CDATP
COMMUNICATIONS IN
DEVELOPMENT AND ASSEMBLING OF TEXTILE PRODUCTS

Overview on natural dyes and their IR-spectra – Part I: Plant based dyes with naphthoquinone and anthraquinone structure

Boris Mahltig

Hochschule Niederrhein, Faculty of Textile and Clothing Technology, Mönchengladbach, Germany
*Corresponding author *E-mail address:* boris.mahltig@hs-niederrhein.de

INFO

CDATP, ISSN 2701-939X
Peer reviewed article
2024, Vol. 5, No. 1, pp. 20-37
DOI 10.25367/cdatp.2024.5.p20-37
Received: 02 March 2023
Accepted: 27 July 2023
Available online: 07 April 2024

ABSTRACT

This is the first paper of a series of review articles reporting on natural dyes, their origin and infrared spectra (IR spectra). One aim of this review series is to compare IR spectra of natural dyes from different origin and discuss if this spectroscopic method can be used as versatile tool for the identification of natural dyes and their origin. This part I of the review series is related to four natural dyes based on the chemical structures of naphthoquinone and anthraquinone. Especially discussed are Lawson, juglone and alizarin, which are related to the natural products henna, walnut hull and madder root. Also, the natural dye based on alkanna root is investigated. Compared are the IR spectra of these natural dyes gained from different suppliers with the IR spectra of the pure chemical substances related to the natural dyes. A discussion with spectra from literature is supported. The aim of this review paper is to support infrared spectroscopic data of natural materials (natural dyes) to enable further material identification and also quality control supporting people working in the fields of fiber analytics or with production processes using natural dyes.

Keywords
natural dyes,
infrared spectroscopy,
plant based dyes,
madder,
Lawson,
henna,
juglone,
alkanna,
alizarin

1 Introduction

Dyeing as process leading to colored textile materials is probably one of the most important processes in the textile industry. While historically natural dyes are used for the coloration of textiles, nowadays in most industrial production processes synthetic dyestuffs are used [1-5]. Prominent examples are acid dyes used for nylon fibers, reactive dyes for cotton or disperse dyes for polyester fiber materials [4,6].

Nevertheless, the interest in coloration of textiles using natural dyes is still present, especially in the private handcraft segment. This interest is reflected by a huge number of publications and books in this field [7-11]. Also, due to the popular trend of sustainability, the use of natural dye stuffs can be promoted in the near future [9,12-14]. The application of natural dyes to realize bio-based antimicrobial functionalized textiles is discussed as innovative method for production of metal free antimicrobial products [15-19]. Following the current trend of sustainability and the demand for environmentally friendly products an international standard for natural dyed textile goods was established – Natural Organic Dye Standard (NODS). This standard lists natural based dyes, maximum limits of inorganic metal ions on the dyed product, prohibited substances and also demanded fastness properties [20].

With this background, a series of review articles on natural dye stuffs, their origin, properties, applications and infrared spectra is supported. This current paper is part I of this series and related to four plant based dyes with naphthoquinone or anthraquinone structure. Please compare the basic chemical structures of naphthoquinone and anthraquinone in Figure 1 with the structure of the basic unit benzoquinone. For all discussed materials, exclusively for this review paper infrared spectra (IR-spectra) are recorded and discussed by comparison to IR spectra reported in the literature. The infrared spectroscopy (IR spectroscopy) is a broadly used method in analytical chemistry and it can be also used for the identification and structural analysis of textile fiber and leather materials [21-25]. Infrared spectroscopy can be also a helpful method for investigation and identification of historical textiles [26,27].

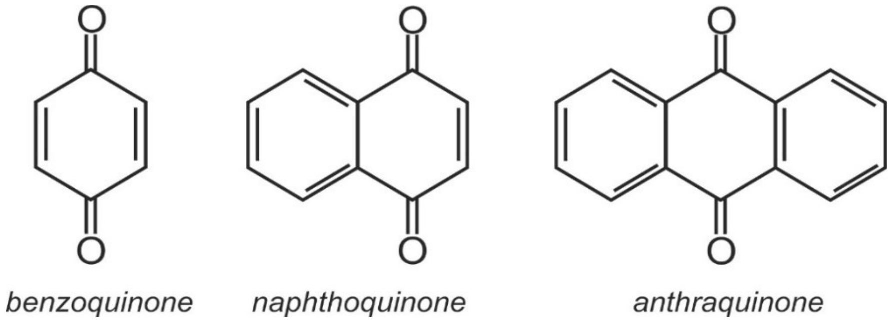


Fig. 1 Basic chemical structures of benzoquinone, naphthoquinone and anthraquinone.

One aim of the review series is to support infrared spectroscopic data of natural materials (natural dyes) to enable further material identification and also quality control supporting people working in the fields of fiber analytics or with production processes using natural dyes. The current paper is related to four natural dyes with naphthoquinone and anthraquinone structure as chromophore. The actually presented dyes are summarized in table 1 together with the related plant of origin. The IR spectra of these natural materials are further discussed by comparison with spectra of synthetic dye products.

Table 1. Overview on the four discussed natural dyes, together with the plant of origin and the main colored component.

Dye	Plant of origin	Color	Main component
C.I. Natural Red 8	Madder root	Red	Alizarin CI75330
C.I. Natural Orange 6	Henna	Orange	Lawson CI75480
C.I. Natural Brown 7	Walnut hull	Brown	Juglone CI75500
C.I. Natural Red 20	Alkanna root	Red	Alkannin CI75530

2 Materials and Methods

2.1 Dyestuffs

In the current overview four different types of natural dyes are discussed which are based on the chemical structures of anthraquinone and naphthoquinone. The natural dyes and natural materials are gained from three different suppliers – Kremer Pigmente GmbH (Aichstetten, Germany), Pflanzenfärbershop (Hückelhoven-Baal, Germany) and Das Wollschaf (Zweibrücken, Germany). Reference measurements are done with related synthetic chemicals which are supplied by the companies Carl Roth GmbH (Karlsruhe, Germany) and Merck (Darmstadt, Germany). An overview on presented materials and related suppliers is given in Table 2. As references, the product web pages of the supplier are mentioned supporting general information and especially information on dyeing recipes and chemical safety. These materials are investigated by infrared spectroscopy as received and no further treatment or purification is performed. The infrared spectroscopic investigations are done on the dye materials without application on textiles.

