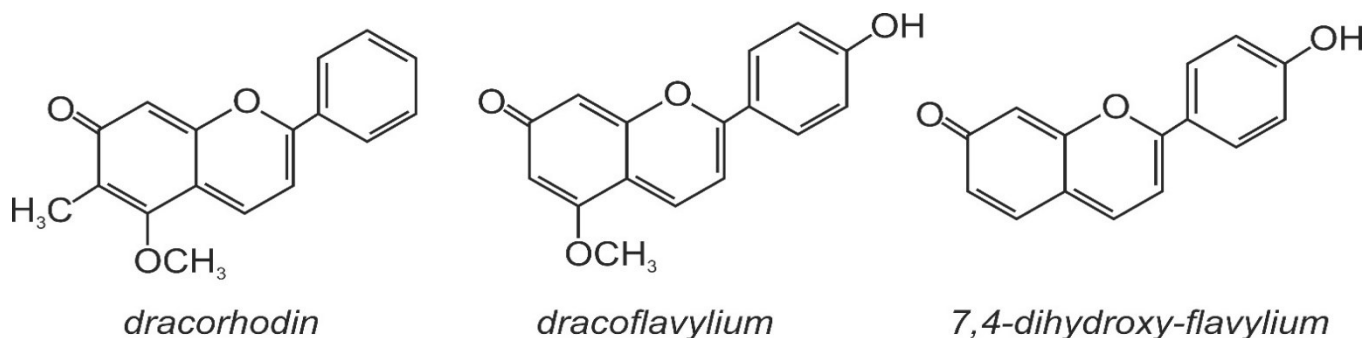


Fig. 22 Chemical structures of dracorhodin, dracoflavylium and 7,4-dihydroxy-flavylium (pictures left to right) as further colored components in red dragon palm resin.

The IR spectra recorded from two different products of dragon palm resin are shown in Figure 23. The IR spectra of both products from different suppliers are mainly similar and in good accordance to an IR-spectrum reported in literature [94]. For this, the identification of dragon palm resin product by IR spectroscopy is possible. The broad signal at 3279 cm⁻¹ is related to O-H stretching vibrations from hydroxy groups. However, dracorubine dye does not contain hydroxy groups, so this signal is caused by other hydroxy containing components in the resin as dracoflavylium or 7,4-dihydroxy-flavylium. The weak signal at around 3015 cm⁻¹ is assigned to C-H stretching vibrations of hydrogen atoms bonded to aromatic ring systems. The peaks at 2931 cm⁻¹ and 2857 cm⁻¹ are assigned as well to C-H stretching vibration but to hydrogen atoms at aliphatic units, as the methyl groups -CH₃ which are attached to the different types of colored components in dragon palm resin (compare Figure 22). The signals at around 1509 cm⁻¹ and 1450 cm⁻¹ can be assigned to C=C stretching vibrations in the aromatic ring system. The most prominent signal at 1152 cm⁻¹ can be attributed to C-O stretching vibrations [93]. The strong signal at 1597 cm⁻¹ and the shoulder at around 1652 cm⁻¹ can be assigned to C=O stretching vibrations of keto groups in different arrangements, with and without formed intermolecular hydrogen bridge bonds to other hydroxy groups.

