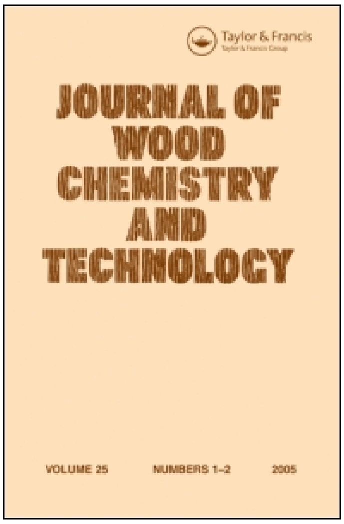

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THE REACTION OF SYRINGOL WITH CHLORINE DIOXIDE

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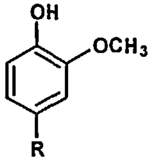
ABSTRACT

Syringol **2** (R=H) reacted with chlorine dioxide to give the dione **7** and its benzilic acid rearrangement product **8a** as the major products. Other products were the dimethoxybenzoquinones **3a** and **3b**, 3-chlorosyringol **4b**, chlorocyclopropenone **5**, 2-furoic acid **6a** and the dichloromethylenefuranones **10a** and **10b**. Two samples of effluent from chlorine dioxide bleaching contained the dione **7**, while one sample contained the furanone **10a**, and one contained the isomer **10b**.

INTRODUCTION

Several studies have been carried out on the reactions of softwood lignin model compounds with chlorine dioxide. Thus, guaiacols **1** react to produce a variety of products including quinones, muconic acid esters and lactones, and further degradation products[1-3]. The reactions of hardwood lignin model compounds **2** have not been studied with the exception of syringol **2** (R=H) itself, which was reported to give 2,6-dimethoxybenzoquinone **3a**, 4-chlorosyringol **4a** and an unidentified compound[1]. During a recent investigation of reactions of chlorine dioxide with lignin model compounds it was found that the products obtained in water were different from those obtained when an alcohol cosolvent was used[4]. Since *t*-butanol was used as a cosolvent in the reported reaction of syringol with chlorine dioxide, the reaction was reinvestigated in pure water, a condition which is more representative of actual bleaching. A number of additional products were identified and are reported in this paper. Samples of effluent from chlorine dioxide bleaching were also investigated for the presence of the newly identified products.



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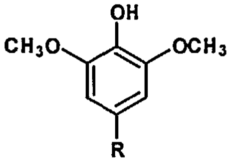

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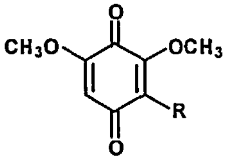
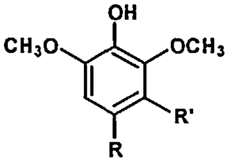


3a R = H
3b R = Cl



4a R = Cl, R' = H
4b R = H, R' = Cl

RESULTS AND DISCUSSION

Reaction of Syringol with Chlorine Dioxide

Analysis of the ethyl acetate extract of the reaction product by GCMS (gas chromatography/mass spectrometry) showed that several products were formed (Figure 1), most of which were chlorinated. The broad peak No.11 was identified as the previously reported[1] 2,6-dimethoxybenzoquinone **3a** by comparison with a standard and subsequent isolation (see below). Peak Nos. 5 and 10 were identified as unreacted syringol **2** (R=H) and 3-chlorosyringol **4b** respectively, by comparison of their retention times and mass spectra with standards. Syringol chlorinates first in the 3-position[5]. The mass spectrum of peak No. 1 had a molecular ion M^+ at m/z 88, a base peak at m/z 60 (M^+ - 28) and contained one chlorine atom. The only reasonable structure for this compound is chlorocyclopropenone **5** which has previously been reported in bleaching

