

## REACTIONS OF LIGNIN CHROMOPHORES OF THE ENAL AND ENONE TYPES WITH SULFITE

Knut Lundquist,<sup>a</sup> Jim Parkås,<sup>a\*†</sup> Magnus Paulsson,<sup>a‡</sup> and Cyril Heitner<sup>b</sup>

In NaHSO<sub>3</sub>-solutions of coniferaldehyde and its methyl ether (models for lignin chromophores of the cinnamaldehyde type) a dynamic equilibrium between the aldehydes and their hydrogen sulfite adducts is set up. A comparatively slow addition of hydrogen sulfite to the double bond leading to 1,3-disulfonic acid derivatives occurs; coniferaldehyde reacts slower than its methyl ether. In Na<sub>2</sub>SO<sub>3</sub>-solution both aldehydes are rapidly converted to 1,3-disulfonic acid derivatives. The results suggest that in both NaHSO<sub>3</sub>-solution and Na<sub>2</sub>SO<sub>3</sub>-solution the free cinnamaldehydes and sulfite ion are the reactants in the formation of disulfonic acid derivatives. Alkaline treatment of the 1,3-disulfonic acids leads to regeneration of the cinnamaldehydes. On prolonged storage in Na<sub>2</sub>SO<sub>3</sub>-solution, the 1,3-disulfonic acid derivative of the methyl ether of coniferaldehyde undergoes reactions leading to colored products and regeneration of the cinnamaldehyde on alkaline treatment fails. A model compound representative of lignin chromophores of enone type (*trans*-3,3',4,4'-tetramethoxychalcone) rapidly undergoes addition to the double bond with formation of a sulfonic acid derivative in Na<sub>2</sub>SO<sub>3</sub>-solution. Treatment of a second model of enone type, 2,6-dimethoxy-*p*-quinone, with NaHSO<sub>3</sub>/Na<sub>2</sub>SO<sub>3</sub>-solution results in formation of a sulfonic acid derivative. The reactions of lignin chromophores of the enone and enal types with hydrogen sulfite/sulfite are discussed.

*Keywords:* Cinnamaldehyde, Chalcone, Chromophore, Lignin, Model compounds, Pulping, Sulfonation

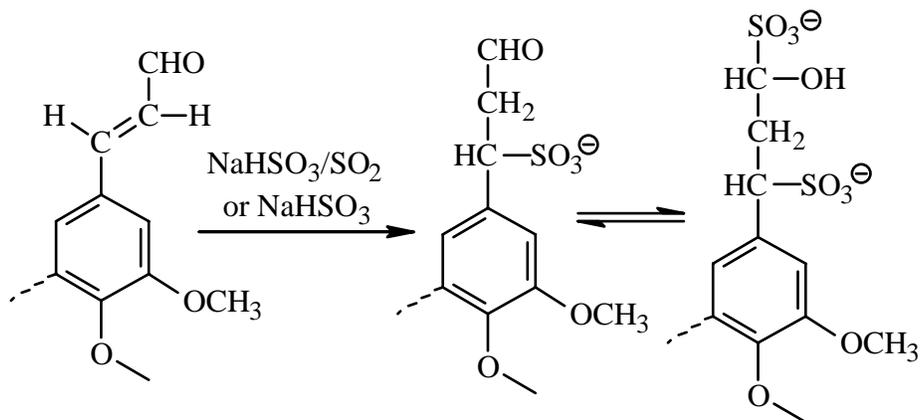
*Contact information:* a: Forest Products and Chemical Engineering, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden; b: Paprican, 570 St. John's Blvd., Pointe Claire, Quebec H9R 3J9, Canada; †: Present address: Södra Cell AB, R&D, SE-43024 Väröbacka, Sweden; ‡: Present address: EKA Chemicals AB, SE-44580 Bohus, Sweden.

\*Corresponding author: [jim.parkas@sodra.com](mailto:jim.parkas@sodra.com)

## INTRODUCTION

Several pulping processes are based on delignification effected by sulfurous acid and/or salts of sulfurous acid (Rydholm 1965). Salts of this acid are also used as impregnation chemicals in certain chemithermomechanical pulping processes in order to facilitate pulping and improve pulp quality (Lindholm and Kurdin 1999). Of interest in these contexts are the reactions of salts of sulfurous acid with lignin chromophores of the enal [e.g. cinnamaldehyde units (Adler 1977; Lundquist 1992)] and enone types (e.g. quinone units). Cinnamaldehyde groups not only contribute to the color of the pulp but also may play a role in the light-induced yellowing of the pulp (Gellerstedt and Pettersson 1975). It is known that lignin units of the cinnamaldehyde type are sulfonated on acid sulfite pulping or bisulfite pulping (Fig. 1) (Adler and Elmer 1948; Mothershead and Glennie 1964; see also Kratzl 1948). Experiments with the model compounds

coniferaldehyde (**1**) and its methyl ether (**2**) show that sulfonation occurs on treatment with acid sulfite (Aulin-Erdtman 1953), and experiments with compounds of type **2** show that this also occurs on treatment with bisulfite and neutral sulfite (Suckling 1991) [see also the studies of the sulfonation of cinnamaldehyde by Tiemann (1898) and Kratzl and Däubner (1944)].



**Fig. 1.** Formation of sulfonic acid derivatives of lignin units of the cinnamaldehyde type on acid sulfite and bisulfite pulping.

Noteworthy also is the isolation of small amounts of the disulfonic acid derivative **6a** from the reaction mixture obtained on neutral sulfite cooking of **2** (Gellerstedt et al. 1977). According to Heitner and Min (1987) the effect of sulfite treatment on increasing the brightness of chemithermomechanical pulp can be attributed to sulfonation of cinnamaldehyde groups.