Table 2. Reported plant based natural materials and their synthetic reference chemicals.

No.	Content	Form	Supplier	References
C1	Synthetic dye, Alizarin	Powder; p.a.	Roth	[28]
C2	Madder root	Extract	Pflanzenfärbershop	[29]
C3	Madder root	Small pieces from Iran	Pflanzenfärbershop	[30]
C4	Madder root	Ground with pieces	Kremer	[31]
C5	Madder root	Cutted root from Turkey	Kremer	[32]
C6	Synthetic compound, Lawson	Powder	Merk	[33]
C7	Henna Red	Powder	Pflanzenfärbershop	[34]
C8	Henna Red	Powder	Kremer	[35]
C9	Henna Red	Powder	Wollschaf	[36]
C10	Henna Black	Powder	Kremer	[37]
C11	Synthetic compound, Juglone	Powder	Merk	[38]
C12	Walnut hull	Pieces	Pflanzenfärbershop	[39]
C13	Walnut hull	Pieces	Kremer	[40]
C14	Walnut, dried	Complete nut	German garden, collected February 2023	---
C15	Alkanna	Cut pieces	Wollschaf	[41]
C16	Alkanna	Cut pieces	Pflanzenfärbershop	[42]

2.2 Analytical Methods

The infrared spectra (IR spectra) of investigated dyes and natural materials are recorded with a FT-IR spectrometer IRTracer-100 from Shimadzu (Japan) using a Specac Golden Gate ATR unit. The IR spectra are taken from the plant based natural materials without any further treatment or cleaning of these materials. Photographic images with enhanced magnification are taken by using a Dino-Lite Premier Digital Microscope. Scanning electron microscopy (SEM) is done by using TM4000Plus Tabletop microscope from Hitachi (Japan).

3 Discussion of the dyes

3.1 Natural Red 8

The dye Natural Red 8 is originated from madder root (Rubia tinctorum) with alizarin as the main colored component. Alizarin is a red dye based on the anthraquinone chemical structure [1]. The alizarin content of the madder root is around 3% [43]. The root is usually harvested from plants after three year or older [44]. Additional to alizarin the madder root contains also anthraquinone based dyes as e.g. pseudopurpurin, rubiadin and munjistin [1, 45, 46]. The composition of different color components in madder root also depends on the country of origin of this plant [47]. The chemical structure of alizarin is shown in Figure 2. The chemical name is 1,2-dihydroxyanthraquinone with the sum formula $C_{14}H_8O_4$ and the molecular weight of 240 g/mol. The CAS number of alizarin is 72-48-0 [20]. For alizarin the LD50 value is 1000 mg/kg (oral/rat) [48]. As far as the suppliers disclose, the currently investigated madder materials are originated from the countries Turkey and Iran.

The dyeing properties of natural madder dye on wool and cotton fibers as function of alkaline pH is intensively presented by Montazer et al. and Zhu et al. [49-51]. Good overviews on the influence of different mordants on the fastness properties, UV-protective and antimicrobial functionality are given by Zarkogianni et al. and Ibrahim et al. [45, 52]. The use of a tin chloride based mordant for dyeing with madder and henna is described by Yusuf et al. [53]. Further the use of zinc sulfate and magnesium sulfate as additives (so-called meta mordants) can improve the dyeing results for madder on wool yarns [54]. For dyeing with madder extract also bio-based mordants with tannin as environmentally friendly alternative to conventional metal mordants are evaluated [46]. Other green dyeing processes using different types of bio-based mordants are presented by Hosseinnezhad et al. [55-58]. A further innovative approach to improve the dyeing of cotton with madder was presented recently by Gupta et al. [59]. These researchers use silica and titania nanosols in a sol-gel process to improve dyeing properties and to implement further UV protective properties [59]. However, it should be kept in mind that the application of sol-gel technology in combination with synthetic dye stuff on textiles is under investigation for already more than twenty years [60-63].

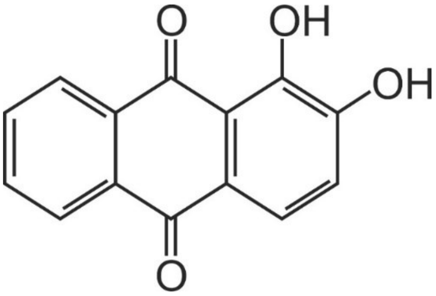


Fig. 2 Chemical structure of Alizarin the main colored compound in madder root.

Figure 3 presents the photograph of madder root pieces (product C5) and magnified photograph of a cut pieces from madder root (product C3). The color impression of this natural product can be described with dark brown or red brown.

Fig. 3 Photographs of madder root (product C5) (left) and cut piece of madder root (product C3). Photographic image with higher magnification (right).

Images taken with scanning electron microscopy SEM from madder root pieces are presented in Figure 4 and Figure 5. Figure 4 shows overview images in low magnification, while Figure 5 presents a cross section of a madder root piece in higher magnification. The vascular openings in the cross section of madder root are clearly visible (Figure 5).

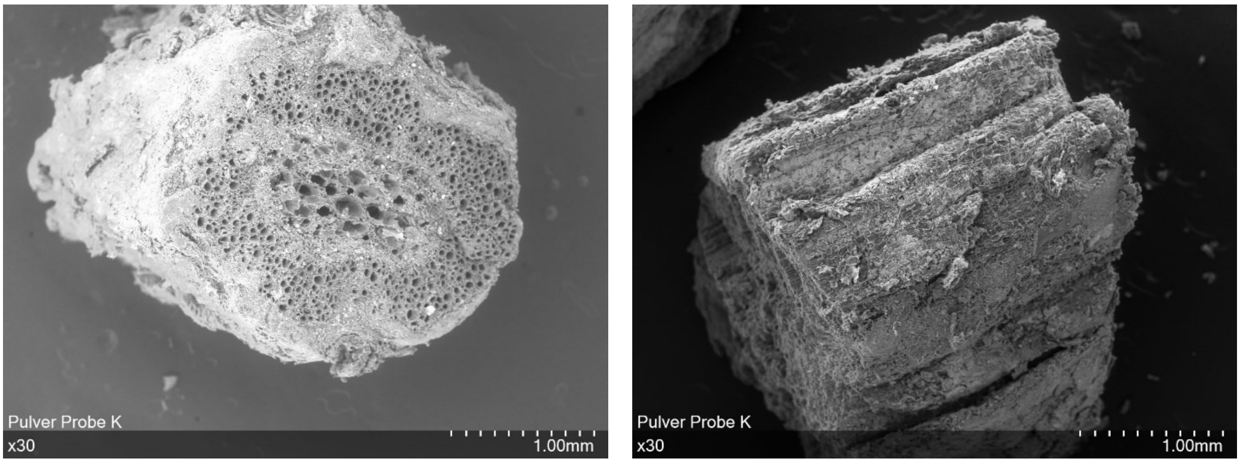


Fig. 4 Pieces of madder root (product C3), images taken by scanning electron microscopy (SEM) in low magnification – cross section of madder root (left) and surface of madder root (right).

