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Predominant formation of aromatic aldehyde and acid from a dimeric *β-O*-4-type lignin model compound under hydrogen peroxide bleaching conditions with high pH levels

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Abstract When a dimeric non-phenolic *β-O*-4-type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (veratrylglycerol-*β*-guaiacyl ether (VG)), was treated under alkaline oxygen or hydrogen peroxide bleaching conditions (O_2 or H_2O_2 system, respectively), 3,4-dimethoxybenzaldehyde (veratraldehyde) and 3,4-dimethoxybenzoic acid (veratric acid) formed with yields dependent on the system. The yield of veratraldehyde based on the mole amount of disappearing VG (VG disappearance) was about 30% in the O_2 system at a high pH level. However, the total yield of veratraldehyde and veratric acid was 70–80% based on VG disappearance in the H_2O_2 system at high pH levels, where H_2O_2 was added stepwise. A prolonged reaction with the further stepwise addition of H_2O_2 at the high pHs would further increase the formations of veratraldehyde and veratric acid with maintaining the yields based on VG disappearance. The yields (70–80%) are higher than those reported in the previous study, which employed VG, oxygen, and 1,10-phenanthroline and copper (II) sulfate as the catalysts. The high yields in the H_2O_2 system with high pH levels can be explained by the reactivity of oxyl anion radical, which is the most responsible active oxygen species at these high pHs and preferably attacks the aliphatic side-chain of VG rather than the aromatic nucleus.

Keywords Lignin · Syringaldehyde · Vanillin · Veratraldehyde · Veratric acid
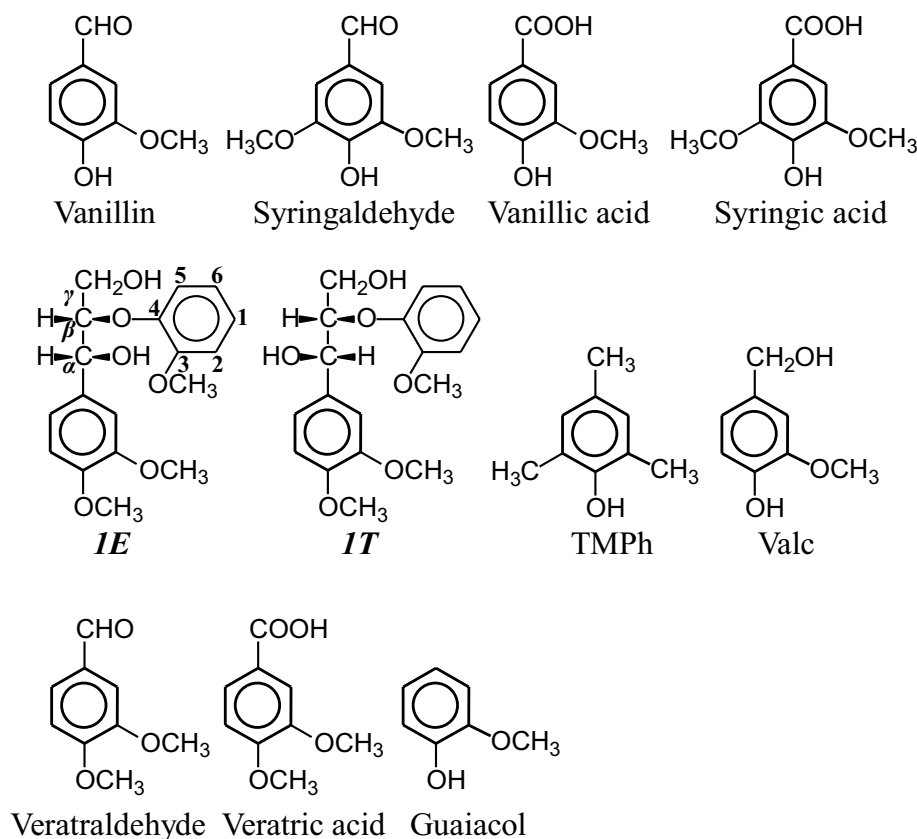
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Introduction

Woody biomass has recently attracted interest due to its potential as a raw material for high value-added material, fine chemicals, and others. The major two components of wood cell walls, cellulose and hemicelluloses, have actually been utilized for these purposes. The other major component, lignin, has been expected to be useful as a replacement for petroleum, but sufficient utilization has not yet been attained. Lignin is currently utilized as an energy source almost only in pulp and paper mills, where it is burned to supply energy for the mill operations. It is reasonable, therefore, to attempt to utilize lignin as a high value-added material and obtain fine chemicals from lignin. The best method for obtaining such lignin-origin fine chemicals, 4-hydroxy-3-methoxybenzaldehyde (vanillin, Fig. 1), 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde, Fig. 1), 4-hydroxy-3-methoxybenzoic acid (vanillic acid, Fig. 1), and 4-hydroxy-3,5-dimethoxybenzoic acid (syringic acid, Fig. 1), is the traditional alkaline nitrobenzene oxidation [1, 2], although it is not suitable for practical application due to the toxicity of nitrobenzene.