In connection with studies of the light-induced yellowing of mechanical pulps (Parkås et al. 2001) we found it was of interest to obtain a more detailed knowledge about the sulfonation reactions of lignin chromophores of the enal and enone types. To elucidate the reaction sequences leading to sulfonation and other modifications of chromophores of enal type, we have studied the reactions of the lignin-related cinnamaldehydes **1** and **2** in NaHSO<sub>3</sub>-solution and Na<sub>2</sub>SO<sub>3</sub>-solution. The sulfonation of a model compound representative of lignin chromophores of the enone type, *trans*-3,3',4,4'-tetramethoxychalcone (**12**), in a Na<sub>2</sub>SO<sub>3</sub> solution was examined. Sulfonation experiments with a quinone (**17**), representative of a second type of enone chromophore, were also carried out. To study the initial reactions and the course of the reactions we have carried out the experiments with model compounds at low temperature (22 °C). The reactions of lignin chromophore models with salts of sulfurous acid result in decolorization or color changes. We have followed these changes by UV/VIS spectroscopy. It was found that this technique could also with advantage be applied in studies of the course of the reactions, particularly in the case of models of the cinnamaldehyde type. The reactions lead to changes of the conjugated systems, which in turn result in dramatic changes of the spectral properties. The thorough and comprehensive studies of the UV properties of lignin models (including compounds of the type examined in this paper) by Aulin-Erdtman (Aulin-Erdtman 1953; Aulin-Erdtman

and Hegbom 1956) and other studies of the UV properties of lignins and model compounds served as a basis for our investigations (for reviews see Goldschmid (1971), Lin (1992), see also Silverstein et al. 1991).

## EXPERIMENTAL

### Chemicals and Starting Materials

(*E*)-3-(4-hydroxy-3-methoxyphenyl)propenal (coniferaldehyde) (**1**) (Iliefski et al. 2003), (*E*)-3-(3,4-dimethoxyphenyl)propenal (**2**) (Iliefski et al. 1998), (*E*)-3-(3,4-dimethoxyphenyl)-2-propen-1-ol (**7**) (Li and Lundquist 1995), *trans*-3,3',4,4'-tetramethoxychalcone (**12**) (Li et al. 1993), deoxyveratrin (**14**) (Kubiczek 1946) and sodium 1-(4-hydroxy-3-methoxyphenyl)propane-1-sulfonate (Adler et al. 1962) were prepared according to methods described in the literature. Buffer solution at pH 12 was prepared by adding 0.1 M NaOH (26.9 ml) to 0.05 M Na<sub>2</sub>HPO<sub>4</sub> (50 ml). Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> were purchased from Merck. Hydroquinonesulfonate (**16**) (potassium salt) and 2,6-dimethoxy-*p*-benzoquinone (**17**) were purchased from Aldrich.

**Wiesner Reaction** (Nakano and Meshitsuka 1992; see also Sarkanen and Ludwig 1971)

Three drops of the samples were added to 5 ml of a mixture of equal amounts of 0.1 M phloroglucinol in 60% ethanol and 4 M hydrochloric acid in ethanol-water 2:1. A red or violet color appearing within 3 min was taken as evidence for the presence of cinnamaldehydes (**1** or **2**).

### Thin Layer Chromatography (TLC)

TLC was performed on silica gel plates (Merck, Kieselgel 60 F<sub>254</sub>) with methylene chloride-ethyl acetate (10:1) (*R<sub>f</sub>* values: sulfonic acid salts, 0.00; **1**, 0.28; **17**, 0.30; **2**, 0.37; veratraldehyde, 0.45), butanol-propanol-water-acetic acid (22:18:10:1) (Glennie 1966) (*R<sub>f</sub>* values: disulfonic acid derivatives (**4a** and **6a**), 0.0-0.1; **13**, 0.38; sodium 1-(4-hydroxy-3-methoxyphenyl)propane-1-sulfonate, 0.39; hydroquinone-sulfonate (**16**) (potassium salt), 0.43; veratraldehyde, 0.63; **2**, 0.65; **1**, 0.68). Spots were made visible with UV light and by spraying with formalin-H<sub>2</sub>SO<sub>4</sub> (1:9) and subsequent heating. Cinnamaldehydes were also detected by spraying with a mixture of equal amounts of 0.1 M phloroglucinol in 60% ethanol and 4 M hydrochloric acid in ethanol-water 2:1.

### UV Spectroscopy

UV spectra were recorded with a Varian Cary 4 UV-Visible Spectrophotometer. Absorption maxima for reference compounds (solvent, 95% ethanol): **1**, λ<sub>max</sub> 342 nm (ε<sub>max</sub> 24000), λ<sub>max</sub> 242 nm (ε<sub>max</sub> 10700); **2**, λ<sub>max</sub> 338 nm (ε<sub>max</sub> 22200), λ<sub>max</sub> 247 nm (ε<sub>max</sub> 11600); 3-(3,4-dimethoxyphenyl)-2-propen-1-ol (**7**), λ<sub>max</sub> 262 nm (ε<sub>max</sub> 16900); **12**, λ<sub>max</sub> 364 nm (ε<sub>max</sub> 24900), λ<sub>max</sub> 239 nm (ε<sub>max</sub> 13800); **14**, λ<sub>max</sub> 306 nm (ε<sub>max</sub> 8900), λ<sub>max</sub> 277 nm (ε<sub>max</sub> 13000).

### Sulfonation of Coniferaldehyde (1) and its Methyl Ether (2) by Treatment with 1 M NaHSO<sub>3</sub>

Coniferaldehyde (1) (55 mg) or its methyl ether (2) (56 mg) was dissolved in 20 ml 1 M NaHSO<sub>3</sub> (magnetic stirring) at 22 °C. Complete dissolution required 1-2 h. The UV spectra of samples of the reaction mixtures diluted with water (1:100 and 1:500) were recorded after different periods of time. The reaction mixtures were also examined by TLC. The Wiesner reagent was used for the detection of cinnamaldehydes in the reaction mixtures.

### Sulfonation of Coniferaldehyde (1) and its Methyl Ether (2) by Treatment with 1 M Na<sub>2</sub>SO<sub>3</sub>

Coniferaldehyde (1) or its methyl ether (2) (about 70 mg) was dissolved in 20 ml 1 M Na<sub>2</sub>SO<sub>3</sub> (magnetic stirring) at 22 °C. To facilitate dissolution the aldehydes were ground in a mortar. Complete dissolution required about 2 h. UV spectra of samples of the solutions diluted with water (1:100 and 1:500) were recorded after different periods of time. To suppress ionization the samples from experiments with coniferaldehyde were acidified (2 ml of 0.4 M HCl were added to a 1 ml sample) prior to dilution and recording of the UV spectra. The reaction mixtures were also examined by TLC. The Wiesner reagent was used for the detection of cinnamaldehydes in the reaction mixtures.

### Regeneration of 2 Reacted with 1 M Na<sub>2</sub>SO<sub>3</sub> Solution

A sample (1 ml) of a solution of 2 in 1 M Na<sub>2</sub>SO<sub>3</sub> was acidified with 2 M hydrochloric acid (1 ml). The solution was concentrated to dryness and the residue dissolved in 100 ml pH 12 buffer. UV spectra of the solution were recorded after different periods of time.