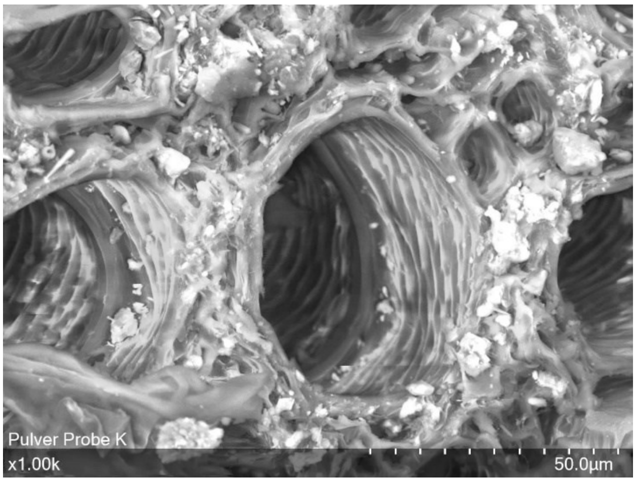


Fig. 5 Cross section of a madder root (product C3) in higher magnification taken by SE).

The infrared spectrum of alizarin is compared with the IR spectra of extract from madder root and different madder root materials (Figure 6). The IR spectrum of the synthetic alizarin is almost not similar to the IR spectra of the madder root based materials. The IR spectrum of alizarin exhibits a broad signal at 3256 cm^{-1} related to the O-H stretching vibration of the hydroxy group [64]. A very weak signal appears at 3078 cm^{-1} which is assigned to the C-H stretching vibration of the hydrogen atoms attached to the aromatic system of anthraquinone [65].

The signal at 1661 cm^{-1} can be assigned to the C=O stretching vibration of the keto group at the aromatic ring system. The second peak at 1632 cm^{-1} can be as well assigned to a C=O stretching vibration but the related C=O bond is weakened by an intramolecular hydrogen bridge bond to the neighboring hydroxy group [66]. The strongest peak at 1281 cm^{-1} is related to the C-O stretching vibration between the hydroxy groups and the aromatic ring system [66]. The peak at 748 cm^{-1} is assigned to O-H deformation vibration [66]. The peak at 1584 cm^{-1} can be assigned to overtone and combination vibration of the aromatic ring system [65]. The peak at 1449 cm^{-1} is assigned to C=C stretching vibration [65].

The extract from madder root is supposed to contain a significant amount of alizarin solved during the extraction procedure. However, of course also other soluble components are probably solved and be finally also part in the madder extract. The recorded IR spectrum of the madder extract is therefore different from the one recorded from nearly pure synthetic alizarin.

The IR spectra of product C2 (madder root extract) exhibits also the broad signal at 3285 cm^{-1} caused by O-H stretching vibration. However, in contrast to alizarin for product C2 a medium signal at 2930 cm^{-1} is determined, which is related to C-H stretching vibration of aliphatic CH components. This signal is one hint for aliphatic compounds in the madder root extract. The signal at 1634 cm^{-1} (spectrum C2) can be assigned to the C=O stretching vibration of alizarin. However, the strongest signal at 1018 cm^{-1} occurring for the madder root extract has no corresponding signal in the spectrum of the synthetic alizarin.

The IR spectra of the two madder products C3 and C4 correspond mainly with the spectrum of the madder extract (product C2). First main difference is the occurring of two signals at 2918 cm^{-1} and 2860 cm^{-1} related to the C-H stretching vibration from -CH$_2$- methylene units. The signal at 2918 cm^{-1} is related to the asymmetric vibration and the signal at 2860 cm^{-1} is related to symmetric vibration of this methylene unit [65]. The second main difference is the presence of the small signal at 1736 cm^{-1}. This signal at 1736 cm^{-1} is probably related to a C=O stretching vibration of an ester group. The related ester component is obviously not soluble in the extraction process and therefore not appearing in the spectrum of the madder extract. A possible source could be the ester compounds from fatty acids which are content of the root.

