

# Reactivity of Ferulic Acid and Its Derivatives toward Hydrogen Peroxide and Peracetic Acid

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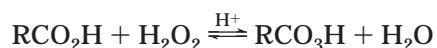
The reactions of ferulic acid and its derivatives with hydrogen peroxide and peracetic acid in lignin-retaining bleaching conditions have been investigated to determine their susceptibility to oxidative degradation. The conjugated side chain of ferulic acid and its etherified or esterified derivative was shown to be fairly stable, especially to hydrogen peroxide. The major reaction was trans–cis isomerization that possibly involved a radical mechanism but did not cause bond cleavage. The peracetic acid reaction increased the rate of trans–cis isomerization and was also accompanied by a minor cleavage of the side chain. Esterification did not have a substantial effect on the reactivity of ferulic acid, but 4-*O*-etherification significantly stabilized it against these two oxidants. By contrast, aldehyde substitution tremendously enhanced the susceptibility of the cinnamyl side chain to oxidative degradation, as evidenced by an intensive degradation of coniferaldehyde.

**Keywords:** *Hydrogen peroxide; peracetic acid; oxidation; ferulic acid; ferulate; coniferaldehyde*

## INTRODUCTION

Our previous article reported that only a small amount of ferulic and *p*-coumaric acid was removed from wheat straw by hydrogen peroxide treatment under practical bleaching condition (Pan et al., 1998). The present study was aimed at further assessing the reactivity of these phenolic acids toward hydrogen peroxide and a stronger oxidant, peracetic acid.

Hydrogen peroxide and peracetic acid as chlorine-free bleaching agents have become increasingly important in today's bleaching technology for the pulp and paper industry. Both of the oxidants are versatile and can be used in electrophilic or nucleophilic reactions of organic compounds depending upon the reaction media chosen (Dence, 1994a). Peracetic acid may be regarded as an activated derivative of hydrogen peroxide, HOOH, in which one hydrogen atom is replaced by an acyl group. The active oxygen of hydrogen peroxide, which is not readily available for oxidation of organic compounds, can be transformed to the active peroxyacid form by direct oxidation of acetic acid with hydrogen peroxide in the presence of mineral acid as a catalyst (Plesnicar, 1978), as described in the equation shown below. As a result,



the higher oxidizing power of peracetic acid allows it to react with organic substrates to a greater extent or to be used in oxidation reactions under more moderate conditions than hydrogen peroxide. Peracetic acid has been well documented as an epoxidizing/hydroxylating agent for olefinic bonds in organic chemistry (Plesnicar, 1978). Alternatively, peracetic acid can be generated *in situ* by adding an activator such as tetraacetylenediamine (TAED) in alkaline hydrogen peroxide solution (Davies and Deary, 1991). It is reported that the

use of TAED-activated hydrogen peroxide allows the attainment of enhanced bleaching for laundry (James and MacKirdy, 1990; Grime and Clauss, 1990) and also paper-making pulps (Turner and Mathews, 1998).

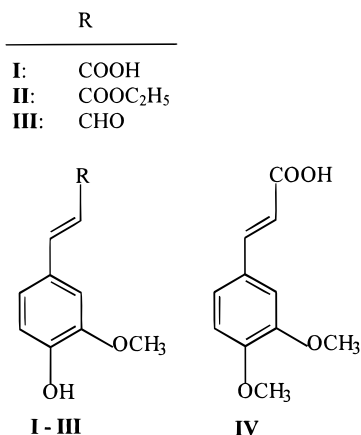
In lignin-retaining bleaching of paper-making pulps, nucleophiles preferentially attack conjugated carbon–carbon double bonds and carbonyl groups such as those found in cinnamaldehyde and quinonoid structures but not electron-rich aromatic rings (Dence, 1994a). Consequently, chromophores are removed with little dissolution of lignin. The mechanism of hydrogen peroxide bleaching involves nucleophilic attack by perhydroxyl anion (HOO<sup>-</sup>). The p*K*<sub>a</sub> for its formation is 11.6 at 25 °C (Legrini et al., 1993). In practice, to promote hydrogen peroxide bleaching, the addition of sufficient alkali is required for formation of an adequate concentration of HOO<sup>-</sup> ions. Since the p*K*<sub>a</sub> of peracetic acid is 8.2 (Plesnicar, 1978), its bleaching reaction can be performed at a lower pH. Under neutral or moderately alkaline conditions, peracetate ion, CH<sub>3</sub>COO<sup>-</sup>, like the perhydroxyl ion (HOO<sup>-</sup>), is a strong nucleophile, leading to selective removal of chromophores.

