

Fluorescence Characteristics of Lignin Model Compounds.

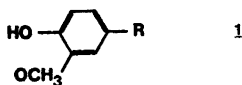
I. Styrene Derivatives

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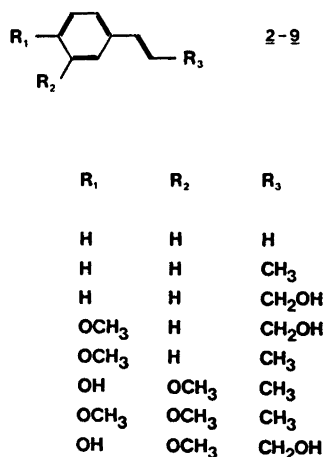
The UV fluorescence and excitation spectra of some lignin models with styrene skeleton (2–9) have been investigated. Auxochromic groups in the β -position cause minor changes in the spectroscopic properties of the styrene chromophore, whereas *para*-substitution significantly affects both the position of the 0–0 band and the Franck-Condon transition. A methoxyl group in the *meta*-position to the propene side chain alters the vibrational pattern of the spectrum, but the energy shifts remain unaltered. The intensity of emission is great upon excitation in the α -band, but shows a major decrease on excitation in the *A*-band for all the compounds. It is concluded that an increase in the rate constants for some similar nonradiative processes is the reason for the fall in emissive intensity on scanning the exciting wavelength from the α -band into the *A*-band. A corrigendum to previously reported pK_a^* -values for isoeugenol 7 and coniferyl alcohol 9 is included. They are estimated to be 4.0 and 3.1 ± 0.5 , respectively.

Most aromatic elements in softwood lignins are of the guaiacyl type (1-hydroxy-2-methoxyphenyl type) carrying different substituents in the 4-position (1).



Substances with related structures are frequently used as lignin models.¹ This is a report on the UV-fluorescence characteristics of lignin models with a styrene skeleton (2–9).

A preliminary communication on the room temperature fluorescence spectra of these compounds is given in Ref. 2.



EXPERIMENTAL

Emission and excitation spectra were measured on a Hitachi Perkin-Elmer spectrofluorimeter model MPF-2A. The spectra were corrected by a procedure described previously.³ The excitation spectra were measured as the total emissive intensity perpendicular to incident light on solutions (5–20 ppm) in ethanol and cyclohexane at 298 K in 1 cm cells, and in ethanol at 77 K in a cylindrical cell. The solvents were checked for spectral purity before use. The spectra were measured on freshly prepared deaerated solutions. The ethanol was Alko AaS spectrograde. The cyclohexane was purified by procedures outlined by Perrin *et al.*⁴ Styrene 2, manufactured by Shell Ltd. (Holland), was chromatographically pure. *trans*-1-Phenyl-1-propene 3 was Fluka *purissimum* grade. Cinnamic alcohol 4 and anethole 6 were Fluka *purum* grade, purified by recrystallization and distillation *in vacuo*, respectively. Isoeugenol methyl ether (1,2-dimethoxy-4-

propenylbenzene) 8 was Merck *purissimum* grade, purified by distillation *in vacuo*. 4-Methoxycinnamic alcohol 5 was synthesized by standard procedures and purified by recrystallization from ether-petroleum ether, m.p. 80 °C. Isoeugenol 7 and coniferyl alcohol (3-(4'-hydroxy-3'-methoxy)-2-propene-1-ol) 9 were purified as described previously.⁵

RESULTS AND DISCUSSION

In the UV-absorption spectra of the compounds under investigation two bands can be recognized at wavelengths greater than 220 nm.⁵ The strong bands at about 250–270 nm have been assigned to interaction between the conjugated side chain and the benzene nucleus, or $p-\pi^*$ bands resulting from the transfer of p -electrons from oxygen substituents (in OH and OCH₃) to the benzene ring, or combinations of these bands, whereas the weak bands at 270–310 nm are due to transitions of the local excitation type occurring in the benzene nucleus ($\pi-\pi^*$ benzenoid bands).^{7,8} The former band is referred to as the *A*-band, ¹*L*_a (*K*-band), the latter as the α -band, ¹*L*_b (*B*-band).⁹ The α -band shows a well-defined vibrational structure in absorption spectra of styrene 2, 1-phenylpropene 3 and cinnamic alcohol 4 at room temperature. The corresponding vibrational pattern of the α -band is recognizable in excitation spectra of the ring substituted compounds measured at 77 K in ethanol solution.

Inspection of the fluorescence, absorption and excitation spectra with respect to the mirror symmetry wave number¹⁰ reveals the following facts. In spectra of a particular com-

pound measured in ethanol at 77 K or in cyclohexane at 298 K the 0–0 bands coincide within the limits of error. The Franck-Condon transitions in the emission spectra are sensitive to the variations in solute-solvent interaction.¹¹ In Table 1 the Stokes' losses in spectra measured in cyclohexane solution at room temperature are given. They are defined as the energy difference between the observed 0–0 bands and the Franck-Condon transitions ($\bar{\nu}_{\max}$ of fluorescence). The Stokes' loss in ethanol is greater than in cyclohexane. For compounds 4, 5, 6, and 8, which contain no phenolic hydroxyl group, this increase is small, 0–100 cm⁻¹, but it amounts to 250 cm⁻¹ for isoeugenol 7 and 600 cm⁻¹ for coniferyl alcohol 9 (Table 1).