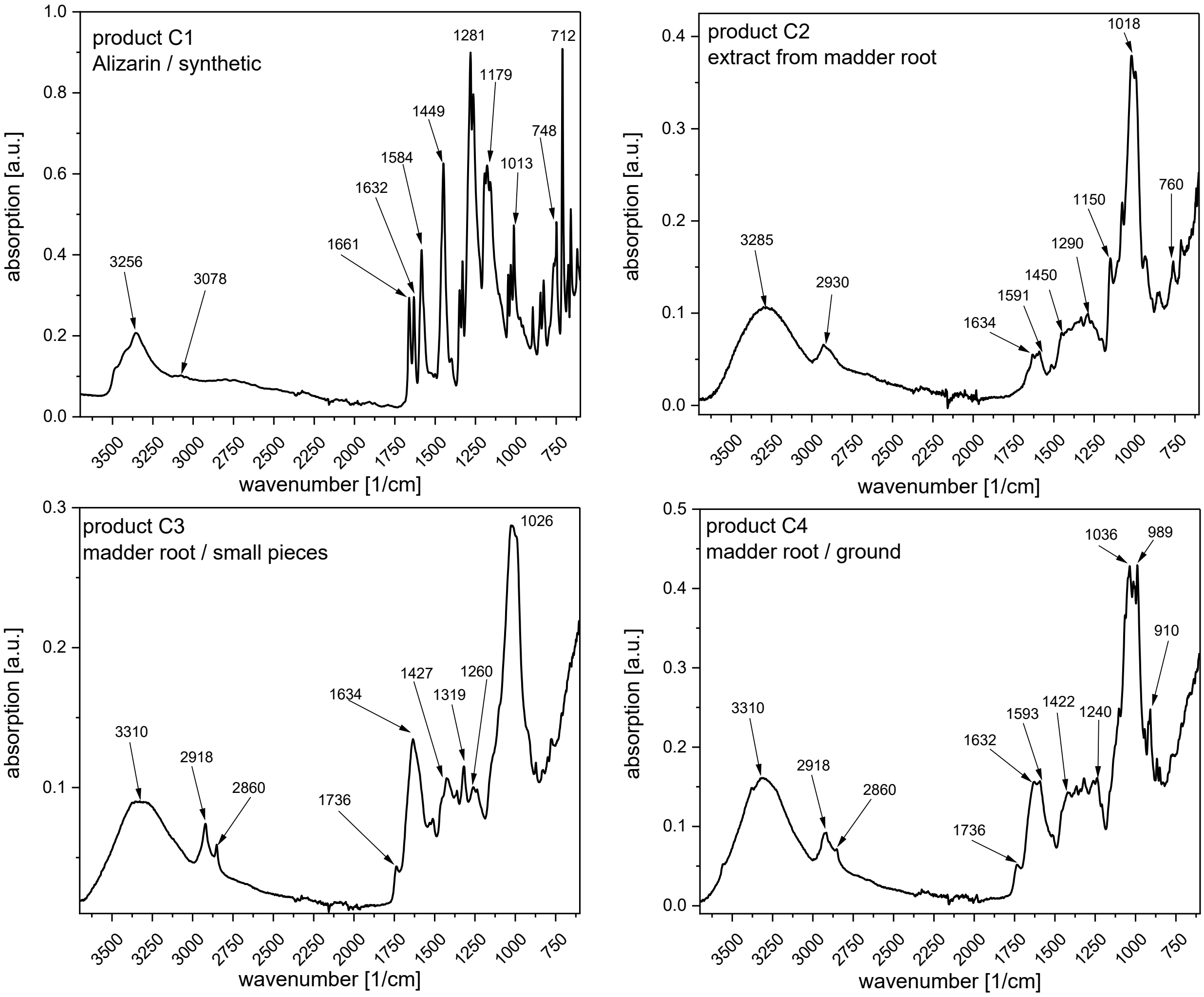


Fig. 6 Comparison of IR spectra of the synthetic dye Alizarin with several madder products. Shown are the products C1 to C4 (compare Table 2).

The infrared spectrum of a complete madder root (product C5) is presented in Figure 7. This spectrum of madder root is with six main signals (1735 cm^{-1}, 1636 cm^{-1}, 1421 cm^{-1}, 1320 cm^{-1}, 1008 cm^{-1} and 874 cm^{-1}) in good accordance to the IR spectra of the two madder root products C3 and C4. The strongest peak at 1008 cm^{-1} appears at a bit lower wavenumber compared to the dominant peak at the comparing products C3 and C4. Altogether it can be concluded that for the identification of madder based products by infrared spectroscopy mostly the main signals in the range of 1740 cm^{-1} to 870 cm^{-1} are suitable.

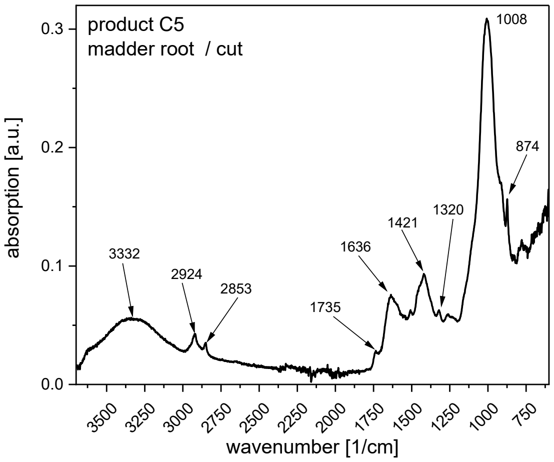
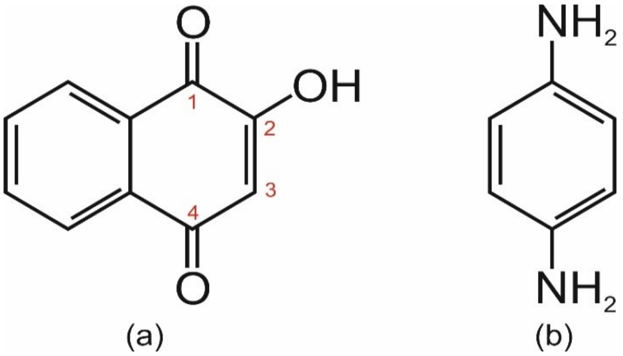


Fig. 7 IR spectrum of cut madder root (product C5).

3.2 Natural Orange 6

Natural Orange 6 is originated from henna plant (Lawsonia inermis) with the chemical compound Lawson as main dye component. Lawson is an orange compound based on the chemical structure of naphthoquinone. The chemical structure of Lawson is presented in Figure 8 and its chemical name is 2-hydroxy-1,4-naphthoquinone. The sum formula is $C_{10}H_6O_3$ and the molecular weight 174 g/mol. The CAS number is 83-72-7. The content of Lawson in dried henna leaves is reported to be in maximum 1% [67]. Henna powder is usually offered as the color product red henna. Henna powder is gained by grinding leaves of the henna plant [68]. Also offered is the product black henna which is a combination of the natural product red henna with the component para-phenylenediamine (PPD) (see chemical structure in Fig. 8). Skin irritation and sensitization are reported for application of black henna in tattoo applications [69,70]. A detailed study reporting the acute toxicity of aqueous extraction of the root of henna plant is supported by Mudi et al. [71]. They reported a slight toxicity for these extracts and concluded that Lawson is for this one of the main components [71].

Henna extracts and Lawson are described for dyeing of wool and nylon yarns [72,73]. An environmental bio-based mordant with chitosan is reported by Alebeid et al. for dyeing with henna extract on wool [74]. The application of henna dye on polyester fabric is reported for using a high temperature process without the need of metallic mordants [75].



(a) (b)

Fig. 8 (a) Chemical structure of Lawson the main colored component in the henna dye. The positions of first four carbon atoms in the aromatic ring system are indicated with red numbers – (b) chemical structure of para-phenylenediamine (PPD).

