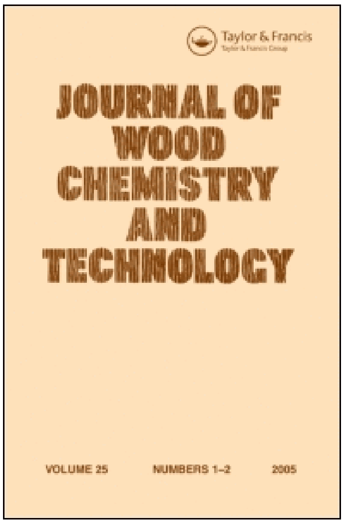

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UV–VIS. SPECTROSCOPIC CHARACTERISTICS OF FERULIC ACID AND RELATED COMPOUNDS

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ABSTRACT

The UV–Vis. absorption of ferulic acid and related compounds may be considerably augmented by substitution and environment. Among the circumstances investigated in the present study, esterification (mostly to polysaccharides in plant cell wall), dehydrodimerization and inclusion in a cellulose matrix substantially cause the absorption to increase and extend into the visible region. As a result of the combination of these three effects, dehydrodiferulate type units appear to be the most likely chromophore among the ferulic acid-derived structures.

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INTRODUCTION

Ferulic acid occurs widely in cell walls of graminaceous plants.[1] As a bifunctional molecule with carboxylic and phenolic bonding sites, it provides an ester–ether bridge and is implicated in cross-linking cell wall components, such as polysaccharides and lignin.[2] On the other hand, the cross-link between polysaccharides is reported to involve dimerization of ferulates via oxidative coupling dehydrodimerization by the action of peroxidases.[3,4]

While its ester linkage to carbohydrates is well defined,[1,2,5] how ferulic acid and its dimers attach to lignin remains yet to be clearly understood. An earlier NMR study suggests that ferulic acid is associated with lignin through ether linkages.[6,7] From experiments with model compounds, Scalbert et al.,[8] proposed the formation of benzyl aryl ether linkages through addition of ferulic acid to quinone methides. More recently, Ralph and coworkers reported that the bonding patterns between ferulic acid and lignin do not just involve alkyl aryl ethers but, like coniferyl alcohol during lignification, ferulic acid may undergo oxidative coupling reactions to incorporate into lignins.[9,10]

It is well documented that ferulic acid and its derivatives can profoundly contribute to the growth, mechanical properties and biodegradability of plant cell walls.[1,2,5,11] However, there is little knowledge about their impact on the papermaking properties of fibers obtained from graminaceous plants, such as wheat straw. In chemical pulping processes, ferulic acid and its derivatives would be dissolved along with lignin. In high yield pulping, straws are softened by mild chemical treatment and disintegrated by mechanical action, thereby retaining most of the fiber components. But, the wheat straw pulps made by this process have a strong yellowness and are difficult to bleach.[12] While the fundamental causes are unclear, this poor bleaching response could be attributed to a generally held belief that, in contrast to wood pulps, wheat straw pulps contain a greater amount of non-lignin coloring substances that are resistant to hydrogen peroxide, a common bleaching reagent. Ferulic acid and its derivatives are some of them and their existence in wheat straw is well documented.[13,14] But, their actual quantity is very likely underestimated because most reports only cover monomers and some identified dimers and analytical techniques need to be improved to determine ferulic acid units linked in other ways.

Our earlier study has demonstrated that ferulic acid and its derivatives are fairly unreactive with hydrogen peroxide and undergo bond cleavage only to a small extent with peracetic acid.[15] Under the identical treatment, coniferaldehyde compounds, well-known chromophores in the wood pulps, are almost completely degraded. Therefore, it is of interest to understand the possible contribution of ferulic acid and its derivatives to the yellowness and poor bleachability of wheat straw pulps. The objective of the present investigation is to characterize ferulic acid and related compounds as probable chromophores in wheat straw by means of UV–Vis. spectroscopy.

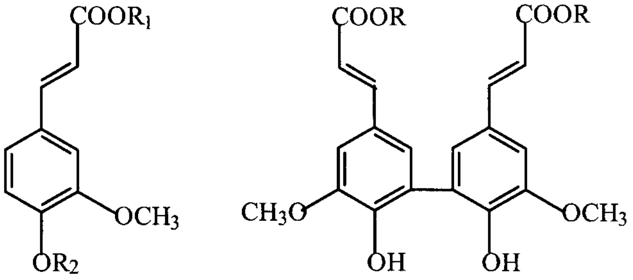
EXPERIMENTAL

Materials

The model compounds studied in this investigation were predominantly the *trans* isomers and are shown in Fig. 1. Ferulic acid (**I**), ethyl ferulate (**II**) and 3,4-dimethoxycinnamic acid (**III**) were purchased from Aldrich Chemical Company and used without further purification. 5,5′-Diferulic acid (**IV**) and diethyl 5,5′-diferulate (**V**) were synthesized according to Quideau and Ralph.[16]