In the present investigation, ferulic acid and its related model compounds were reacted with hydrogen peroxide and peracetic acid under typical lignin-retaining bleaching conditions. The reaction substrates were selected to assess the effect of 4-*O*-etherification and esterification on the reactivity of ferulic acid. The reactions were followed spectrophotometrically, and reaction products were determined quantitatively and qualitatively. Analysis of the disappearance rate of the substrates and identification of reaction products allow the assessment of the reactivity of the side chain of ferulic acid toward hydrogen peroxide and peracetic acid.

## EXPERIMENTAL PROCEDURES

**Materials.** The model compounds studied in this investigation were predominantly the trans isomers and are shown in Figure 1. Ferulic acid (**I**), ethyl ferulate (**II**), coniferaldehyde

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**Figure 1.** Model compounds studied: ferulic acid (I), ethyl ferulate (II), coniferaldehyde (III), and 3,4-dimethoxycinnamic acid (IV).

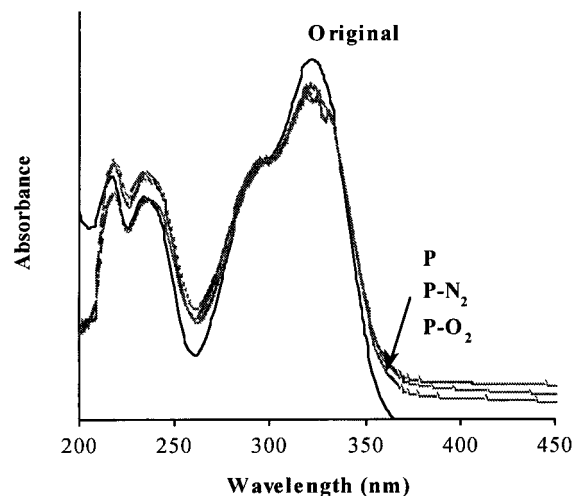
(III), 3,4-dimethoxycinnamic acid (IV), and acetovanillone were purchased from Aldrich Chemical Co. and used without further purification. Other reagents, including 30% hydrogen peroxide and 32% equilibrium peracetic acid solutions, were commercial products and employed as received.

**Reaction of Model Compounds with Hydrogen Peroxide and Peracetic Acid.** Each oxidation was performed in a 50 mL three-necked flask capped with rubber septa at 50 °C in an oil bath. Each run employed approximately 0.5 mmol of substrate and 2.0 mmol of oxidant. In the case of hydrogen peroxide, the model compounds were dissolved in 30 mL of pH 11.2 phosphate buffer solution containing 4 mg of metal chelating agent (DTPMPA). After the materials were completely dissolved, the required amount of hydrogen peroxide was added through a syringe. For the peracetic acid reactions, the model compounds were dissolved in 15 mL of ethanol and then mixed with 15 mL of aqueous peracetic acid solution preadjusted to pH 7 with NaHCO<sub>3</sub> solution. In the experiments under nitrogen or oxygen, the gas was continuously passed into the reaction mixture and vented through a needle. In the case of nitrogen, the substrate solution had been purged with nitrogen for 10 min before addition of hydrogen peroxide or peracetic acid. During the 4 h reaction period, the reaction mixture was shaken occasionally and aliquots (1 mL) of the reaction solution were withdrawn with a syringe at chosen intervals for UV-vis and GC analyses, respectively.

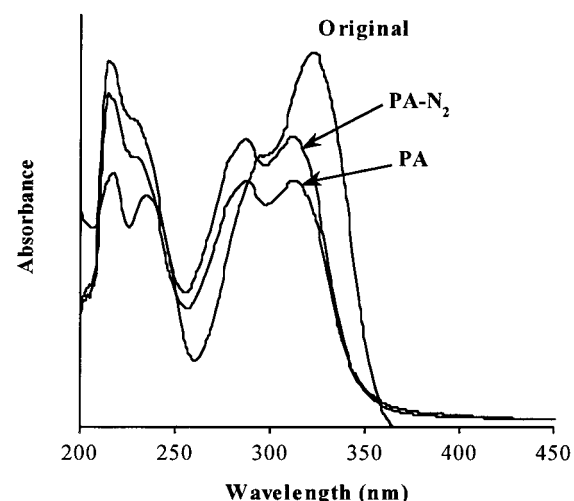
**Workup Procedure of Reaction Solutions.** Duplicate samples of the reaction mixture were immediately transferred to vials containing 1 mL of 5% sodium metabisulfite solution in order to quench any remaining hydrogen peroxide or peracetic acid and to bring the sample solution to pH < 7. To prepare samples for GC analysis, the sample in the vial was diluted with 20 mL of 50% aqueous methanol solution and acidified to pH 2.5 with 10% HCl solution. After 2.0 mg of acetovanillone (internal standard) was added, the mixture was extracted with 3 × 20 mL ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure.