The infrared spectrum of the synthetic chemical Lawson is show in Figure 9. Compared to the IR spectra of henna dye products (Figure 10), the spectrum of the pure substance is significantly different and cannot be used for the identification of the natural henna products. The IR spectrum of synthetic Lawson exhibits a weak signal at 3333 cm^{-1} and a broad signal at 3155 cm^{-1}, both signals are related to O-H stretching vibrations of the hydroxy group. The hydroxy group in Lawson can form intramolecular hydrogen bridge bonds to the keto group in position 1 in the same molecule. Also, intermolecular hydrogen bridge bonds to polar groups of other molecules are possible. By this, the different peaks for the O-H stretching vibration can be explained. The two weak signals at 3077 cm^{-1} and 3016 cm^{-1} are related to C-H stretching vibrations of hydrogen atoms bonded to the aromatic ring system [65]. The signal at 3077 cm^{-1} is probably assigned to the hydrogen atom in the position 3 of the Lawson structure – between the keto group and the hydroxy group. The peaks at 1677 cm^{-1} and 1640 cm^{-1} are assigned to the C=O stretching vibration of the keto groups. Here, peak 1677 cm^{-1} is related to the keto group in position 4 of the Lawson molecule. The keto group in position 1 is weakened by an intermolecular hydrogen bridge bond to hydroxy group in position 2, so the related peak appears at lower wavenumber with 1640 cm^{-1}. The peak at 1579 cm^{-1} can be assigned to overtone and combination vibration of the aromatic ring system [65]. The peak at 1215 cm^{-1} is probably assigned to C-O stretching vibration of the hydroxy group.

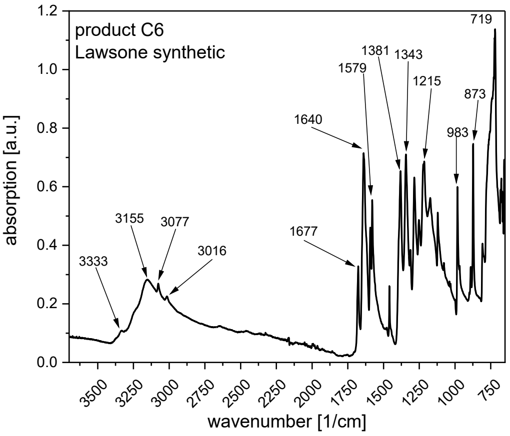


Fig. 9 IR spectrum of synthetic Lawson (product C6).

The IR spectra of different henna dye products are compared in Figure 10. The products C7, C8 and C9 are all from red henna but from different suppliers. Product C10 is named henna black and is supplied by the company Kremer Pigmente. The IR spectra of all three henna red samples are nearly similar with eight prominent peaks in the region around 3285 cm^{-1}, 2920 cm^{-1}, 2850 cm^{-1}, 1730 cm^{-1}, 1626 cm^{-1}, 1317 cm^{-1}, 1235 cm^{-1} and 1025 cm^{-1}. The determined IR spectra for henna red are mainly similar to one IR-spectrum reported in literature for henna dye [74]. The broad signal around 3285 cm^{-1} is related to O-H stretching vibrations. The both peaks at around 2920 cm^{-1} and 2850 cm^{-1} are related to C-H stretching vibration at aliphatic compounds containing -CH$_2$- methylene units. The signal at 2920 cm^{-1} is related to the asymmetric vibration and the signal at 2850 cm^{-1} is related to symmetric vibration of this methylene unit [65]. The appearance of both signals indicates the presence of some aliphatic compounds in the henna dye which are additionally present to Lawson. A further hint on an additional component is the presence of the medium signal around 1730 cm^{-1} which is probably related to a C=O stretching vibration of an ester group, which is not part of the Lawson structure. The strong signal around 1626 cm^{-1} can be assigned to the C=O stretching vibration of the keto groups at the aromatic ring system of Lawson. Earlier Saadaoui et al. published an IR spectrum for henna extract [76]. This reported IR spectrum exhibit significant differences to synthetic Lawson and the actually investigated henna red products. One main difference is that the reported IR spectrum from henna extract does not contain any signal at 1730 cm^{-1} which is related to an ester compound [76]. Probably this ester component is not solved during the extraction procedure.

The infrared spectrum of product C10 – henna black – contains a certain similarity to the IR spectra of the other three products from henna red. One main difference in the IR spectrum of henna black is the signal at 1589 cm^{-1} which appears at significantly lower wavenumber compared to the comparable signal at 1626 cm^{-1} for the henna red products. Henna black is gained from henna red by addition of para-phenylenediamine, which exhibits with -NH_2 primary amino groups. The N-H stretching vibration cannot be specified, because of the broad signal at around 3280 cm^{-1}. However, the peak at 1589 cm^{-1} can be assigned to a deformation vibration of the -NH_2 group [65]. Altogether it can be stated that henna red products from different origin can be identified by infrared spectroscopy, if the eight significant signals are determined.