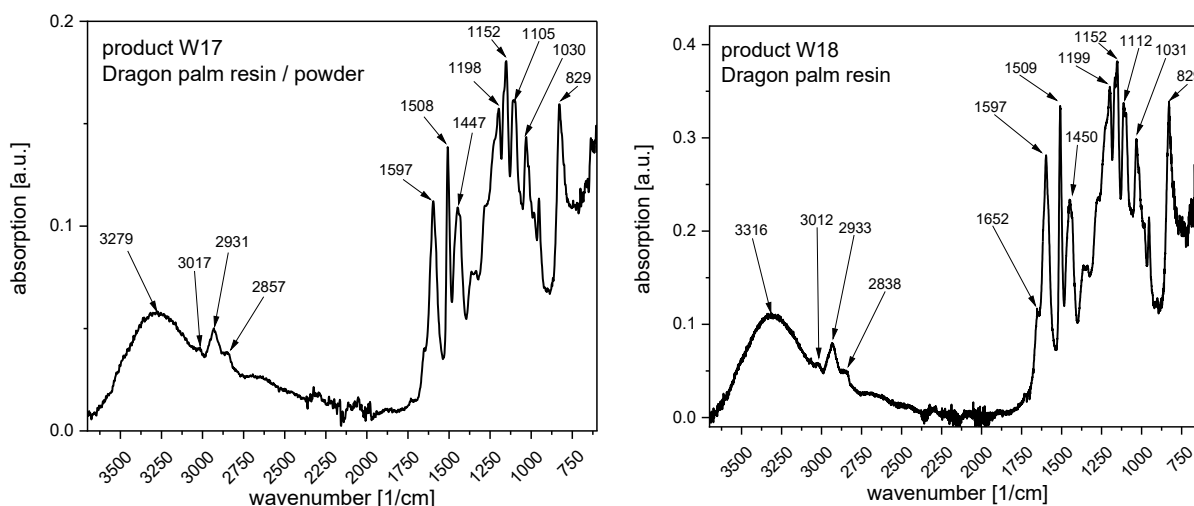


Fig. 23 IR spectra of dragon palm resin products (samples W17 and W18).

3.7 Osage Yellow

Osage yellow is a water insoluble dye product made of wood flour [54]. It is produced and supplied by the company Kremer Pigmente and dedicated especially for recipes used for treatment of wood surfaces. Further details on production processes or origin of used wool flour are not disclosed by the producer, so a discussion of the main colored component and its chemical structure is not possible. Nevertheless, the infrared spectrum from osage yellow powder is recorded and main signal can be discussed (Figure 24). The broad signal at 3340 cm^{-1} is probably related to O-H stretching vibrations from hydroxy groups. Remarkable is that for the range from 2800 cm^{-1} to 3100 cm^{-1} even no weak signal or shoulder are detected, so no signal related to C-H stretching vibration can be determined. In a certain way this measurement result is similar to the infrared spectra of other wood extract exhibiting also only weak signals in this spectral range. Also, for the infrared spectrum of the dye morin as main colored component in old fustic wood no clear signal in this spectral area is reported [95]. The signal at 1695 cm^{-1} and 1616 cm^{-1} are probably related to C=O stretching vibration of keto group attached to an aromatic ring system building up the chromophore. This product W18 can be expected to be an extract gained from a colored wood. However, the type of wood or the used method for extraction cannot be identified by infrared spectroscopy.

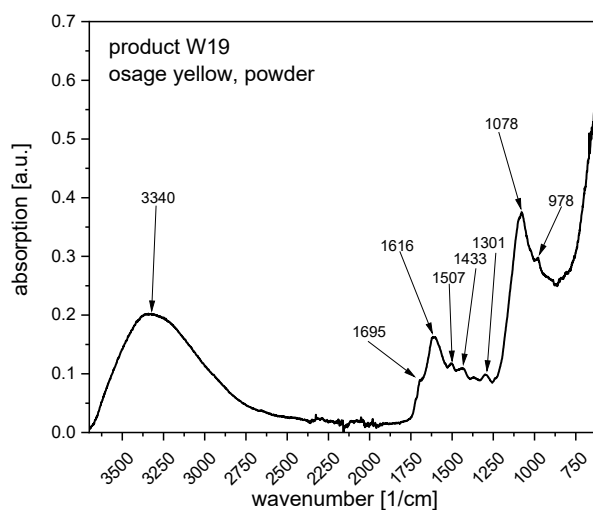


Fig. 24 IR spectrum of osage yellow, powder.

3.8 Dyer Bark

Wood based natural dyes can be gained from different parts of the original tree, as the wood, heart wood or the bark. For example, the dye components brazilin and brazilein are gained from heart wood (brasil wood) [96]. In case, the heart wood is the source for the dye component, the complete tree has to be sacrificed for dye production. In contrast, by using barks as source for dye extraction a more sustainable production of natural dyes might be possible. With this background, in this final section a view on a selection of different barks offered for dyeing purposes is given. The infrared spectra of two different samples of buckthorn bark are presented in Figure 25. These samples are gained from two different suppliers. From buckthorn (*Rhamnus frangula*) the bark (*Frangulae Cortex*) is used for dyeing. Additional to the bark, also other parts of the buckthorn are reported to be used for dyeing, as e.g. berries or leaves [97]. As dyeing components in the buckthorn bark, derivatives from anthracene are mentioned [4,5,98]. Other dye components reported for extracts from buckthorn are, gallic acid, ellagic acid, quercetin, rhamnetin, rhamnazin and emodin [5,99,100]. For this, a broad range of different dye components are identified in the literature, making a structural discussion of the determined infrared spectra difficult. The infrared spectra from both products W20 and W21 are clearly different from each other, even if both are from buckthorn products (Figure 25). The infrared spectrum of product W21 has a certain similarity to the spectra from different wood samples presented in Figures 2 and 3. By this, it is not possible to distinguish buckthorn bark from other wooden samples using the infrared spectroscopy. The differences between the infrared spectra from W19 and W21 may be explained by irregularities in the sample morphology. In contrast to pure wood samples, product samples from bark are often less regular containing different components of bark and wood.