Many studies have been published describing the conversion of lignin into these fine chemicals [3–28]. Wu et al. showed that the total yield of vanillin and syringaldehyde is about 12% when *Populus* wood is steam-exploded in the presence of Cu^{2+} and Fe^{3+} [4]. Fargues et al. showed that the maximum vanillin yield is about 10% when *Pinus spp.* wood is treated in an alkaline solution under oxygen pressure [7]. Araujo et al. indicated that the vanillin yields are 3–8% when kraft lignin derived from *Pinus* spp. wood is treated in an alkaline solution under oxygen pressure [18]. Azarpira et al. indicated that about 50% of vanillin is obtained when a dimeric *β-O*-4-type lignin model compound is treated in an alkaline solution under oxygen

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pressure in the presence of catalysts, 1,10-phenanthroline and CuSO₄ [24]. Roughly speaking, around 10% and 50% of vanillin can be obtained from a macromolecular lignin sample and lignin model compounds, respectively, in the presence of special catalysts.

In our previous studies, the diastereomeric *erythro* (*E*) or *threo* (*T*) isomer of a dimeric non-phenolic *β-O*-4-type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (*1E* or *1T*, respectively, Fig. 1), was individually treated with alkaline oxygen or hydrogen peroxide to examine the *E* or *T* stereo-preference of active oxygen species (AOS) generated in the system under conditions simulating a practical pulp bleaching process [29, 30]. This study reports that 3,4-dimethoxybenzaldehyde (veratraldehyde, Fig. 1), which is an analogue of vanillin, was obtained as the major degradation product in the above-described alkaline oxygen treatments while veratraldehyde and 3,4-dimethoxybenzoic acid (veratric acid, Fig. 1), which is an analogue of vanillic acid, were obtained as the major degradation products with high yields in the above-described alkaline hydrogen peroxide treatments at high pH levels. It should be emphasized that special catalysts, such as 1,10-phenanthroline and CuSO₄ used in the previous report [24], were not employed in this study, which is significantly different from previous reports [4, 24].

Although compound *1*, veratraldehyde, and veratric acid consist of the 3,4-dimethoxy aromatic nucleus, which does not exist in native lignin, and hence, the reaction of compound *1* is not completely the same as those of native lignin, the results obtained in this study significantly contribute to progress in basic knowledge on the formation of vanillin and vanillic acid from native lignin.

Materials and methods

Materials

All chemicals except compound *1* were commercially available and used without further purification [29, 30]. The synthesis of compound *1* and separation of the *E* and *T* isomers were described in our previous studies [29, 30]. The ¹H- and ¹³C-NMR spectral data of compound *1* were reported in our previous study [29].

Alkaline oxygen treatment simulating an oxygen delignification process (O₂ system)

A phenolic compound, 2,4,6-trimethylphenol (TMPh, Fig. 1) or 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, Valc, Fig. 1), was used as the generator of

AOS. When TMPh or Valc was employed, the system is described as the O_2-TMPh or O_2-Valc system, respectively, in the following text.

The reaction conditions were as follows: NaOH concentration in the O_2-TMPh system: 0.5 mol/L, NaOH concentration in the O_2-Valc system: 0.5 or 0.1 mol/L, oxygen pressure in the O_2-TMPh system: 1.1 or 0.4 MPa (1.0 or 0.3 MPa as gauge level, respectively), oxygen pressure in the O_2-Valc system: 1.1 MPa (1.0 MPa as gauge level), initial concentration of compound *1E* or *1T*: 1.0 mmol/L, initial concentration of TMPh or Valc: 10 mmol/L, ferric ion added (as $FeCl_3$): 0.36 mmol/L, temperature: 95 °C, rise in temperature: 10 min, reaction period: 360 min, volume of solution: 300 mL. The detailed procedures were described in our previous study [29].

In some reactions in the O_2-Valc system employing 0.5 mol/L NaOH, Valc was added five times stepwise at intervals of about 60 min. The amount of Valc added at each step was 3.0 mmol.

Alkaline hydrogen peroxide treatment simulating a hydrogen peroxide bleaching process (H_2O_2 system)

The reaction conditions were as follows: initial pH: 13.3, 12.8, 11.9, 11.5, 11.0, 10.5, or 9.5 (adjusted by adding an aqueous NaOH solution), initial concentration of compound *1E* or *1T*: 1.0 mmol/L, ferric ion added (as $FeCl_3$): 0.36 mmol/L, temperature: 95 °C, reaction period: 120 min, volume of solution: 30 mL. The addition of 20 μL of a 30% hydrogen peroxide solution was repeated ten times at intervals of 10 min [30]. The total amount of hydrogen peroxide added was about 1.8 mmol. The detailed procedures were reported in our previous study [30]. This system is described as the H_2O_2 system in the following text.