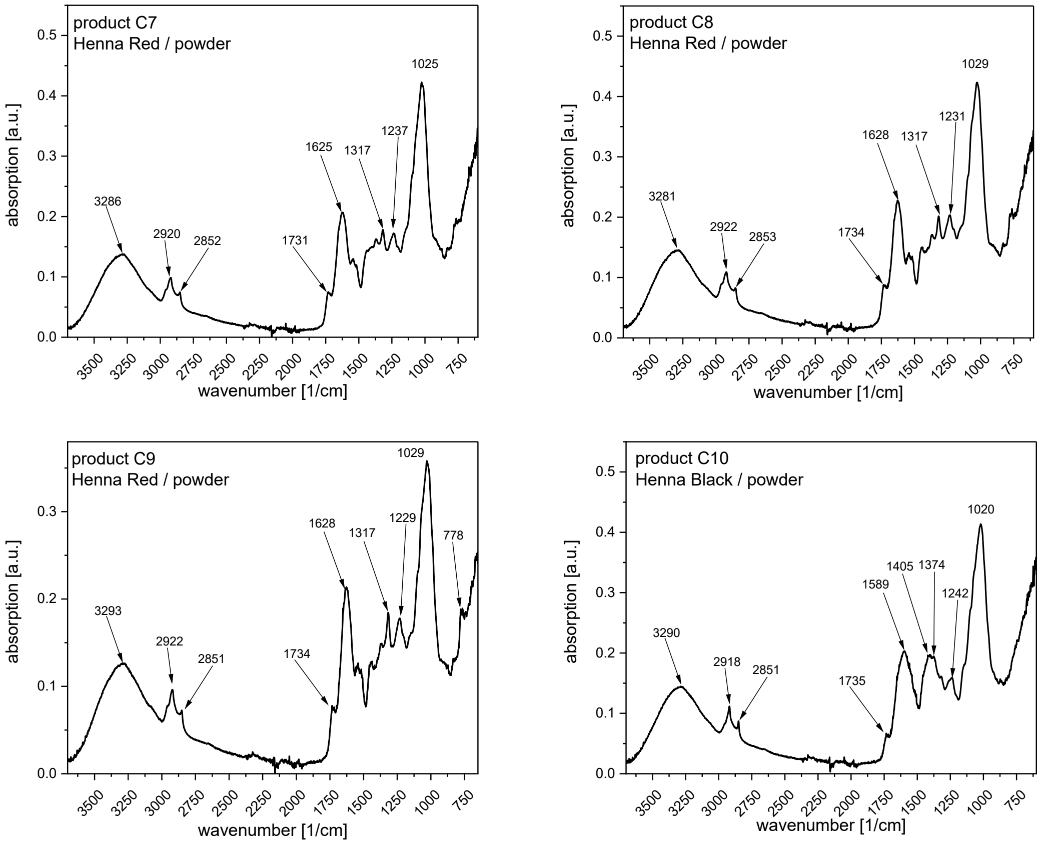


Fig. 10 Comparison of IR spectra of several henna products. Shown are the products C7 to C10 (compare Table 2).

3.3 Natural Brown 7

The dye Natural Brown 7 is originated from the walnut tree (Juglandis nuc.) – mainly from the hulls of the walnut. The main dye component of natural brown 7 is the chemical compound juglone [1]. Juglone is based also on the chemical structure of naphthoquinone and its chemical name is 5-hydroxy-1,4-naphthoquinone (compare Figure 11). Juglone is an isomer with Lawson containing the same sum formula $C_{10}H_6O_3$ and the same molecular weight 174 g/mol. However, compared to Lawson, juglone exhibits a higher toxicity [77,78]. Additional to juglone also other colored compounds are identified in green walnut hulls [79,80]. By combination of juglone extracts with iron, alum and copper mordant, different shades of brown can be realized on wool fibers [81,82]. The light fastness is especially improved by combination with copper mordant. Further, UV protective properties can be implemented on wool by these applications [83]. Beside using metal compounds as mordant, an interesting and sustainable approach is the combination of walnut bark-based juglone with bio-based mordants [83]. The dyeing with nearly pure juglone is reported for fiber substrates from wool, human hair, silk, nylon and polyester [84]. In the mentioned study, the researchers claim to use natural dye juglone but probably synthetic juglone was used [84].

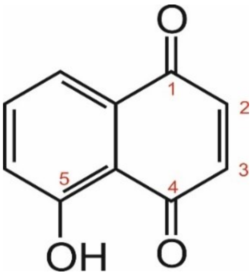


Fig. 11 Chemical structure of Juglon the main colored component in walnut hull. The positions of first four carbon atoms in the aromatic ring system are indicated with red numbers.

Figure 12 shows photographs from different walnut products (products C13 and C14). The dark brown coloration of dried walnut is visible. Fresh walnut exhibits a green hull. The presented brown hull is gained after several months outdoor storage under environmental conditions.

Fig. 12 Photograph of complete walnut with dried hull (product C14) (left image) and photographic image with higher magnification of a dried piece of walnut hull (product C13) (right image).

The infrared spectrum of the synthetic compound juglone is shown in Figure 13. The signal at 3236 cm^{-1} is related to the O-H stretching of the hydroxy group. The three signals at 3062 cm^{-1}, 2968 cm^{-1} and 2924 cm^{-1} are assigned to the C-H stretching vibration. The peaks at 1663 cm^{-1} and 1624 cm^{-1} are assigned to the C=O stretching vibration of the keto-groups. The signal at 1663 cm^{-1} is probably related to the keto group in position 1 of the juglone structure. The signal at 1624 cm^{-1} is assigned to the keto group at position 4. Probably this keto bond is weakened by hydrogen bridge bond formation to the hydroxy group in position 5 [85]. The peak at 1459 cm^{-1} can be assigned to C=C stretching vibration in the aromatic ring system [65].

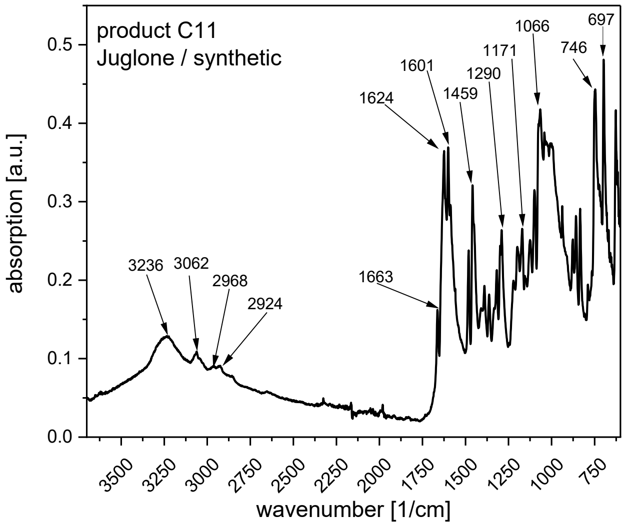


Fig. 13 IR spectrum of synthetic Juglone (product C11).

The IR spectra of two products from walnut hull offered for dyeing purposes (products C12 and C13) are presented in Figure 14. The spectra of these both samples are significantly different from each other and exhibit also strong difference to the spectrum of synthetic juglone (compare Fig. 13). A determination of those products by infrared spectroscopy is therefore not possible. Remarkable is the strong peak at 1701 cm^{-1} at product C12 which is related to a shoulder at the spectrum of the product C13. These signals are probably related to C=O stretching vibration of ester or keto components which are part of the walnut hull. In literature an IR spectrum from a dye extract of walnut is reported [66]. For this extract the main peak assigned to C=O vibration appears at 1639 cm^{-1}, which is related to the keto group bonded to the aromatic ring system. Further peaks related to C=O vibration of other groups are not reported. These compounds probably present in the walnut hull are not solved by the extraction process. An excellent overview on different extraction processes for green walnut hulls and extracted components is reported by Mirjalili et al. [86]. These researchers identified in the extracts several derivatives of juglone and supported their infrared spectra.