**GC Analysis.** The dried extracts of oxidation products were silylated with 0.5 mL of pyridine and 0.25 mL of bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 70 °C for 15 min. Trimethylsilylated (TMS) derivatives of the products were separated on a HP 5890 gas chromatograph (splitless injection) equipped with a BPX70 column (25m × 0.32 mm × 0.25 μm) and a flame ionization detector using helium as the carrier gas (linear velocity 27 cm/s at 50 °C). Injector and detector temperatures were 250 and 350 °C, respectively. The column was held at 50 °C for 2 min and ramped to 270 °C at 10 °C/min. The amounts of individual components were calculated using response factors determined by running the authentic standards.

**UV-vis Spectrometry.** UV-vis spectra were recorded on a Varian Cary 1E UV-visible Spectrophotometer using methanol-water (1:1, v/v) as the solvent.



**Figure 2.** UV spectral changes during the reaction of ferulic acid (I) with hydrogen peroxide (P) after 4 h of reaction time.



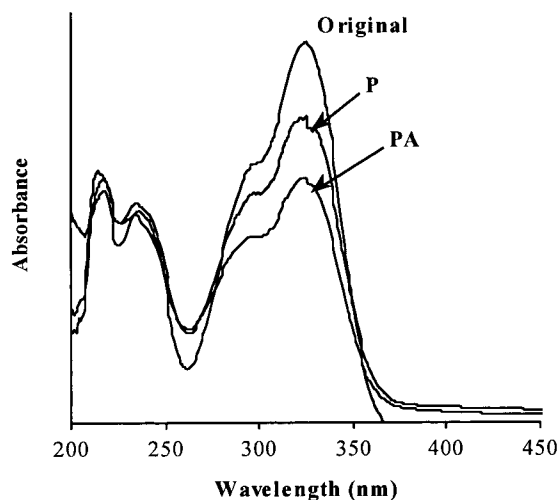
**Figure 3.** UV spectral changes during the reaction of ferulic acid (I) with peracetic acid (PA) after 4 h of reaction time.

**Mass Spectrometry.** GC-MS analyses were conducted on a Micromass AutoSpec instrument using the same column and temperature program as in the GC analyses. The electron energy used was 70 eV.

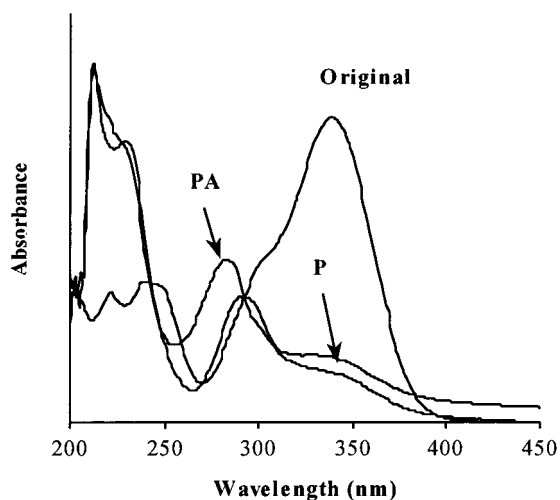
## RESULTS AND DISCUSSION

**Spectral Changes.** In the present investigation, reactions were periodically monitored by UV-vis spectroscopy. This allowed a quick assessment of the reactivity of substrates toward hydrogen peroxide and peracetic acid in different reaction media. Figure 2 shows that ferulic acid (I) was only slightly reactive to hydrogen peroxide. The presence of oxygen during the reactions did not affect the consumption of the starting material. On the other hand, the peracetic acid reaction resulted in a pronounced change in UV absorption, as revealed by Figure 3. It appeared that peracetic acid not only destroyed ferulic acid (I) but also produced products that had absorption maxima at lower wavelengths. In contrast to the observation in the hydrogen peroxide reaction, excluding oxygen reduced the rate of consumption of the substrate by peracetic acid.

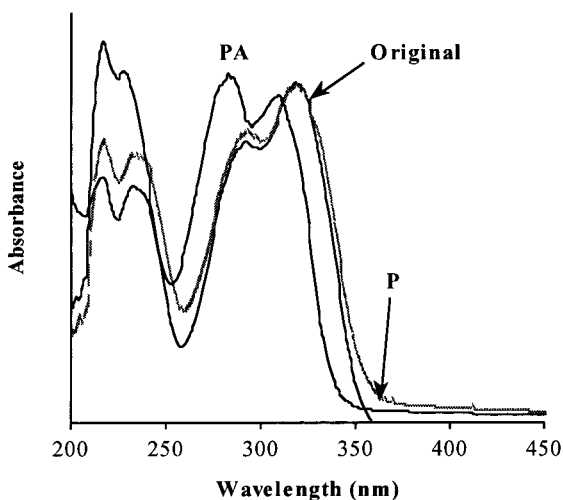
To assess the effect of substitutes on the reactivity of the cinnamyl side chain, three derivatives of ferulic acid were investigated and the results are shown in Figures 4–6. Ethyl ferulate (II) reacted with hydrogen peroxide



**Figure 4.** UV spectral changes during the reaction of ethyl ferulate (**II**) with hydrogen peroxide (P) and peracetic acid (PA) after 4 h of reaction time.