### Sulfonation of *Trans*-3,3',4,4'-tetramethoxychalcone (12)

A mixture of *trans*-3,3',4,4'-tetramethoxychalcone (12) (102 mg), dioxane (2 ml) and 10 ml 1 M Na<sub>2</sub>SO<sub>3</sub> was stirred at room temperature (22 °C). Complete dissolution of the chalcone required 4 h. TLC showed that, excepting traces of the starting material, only one compound was present in the solution. The UV spectrum of the solution, recorded after dilution with water (1:500), similarly showed that 12 was essentially absent. A portion of the solution (5 ml) was acidified with 4 M hydrochloric acid (1.75 ml), and the solvents were removed by film evaporation. The <sup>1</sup>H NMR spectra [recorded at 400 MHz with a Varian Unity 400 instrument (temperature, ≈293 K)] of the residue and a fraction of the residue (30 mg, obtained by leaching of the residue with butanol) dissolved in D<sub>2</sub>O were recorded (internal reference, the sodium salt of 3-(trimethylsilyl)propane sulfonic acid). The two spectra did not differ significantly. Based on the examinations it was concluded that the product consisted of the sulfonic acid salt 13. <sup>1</sup>H NMR spectrum of the fraction obtained by leaching with butanol: δ 3.67 (3H, s, OCH<sub>3</sub>), 3.78 (3H, s, OCH<sub>3</sub>), 3.79 (3H, s, OCH<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 3.70 (1H, dd, J= 4.2 and 16.4 Hz, CH<sub>2</sub>), 3.87 (1H, dd, J= 10.6 and 16.4 Hz, CH<sub>2</sub>) 4.60 (1H, dd, J= 4.2 and 10.6 Hz, >CH-SO<sub>3</sub>Na), 6.69 (1H, d, J= 8 Hz, H-Ar), 6.94 (1H, d, J= 8 Hz, H-Ar), 7.04 (1H, dd, J= 2 and 8 Hz, H-Ar), 7.10 (1H, d, J= 2 Hz, H-Ar), 7.11 (1H, d, J= 2 Hz, H-Ar), 7.41 (1H, dd, J= 2 and 8 Hz, H-Ar).

### Treatment of 2,6-dimethoxy-*p*-benzoquinone (**17**) with 1 M Na<sub>2</sub>SO<sub>3</sub> and 1 M Na<sub>2</sub>SO<sub>3</sub>-1 M NaHSO<sub>3</sub> (1:1)

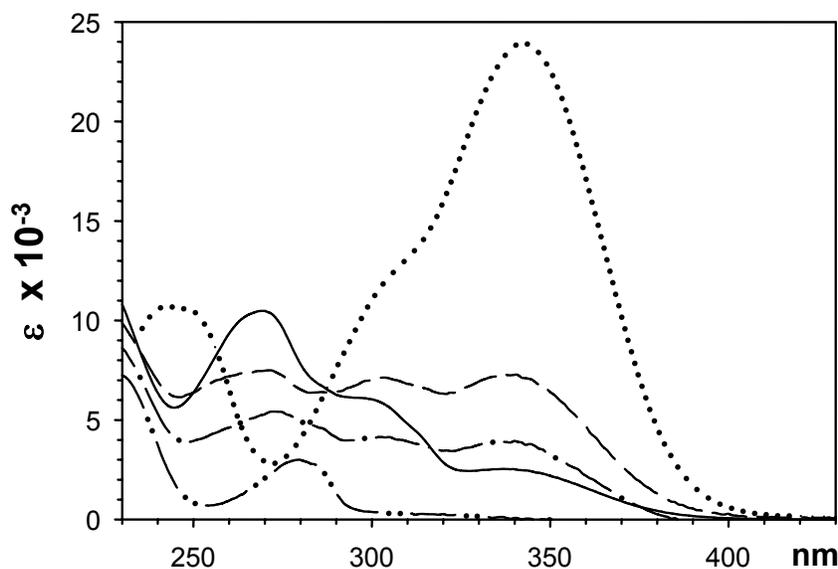
a. 2,6-Dimethoxy-*p*-benzoquinone (**17**) (ca. 50 mg) was dissolved in 10 ml 1 M Na<sub>2</sub>SO<sub>3</sub>-1 M NaHSO<sub>3</sub> (1:1). Dissolution occurred almost immediately and the solution was colorless. No starting material was present in the solution (TLC). TLC [eluent, butanol-propanol-water-acetic acid (22:18:10:1)] exhibited only one spot (R<sub>f</sub> value 0.38). Based on comparisons with R<sub>f</sub> data published by Glennie (1966) and the R<sub>f</sub> value for hydroquinonesulfonate (**16**) (potassium salt) we attribute the spot to **18**.

b. 2,6-Dimethoxy-*p*-benzoquinone (**17**) (ca. 50 mg) was dissolved in 10 ml 1 M Na<sub>2</sub>SO<sub>3</sub>. Dissolution required 1-2 h. The solution acquired a yellow color. No starting material was present in the solution (TLC). TLC [eluent, butanol-propanol-water-acetic acid (22:18:10:1)] showed only materials with very low R<sub>f</sub> value (< 0.1). Based on comparisons with R<sub>f</sub> data published by Glennie (1966) disulfonic acids may be present in the product.