UV–Vis Spectrometry

UV–Vis spectra were recorded on a Varian Cary 1 E UV–Visible Spectrophotometer. Fifty percent aqueous 2-methoxyethanol was employed



I: $R_1 = R_2 = H$
II: $R_1 = C_2H_5; R_2 = H$
III: $R_1 = H; R_2 = CH_3$

IV: $R = H$
V: $R = C_2H_5$

Figure 1. Model compounds: ferulic acid (**I**), ethyl ferulate (**II**), 3,4-dimethoxycinnamic acid (**III**), 5,5′-diferulic acid (**IV**) and diethyl 5,5′-diferulate (**V**).

as solvent and iron (**III**) nitrate solution was used to make up the ferric complexes of the model compounds. The solid state spectra were obtained by impregnating the compounds into very thin paper sheets (10 g/m^2) made of pure cellulose fibers (Whatman filter paper).

RESULTS AND DISCUSSION

The monomeric model compounds demonstrate the effect of 4-*O*-etherification and esterification on the UV–Vis. absorption of ferulic acid. As shown in Fig. 1, compounds **II** and **III** are representative of ferulic acid molecules ester-bonded to polysaccharides or ether-bonded to lignin in plant cell walls. Figure 2 shows that absorption of ferulic acid (**I**) does not extend into the visible region (above 400 nm). Esterification results in a bathochromic shift in the absorption curve, as indicated by λ_{max} 325 nm for ethyl ferulate (**II**) against λ_{max} 310 nm for ferulic acid (**I**). But the absorption of ethyl ferulate (**II**) still falls within the region of below 400 nm. On the other hand, 4-*O*-etherification has little effect on the absorption of ferulic acid, as

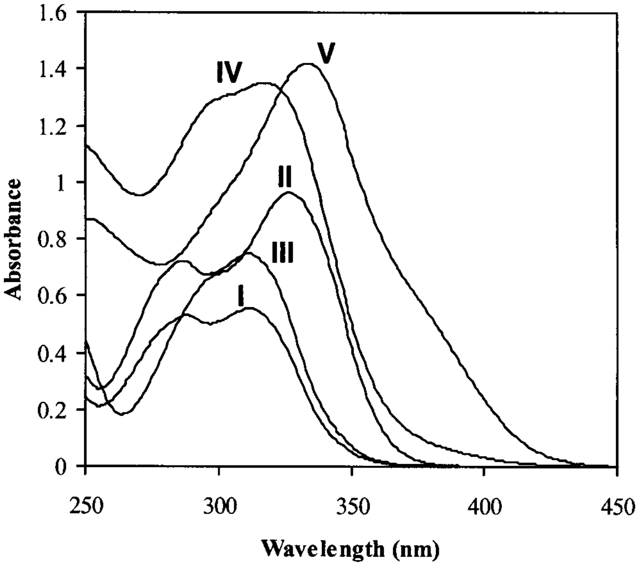


Figure 2. UV–Vis. absorption spectra of model compounds in 50% aqueous 2-methoxyethanol; ferulic acid **I** (4.2×10^{-5} M), ethyl ferulate **II** (5.1×10^{-5} M), 3,4-dimethoxycinnamic acid **III** (4.8×10^{-5} M), 5,5′-diferulic acid **IV** (4.2×10^{-5} M) and diethyl 5,5′-diferulate **V** (4.5×10^{-5} M).

shown by compound (**III**). Overall, monomeric ferulic acid and its derivatives do not appear to be potential color sources.

As pointed out earlier, ferulic acid is able to undergo dimerization through peroxidase-mediated oxidative coupling to produce dehydrodiferulic acid, which may cross-link polysaccharides. The sole ferulic acid dehydrodimer reported from plant cell walls until recently is the 5,5′-coupled dehydrodiferulic acid, commonly referred to as diferulic acid. The more recent determination (and authentication) of a range of diferulates from grasses[9] stems from a recognition that radical coupling of ferulates, necessary to produce the 5,5′-dehydrodimer, can produce other dehydrodimers by anticipated β,5′-, β,β′-, β-*O*-4′-, and 4-*O*-5′-coupling reactions, analogous to those observed for coniferyl alcohol during lignification. Unless the radical coupling is directly controlled by an enzyme or a dirigent protein, other dimers would be expected to be more prevalent than the 5,5′ dimer, as found in many plant materials.[17] Apparently, dimerization of ferulic acid and ferulate occurs in plant cell walls to an extent greater than that used to be thought previously.