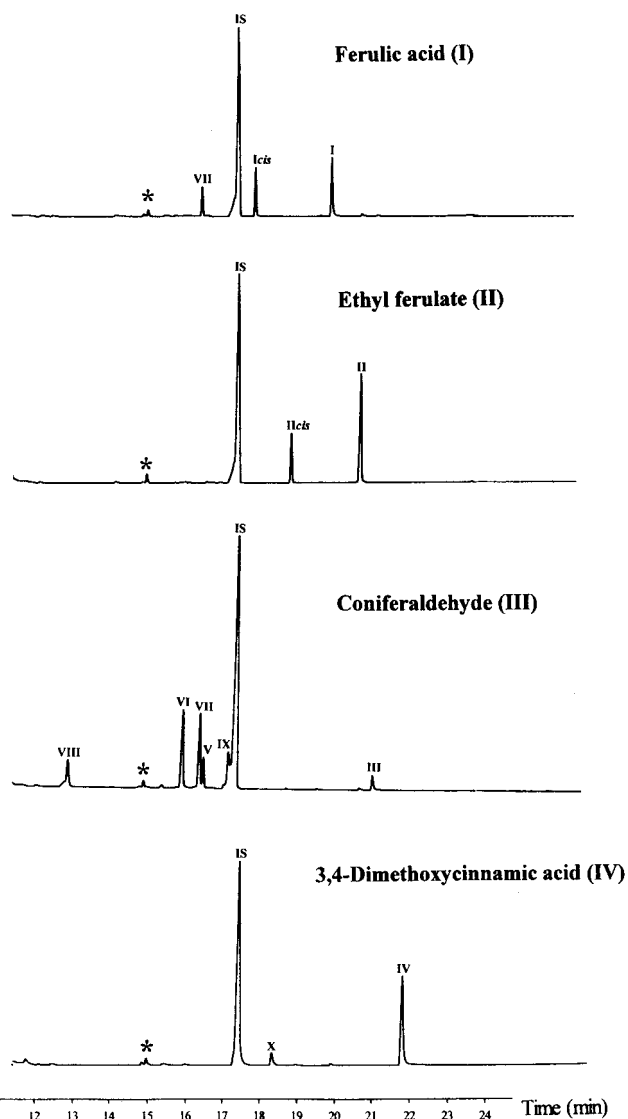


**Figure 5.** UV spectral changes during the reaction of coniferaldehyde (**III**) with hydrogen peroxide (P) and peracetic acid (PA) after 4 h of reaction time.



**Figure 6.** UV spectral changes during the reaction of 3,4-dimethoxycinnamic acid (**IV**) with hydrogen peroxide (P) and peracetic acid (PA) after 4 h of reaction time.

to some extent. Again, peracetic acid resulted in a more pronounced reaction than did hydrogen peroxide. Coniferaldehyde (**III**) showed a great reactivity. Both



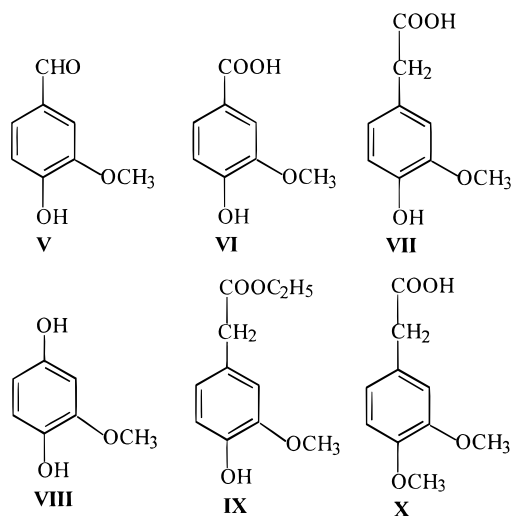
**Figure 7.** GC chromatograms of trimethylsilylated derivatives from peracetic acid reaction products of ferulic acid (**I**), ethyl ferulate (**II**), coniferaldehyde (**III**), and 3,4-dimethoxycinnamic acid (**IV**). IS (internal standard): acetovanillone. Asterisk (\*) denotes impurities.

hydrogen peroxide and peracetic acid almost completely destroyed this aldehyde derivative. However, as shown in Figure 5, these two oxidants gave a different composition of reaction products. It has been found that the peracetic acid produced more phenylcarboxylic-acid-related compounds so that the absorption maxima shifted to lower wavelengths (Pan et al., 1999). Unlike compounds **I–III**, 3,4-dimethoxycinnamic acid (**IV**) showed very little reactivity toward either hydrogen peroxide or peracetic acid. This compound virtually did not react with hydrogen peroxide. The peracetic acid reaction caused a shift of the absorption curve, but it did not considerably decrease the absorbance.