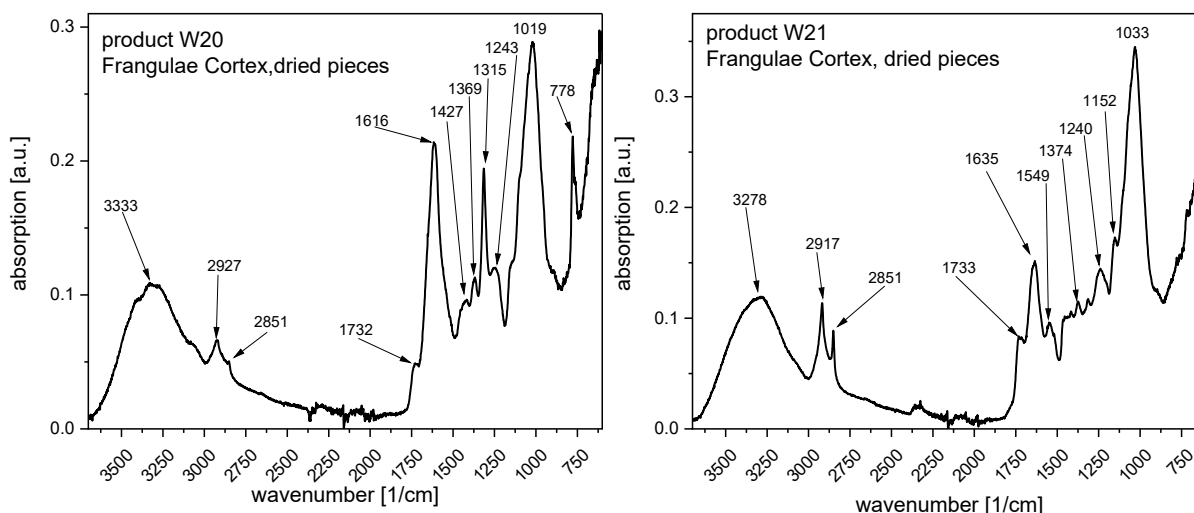


Fig. 25 Comparison of IR spectra of two different samples from buckthorn bark / *Frangulae Cortex*, dried pieces.

For the current overview, additional to buckthorn three further barks from different trees are considered – linden, purple willow and apple tree. The bark from linden is named also as *Tiliae Cortex* and the bark from purple willow as *Salix purpures* [57,58]. The bark from apple tree are basically thin branches from apple tree which are grinded [59]. The infrared spectra of these three product samples W22, W23 and W24 are shown and compared in Figure 26. The IR spectra of W22 and W23 are nearly identical to each other and also quite similar to the infrared spectra of different wood samples presented above in Figure 2 and 3. For this, it is not possible to distinguish these bark samples from other wooden materials using the infrared spectroscopy. The infrared spectrum of product W24 is as well quite similar to the spectra recorded from other wooden samples but it does not exhibit a clear peak in the range of 1710 cm^{-1} to 1740 cm^{-1} . Instead a broad signal at 1613 cm^{-1} is recorded which exhibits a very slight shoulder at around 1740 cm^{-1} . If it is assumed that the signal at 1613 cm^{-1} is caused by a C=O stretching vibration of an amide group, a strong signal here is related to a significant content of protein in product W24. Such a high protein content might be typical for freshly grinded small branches.