Hydrogen peroxide treatment in Fenton system

The reaction conditions were as follows: initial pH: 5.5 (without any acid or alkali added), initial concentration of compound *1E* or *1T*: 1.0 mmol/L, ferrous ion added (as $FeCl_2$): 0.36 mmol/L, temperature: 95 °C, reaction period: 120 min, volume of solution: 30 mL. The addition of 20 μL of a 1% hydrogen peroxide solution was repeated ten times at the intervals of 10 min [30]. The total amount of hydrogen peroxide added was about 60 μmol, which was 1/30 in the above H_2O_2 system. The detailed procedures were described in our previous study [30].

Quantification of degradation products

The detailed work-up procedures for quantification were described in our previous studies [29, 30]. Quantification was on the basis of a calibration line prepared for compound *1* or each degradation product with an internal standard compound, 4-chlorophenol. The quantification was conducted using a high performance liquid chromatograph (HPLC, LC-10A, Shimadzu Co., Kyoto, Japan) equipped with a photodiode array detector (SPD-M10A, Shimadzu Co.).

Conditions of HPLC for the analysis of compound *1* and neutral degradation products were described in our previous studies [29, 30]. Those for the analysis of acidic degradation products were as follows: column: Luna 5u C18 (2) 100 A (150 mm × 4.6 mm, Phenomenex Inc., Torrance, CA, USA), oven temperature: 40 °C, flow rate: 1.0 mL/min, solvent system: gradient CH_3OH/aqueous 1% CH_3COOH (v/v) from 15/85 to 20/80 for 45 min, gradient to 44/56 for 5 min and maintained for 15 min, gradient to 15/85 immediately and maintained for 5 min, total time 70 min.

In this study, the four main degradation products were identified as veratraldehyde, veratric acid, vanillin, and 2-methoxyphenol (guaiacol, Fig. 1). The identifications of these compounds were based on the following observations. (1) When the four authentic compounds were analyzed by the above described HPLC method, the retention times and UV-visible spectra from 190 to 800 nm of their peaks were exactly the same as those of the suspected peaks appearing on the HPLC chromatogram of a reaction solution. (2) When the four authentic compounds were added to a reaction solution for the HPLC analysis, the obtained HPLC chromatogram was the same as that of the original reaction solution without the addition of the four authentic compounds except the areas of the corresponding four peaks.

Results and discussion

Description of the O_2-TMPh or O_2-Valc system

As basic knowledge about the O_2-TMPh or O_2-Valc system, the followings were indicated in our previously published papers [31–36]. Compound *1* is quite stable without oxygen under otherwise the same conditions [35]. A non-phenolic lignin model compound such as compound *1* is not directly attacked by molecular oxygen but by AOS generated in either system accompanying the reaction between molecular oxygen and a co-existing phenolic compound, TMPh or Valc, which is the generator of AOS [32, 35]. A major AOS is negatively charged oxyl anion radical (O⁻), the conjugate base of hydroxyl radical (HO·), in either of the O_2-TMPh or O_2-Valc system before TMPh or Valc, respectively, disappears from the system owing to the high pH levels [32]. Other neutral AOS, which are peroxyl radicals generated by the reaction between molecular oxygen and the phenoxyl radical derived from TMPh, can participate in the O_2-TMPh

system [34, 36]. After the disappearance of TMPh or Valc, AOS are produced as radicals generated in chain-type reactions propagating in either system. O^- preferentially attacks the side-chain of a non-phenolic lignin model compound analogous to compound *1* rather than the aromatic nucleus [29, 32, 35].

FeCl$_3$ (20 ppm as Fe^{3+}) was added to simulate a practical oxygen delignification process. Almost all Fe^{3+} precipitated and aggregated as oxides and/or hydroxides during the reaction under the employed conditions.

Degradation products in the O$_2$-TMPh system

In our previous study, compound *1E* or *1T* was individually reacted with AOS in the O$_2$-TMPh system to examine the stereo-preference of the AOS [29]. Identified and quantified degradation products in the O$_2$-TMPh system are described below. The upper rows of Table 1 list the recovery yield of compound *1* and yields of veratraldehyde and guaiacol based on the initial mole amount of compound *1* at the prescribed reaction times and those of veratraldehyde and guaiacol based on the mole amount of disappearing compound *1* by the prescribed reaction times. All the yields of veratraldehyde referred to and discussed in this section are based on the mole amount of disappearing compound *1* by the prescribed reaction times. Guaiacol was not detected at all in any reaction in the O$_2$-TMPh system at a reaction time of 360 min.