The characteristics of the fluorescence spectra measured in ethanol solution at 77 K are also listed in Table 1. Vibrational fine structure is found in all the spectra, a pattern of five bands can be recognized, either as shoulders or as maxima. It is also noteworthy that the 0–0 band is recognizable in the spectra. In spectra of the polar solutes run at higher temperatures in ethanol or cyclohexane solution the vibrational structure is obscured. Typical fluorescence spectra at 77 K in ethanol are seen in Fig. 1–3. No phosphorescence could be detected for the compounds investigated.

For most molecules in condensed media, the fluorescence quantum yield is independent of the wavelength of the exciting light, and an excitation spectrum gives the same information as an absorption spectrum.¹² Fluorescence quantum yield dependence of the wavelength of the exciting light has been found for retinals.^{13,14}

Table 1. Fluorescence characteristics of lignin model compounds with a styrene skeleton.

	Maxima (italics) or shoulders in fluorescence emission spectra in ethanol at 77 K (cm ⁻¹)					Stokes loss in cyclohexane at 298 K (cm ⁻¹)	Increase of Stokes loss in ethanol solution at 298 K with respect to Stokes loss in cyclohexane (cm ⁻¹)
2	<i>34 246</i>	<i>33 222</i>	<i>32 786</i>	32 258	31 746		
3	<i>34 013</i>	<i>33 003</i>	<i>32 467</i>	31 847	31 446		
4	<i>34 130</i>	<i>33 003</i>	<i>32 467</i>	31 948	<i>31 545</i>	1557	
5	<i>32 787</i>	<i>32 258</i>	<i>30 960</i>		29 761	2206	94
6	<i>32 280</i>	<i>32 051</i>	30 864	<i>30 581</i>	29 535	1885	92
7	<i>32 467</i>	<i>31 446</i>	30 910	<i>30 120</i>	28 818	2437	541
8	<i>32 786</i>	<i>31 847</i>	<i>31 152</i>	<i>30 487</i>	29 940	2840	90
9	<i>32 362</i>	<i>31 348</i>	<i>30 864</i>	<i>30 030</i>	28 901	2332	660
	± 200	± 200	± 200	± 200	± 200		

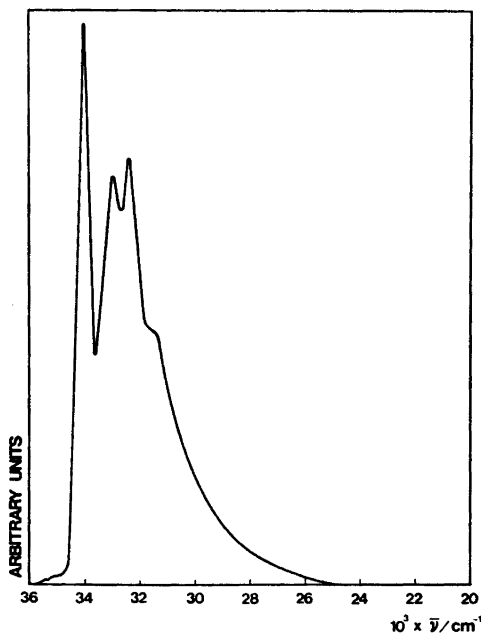


Fig. 1. Fluorescence emission spectrum of *trans*-1-phenyl-1-propene **3** at 77 K in ethanol solution.

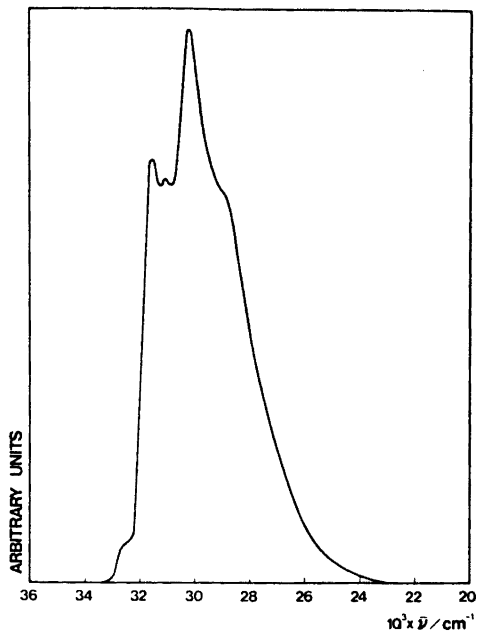


Fig. 3. Fluorescence emission spectrum of co-feneryl alcohol **9** at 77 K in ethanol solution.



Fig. 2. Fluorescence emission spectrum of anethole **6** at 77 K in ethanol solution.