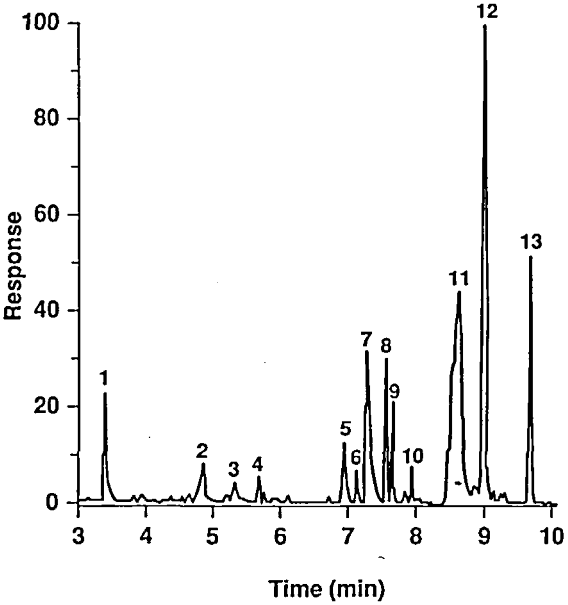
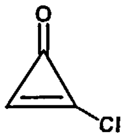


Figure 1. Ion chromatogram of the ethyl acetate extract from the reaction of syringol with chlorine dioxide.

effluent[6]. Peak No. 2 was identified by library search as either 2- or 3-furoic acid (6a or 6b). Subsequent isolation (see Experimental) and comparison with standards established peak No. 2 was 2-furoic acid 6a, a compound which has been previously reported in bleaching effluent[7], and which could result from the cyclization and aromatization of a number of ring opened precursors. Peak Nos. 6, 7, 8, 9, 12 and 13 all had mass spectra indicating the presence of chlorine while peaks Nos. 3 and 4 gave poor mass spectra.



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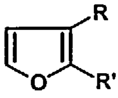
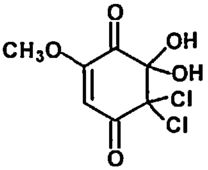


6a R = H, R' = COOH
6b R = COOH, R' = H

When the extract from the reaction was concentrated, pure 2,6-dimethoxybenzoquinone **3a** crystallized in 8% yield. Fractionation of the rest of the product on silica gel resulted in the isolation of a fraction containing a mixture of 2-furoic acid **6a** (peak No. 2) and peak No. 9 (Figure 1), a fraction containing peak No. 12, about 70% purity by GC, and fractions containing mixtures of peak Nos. 7, 8, 13, chlorocyclopropenone **5** (peak No. 1) and an additional 5% yield of 2,6-dimethoxybenzoquinone **3a** (peak No. 11) in various proportions. Crystallization of the compound giving peak No. 12 gave chloro-2,6-dimethoxybenzoquinone **3b** (5% yield), identified by comparison of its melting point and ^{1}H NMR spectrum with literature values[8], and by its mass spectral fragmentation pattern which was similar to that of 2,6-dimethoxybenzoquinone **3a**. Chloro-2,6-dimethoxybenzoquinone **3b** likely results from oxidation of 3-chlorosyringol **4b** since a separate experiment with the latter as substrate gave **3b** as one of the major products.

The major product of the reaction (peak No. 7, Figure 1) was isolated from fractions containing this compound by trituration with toluene followed by crystallization. The melting point and ^{1}H NMR spectrum agreed with literature values[8] for the dione **7**. A weak molecular ion M^+ was present in the mass spectrum at m/z 222 (loss of H_2O from **7**), and two chlorine atoms were indicated present when the compound was introduced directly into the mass spectrometer on a probe. The mass spectrum of the same compound obtained by GCMS of the crude reaction produce (Figure 1) showed no peaks above m/z 160. Evidently, the dione **7**, in addition to losing water of hydration in the mass spectrometer as expected, readily loses a chlorine atom and carbon monoxide when analyzed by GCMS. Initially, the ^{13}C NMR of this compound was also somewhat confusing as one carbon appeared to be missing. After confirming the structure by X-ray crystallography, a ^{13}C NMR spectrum obtained with much better signal to noise revealed a new peak at δ 89.3 which was attributed to the carbon bearing the two hydroxyl groups. The dione **7** results from addition of hypochlorous acid to chloro-2,6-dimethoxybenzoquinone **3b** followed by acid-catalyzed hydrolysis of the hemi-ketal.

Initially, it was found that the compound responsible for peak No. 13 (Figure 1) could be obtained by methylation of the dione **7** with diazomethane in ether/methanol. Subsequently, it was found this compound could be obtained simply by dissolving the dione **7** in methanol. Benzilic acid rearrangement of the dione **7** with sodium bicarbonate as reported[8] gave the cyclopentenonecarboxylic acid **8a**. Methylation of **8a** with diazomethane gave **8b**, the same compound obtained by dissolving the dione **7** in methanol and which was the compound responsible for peak 13 (Figure 1). Evidently, the dione **7** undergoes a benzilic acid rearrangement in methanol to give the methyl ester **8b**, directly. The combined yields of the dione **7** and its benzilic acid rearrangement product **8a**, which eluted from silica with and slightly after **7**, were estimated to be 20%.