**Identification of Reaction Products.** Figure 7 shows the GC separation of the trimethylsilylated derivatives of reaction mixtures obtained from peracetic acid reactions of ferulic acid (**I**), ethyl ferulate (**II**), coniferaldehyde (**III**), and 3,4-dimethoxycinnamic acid (**IV**). Overall, hydrogen peroxide reacted with these substrates to a smaller extent or to give fewer products. The products were identified by comparison of their retention times with those of authentic compounds and

**Table 1. Mass Spectrometric Data of Trimethylsilylated Derivatives from Hydrogen Peroxide and Peracetic Acid Reaction Products**

compound	MS ( <i>m/z</i> )
<b>I</b>	338 (M, 100), 323 (65), 308 (60), 293 (26), 279 (9), 249 (48), 219 (21), 191 (9), 175 (7), 146 (14), 73 (45), 59 (4), 45 (5)
<b>Icis</b>	338 (M, 100), 323 (45), 308 (44), 293 (21), 279 (7), 249 (35), 219 (14), 191 (7), 175 (5), 146 (6), 73 (30), 59 (3), 45 (5)
<b>II</b>	294 (M, 88), 279 (20), 264 (100), 249 (19), 236 (8), 219 (18), 192 (20), 73 (21), 59 (3), 45 (4)
<b>IIcis</b>	294 (M, 86), 279 (27), 264 (100), 249 (30), 236 (11), 219 (25), 192 (27), 73 (34), 102 (7), 59 (5), 45 (5)
<b>III</b>	250 (M, 100), 235 (19), 220 (97), 207 (6), 192 (55), 177 (13), 166 (14), 151 (7), 117 (7), 102 (8), 89 (15), 73 (58), 59 (13), 45 (16)
<b>V</b>	224 (M, 40), 209 (48), 194 (100), 165 (9), 151 (5), 137 (10), 121 (3), 104 (8), 89 (9), 73 (27), 59 (6), 45 (9)
<b>VI</b>	312 (M, 75), 297 (100), 282 (31), 267 (53), 253 (37), 223 (64), 193 (35), 165 (10), 126 (16), 89 (10), 73 (82), 59 (8), 45 (17)
<b>VII</b>	326 (M, 77), 311 (38), 296 (9), 267 (28), 238 (4), 223 (7), 209 (58), 193 (12), 179 (32), 163 (6), 149 (8), 73 (100), 59 (5), 45 (10)
<b>VIII</b>	284 (M, 80), 269 (14), 254 (100), 239 (10), 209 (4), 179 (5), 112 (5), 73 (27), 59 (3), 45 (5)
<b>IX</b>	282 (M, 80), 267 (32), 252 (71), 238 (6), 223 (10), 209 (100), 193 (15), 179 (73), 163 (5), 149 (15), 73 (42), 59 (5), 45 (6)

**Figure 8.** Structures of hydrogen peroxide and peracetic acid reaction products: vanillin (**V**), vanillic acid (**VI**), homovanillic acid (**VII**), methoxyhydroquinone (**VIII**), ethyl homovanillate (**IX**), and homoveratric acid (**X**).

confirmed by mass spectrometric data given in Table 1. Figure 8 illustrates the structures of identified products.

As shown in Figure 7, ferulic acid (**I**) gave two products with the starting material remaining in a considerably large amount. Compound **Icis** was assigned to *cis*-ferulic acid because Compounds **I** and **Icis** had a nearly identical mass spectrum, as shown in Table 1. This observation indicated that the reaction substrate underwent isomerization to its *cis* form under our experimental conditions. The second product was homovanillic acid (**VII**), which was found only in the peracetic acid reaction. The formation of this compound would suggest that the peracetic acid attack on the olefinic double bond of ferulic acid could cause the cleavage of the side chain.

By contrast, ethyl ferulate (**II**) only gave one product. Similarly, this product was the *cis* form of **II** due to isomerization. Moreover, only trace amounts of ferulic acid (**I**) were observed when ethyl ferulate (**II**) was reacted with hydrogen peroxide. This indicated that the occurrence of saponification of **II** was very limited under our experimental conditions (pH  $\approx$  11).