## RESULTS AND DISCUSSION

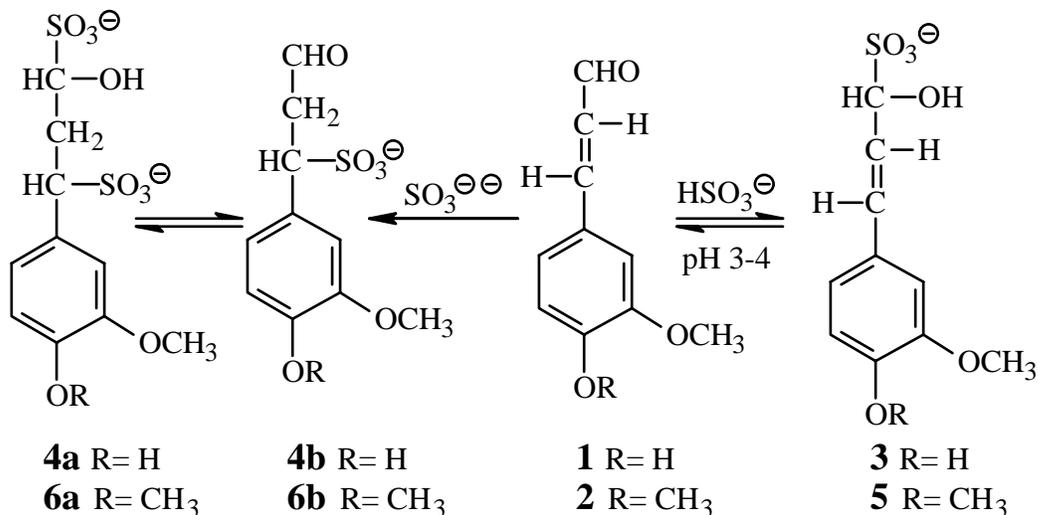
### Reactions of Coniferaldehyde (**1**) and its Methyl Ether (**2**) in 1 M NaHSO<sub>3</sub>

Solutions of cinnamaldehydes **1** and **2** in 1 M NaHSO<sub>3</sub> were examined by UV spectroscopy and TLC after different periods of time. UV spectra of a solution (diluted with water) obtained in an experiment with **1** are shown in Fig. 2.

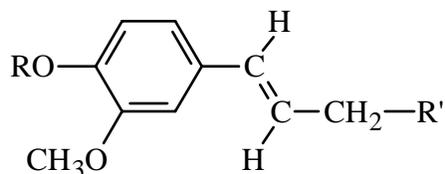


**Fig. 2.** The UV spectrum of a solution of coniferaldehyde (**1**) in 1 M NaHSO<sub>3</sub> after 5 h (----), 25 h (- · - · -) and 100 h (- · - · - · -). The solution was diluted with water 1:500 before the recording of the spectra. The solution stored for 5 h was also diluted with water 1:100 (——). The UV spectrum of **1** in 95% ethanol (· · · · ·) is also shown.  $\epsilon$  is calculated from the initial concentration of **1**.

The presence of starting material in the solution could be demonstrated by TLC and the Wiesner reaction. Even after several days the solution showed a weak but distinct Wiesner reaction.



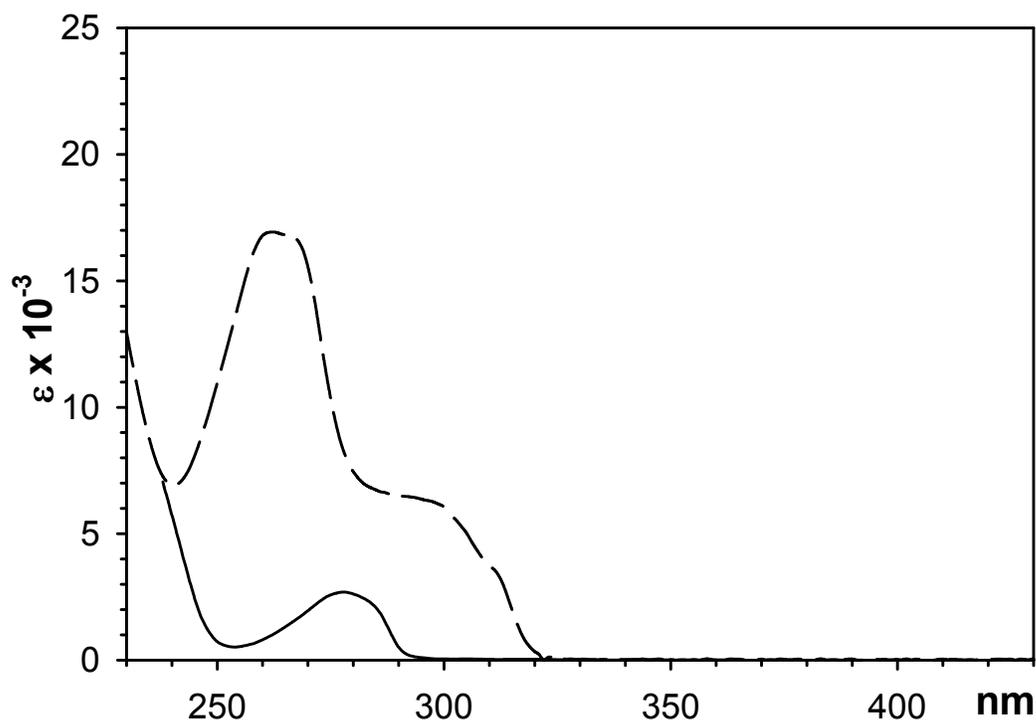
**Fig. 3.** Reactions of coniferaldehyde (**1**) and its methyl ether (**2**) in 1 M NaHSO<sub>3</sub>. A dynamic equilibrium is set up between the aldehydes and the corresponding hydrogen sulfite adducts (**3** and **5**). A slow conversion to **4** and **6** occurs.



- 7** R= CH<sub>3</sub>, R'= OH  
**8** R= H, R'= OH  
**9** R= H, R'= SO<sub>3</sub>Na