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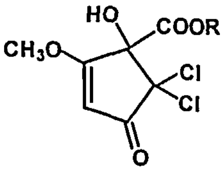

8a R = H
8b R = CH_3

When the mixture of 2-furoic acid (peak No. 2) and the compound responsible for peak No. 9 (Figure 1) was separated by preparative thin-layer chromatography on silica gel, a small quantity of the latter was obtained pure. After crystallization, the compound had a melting point of 141-142°C. The mass spectrum of the compound

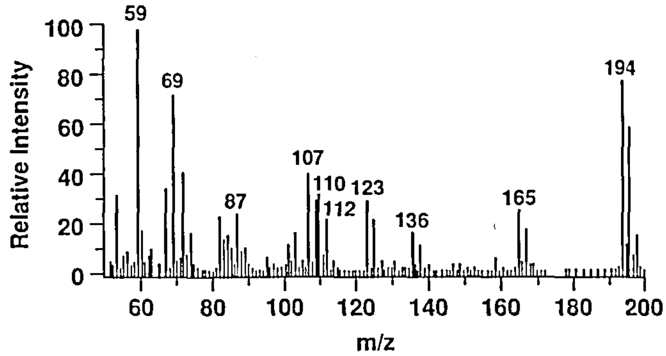

Figure 2. Mass spectrum of the dichloromethylenefuranone **10a**.

(Figure 2) had a molecular ion M^+ at m/z 194 and two chlorine atoms were indicated present by the isotope ratio. High resolution mass spectrometry established the molecular formula was $C_6H_4Cl_2O_3$. The ^1H NMR spectrum indicated a methoxyl group and one olefinic hydrogen (δ 6.56) were present which accounted for all the hydrogen atoms. The ^{13}C NMR spectrum contained six signals including one for a carbonyl group but the structure could not be elucidated. The crystals obtained by crystallization from acetone/hexane were not suitable for X-ray crystallography, however, during the course of attempting to get additional NMR data in dmso-d_6, larger crystals formed which were used for an X-ray structure determination. The structure of the compound was determined to be the dichloromethylenefuranone **10a** (Figure 3). Peak Nos. 8 and 9 (Figure 1) gave mass spectra indicating they were isomeric so the compound responsible for peak No. 8 is probably the isomer **10b**. The mechanism of formation of the furanones could involve decarboxylation of **8a** to the dichlorocyclopentenedione **9**, followed by ring opening and reclosure as shown in Figure 3, similar to that reported previously for the conversion of other chlorinated 1,3-cyclopentenediones to furanones[9].