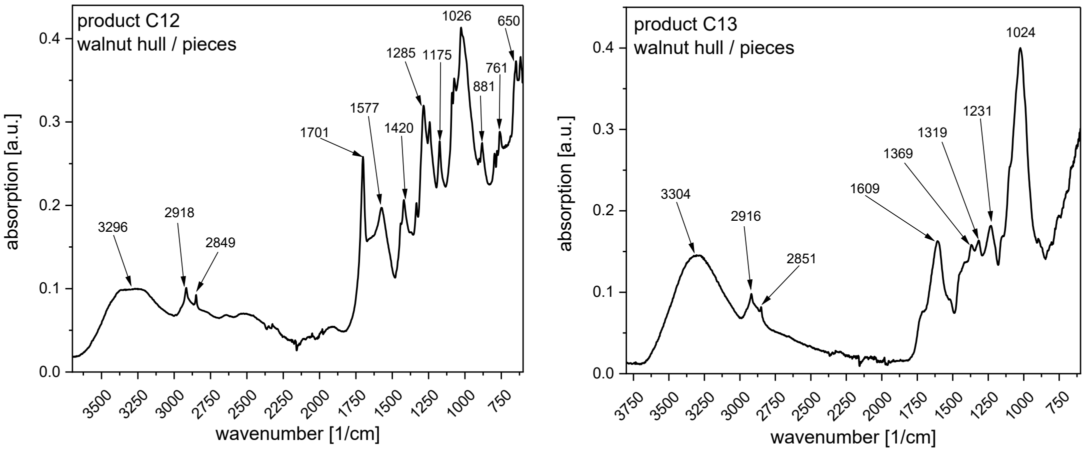


Fig. 14 Comparison of IR spectra of several walnut hull products. Shown are the products C12 and C13 (compare Table 2).

The IR-spectrum recorded from product C14 is given in Figure 15. For this spectrum, a small sample of the dried hull was removed from a complete nut. This IR-spectrum from product C14 shows some similarities with the spectrum of C13, with the signals at 1612 cm^{-1} and 1017 cm^{-1}. However, also significant differences are clear, as the additional medium signal at 1736 cm^{-1}, which is probably related to the C=O stretching vibration of an ester group. By view on the clear differences in the IR-spectra of different walnut products offered for dyeing purposes, it is clear that for these products a systematic identification by using infrared spectroscopy is very challenging.

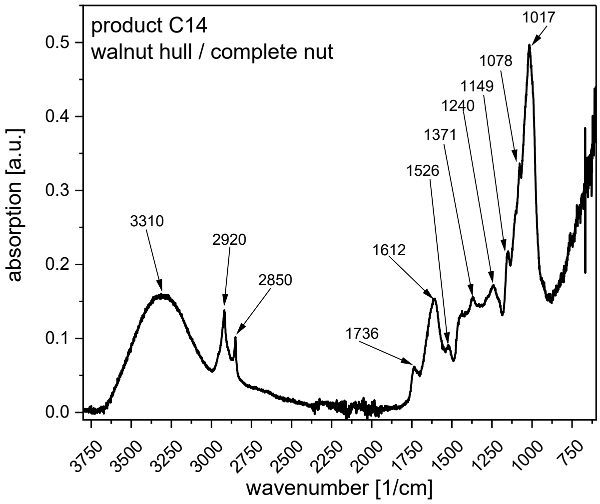


Fig. 15 IR spectrum of walnut hull from complete nut (product C14).

3.4 Natural Red 20

Natural Red 20 is a natural dye originated from the root of the plant Alkanna tinctorial [1]. The main dye component in the alkanna root is the compound alkannin (see Figure 16) with the sum formula $C_{16}H_{16}O_5$ and the molecular weight 288 g/mol. Alkannin exhibits a naphthoquinone unit as part of its chromophore. The CAS number of alkannin is 517-88-4 [20]. A good overview on dyeing wool with alkanna root extract under consideration of a broad range of different metal mordants is given by Eser et al. [87]. These scientists distinguish in their description systematically between pre-mordanting method, meta-mordanting method and post-mordanting method. Extracts from alkanna root were applied on wool and silk with conventional metal based mordant and bio-based mordant for the development of sustainable alkannin colorant eco-dyeing [88,89].

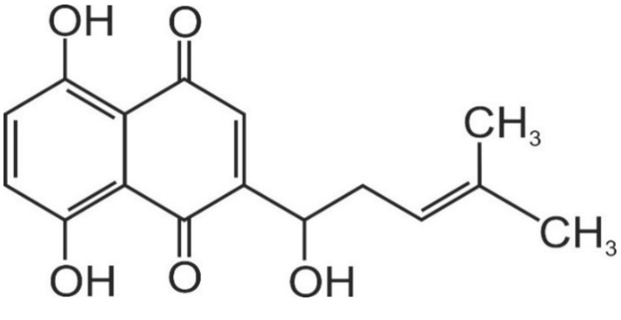


Fig. 16 Chemical structure of Alkannin - one main colored compound in Alkanna root.

The currently investigated alkanna products C15 and C16 are cut pieces of the red alkanna root (compare photograph in Figure 17). The red brown coloration of this natural product is clearly visible. SEM images of alkanna pieces (product C15) recorded in different magnification are compared in Figure 18. The structure of plant cells can be clearly identified in the SEM image recorded in higher magnification.

Fig. 17 Alkanna cut pieces. Photographic image with higher magnification (product C15).