**Formula Fig. 1**

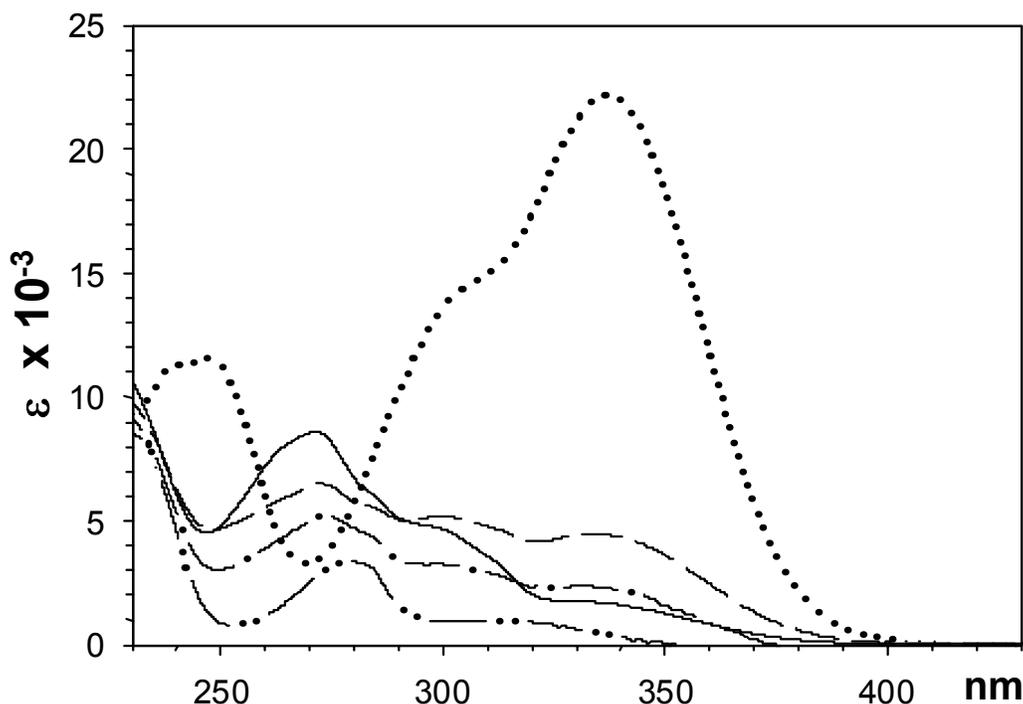
The reactions leading to the spectral changes are shown in Fig. 3. From comparisons of the UV spectra (Fig. 2) with the spectra of **1**, the sulfonic acid derivative **6** prepared according to Aulin-Erdtman (1953), 3-(3,4-dimethoxyphenyl)-2-propen-1-ol (**7**) (Fig. 4), coniferyl alcohol (**8**) [solvent 95% ethanol:  $\lambda_{\max}$  = 266 nm,  $\epsilon_{\max}$  = 15100, aqueous solution:  $\lambda_{\max}$  = 261 nm,  $\epsilon_{\max}$  = 15100 (Aulin-Erdtman and Hegbom 1957)] and salts of 3-(4-hydroxy-3-methoxyphenyl)-2-propene-1-sulfonic acid (e.g. **9**) ( $\lambda_{\max}$  = 267 nm,  $\epsilon_{\max}$  = 15600 [Schubert et al. 1967]), it could be concluded that an equilibrium is initially set up between the starting material and the hydrogen sulfite adduct **3** (Fig. 3).



**Fig. 4.** UV spectra of **6** [**2** sulfonated according to Aulin-Erdtman (1953)] (—) and 3-(3,4-dimethoxyphenyl)-2-propen-1-ol (**7**) (---). The spectrum of **6** closely resembles that of **4** (Aulin-Erdtman 1953).

That an equilibration rapidly occurs is evident from comparisons of the spectra obtained on dilution of the solution with water 1:100 and 1:500 (Fig. 2, cf. Fig. 4). As judged from UV spectral examinations, equilibration after dilution required < 20 min. On the basis of comparisons with the spectra in Fig. 4, it can be concluded from the spectra recorded after different periods of time (Fig. 2) that a slow conversion to the sulfonic acid derivative **4** occurs (Fig. 3). A weak Wiesner reaction suggests that traces of **1** were present in the solution even after 100 h. TLC [eluent: butanol-propanol-water-acetic acid (22:18:10:1)] showed a spot with very low  $R_f$  value and streaking ranging from  $R_f$  0.1 to  $R_f$  0.5. Based on literature data (Glennie 1966) and the use of the sodium salt of 1-(4-hydroxy-3-methoxyphenyl)propane-1-sulfonic acid as a reference compound ( $R_f$  0.39), we attribute the low  $R_f$  value spot to the 1,3-disulfonic acid salt **4a** and the streaking to monosulfonic acid salts (**3** and **4b**).

UV spectra of a solution of **2** in 1 M NaHSO<sub>3</sub> (diluted with water) recorded after different periods of time are shown in Fig. 5.



**Fig. 5.** The UV spectrum of a solution of the methyl ether of coniferaldehyde (**2**) in 1 M NaHSO<sub>3</sub> after 5 h (----), 25 h (- · - · -) and 100 h (- · - · - · -). The solution was diluted with water 1:500 before the recording of the spectra. The solution stored for 5 h was also diluted with water 1:100 (——). The UV spectrum of **2** in 95% ethanol (· · · · ·) is also shown.  $\epsilon$  is calculated from the initial concentration of **2**.

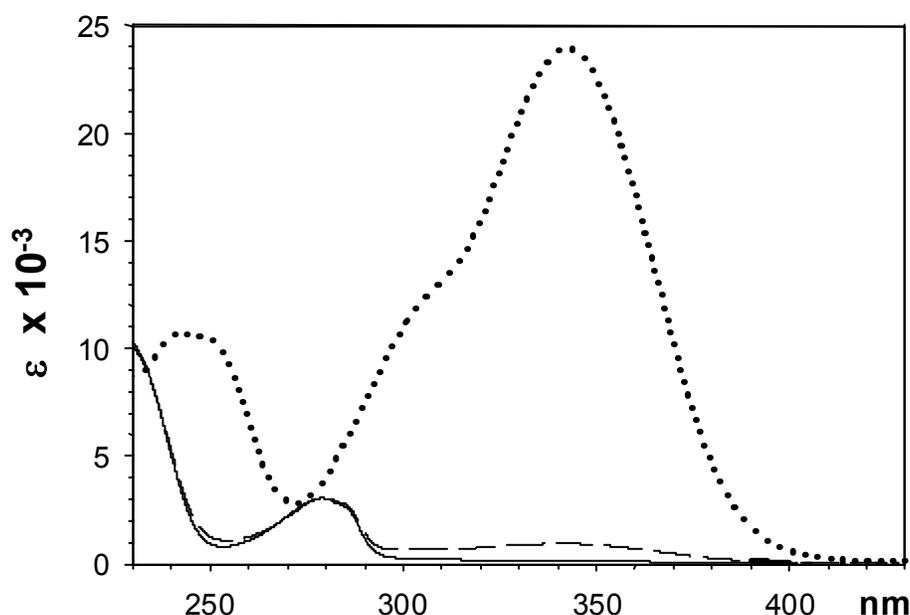
Comparisons with the spectra in Figs. 2 and 5 suggest that **1** and **2** react with 1 M NaHSO<sub>3</sub> in an analogous manner (Fig. 3). However, the rate of addition to the double bond differs. The non-phenolic cinnamaldehyde **2** adds hydrogen sulfite to the double bond more rapidly than does the phenolic cinnamaldehyde **1**. This is evident from comparisons of the absorbance at 260-270 nm (attributed to **3/5**) in the UV spectra in Figs. 2 and 5 and is also in accordance with results from examinations by TLC and the Wiesner reagent. Thus the solution of **2** in 1 M NaHSO<sub>3</sub> gave a very weak Wiesner reaction after 72 h, and TLC showed that an only trace of **2** was present in the solution. After 100 h **2** could not be detected by the Wiesner reaction or TLC. TLC with the eluent butanol-propanol-water-acetic acid (22:18:10:1) showed spots and streaking that can be attributed to sulfonic acids (cf. the results from the TLC examination of the solution of **1** described above). The UV spectra of the solutions of **2** stored for a long period of time (e.g. 100 h) show some absorbance in the region above 300 nm (Fig. 5) that cannot be attributed to the sulfonic acids formed or the starting material. This UV absorbance is attributed to formation of condensation products (Fig. 6) (cf. Suckling 1991).