Figure 7 reveals that the reaction of coniferaldehyde (**III**) was far more pronounced than that of the above two substrates. It formed five products and only a very small amount of the starting material remained. It is well-known that the reaction of coniferaldehyde structures with hydrogen peroxide involves oxidative cleavage of the  $\alpha,\beta$  double bond, which is initiated by nucleophilic attack on  $C_\alpha$  followed by formation of epoxide intermediate (Reeves and Pearl, 1965; Geller-

stedt and Agnemo, 1980). The double-bond rupture leads to the formation of vanillin (**V**). Subsequently, this benzaldehyde can be readily oxidized to the corresponding benzoic acid, i.e., vanillic acid (**VI**). Also, vanillin (**V**) as a *p*-hydroxybenzaldehyde may be further oxidized to methoxyhydroquinone (**VIII**) by the Dakin reaction with hydrogen peroxide (Dence, 1994b) or the Baeyer–Villiger reaction with peracetic acid (Strumila and Rapson, 1975; Nimz and Schwind, 1979). On the other hand, the formation of homovanillic acid (**VII**) would suggest that the side-chain cleavage could involve mechanisms other than the well-known  $\alpha,\beta$  double-bond scission. In addition, ethyl homovanillate (**IX**) was found only in the peracetic acid reactions. This product probably resulted from the esterification of homovanillic acid (**VII**) by ethanol used as solvent in the peracetic acid reaction. More detailed results concerning the reaction of coniferaldehyde-type structures will be published elsewhere (Pan et al., 1999).

As can be seen in Figure 7, 3,4-dimethoxycinnamic acid (**IV**) gave small amounts of one product, homoveratric acid (**X**). Similar to homovanillic acid (**VII**), this product was not found in the hydrogen peroxide reaction. 3,4-Dimethoxycinnamic acid (**IV**) was virtually unreactive to hydrogen peroxide. This result explained the change in the UV absorption of this substrate due to the peracetic acid reaction, as shown in Figure 6.

**Rates of Disappearance of Substrates and Yields of Reaction Products.** To further analyze the course of the consumption of the substrates and the course of the formation of products, quantitative data are given in Tables 2–4. The amounts of starting materials remaining upon hydrogen peroxide or peracetic acid reaction (Table 2) were consistent with those observed by UV absorption measurements (Figures 2–6). Overall, ferulic acid (**I**) and ethyl ferulate (**II**) showed a similar reactivity to either hydrogen peroxide or peracetic acid. Both were partially consumed by the reactions. Peracetic acid resulted in a greater extent of consumption of substrates than did hydrogen peroxide. The effect of nitrogen atmosphere on the rate of reaction was not clearly observed. Excluding oxygen from the reaction system slowed the reaction of ferulic acid (**I**) with peracetic acid and the reaction of ethyl ferulate (**II**) with hydrogen peroxide but appeared to have little effect on the other degradation reactions. Moreover, addition of oxygen to the hydrogen peroxide reaction of ferulic acid (**I**) did not seem to increase the rate of reaction.

Table 2 shows that either hydrogen peroxide or peracetic acid reacted nearly completely with coniferaldehyde (**III**). The aldehyde substituent makes the side chain of cinnamyl structures highly susceptible to oxidative degradation. By contrast, 3,4-dimethoxycinnamic acid (**IV**) showed no reactivity to hydrogen peroxide and was recovered in almost 100% yield.

**Table 2. Amounts (%) of Remaining Starting Materials upon Hydrogen Peroxide and Peracetic Acid Reactions**

reaction conditions		ferulic acid (I)	ethyl ferulate (II)	coniferaldehyde (III)	3,4-dimethoxycinnamic acid (IV)
H <sub>2</sub> O <sub>2</sub>	4 h	87.1	74.0	2.4	99.2
	N <sub>2</sub> , 4 h	87.5	92.6	1.3	99.9
	O <sub>2</sub> , 4 h	89.0			
CH <sub>3</sub> CO <sub>3</sub> H	1 h	59.4	84.2	6.3	98.4
	4 h	48.7	58.0	5.3	96.8
	N <sub>2</sub> , 4 h	76.8	58.3	1.5	101

**Table 3. Yield (mol %) of Main Products Obtained from the Hydrogen Peroxide and Peracetic Acid Reactions of Ferulic Acid (I), Ethyl Ferulate (II), and 3,4-Dimethoxycinnamic Acid (IV)**

reaction conditions		ferulic acid (I)		ethyl ferulate (II) II <sub>cis</sub>	3,4-dimethoxycinnamic acid (IV) homoveratric acid (X)
		I <sub>cis</sub>	homovanillic acid (VII)		
H <sub>2</sub> O <sub>2</sub>	4 h	13.9		17.2	
	N <sub>2</sub> , 4 h	1.8		7.5	
CH <sub>3</sub> CO <sub>3</sub> H	1 h	32.6	4.5	19.4	3.4
	4 h	35.9	6.0	22.9	5.8
	N <sub>2</sub> , 4 h	19.4	3.9	13.9	2.1