Three clear and several broad peaks appeared on the chromatogram of the HPLC analysis (monitored at 280 nm) for any reaction at an oxygen pressure of either 1.1 or 0.4 MPa. One clear peak was identified as that of veratraldehyde. The other clear peaks were those of compound *1* and the internal standard compound, 4-chlorophenol. The formation of veratraldehyde indicates that the carbon–carbon bond cleaved between the α- and β-position at the side-chain. The yield of veratraldehyde was 28 or 26%, respectively, in the reactions of compound *1E* or *1T* at an oxygen pressure of 1.1 MPa and a reaction time of 45 min, when TMPh disappeared from the system. The yield became 30 or 19%, respectively, at a reaction time of 360 min. The yield was 36 or 33%, respectively, at an oxygen pressure of 0.4 MPa and a reaction time of 120 min, when TMPh disappeared from the system. The yield became 35 or 34%, respectively, at a reaction time of 360 min. The yields were higher at an oxygen pressure of 0.4 than 1.1 MPa. We previously suggested that the above-described neutral AOS generated in the O$_2$-TMPh system are peroxyl radicals derived from TMPh and their formation is enhanced by high oxygen pressure [34, 36]. Therefore, the neutral AOS would be generated more frequently at 1.1 than at 0.4 MPa. Because the neutral AOS can attack the aromatic nuclei of compound *1* more frequently than O^- owing to the absence

of the electrostatic repulsion between the π-electron system of the aromatic nuclei and O^-, the aromatic nuclei can be degraded or converted to another-type more frequently at 1.1 than at 0.4 MPa and consequently the yields of veratraldehyde are to be lower at 1.1 than at 0.4 MPa. Because the amount of detected veratraldehyde monotonically increased with progress of the reaction until a reaction time of about 180 min and was maintained at the same level after that, veratraldehyde is considered to be stable in the O$_2$-TMPh system.

The peak of veratric acid did not appear even under the HPLC conditions for the analysis of acidic degradation products. Although we previously confirmed that the β-O-4 bond of compound *1* cleaves and a small amount of guaiacol is liberated in the O$_2$-Valc system [35], almost no guaiacol was detected in the O$_2$-TMPh system. Guaiacol is commonly oxidized by molecular oxygen.

Degradation products in the O$_2$-Valc system

In our previous study, compound *1E* or *1T* was individually reacted with AOS in the O$_2$-Valc system to examine the stereo-preference of the AOS [29]. Identified and quantified degradation products in the O$_2$-Valc system are described below. The lower rows of Table 1 list the recovery yield of compound *1* and yields of veratraldehyde and guaiacol. The yields referred to and discussed in this section indicate those based on the mole amount of disappearing compound *1* by the prescribed reaction times, unless the base of the yield is described.

The peak of veratraldehyde appeared as one of three clear peaks of degradation products on the chromatogram of the HPLC analysis (monitored at 280 nm) for the reactions using either 0.5 or 0.1 mol/L NaOH. Several broad peaks of degradation products also appeared, but have not yet been identified. The yield of veratraldehyde was 33 or 25% in the reactions of compound *1E* or *1T*, respectively, using 0.5 mol/L NaOH (O$_2$: 1.1 MPa) at a reaction time of 60 min, when Valc disappeared from the system. The yield became 31 or 20%, respectively, at a reaction time of 360 min. The yield was 27 or 36%, respectively, in the reaction using 0.1 mol/L NaOH (O$_2$: 1.1 MPa) at a reaction time of 60 min, when Valc disappeared from the system. The yield became 16 or 17%, respectively, at a reaction time of 360 min. Many of these yields are similar to those in the O$_2$-TMPh system.

One of the other clear peaks was successfully identified as that of vanillin. When Valc was solely treated in the O$_2$-Valc system (0.5 mol/L NaOH, 1.1 MPa O$_2$) without adding compound *1*, the yield of vanillin was 1.7% based on the initial mole amount of Valc at a reaction time of 60 min, when Valc disappeared. Because the absolute amount of vanillin detected in the O$_2$-Valc

Table 1 Recovery yield of compound *1* and yields of veratraldehyde and guaiacol in the O_2-TMPh or O_2-Valc system