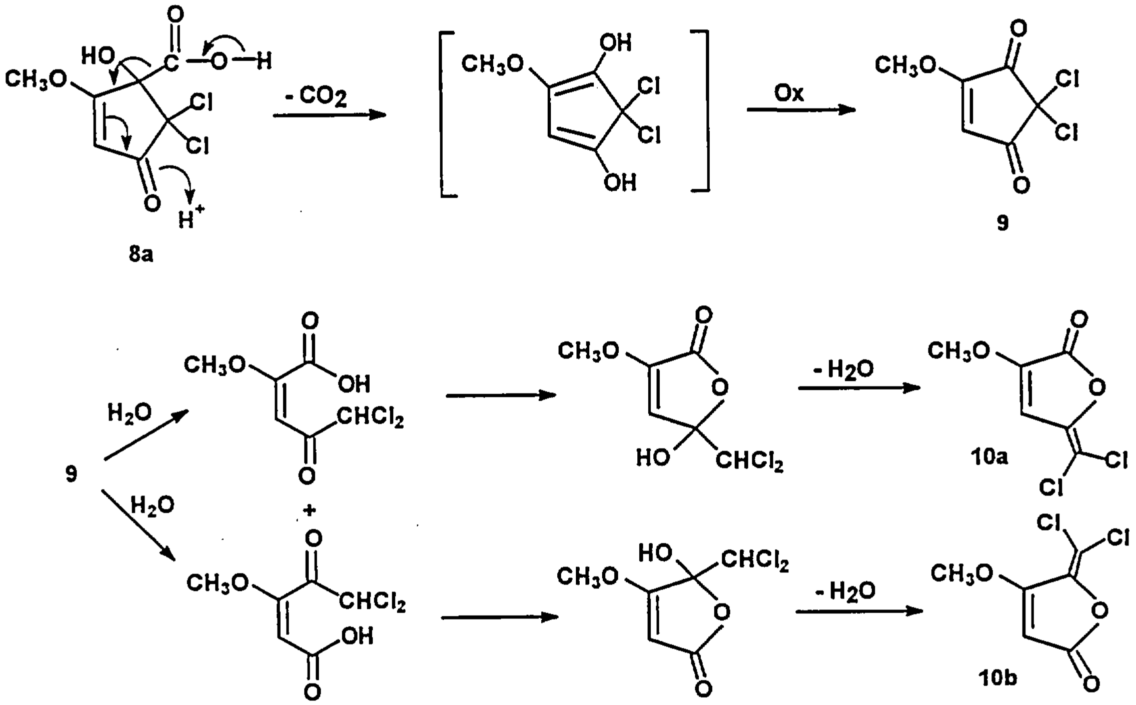

Figure 3. Proposed mechanism for the formation of the dichloromethylenefuranones 10a and 10b.

Analysis of Effluents from Chlorine Dioxide Bleaching

The dione **7** was clearly present in the sample of effluent from the bleaching of conventional pulp (sample C) and the sample from the bleaching of oxygen-prebleached pulp (sample B). The furanone **10a** was present in sample B, while the isomer **10b** was present in sample C. None of these compounds were found in sample A, which was from the bleaching of pulp produced by extended delignification and prebleached with oxygen. The quinones **3a** and **3b** were not found in any of the samples. Compounds **7**, **10a** and **10b** have not been previously reported in bleaching effluent, and although the concentrations were not determined in the present study, they are likely present in the low µg/L range. The fact that these compounds were found in effluents from the bleaching of a softwood pulp indicates they can also originate from guaiacol units.

EXPERIMENTAL

General

Melting points were determined on a Fisher Johns apparatus and are uncorrected. Column chromatography was performed on silica gel, 80-200 mesh. Preparative thin layer chromatography was performed on silica gel 60F 254 precoated aluminum plates, 0.20 mm thickness. Gas chromatography (GC) was done on a Hewlett Packard 5890 Gas Chromatograph equipped with a 25 m HP-1 capillary column and gas chromatography/mass spectrometry on a Hewlett Packard 5890 Gas Chromatograph equipped with a 30m DB-5 capillary column coupled to a Fisons 70-250S high resolution mass spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a Varian UNITYplus 500MHz NMR spectrometer. Proton and carbon chemical shifts of 7 and **10a** were assigned and verified according to the X-ray structures by a $^1H/^{13}C$ correlation experiment (HSQC) as well as a long range $^1H/^{13}C$ multiple bond correlation experiment (HMBC). Signal positions are given in ppm (δ) relative to Me_4Si. X-ray crystallography was done on a Siemans P4 diffractometer at 173°K.

Reaction of Syringol with Chlorine Dioxide

Syringol (6.16 g, 0.04 moles) was added to a stirred solution of chlorine dioxide (8.1 g, 0.12 moles) in water (810 mL) at room temperature. The flask was stoppered with a pressure-release stopper and heated at 60°C (bath) with stirring and protected from light for 30 min. After cooling, sodium chloride (80 g) was added, and the product extracted with ethyl acetate (5 x 100 mL). The combined extracts were dried ($MgSO_4$) and, after analysis by GCMS, concentrated to about 20 mL. The 2,6-dimethoxybenzoquinone **3a** (570 mg, 8% yield) which crystallized was filtered, and the filtrate evaporated to give an orange oil (3.2 g). Fractionation on silica gel (200 g) and elution with hexane:ethyl acetate, 4:1 containing 5% acetic acid gave a mixture of syringol **2**, 3-chlorosyringol **4b**, 2-furoic acid **6a** and **10a** (180 mg). Further separation by preparative thin layer chromatography on silica gel using hexane:ethyl acetate, 6:1, gave **10a** (16 mg), mp 141-142°C after crystallization from acetone/hexane. ^1H NMR ($CDCl_3$): 3.93 (s, 3H, OCH_3), 6.56 (s, 1H, olefinic). ^{13}C NMR ($CDCl_3$, ^{13}C-^1H undecoupled): 59.1 (J = 146.5 Hz, OCH_3), 106.3 (J = 181.7 Hz, = CH), 106.4 ($=CCl_2$), 144.0 (J = 5-6 Hz, $\underline{C}=CCl_2$), 149.4 ($\underline{C}OCH_3$), 161.9 (J = 8 Hz, C=O). MS(%): 196 (M^+ + 2, 55), 194 (M^+, 75), 167(15), 165(22), 138(10), 136(14), 125(18), 123(28), 107(40), 71(40), 69(75), 59(100). Calc'd. mass for $C_6H_4Cl_2O_3$: 193.9537; found: 193.9544. Structure determined by X-ray. 2-Furoic acid (41 mg), identical with an authentic sample was also isolated from the plate.