**Table 4. Yield (mol %) of Products Obtained from the Hydrogen Peroxide and Peracetic Acid Reactions of Coniferaldehyde (III)**

reaction conditions		vanillin (V)	vanillic acid (VI)	homovanillic acid (VII)	methoxyhydroquinone (VIII)
H <sub>2</sub> O <sub>2</sub>	4 h	0.8	13.5	7.3	20.4
	N <sub>2</sub> , 4 h	trace	8.9	6.6	21.6
CH <sub>3</sub> CO <sub>3</sub> H	1 h	7.1	13.6	10.9	10.1
	4 h	5.2	15.8	11.6	4.8
	N <sub>2</sub> , 4 h	2.1	14.9	12.7	6.4

However, there was a slight consumption of this substrate by peracetic acid.

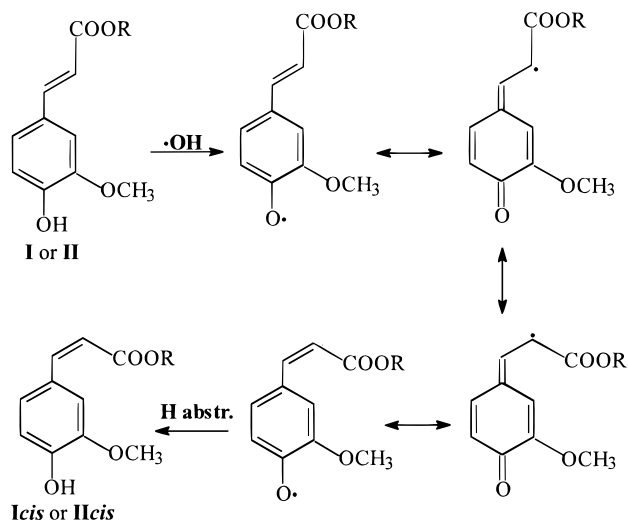
As revealed by Table 3, the major products obtained from the reactions of ferulic acid (I) and ethyl ferulate (II) were the *cis* isomers. Both the reactions produced trace amounts of vanillin (V) and vanillic acid (VI). In addition, the peracetic acid reaction of ferulic acid (I) produced up to 6% of homovanillic acid (VII). It appeared that *trans*-*cis* isomerization occurred to a greater extent with peracetic acid than with hydrogen peroxide. Furthermore, excluding oxygen from the reactions with either of the oxidants significantly reduced the formation of *cis* isomers. It should be pointed out that the yields of the *cis* products given in Table 3 were obtained by using the GC response factors of their *trans* counterparts (assuming the same value for both the *trans* and *cis* isomers of ferulic acid and ethyl ferulate, respectively). Combination of the results in Tables 2 and 3 indicated that in most cases the sum of the yields of the *trans* and *cis* isomers was around 90% or higher for both ferulic acid (I) and ethyl ferulate (II). In a few cases the peracetic acid reaction gave a total recovered material yield of 70–80%. In addition to the observed homovanillic acid (VII) and traces of vanillin (V) and vanillic acid (VI), the discrepancy of mass balance could be due to other reactions by peracetic acid, e.g., ring-opening reaction, forming more intensively degraded products.

Unlike the free phenolic substrates, the reaction of 3,4-dimethoxycinnamic acid (IV) had a good mass balance. The 4-*O*-methylated compound was more stable to oxidation by either hydrogen peroxide or peracetic acid. The only reaction seen was the slight side-chain cleavage by peracetic acid to produce homoveratric acid (X). The magnitude of this reaction appeared to be similar to that observed for ferulic acid (I).

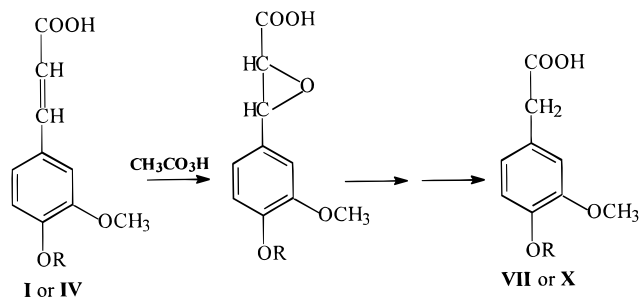
Table 4 reports the yields of products obtained from the reaction of coniferaldehyde (III) with hydrogen