System	Yield based on the initial mole of compound *1* (%)[a]								Yield (%)[b]			
	1E		1T		Veratraldehyde		Guaiacol		Veratraldehyde		Guaiacol	
	Dis[c]	360[d]	Dis[c]	360[d]	Dis[c]	360[d]	Dis[c]	360[d]	Dis[c]	360[d]	Dis[c]	360[d]
TMPh	75	57	–	–	7	13	0[f]	0[f]	28	30	0[f]	0[f]
(O₂: 1.1 MPa)[e]	–	–	81	57	5	8	0[f]	0[f]	26	19	0[f]	0[f]
TMPh	78	66	–	–	8	12	0[f]	0[f]	36	35	0[f]	0[f]
(O₂: 0.4 MPa)[e]	–	–	73	61	9	13	0[f]	0[f]	33	34	0[f]	0[f]
Valc	85	77	–	–	5	7	2	0	33	30	13	0
(NaOH: 0.5 mol/L)[g]	–	–	84	75	4	5	2	0	25	20	12	0
Valc	93	88	–	–	2	2	1	0	27	16	14	0
(NaOH: 0.1 mol/L)[g]	–	–	94	88	2	2	1	0	36	17	18	0
Valc stepwise[h]	–	55	–	–	–	14	–	0	–	31	–	0

[a] In case of compound *1*, recovery yield is shown

[b] based on the mole amount of disappearing compound *1* by a reaction time of Dis[c] or 360 min[d]

[c] at a reaction time when TMPh or Valc disappeared (45 min in the TMPh system under 1.1 MPa O_2, 120 min in the TMPh system under 0.4 MPa O_2, 60 min in the Valc system)

[d] at a reaction time of 360 min

[e] NaOH: 0.5 mol/L

[f] Not exactly 0 but negligible amount

[g] O_2: 1.1 MPa

[h] Valc was added stepwise at intervals of about 60 min. The yields displayed are not those at a reaction time of exactly 360 min. NaOH: 0.5 mol/L, O_2: 1.1 MPa

system containing compound *1* at a reaction time of 60 min was almost the same as that in the O_2-Valc system without compound *1* and vanillin was not detected in the O_2-TMPh system, the detected vanillin in the O_2-Valc system would have originated not from compound *1* but mostly from Valc.

The last clear peak was successfully identified as that of guaiacol, which confirms that the *β-O*-4 bond of compound *1* certainly cleaves in the O_2-Valc system. The yield was 12–18% in the reaction of compound *1E* or *1T* using 0.5 or 0.1 mol/L NaOH at a reaction time of 60 min, when Valc disappeared. A similar amount of guaiacol was also detected in the reaction of compound *1* in the O_2-Valc system of our previous study [35]. Guaiacol was not detected at all at a reaction time of 360 min. The relatively low yield of guaiacol at a reaction time of 60 min and its disappearance at a reaction time of 360 min result from the fact that molecular oxygen directly oxidizes guaiacol. Because almost no guaiacol was detected in the O_2-TMPh system, however, the *β-O*-4 bond of compound *1* may be cleaved more frequently in the O_2-Valc than in the O_2-TMPh system. In contrast, the yields of veratraldehyde were not different between the O_2-TMPh and O_2-Valc systems. Therefore, the mechanism of the side-chain degradation is suggested to be different between these systems, leading to similar amounts of veratraldehyde but different amounts of guaiacol.

The peak of veratric acid did not appear even under the HPLC conditions for the analysis of acidic degradation products.

When Valc was added five times (total amount of Valc added: five times of the common reaction) stepwise at intervals of about 60 min in the O_2-Valc system containing compound *1E* and using 0.5 mol/L NaOH (O_2: 1.1 MPa), the yields of compound *1E* were 80, 76, 65, 59, and 56% based on its initial amount at reaction times of about 70, 140, 215, 285, and 360 min, respectively. The degradation of compound *1E* at a reaction time of 360 min was much greater than that in the common reaction of the O_2-Valc system (yield: 77% based on its initial amount). However, the enhancement of the degradation of compound *1E* became smaller with repeating the addition of Valc. The yield of veratraldehyde was 31% at a reaction time of 360 min either in this case or in the common reaction of the O_2-Valc system. The proportion of the amount of varatraldehyde formation to that of disappearing compound *1E* was constant during the reaction. These results suggest that the formation of veratraldehyde is enhanced by repeating the addition of Valc but the yield of veratraldehyde based on the initial amount of compound *1E* cannot reach a value high enough to emphasize that the alkaline oxygen treatment affords veratraldehyde with a high yield.