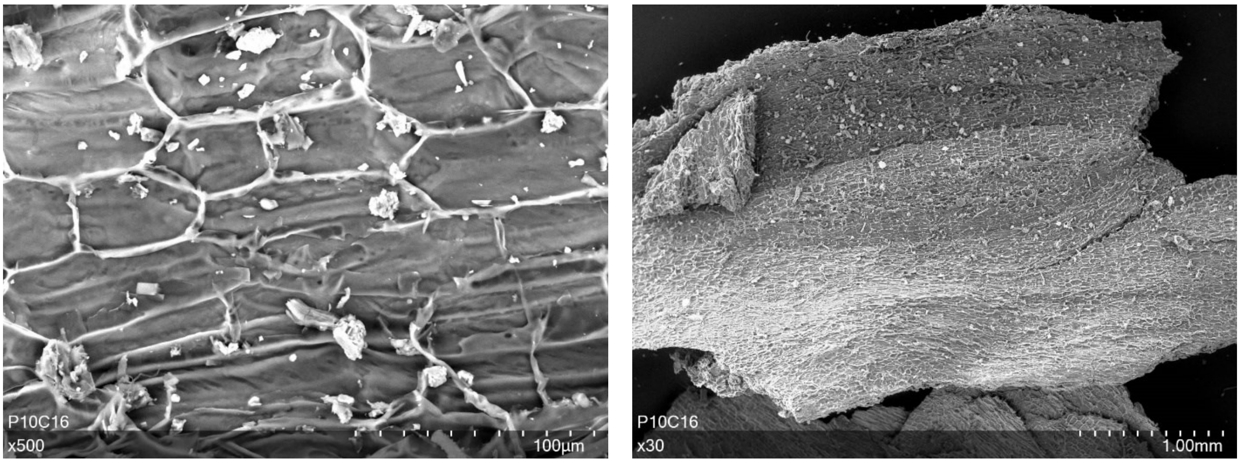


Fig. 18 Pieces of alkana (product C15), images taken by scanning electron microscopy (SEM) in different magnification.

The infrared spectra of the investigated alkanna products C15 and C16 are shown in Figure 19. For product C15, the IR spectrum exhibits a broad signal at 3305 cm^{-1} assigned to O-H stretching vibration of hydroxy groups. The signals at 2916 cm^{-1} and 2850 cm^{-1} are related to C-H stretching vibration. The signal at 2916 cm^{-1} is related to the asymmetric vibration and the signal at 2850 cm^{-1} is related to symmetric vibration of the methylene unit $-CH_2-$ [65]. The signal at 1719 cm^{-1} is probably related to the C=O stretching vibration of an ester group or a keto group. The strong signal at 1608 cm^{-1} may be assigned to C=O stretching vibration of the keto group of alkannin dye. This keto group is probably weakened by the formation of a hydrogen bridge bond to the neighboring hydroxy group, so the peak is shifted to lower wavenumbers.

It should be considered that the alkanna pieces contain beside the dye alkannin many other components, especially the ester group assigned signal at 1719 cm^{-1} is related to this. A reported IR spectrum for alkanna extract does not exhibit any ester related peaks, so this ester component is probably not soluble in the extraction process [90]. One main signal in the reported IR spectrum from alkanna extract appears at 1603 cm^{-1} and can be set in relation to the signal determined at 1608 cm^{-1} for the alkanna piece. Other peaks in the fingerprint area are mainly not similar [90]. Both main signals at around 1608 cm^{-1} and 1718 cm^{-1} are also determined in the infrared spectrum of alkanna product C16 (Figure 19). The other four dominant signals in the fingerprint area can be also identified for both alkanna products, so the infrared spectroscopy can be a helpful tool to identify this natural color material.

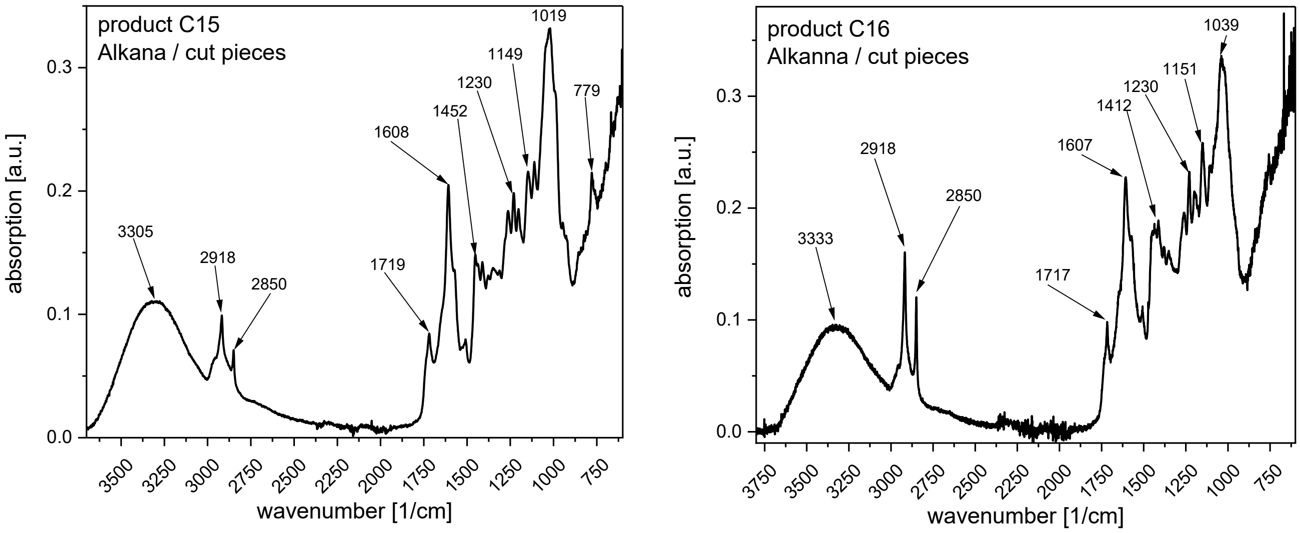


Fig. 19 Comparison of IR spectra of several alkanna products. Shown are the products C15 and C16 (compare Table 2).

4 Conclusions

Four different natural dyes originated from the plants – madder, henna, walnut and alkanna – are presented together with their related infrared spectra. A comparison of the IR spectra with the spectra of pure synthetic chemicals – alizarin, Lawson and juglone – is performed. An identification of the natural dyes by comparison with the IR spectra of the related synthetic substances is not possible, probably because of by-products in the natural materials. All investigated natural compounds exhibit an infrared signal in the range of 1740 to 1715 cm^{-1} which is probably related to a C=O stretching vibration from an ester group. One possible explanation for this can be the presence of esters from fatty acids.

Nevertheless, the natural materials of madder root, henna plant and alkanna from different suppliers exhibit similar typical IR signals and can be identified by them. For walnut hull based materials this identification by infrared spectroscopy is more challenging. Finally, it can be concluded that for natural dye materials the infrared spectroscopy can be a valuable tool for identification and discussion of chemical structure of containing compounds.

Acknowledgements

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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