Lowering of the pH of the reaction mixtures led to slower formation of **4** and **6**. This is consistent with the assumption that the free aldehyde and sulfite ion are reactants in the formation of **4** and **6** (Fig. 3). To further elucidate this point we have studied the reactions of **1** and **2** in 1 M Na<sub>2</sub>SO<sub>3</sub> (see below).

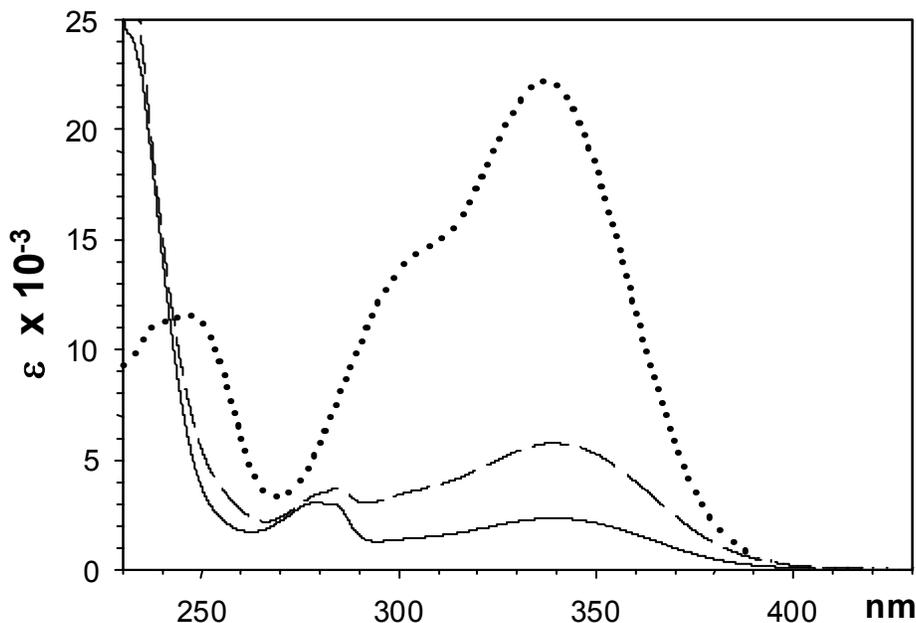
### Reactions of Coniferaldehyde (**1**) and its Methyl Ether (**2**) in 1 M Na<sub>2</sub>SO<sub>3</sub>

Experiments with cinnamaldehydes **1** and **2** of the aforementioned type in which 1 M NaHSO<sub>3</sub> had been replaced by 1 M Na<sub>2</sub>SO<sub>3</sub> were carried out. UV spectra of the solutions (diluted with water, in the case of **1** after acidification) recorded after different periods of time are shown in Figs. 8 and 9.

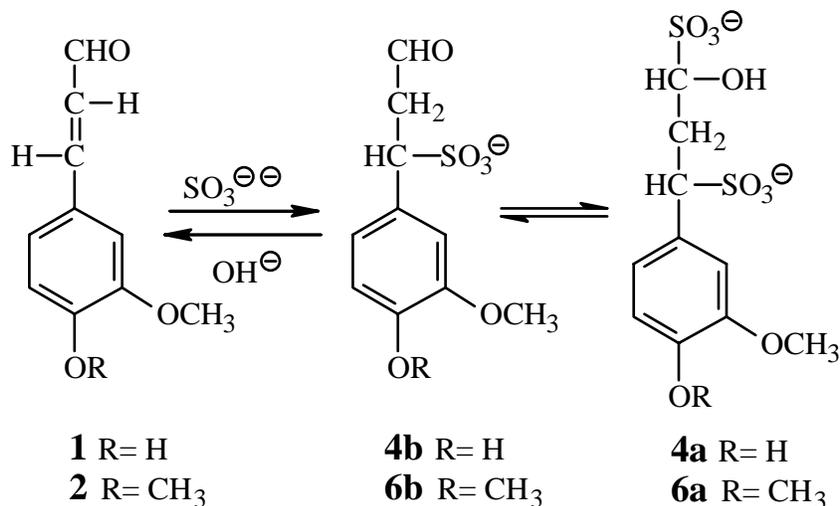


**Fig. 8.** The UV spectrum of a solution of coniferaldehyde (**1**) in 1 M Na<sub>2</sub>SO<sub>3</sub> after 1.5 h (—) and 24 h (---). The solution was diluted with water (1:100) before the recording of the spectrum. The UV spectrum of **1** in 95% ethanol (· · · · ·) is also shown.  $\epsilon$  is calculated from the initial concentration of **1**.

The spectra suggest that a rapid addition of sulfite to the double bonds occurs with formation of **4** and **6** (Fig. 10) (cf. Fig. 4). Free cinnamaldehydes could not be detected in the solutions by TLC. Only the solution of coniferaldehyde (**1**) gave a weak Wiesner reaction, and on long term storage this reaction became even weaker. The UV absorbance in the region above 300 nm increases on storage of the solutions. This increase is particularly pronounced in experiments with **2** (Fig. 9). Formation of condensation products (cf. Suckling 1991) probably explains the increase of the absorbance above 300 nm (Fig. 6). The formation of **11** on sulfite treatment of **2** has been reported by Suckling (1991).



**Fig. 9.** The UV spectrum of a solution of the methyl ether of coniferaldehyde (**2**) in 1 M Na<sub>2</sub>SO<sub>3</sub> after 2 h (—) and 29 h (---). The solution was diluted with water (1:100) before the recording of the spectrum. The UV spectrum of **2** in 95% ethanol (····) is also shown.  $\epsilon$  is calculated from the initial concentration of **2**.