Description of the H_2O_2 and Fenton system

As basic knowledge on the H_2O_2 system, the followings were indicated in our previous papers [33–37] or were shown in our previous study [30]. Compound *1* is quite stable without the addition of H_2O_2 under, otherwise, the same conditions [35]. Compound *1* is degraded mostly by $O^{\bar{}}$ generated by the decomposition of H_2O_2 at a pH level sufficiently higher than 11.9, the pK_a value of HO· [30, 35]. The responsible species gradually varies from $O^{\bar{}}$ to HO·, accompanying the decrease of pH through the value of 11.9 [30]. Because of these facts, the reaction in the H_2O_2 system is divided into two relatively high and low initial pH levels (high: ≥11.9, low: <11.9) and discussed separately. Chain-type reactions do not propagate in the H_2O_2 system due to the low oxygen pressure [30, 35]. $O^{\bar{}}$ preferentially attacks the side-chain of a non-phenolic lignin model compound analogous to compound *1* rather than the aromatic nucleus as described above, while HO· rapidly adds to or attacks the aromatic nucleus as well as the side-chain [30]. The 30% H_2O_2 solution (20 μL) was added stepwise ten times at intervals of 10 min, because the degradation of compound *1* was too small to discuss when 200 μL of the solution was initially added at once [30]. The mechanisms of these phenomena were discussed in detail in our previous study [30].

As indicated in our previous study, the degradation of compound *1E* or *1T* became less with decrease of the initial pH from 13.3, showing minimum degradation at an initial pH of 11.9 [30]. The further decrease of the pH dramatically enhanced the degradation [30]. The mechanism was discussed on our previous study [30]. The degradation of compound *1* was severe in the Fenton system even where the amount of employed H_2O_2 was 1/30 of that in the H_2O_2 system [30].

As described above, $O^{\bar{}}$ and/or HO· degrade compound *1* almost exclusively in the H_2O_2 or Fenton system, which is different from the O_2-TMPh or O_2-Valc system. Not only $O^{\bar{}}$ and/or HO· but also other radicals work as AOS in these O_2 systems. It can be explored in the H_2O_2 and Fenton systems, therefore, whether or not veratraldehyde also forms when AOS working in the system are limited only to $O^{\bar{}}$ and/or HO· in the H_2O_2 and Fenton systems.

$FeCl_3$ (20 ppm as Fe^{3+}) was added to simulate a practical hydrogen peroxide bleaching process in the H_2O_2 systems. Almost all Fe^{3+} precipitated and aggregated as oxides and/or hydroxides during the reaction under the employed conditions with the relatively high alkalinities (pH>9–10).

Degradation products in the H$_2$O$_2$ system at high pH levels

In our previous study, compound *1E* or *1T* was individually reacted in the H$_2$O$_2$ system at an initial pH of 13.3 or 12.8 to examine the stereo-preference of O$^-$ and/or HO· [30]. Identified and quantified degradation products in the H$_2$O$_2$ system at the high pH level are described below.

When the reaction was run at either pH and the solution obtained at a reaction time of 120 min (after 30 min from the final addition of H$_2$O$_2$) was analyzed by HPLC (280 nm) under the conditions for quantifying neutral degradation products, four clear peaks of compound *1E* or *1T*, the internal standard compound (4-chlorophenol), veratraldehyde, and guaiacol and one broad peak of veratric acid appeared on the chromatogram. The peak of veratic acid was sharp in the HPLC analysis under the conditions for quantifying acidic degradation products. Table 2 lists the recovery yield of compound *1* and yields of veratraldehyde, veratric acid, and guaiacol at a reaction time of 120 min. All the yields of veratraldehyde, veratric acid, and guaiacol referred to and discussed in this section are based on the mole amount of disappearing

compound *1* by the prescribed reaction times, unless the base of the yield is described.

The yield of veratraldehyde showed a maximum (30–40%, data not shown) at a reaction time of 10–30 min and decreased, thereafter, at either pH. The yield was 12–27% at a reaction time of 120 min. Veratric acid appeared initially at a reaction time of 30 min and monotonically increased thereafter at either pH. The yield was 49–65% at a reaction time of 120 min. When veratraldehyde was treated solely as a starting material without adding compound *1* in the H$_2$O$_2$ system at a pH of 13.3, the formation of veratric acid was always quantitative and 20% of veratraldehyde was remained at a reaction time of 120 min based on its initial amount. Because most molecules of H$_2$O$_2$ dissociate to highly nucleophilic hydroperoxide anion, HO$_2^-$, at this pH, the anion attacks the aldehyde group of veratraldehyde quantitatively affording veratric acid. These observed phenomena indicate that veratric acid formed not directly from compound *1* but *via* veratraldehyde. Therefore, the total yield of veratraldehyde and veratric acid is discussed below.