In this study, we used 5,5′-diferulic acid (**IV**) and diethyl 5,5′-diferulate (**V**) as model compounds to examine the effect of dehydrodimerization on the absorption of ferulic acid and ferulate. As shown in Fig. 2, the 5,5′-dehydrodimerization significantly enhances the UV–Vis. absorption of ferulic acid and ferulate and causes the absorption curves to extend into the visible region. This dehydrodimerization effect was previously observed on coniferaldehyde type compounds.[18] Similar to that observed for the monomeric model compounds, the bathochromic effect caused by esterification is evident for the dimeric compounds. It appears that the 5,5′-coupled dehydrodiferulate is a colored substance in annual plant fiber materials, such as wheat straw.

Ferric complexes with catechols and other phenolic substances are well documented chromophores in wood and other plant fiber materials.[19–21] Wheat straw has a fair amount of iron.[22] Therefore, it is of interest to investigate the effect of ferric ion on the absorption of ferulic acid-based compounds. Figure 3 shows that the presence of ferric ions has a bathochromic effect, but the shift in the absorption spectra occurs to a limited degree. On the other hand, it seems that ferric ions tend to complex with the carboxylic site, not the phenolic site, in ferulic acid or its derivatives. Thus, the addition of ferric ions to the ethyl ferulate (**II**) solution has little effect on its absorption. This could be attributed to a well known fact that iron tends to complex with a compound having two ortho-positioned hydroxyl groups, like catechol. As ferulates are more important as possible chromophores, this result suggests that ferric ions may not play a significant role in the ferulic acid-derived chromophore system.

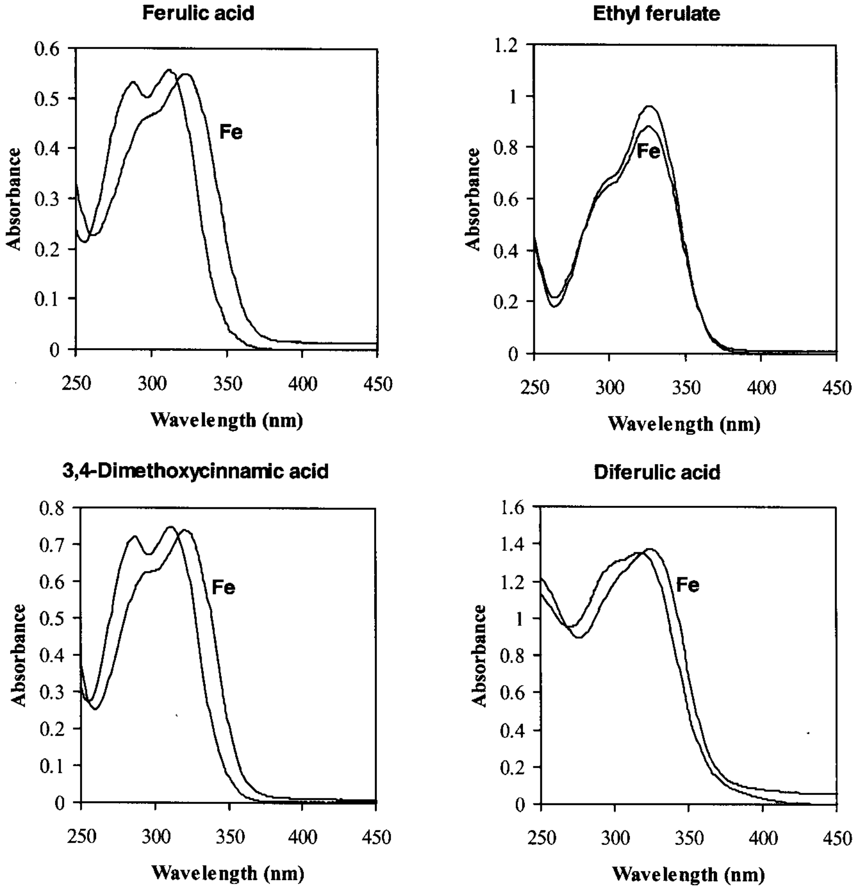


Figure 3. UV–Vis. absorption spectra of model compounds in 50% aqueous 2-methoxyethanol in the presence of iron **III** (1 mole ratio); the compound concentrations are identical to those in Fig. 2.

It is common knowledge from dyestuff chemistry that the absorption curves of colored substances may undergo a bathochromic shift when dried from solution onto cellulose fiber. This proved to be the case with the coniferaldehyde type compounds.[18] As shown in Fig. 4, the solid state spectra exhibit a bathochromic shift for all the model compounds studied here.