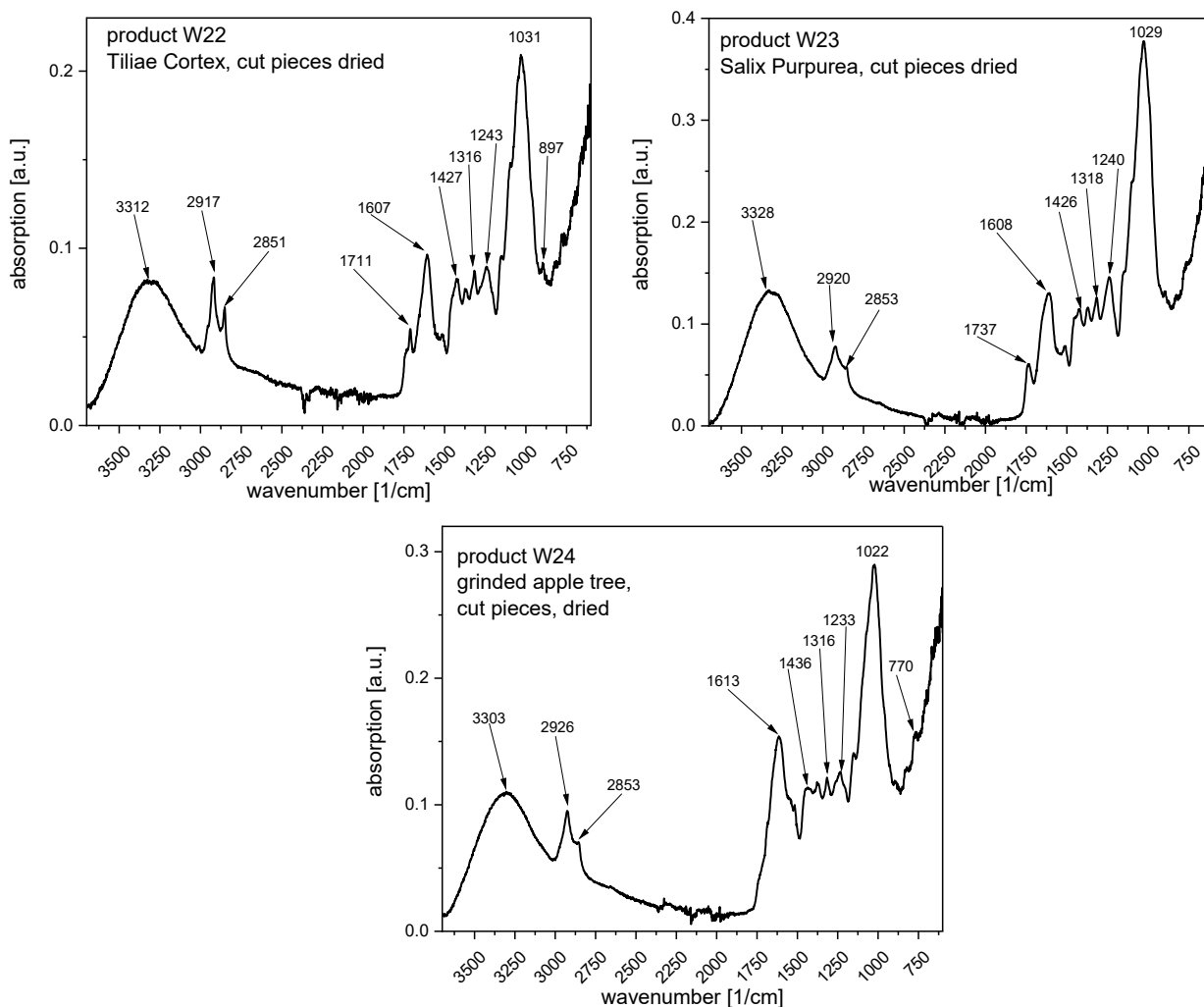


Fig. 26 Comparison of IR spectra of three different types of bark – linden bark / Tiliae Cortex, purple willow bark / Salix Purpurea and apple tree bark / grinded apple tree.

4 Conclusions

Five different types of dye containing wood are discussed and investigated by infrared spectroscopy. Comparison is made to several types of different reference wood materials without any dyeing function. Compared are also the IR spectra of colored wood samples to the related dye extracts. The IR spectra of investigated wooden samples exhibit with exception of brazilwood a strong similarity, so a clear identification of different wood samples is difficult. Nevertheless, the extracts from colored wood exhibit quite typical pattern in their IR spectra, which can be related to some structural groups at the extracted dye components. For this, the IR spectroscopy can be a helpful tool for identification of wood dye extracts or dyes from colored wood. Further, comparative spectroscopic investigations are done with dye products as dragon palm resin, osage yellow and different type of barks. Finally, it can be stated that the actually supported IR spectroscopic data can be helpful for quality control and researchers working in the field of dye analytics as e.g. for historical art pieces or textile materials.

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All product and company names mentioned in this article may be trademarks of their respected owners, even without labeling. There is no conflict of interest and no funding for the presented research.

Conflicts of Interest

The author declares no conflict of interest.

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