**Fig. 10.** Reactions of coniferaldehyde (**1**) and its methyl ether (**2**) in 1 M Na<sub>2</sub>SO<sub>3</sub>. Regeneration of the aldehydes could be accomplished by treatment with pH 12 buffer.

Aulin-Erdtman (1953) showed that the aldehydes **1** and **2** are regenerated when **4** and **6** are treated with pH 12 buffer. We found that **1** was regenerated when a sample of

the Na<sub>2</sub>SO<sub>3</sub> solution was diluted (1:100) with pH 12 buffer (even if the Na<sub>2</sub>SO<sub>3</sub> solution had been kept at room temperature for several days). Similar treatment of the Na<sub>2</sub>SO<sub>3</sub> solution of **2** did not result in a regeneration of **2**. However, acidification followed by evaporation to dryness and dissolution of the residue in pH 12 buffer led to regeneration of **2**. An explanation for the different results obtained with **1** and **2** may be that an equilibrium involving sulfite ion, free cinnamaldehyde, and its sulfonic acid derivative is set up in the buffer solution and that this equilibrium is much more in favor of the sulfonic acid derivative in the case of cinnamaldehyde **2** (Fig. 10). Regeneration of **2** could only be accomplished if the solution was fairly fresh. Attempts to regenerate **2** from Na<sub>2</sub>SO<sub>3</sub> solutions that had been stored for several days at 22°C failed. Evidently, prolonged storage of **2** in Na<sub>2</sub>SO<sub>3</sub> solution leads to formation of products that are not converted to **2** on alkaline treatment. A plausible explanation would be that reversed aldol condensation occurred in the slightly alkaline sulfite solution (**6** → **2** → veratraldehyde + acetaldehyde). It was found that veratraldehyde actually formed, but very slowly. The formation of veratraldehyde is in accordance with observations made by Suckling (1991). The conversion to veratraldehyde contributes to the failure to regenerate **2** on alkaline treatment to a small extent; the main reason for the failure is probably formation of condensation products (Fig. 6) (Suckling 1991).

Aulin-Erdtman (1953) prepared the sulfonic acid derivatives **4** and **6** by subjecting **1** and **2** to conditions similar to those of acid sulfite pulping. Treatment of the obtained sulfonic acid derivatives with pH 12 buffer resulted in regeneration of **1** and **2** but the regeneration was not complete (in particular in the case of **2**) [Aulin-Erdtman (1953)]. The above described studies of the regeneration of the cinnamaldehydes from **4** and **6** provide an explanation of the incomplete regeneration of the cinnamaldehydes observed by Aulin-Erdtman (1953). Acid treatment did not lead to regeneration of the cinnamaldehydes (**1** and **2**) from the sulfonic acid derivatives **4** and **6**. This is in accordance with the literature dealing with sulfonic acids of cinnamaldehydes (see e.g. Mothershead and Glennie 1964).

### Sulfonation of *trans*-3,3',4,4'-tetramethoxychalcone (**12**) by Treatment with Na<sub>2</sub>SO<sub>3</sub>

*Trans*-3,3',4,4'-Tetramethoxychalcone (**12**) was dissolved in 1 M Na<sub>2</sub>SO<sub>3</sub>-dioxane (5:1). Examinations of the solution (TLC and UV) showed that a practically quantitative conversion to the sulfonic acid salt **13** had occurred (Fig. 11). The UV spectrum of the solution illustrates the completeness of the reaction (Fig. 12). The structure of **13** was confirmed by <sup>1</sup>H NMR spectroscopy.

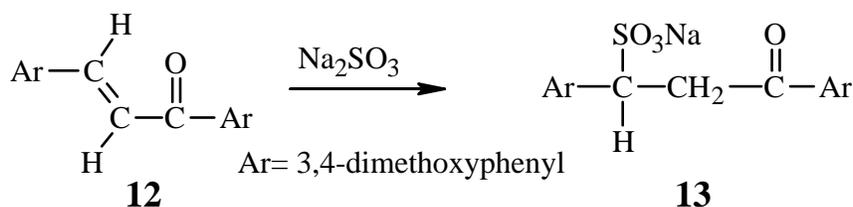
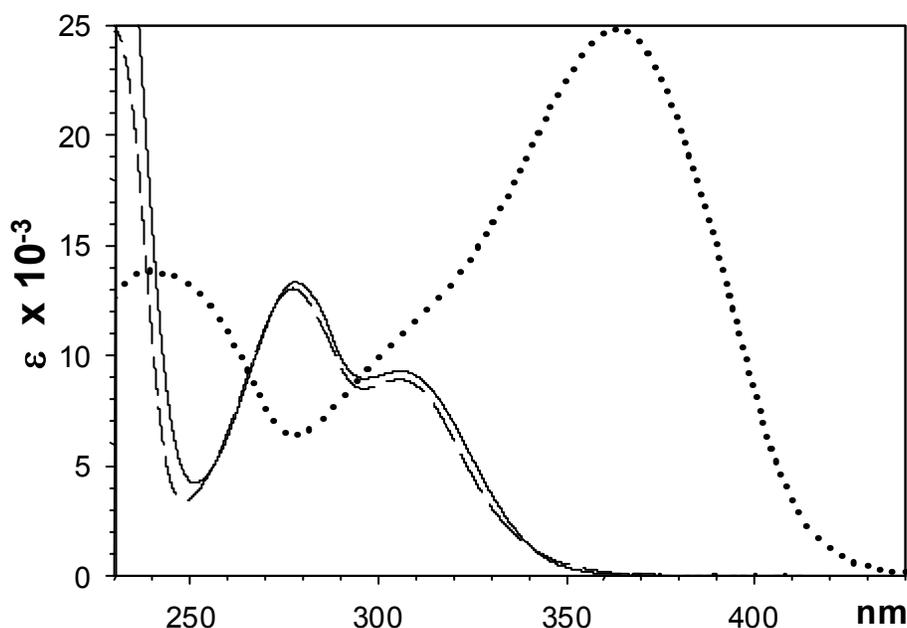
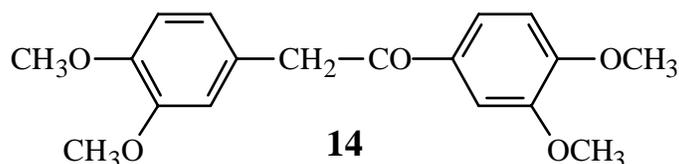


Fig. 11. Sulfonation of *trans*-3,3',4,4'-tetramethoxychalcone (**12**) in 1 M Na<sub>2</sub>SO<sub>3</sub>-dioxane (5:1).