In summary, the UV–Vis. absorption of ferulic acid may be considerably augmented by substitution and environment. It appears that

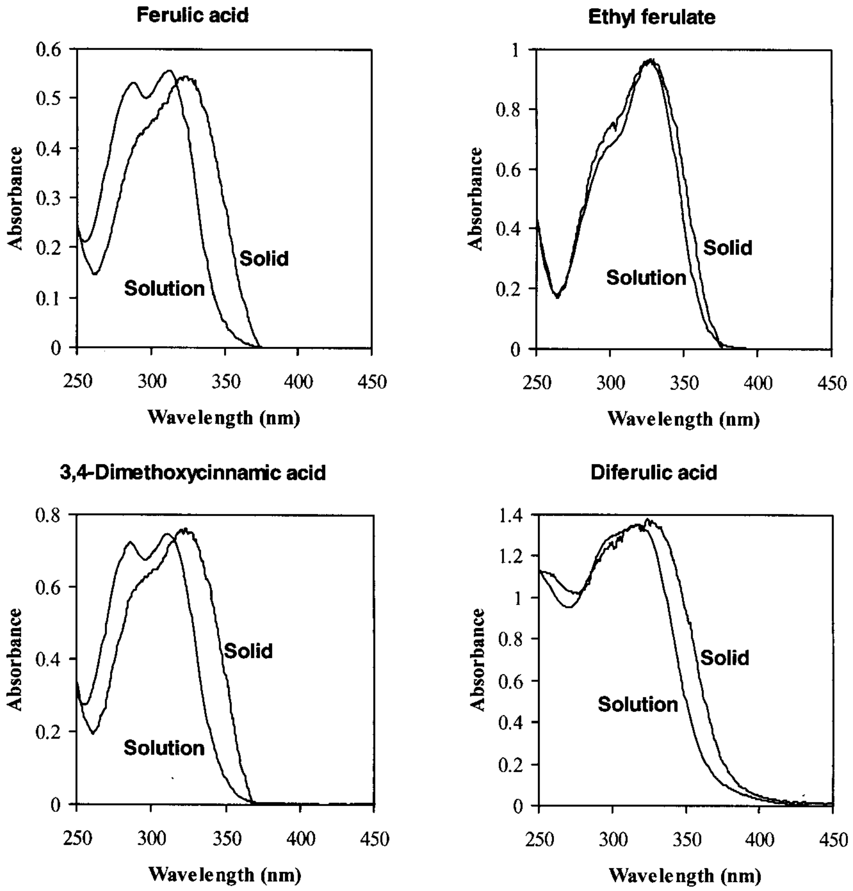


Figure 4. Comparison between solid state (in cellulose matrix) and solution (in 50% aqueous 2-methoxyethanol) UV–Vis. absorption spectra of model compounds.

dehydrodiferulate type units in the solid state could be the most likely chromophore among the ferulic acid-derived structures. Apart from the circumstances discussed above, ferulic acid isomerization would also change its UV–Vis. absorption. It should be noted that the model compounds used in this study are predominantly *trans* isomers, the predominant form in which ferulic acid and its derivatives are naturally present in plants' cell walls.[1] However, the *cis* isomer exists to some extent in the nature as well. More importantly, the *cis* form of ferulic acid is yellow in color.[23] On the other hand, ferulic acid and its derivatives are reported to undergo the *trans–cis* isomerization induced by UV light exposure[24] and via radical mechanisms in peroxide or peracetic acid bleaching.[15,25] While not confirmatory, these facts would suggest that the effect of isomerization on the color of ferulic acid and related compounds should not be neglected.

CONCLUSIONS

The results presented in this paper offer qualitative evidence that ferulic acid-derived structures may contribute to the color of annual plants, including wheat straw, since their presence in the plants' cell walls is well established and their light absorptivity in the visible region is enhanced by dehydrogenative coupling and by inclusion in a cellulose matrix. These two circumstances are available to grown cell walls. This study suggests that dehydrodiferulate type units would be the most likely chromophores among the ferulic acid-derived structures. It should be pointed out that the observation by the present study merely serves to support the generally held belief that annual plant fibers such as wheat straw contain non-lignin and peroxide-resistant chromophores. Ferulic acid and related compounds could be one likely source. Nevertheless, confirmatory and quantitative evidence of the role of ferulic acid and related compounds in contributing to the color of annual plants like wheat straw would not be possible to obtain until several key fundamental questions are resolved, which include the abundance of coloring substances other than lignin and extractives and the estimation of ferulic acid and its derivatives in their entirety. To arrive at that point, the application of many advanced analytical techniques is needed.

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