Continued elution with the same solvent gave chloro-2,6-dimethoxybenzoquinone **3b** (400 mg, 5% yield), mp 144-146°C (Lit.[8] 147-148°C) after crystallization from ethyl acetate. ^{1}H NMR ($CDCl_3$): 3.84 (s, 3H, OCH_3), 4.18 (s, 3H, OCH_3), 5.98 (s, 1H, olefinic),as reported[8]. MS(%): 204(M^+ + 2, 47), 202(M^+, 100), 174(60), 172(77), 159(44), 139(32), 131(46), 114(47), 103(74), 69(97), identical with material obtained by the treatment of 3-chlorosyringol **4b** with chlorine dioxide.

Elution with hexane:ethyl acetate, 1:1, containing 5% acetic acid gave a mixture of **5**, **7** and **8a** (1.35 g) which was triturated with cold toluene to give **7** (750 mg), mp 125-135°C. Recrystallization from acetone/hexane gave colorless needles, mp 146-148°C (Lit.[8] 149°C). ^{1}H NMR [$(CD_3)_2CO$)]: 3.98 (s, 3H, OCH_3), 6.30 (s, 1H, olefinic), 7.09 (s, 2H, D_2O-exchangeable, 2 x OH), as reported[8]. ^{13}C NMR [$(CD_3)_2CO$]: 57.5 (J = 148.5 Hz, OCH_3), 89.3 (C6), 96.2 (C5), 107.9 (J = 168.9 Hz, C3), 161.5 (C2), 183.2 (C1), 186.8 (J = 9-10 Hz, C4). MS(%): 224 (M^+ + 2-18, <3), 222 (M^+-18, <5), 190(12), 188(37), 160(48), 125(17), 69(100), 59(43), 58(64). Structure confirmed by X-ray crystallography. Continued elution with the same solvent and ethyl acetate containing 5% acetic acid gave a mixture of **8a** and **3a** (930 mg). A sample of **8a** was prepared by the benzilic acid rearrangement of **7**. ^{1}H NMR [$(CD_3)_2CO$]: 4.04 (s, 3H, OCH_3), 5.80 (s, 1H, olefinic), as reported[8]. The methyl ester **8b**, prepared by dissolving **7** in methanol containing a drop of triethylamine, had mp 133-134°C (Lit.[8] 130-131°C). ^{1}H NMR ($CDCl_3$): 3.86 (s, 3H, $COOCH_3$), 3.97 (s, 3H, olefinic OCH_3), 4.47 (s, 1H, OH), 5.58 (s, 1H, olefinic), as reported[8].

Analysis of Effluents from Chlorine Dioxide Bleaching

Three samples of combined D + E stage effluents were obtained from a mill bleaching softwood (pine) kraft pulp. One sample (C) was from bleaching conventional pulp, one (B) from bleaching oxygen prebleached pulp, and one (A) from bleaching pulp produced by extended delignification and oxygen prebleaching.

Samples (500 mL) were acidified with 10% HCl (10 mL), treated with sodium chloride (50 g) and extraced with ethyl acetate (5 x 100 mL). The combined extracts from each sample were washed with water (3 x 10mL), dried ($MgSO_4$) and concentrated to 5-10 mL using a rotary evaporator. They were further concentrated using a stream of air to about 0.5 mL and filtered through a cotton plug. A sample of tap water was processed in the same manner as a blank. The concentrates were analyzed by GCMS and the mass spectra compared with those from the reaction of syringol with chlorine dioxide.

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