The total yields of veratraldehyde and veratric acid were 68–78% at a reaction time of 120 min. O$^-$ is most responsible for the degradation of compound *1* at an initial pH

Table 2 Recovery yield of compound *1* and yields of veratraldehyde, veratric acid, and guaiacol in the H$_2$O$_2$ and Fenton systems at a reaction time of 120 min (after 30 min from the final addition of H$_2$O$_2$)

Initial pH	Final pH	Yield based on the initial mole of compound *1* (%)[a]					Yield (%)[b]		
		1E	*1T*	Ald[c]	Acid[d]	G[e]	Ald[c]	Acid[d]	G[e]
13.3	13.3	78	–	6	11	5	27	49	22
		–	76	3	13	6	13	55	25
12.8	12.5	83	–	2	11	3	12	62	18
		–	85	2	10	3	13	65	20
11.9	11.5	94	–	1	4	0	17	58	0
		–	96	1	2	0	26	58	0
11.5	*7.5*	*9*	*–*	*4*	*0*	*3*	*4*	*0*	*3*
		–	*16*	*4*	*0*	*3*	*5*	*0*	*4*
11.0	*6.0*	*0*	*–*	*1*	*0*	*0*	*1*	*0*	*0*
		–	*1*	*1*	*0*	*0*	*1*	*0*	*0*
10.5	*4.0*	*0*	*–*	*0*	*0*	*0*	*0*	*0*	*0*
		–	*0*	*0*	*0*	*0*	*0*	*0*	*0*
9.5	*3.5*	*0*	*–*	*0*	*0*	*0*	*0*	*0*	*0*
		–	*0*	*0*	*0*	*0*	*0*	*0*	*0*
5.5	**3.1**	**1**	**–**	**1**	**0**	**3**	**1**	**0**	**3**
		–	**1**	**0**	**0**	**2**	**0**	**0**	**2**

The roman, italic, and bold rows show the systems at the initially high pH levels, at the initially low pH levels, and of Fenton, respectively

[a] In case of compound *1*, recovery yield is shown.

[b] based on the mole amount of disappearing compound *1* by a reaction time of 120 min

[c] Ald: veratraldehyde

[d] Acid: veratric acid

[e] G: guaiacol

of 13.3 or 12.8. O⁻ does not preferably attack the aromatic nucleus but predominantly the side-chain. This reactivity resulted in the survival of the original 3,4-dimethoxyphenyl aromatic nucleus of compound *1*, the scission of the side-chain of compound *1*, and hence the formation of the large amounts of veratraldehyde and veratric acid. Because the disappearance of compound *1* was still about 22–24% or 15–17% based on its initial amount at an initial pH of 13.3 or 12.8, respectively, at a reaction time of 120 min and the degradation rate of compound *1* was constant throughout the reaction, a prolonged reaction with adding H_2O_2 stepwise must further afford much larger amounts of veratraldehyde and veratic acid with finally attaining the yield of more than 70% even based on the initial mole amount of compound *1*. The above total yields of veratraldehyde and veratic acid (68–78%) are higher than those reported in the previous paper [24], although special catalysts, such as 1,10-phenanthroline and $CuSO_4$ used in the paper [24], were not employed in the H_2O_2 system. In the previous report, less than 5% and 65–70% of veratraldehyde and veratric acid, respectively, as well as 3% of residual compound *1* (which is called compound 2 in this previous report) were obtained based on the initial mole amount of compound *1*, when compound *1* was treated in an aqueous alkaline solution at an oxygen pressure of about 1.3 MPa at 80 °C for 24 h in the presence of catalysts, 1,10-phenanthroline and $CuSO_4$, showing the slightly lower yields of veratraldehyde and veratric acid (less than 5 and 45–50%, respectively) at an oxygen pressure of about 0.3 MPa [24].

The yield of guaiacol showed a maximum at a reaction time of around 30 min (45–65%, data not shown) and decreased thereafter. The yield was 18–25% at a reaction time of 120 min. This result indicates that the *β-O*-4 bond of compound *1* cleaves and guaiacol is attacked by O⁻.

The results observed in the reaction at an initial pH of 11.9 were similar to those at an initial pH of 13.3 or 12.8. However, the results cannot be discussed in detail, because the yields of veratraldehdye and veratric acid were not very reliable owing to the limited amount of the degradation of compound *1* (4–6% based on its initial amount at a reaction time of 120 min).

Degradation products in the H_2O_2 system at low pH levels or in the Fenton system.

In our previous study, compound *1E* or *1T* was individually reacted in the H_2O_2 system at an initial pH of 11.5, 11.0, 10.5, or 9.5 or in the Fenton system to examine the stereo-preference of O⁻ and/or HO· [30]. The degradation of compound *1* in these systems was great especially at the lower pH levels and in the Fenton system. Identified and quantified degradation products in these systems are described below.