In gas phase investigations on the *cis-trans* isomerization of 1-phenyl-propene Rockley and Salisbury⁸ found that the quantum yield of fluorescence is strongly dependent on the excitation wavelength, remaining constant throughout the α -band, and falling to approximately zero in the *A*-band. They assume that a rapid increase in the rate constants for some non-radiative process(es) is the reason for the rapid fall in the fluorescence quantum yield as the excitation wavelength moves from the α -band into the *A*-band.

In the present investigation the excitation spectra of compounds **2-9** were measured in cyclohexane at room temperature and in ethanol at 77 K. In all the spectra it was found that the intensity of emission is strong on excitation in the α -band, and that the emission shows a minimum about the λ_{max} absorption wavelength in the *A*-band. The possibility that this behaviour of model compounds **2-9** is due to impurities is excluded on the same grounds as discussed by Christensen and Kohler.¹³

It has been shown that there is little, if any, increased interaction between the double bond and the benzene ring on excitation in the α -band of styrene.¹³ It was found that the excita-

Table 2. Excitation characteristics of lignin model compounds with a styrene skeleton.

	Maxima in the α -band of excitation spectra of compounds 2–9 at 77 K in ethanol (cm^{-1})		
2	36 496	35 460	34 365
3	36 101	35 088	34 013
4	36 300	35 211	34 130
5		34 013	32 787
6	34 364	33 670	32 467
7	33 898	33 222	32 573
8	33 300	32 788	32 088
9	33 113	32 573	31 847

tion spectra of 2, 3 and 4 are similar. Compounds 5–9 with substituents on the aromatic ring show the same type of difference in absorption and excitation spectra as compounds 2–4. Evidently the slightly electron donating groups in *para*-position to the side chain and the slightly withdrawing groups in the *meta*-position do not affect the interaction between the propene side chain and the aromatic ring. It is concluded that in the solution spectra of styrene 2 and its derivatives 3–9 an increase in the rate constants for some nonradiative process(es) is the reason for the rapid fall in emissive intensity on scanning the excitation wavelength from the α -band into the A-band, and that the nature of the non-radiative process(es) probably is similar in all the cases.

The characteristics of the excitation spectra measured in ethanol solution at 77 K are listed in Table 2.

The excitation spectra show some vibrational fine structure which is not seen in the absorption spectra due to overlap between the α - and A-bands. It is found that the vibrational spacing of the bands in the excitation spectra corresponds to the spacing of bands found in the fluorescence emission spectra.

In previous papers^{5,16} the excited state $\text{p}K_{\text{a}}$ -values ($\text{p}K_{\text{a}}^*$ -values) for a number of lignin phenols have been reported. The calculation was performed using the Förster cycle¹⁷ on values from the structureless absorption and emission spectra in aqueous alcoholic solution. In accordance with the above discussion it seems more justified to estimate the $\text{p}K_{\text{a}}^*$ -values for isoeugenol 7 and coniferyl alcohol 9 with the wavenumber of the center of gravity of the α -band in the excitation spectra as the

value of $\bar{\nu}_{\text{A}}$ and $\bar{\nu}_{\text{A}}'$, respectively. The corrected $\text{p}K_{\text{a}}^*$ -values of isoeugenol 7 and coniferyl alcohol 9 will be 4.0 and 3.1 ± 0.5 , respectively.

The model compounds contain auxochromic groups of three different types: (i) substituent groups attached to the β -carbon atom of the side chain, (ii) substituent groups in the *para*-position to the side chain in the aromatic ring, and (iii) substituents in the *meta*-position of the aromatic ring.

The incorporation of an auxochromic substituent into the styrene chromophore causes significant changes in the fluorescence spectra as well as in the absorption spectra. The substituents of the first type (i) cause only small increases in Stokes loss, and the position of the 0–0 band remains almost unaltered as compared to styrene. Substituents of category (ii) shift the position of the 0–0 band more than 1300 cm^{-1} (10 nm) towards smaller wavenumbers. The shift is largest for the phenolic compounds 7 and 9, 2000 cm^{-1} (17–18 nm), a fact correlating with the greatly enhanced acidity of these compounds in the excited state. The similarity between a hydroxyl group and a methoxyl group as regards auxochromic properties is great enough to make compounds 5–9 analogous with respect to fluorescence emission.

The introduction of a group (iii) substituent, the *meta*-methoxyl group typical for softwood lignins, causes only a minor shift of the 0–0 band and a small change in the Stokes loss in the spectra. The vibrational pattern is, however, altered by introduction of the *meta*-methoxyl group. This corresponds to the findings of Aulin-Erdtman and Sandén.⁷ The effect is related to the effect of the *meta*-methoxyl groups on the excited state acidity of lignin phenols reported previously.¹⁶

The fluorescence intensity of the investigated compounds is linearly dependent on concentration within the range 0.01–~50 ppm. Even smaller concentrations can be detected by fluorescence measurements. No sign of excimer formation could be detected within this concentration range.

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