**Fig. 12.** UV spectrum of *trans*-3,3',4,4'-tetramethoxychalcone (**12**) treated with Na<sub>2</sub>SO<sub>3</sub> solution (—). For comparisons the UV spectra of **12** (·····) and deoxyveratrin (**14**) (---) in 95% ethanol are shown.  $\epsilon$  is calculated from the initial concentration of **12**.



**Formula Fig. 2**

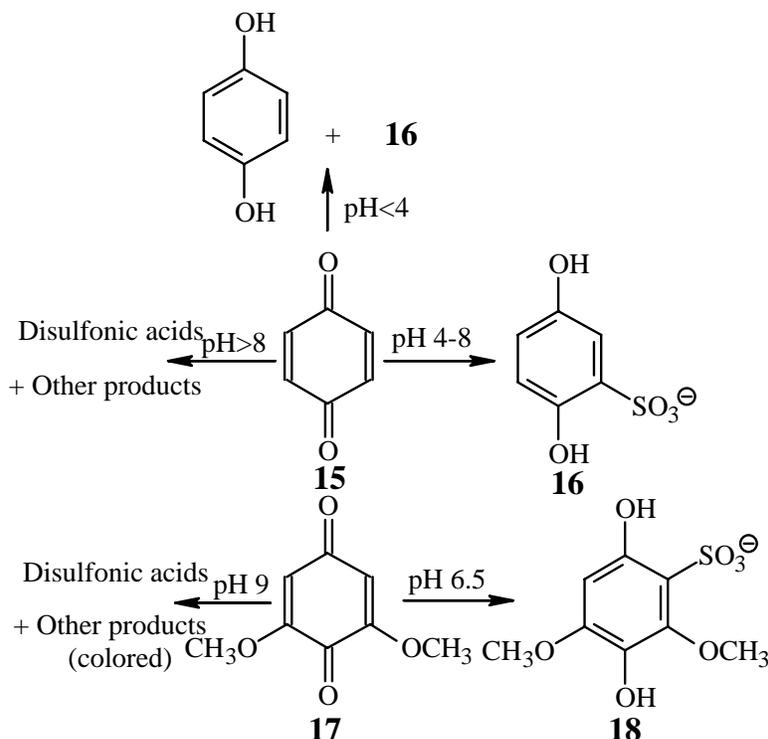
### Reactions of Lignin Chromophores of the Enal and Enone Types with Sulfite

Cinnamaldehydes **1** and **2** are appropriate model compounds for lignin chromophores of the enal type. Compound **2** is representative of the major part of the chromophores of this type, since most of the lignin units are non-phenolic. We think that it is justified to assume that the sulfonation reactions of cinnamaldehyde end groups in lignins are the same as those of the model compounds **1** and **2**.

Based on the results from the cinnamaldehyde study we considered it of interest to examine whether lignin chromophores of the arylconjugated enone type could be expected to react with 1 M Na<sub>2</sub>SO<sub>3</sub> at low temperatures. The chalcone derivative **12** was selected as a model compound representative of such chromophores. It was found that **12** reacted rapidly with formation of the sulfonic acid salt **13** (Fig. 11) under such conditions. Kratzl and Däubner (1944) have demonstrated that sulfonic acid derivatives

structurally related to **13** are formed on acid sulfite cooking of chalcone derivatives and several other compounds of the enone type.

Quinone units represent a second type of lignin chromophores of the enone type. It has been shown that the outcome of reactions of *p*-benzoquinone (**15**) with sulfite is strongly pH-dependent (Fig. 13) (Youngblood 1986). We have made some experiments with the methoxylated quinone **17**. The results (see Experimental) suggest that the reactions of **17** are analogous to those of **15** (Fig. 13).



**Fig. 13.** Reactions of quinones with sulfite.

Arylconjugated enals (such as cinnamaldehydes) and conjugated enones (such as chalcones and quinones) are in all probability important chromophoric groups in pulps. Such groups could also play a role as sensitizers in connection with the photochemical “yellowing” of paper produced from mechanical and chemimechanical pulps. The model compound studies presented in this paper suggest that these types of chromophoric groups can be eliminated by treatment with sulfite under suitable conditions. Sulfite concentration and pH are important factors. Treatment with sulfite at pH about 9 can be expected to generate new chromophoric groups from cinnamaldehyde units and perhaps also from quinone units. It is notable in this context that the optical properties of chemithermomechanical pulp manufactured from Black spruce wood (*Picea mariana*) pretreated with sulfite at pH 4.2 are better than those of such pulp manufactured from wood pretreated with sulfite at pH 8.6 (Argyropoulos and Heitner 1991). It is also of interest to note that formation of chromophores, possibly of quinoid type, was lessened when sulfite was present during refining of *Pinus radiata* wood (Suckling 1995).

## CONCLUSIONS

1. The course and outcome of the reactions of lignin chromophores of the enal and enone types with sulfite are strongly pH-dependent.
2. Based on the experiments with model compounds it can be concluded that in both NaHSO<sub>3</sub>-solution and Na<sub>2</sub>SO<sub>3</sub>-solution the free cinnamaldehyde units and SO<sub>3</sub><sup>2-</sup>-ion are the reactants in the formation of disulfonic acid derivatives. (On treatment with NaHSO<sub>3</sub>-solution an equilibrium is initially set up between cinnamaldehydes **1** and **2** and their sulfite adducts. This is followed by a comparatively slow conversion to disulfonic acid derivatives. Increased acidity leads to slower formation of such derivatives. On treatment with Na<sub>2</sub>SO<sub>3</sub>-solution **1** and **2** are rapidly converted to disulfonic acid derivatives).
3. Cinnamaldehyde units are regenerated on alkaline (but not acid) treatment of their disulfonic acid derivatives, provided the sulfite concentration is low. Prolonged treatment with Na<sub>2</sub>SO<sub>3</sub>-solution irreversibly leads to new types of chromophoric groups.
4. Lignin chromophores of the chalcone type are eliminated on treatment with Na<sub>2</sub>SO<sub>3</sub>-solution.
5. On sulfite treatment quinoid units may be reduced, form sulfonic acids, or give rise to complex, colored products dependent on pH.

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