When the reaction solutions obtained in the H_2O_2 and Fenton systems were analyzed by HPLC, the chromatograms showed the flatter baselines than those obtained in the H_2O_2 systems at the initial high pH levels with at most four clear peaks as described below and no broad peak. This observation suggests that the degradation of compound *1* is accompanied by the destruction of the aromatic nuclei affording non-aromatic degradation products and the following identified aromatics. The four clearest peaks were identified as those of compound *1E* or *1T*, the internal standard compound (4-chlorophenol), veratraldehyde, and guaiacol. Table 2 lists the recovery yield of compound *1* and yields of veratraldehyde, veratric acid, and guaiacol at a reaction time of 120 min. All the yields of veratraldehyde, veratric acid, and guaiacol referred to and discussed in this section are based on the mole amount of disappearing compound *1* by the prescribed reaction times, unless the base of the yield is described.

The yield of veratraldehyde showed a maximum at a reaction time of 10–30 min and then decreased to 0–5% at a reaction time of 120 min, although the maximum yield was dependent on the system. The maximum yield was about 30% in the H_2O_2 system at an initial pH of 11.5 or 11.0, but only 5–10% at the lower pH levels and in the Fenton system. Because the final pH was 7.5, 6.0, 4.0, or 3.5, respectively, the contribution of O⁻ to the degradation of compound *1* decreased and HO· became most responsible for the progress of the reaction. HO· was most responsible during the whole reaction in the Fenton system. As mentioned above, O⁻ preferentially attacks the side-chain of compound *1*, while the aromatic nuclei as well as side-chain are reaction sites of HO·. Thus, the action of HO· can result in the degradation of the aromatic nuclei of compound *1*, which explains why the maximum yield was low in the H_2O_2 systems at the low pH levels and in the Fenton system.

No veratric acid was detected in any reaction during almost the whole period, although the yield of veratraldehyde showed a maximum and then decreased. When veratraldehyde was treated solely as a starting material in the H_2O_2 system at an initial pH of 11.5 without adding compound *1*, the following phenomena were observed. (1) The disappearance of veratraldehyde was much slower than that in the H_2O_2 system at a pH of 13.3, (2) The yield of residual veratraldehyde was 73% based on its initial amount at a reaction time of 120 min. (3) Veratric acid was the only degradation product detected, although the amount was negligible. These results indicate that the reaction of veratraldehyde with H_2O_2 is slow at this pH level and does not frequently afford veratric acid. It is considered that a fairly large amount of H_2O_2 does not dissociate at this pH and that the disappearance of veratraldehyde does not accompany the action of H_2O_2 itself but HO· generated by self-decomposition of H_2O_2. HO· preferably attacks and degrades the 3,4-dimethoxyphenyl aromatic nucleus.

The yield of guaiacol was small in the H_2O_2 system at an initial pH of 11.5. Because the final pH was 7.5 in this system, the responsible species was HO· during most of the reaction and HO· degraded guaiacol liberated by the *β-O-*4 bond cleavage of compound *1*. No guaiacol was detected in the H_2O_2 systems at the other low pH levels, although about 5–10% of guaiacol were detected as the maximum in the middle stage of the reaction. These results may indicate that the *β-O-*4 bond of compound *1* was not frequently cleaved, although it seems to be rational to consider that the *β-O-*4 bond was cleaved and the responsible HO· easily attacked the liberated guaiacol. A similar phenomenon was observed in the Fenton system.

Conclusions

Veratraldehyde formed with a yield of 30–35% based on the amount of disappearing compound *1*, when compound *1* was treated in the O_2-TMPh or O_2-Valc system. The formation of veratraldehyde can be explained by the reactivity of a major AOS, O^-, which preferentially attacks the side-chain of compound *1* rather than the aromatic nuclei. The stepwise addition of Valc in the O_2-Valc system at a pH of 13.3 increased the amount of afforded veratraldehyde with maintenance of the yield based on the amount of disappearing compound *1*. Because the degradation of compound *1* became small with progress of the reaction with the stepwise addition, the yield of veratraldehyde based on the initial mole amount of compound *1* cannot reach a value high enough to compare with those reported in the previous papers.

The total yields of veratraldehyde and veratric acid were mostly more than 70% based on the amount of disappearing compound *1*, when compound *1* was treated in the H_2O_2 systems at the high initial pH levels (13.3 and 12.8). A prolonged reaction must afford larger amounts of veratraldehyde and veratric acid, which makes it possible to say that the total yields based not only on the amount of disappearing compound *1* but also on the initial mole amount of compound *1* are no lower than those shown in the previous paper where compound *1* was subjected to an oxidation system employing the special catalysts, 1,10-phenanthroline and $CuSO_4$ [24]. These high yields result from the reactivity of O^-, the species responsible for the degradation of compound *1*. Almost no veratraldehyde and veratric acid were affored in the H_2O_2 systems at the initial pH levels equal to or lower than 11.5 and in the Fenton system. These results can be explained by the fact that HO· is the species responsible for the degradation of compound *1* and attacks the aromatic nuclei as well as the side-chain.

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