peroxide and peracetic acid. In general, similar products were obtained but in varying yield, with the exception of ethyl homovanillate (IX) that was only present in the peracetic acid reaction. As its GC response factor was not determined, the yield of this product was not calculated but its relative abundance did not significantly vary during the peracetic acid reaction. Among the other products, there seemed to be a correlation between the consumption of vanillin (V) and the formation of methoxyhydroquinone (VIII). As discussed earlier, vanillin can be converted to methoxyhydroquinone (V) by the Dakin reaction, in hydrogen peroxide bleaching or the Baeyer–Villiger oxidation by peracetic acid. It appeared that the hydrogen peroxide reaction conditions might favor the occurrence of the Dakin reaction whereas the peracetic acid tended to oxidize vanillin (V) to vanillic acid (VI). As a consequence, the hydrogen peroxide reaction yielded more methoxyhydroquinone (VIII) and less vanillin (V) and the peracetic acid reaction produced more vanillic acid (VI) and less methoxyhydroquinone (VIII). In addition, peracetic acid gave more homovanillic acid (VII) than hydrogen peroxide.

**Possible Reaction Mechanisms.** In the present investigation, ferulic acid (I) was shown to undergo two reactions: isomerization and side-chain oxidative cleavage. The transformation of *trans*-ferulic acid to its *cis* isomer is reported to occur upon hydrogen peroxide–UV photolysis (Sun et al., 1996). In our case, the reaction mechanisms for isomerization are not clear. However, it required a free phenolic hydroxyl group, and the presence of oxygen promoted this process. The isomerization occurred only with ferulic acid (I) and ethyl ferulate (II) but not with 3,4-dimethoxycinnamic acid (IV). Moreover, the reactions with hydrogen peroxide or peracetic acid under nitrogen significantly reduced the formation of *cis* isomers. The experimental evidence, therefore, suggests the involvement of phe-



**Figure 9.** Proposed mechanism for trans-cis isomerization of ferulic acid (I) and ethyl ferulate (II) during hydrogen peroxide or peracetic acid reaction.



**Figure 10.** Proposed pathway for formation of homovanillic acid (VII) or homoveratric acid (X) from ferulic acid (I) or 3,4-dimethoxycinnamic acid (IV) on peracetic acid reaction.

noxy radicals. We note that reactions using peroxygen reagents including hydrogen peroxide and peracetic acid are inevitably accompanied by their decomposition to more reactive species such as hydroxy radical ( $\text{HO}\cdot$ ) and superoxide radical ( $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ ) (Dence, 1994a). It is proposed in Figure 9 that a hydroxy or hydroperoxy radical initiates hydrogen abstraction from a free phenolic substrate to form a phenoxy radical that can rearrange to a quinone methide radical intermediate. In our study, the reaction temperature of 50 °C, although not very high, is probably sufficient to cause the cis-trans isomerization to some extent. On the other hand, because the experiments were not carried out in the dark, the presence of light may promote the isomerization.

On the other hand, appreciable amounts of homovanillic acid (VII) and homoveratric acid (X) were found only in the reactions of ferulic acid (I) and 3,4-dimethoxycinnamic acid (IV), respectively, with peracetic acid. As peracetic acid has been well documented as an epoxidizing agent for olefinic bonds (Plesnicar, 1978), reaction mechanisms for the formation of these substituted phenylacetic acids might involve epoxide intermediate, as shown in Figure 10. However, it is not clear how the epoxidized side chain of the proposed intermediate splits to give homovanillic acid (VII) or homoveratric acid (X). One possibility could be via decarboxylation followed by further oxidation of the rest of the side chain. One example relevant to this mechanism is the work of Reeves and Pearl (1965) who obtained homoveratric acid in 80% yield from the reaction of (3,4-

dimethoxyphenyl)pyruvic acid with hydrogen peroxide. They attributed this reaction to the decarboxylation of  $\alpha$ -keto acids (Bunton, 1962). On the other hand, involvement of radicals in the side-chain rupture cannot be ruled out.

## CONCLUSIONS

In lignin-retaining bleaching conditions using hydrogen peroxide or peracetic acid, ferulic acid (I) undergoes two reactions: isomerization and side-chain oxidative cleavage. Esterification does not have a substantial effect on the reactivity of ferulic acid, but 4-*O*-etherification fully stabilizes it against isomerization. By contrast, aldehyde substitution tremendously enhances the susceptibility of the cinnamyl side chain to oxidative degradation, as shown by the intensive degradation of coniferaldehyde (III) under the same reaction conditions, leading to the formation of a number of products. On the basis of the results presented here, it would be reasonable to conclude that the conjugated side chain of ferulic acid and its etherified or esterified derivative is fairly stable to the two oxidants studied, especially hydrogen peroxide. The major reaction observed is trans-cis isomerization that possibly involves a radical mechanism but does not cause bond cleavage. The peracetic acid reaction increases the rate of trans-cis isomerization and is also accompanied by a minor cleavage of the side chain.

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