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Occurrence of Some Chlorinated Enol Lactones and Cyclopentene-1,3-diones in Chlorine-Treated Waters

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Enol lactones (5-dichloromethylene-2-furanones) and 2,2-dichlorocyclopentene-1,3-diones, a total of six compounds, were synthesized and subsequently qualitatively and quantitatively determined in a sample of chlorination stage liquor from the bleaching of softwood kraft pulp (CBL), in chlorine-treated natural humic water (HW), and in three samples of drinking water treated with various disinfectants (DW1–3). All the compounds could be observed in the samples, in concentrations ranging from 2 to 170 μg/L in CBL, from 7 to 65 ng/L in HW, and at most a few nanograms per liter in DW1–3. The compounds were found to be weakly mutagenic in the Ames assay (strain TA100 without metabolic activation). The contribution of the compounds to the total mutagenicity in the studied samples was negligible. The compounds were unstable in aqueous solutions at pH 7.0, and under these conditions they were in part converted to 5-(dichloromethyl)-5-hydroxy-2-furanones. In acidified methanol, the enol lactones were partially converted to 5-(dichloromethyl)-5-methoxy-2-furanones.

Numerous studies have shown that the chlorination of humic substances and the chlorine bleaching of pulp leads to the formation of Ames mutagenic compounds (reviewed in refs 1 and 2). Several mutagens have been identified in chlorination stage bleaching liquors from kraft pulp mills (CBL) and in chlorine-treated water containing humic material. The most important of these compounds is the extremely strong mutagen MX, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone. MX has been shown to account for up to 60% of the total TA100 mutagenicity both in CBL and in chlorine-disinfected drinking water (*2–4*). Several mutagenic compounds with structural similarities to MX have been reported to be formed during aqueous chlorination of organic macromolecules (*5, 6*). Of particular interest for the current study is the report of Franzén and Kronberg on the identification of 5-(dichloromethyl)-5-hydroxy-2-furanones (5-dcMHFs) in chlorinated waters (*7*). In an earlier work, they synthesized 5-dcMHFs and used 5-dichloromethylene-2-furanones, also called enol lactones, and 2,2-dichlorocyclopentene-1,3-diones as intermediates (*8*). Previously, it had been shown that 5-dcMHFs, enol lactones, and cyclopentenediones are related and that they can easily be converted to each other (*9–11*). Franzén and Kronberg (*8*) showed that at the conditions used for the methylation of extracts of chlorinated waters for GC/MS analysis, enol lactones are partially converted to 5-methoxy-5-dcMFs, i.e., the identical methoxy derivatives as those used for the determination of 5-dcMHFs. This means that if enol lactones are present in chlorinated waters, they might affect the quantitation of 5-dcMHFs. McKague et al. (*9, 12*) have previously reported some enol lactones and cyclopentenediones to be present in CBL. Thus, we might expect these compounds to be present also in extracts of chlorine-treated humic water and chlorine-disinfected drinking water. In addition, McKague et al. (*9*) reported enol lactones to generate mutagenicity in the Ames assay.

The aim of the current work was to carry out a more comprehensive search for enol lactones and cyclopentene-1,3-diones in softwood chlorination stage liquor from a kraft pulp mill, in chlorine-treated natural humic water, and in drinking water. At the same time, we wanted to ensure that the previously reported concentrations of 5-(dichloromethyl)-5-hydroxy-2-furanones in chlorinated waters were not affected by the presence of enol lactones. We synthesized three different chlorine-substituted enol lactones and cyclopentene-1,3-diones (Figure 1). We used the compounds as authentic standards in the subsequent analytical work. Furthermore, we determined the mutagenicity of the compounds by the Ames assay and studied the chemical stability of the compounds in water under neutral conditions.

Experimental Section

Synthesis of Compounds. 5-Dichloromethylene-2-furanone (EL1, Figure 1) was synthesized and purified as described previously (*8*).

3-Chloro-5-dichloromethylene-2-furanone (EL2) was obtained by treating 3-chloro-5-(dichloromethyl)-5-hydroxy-2-furanone (*8*) with concentrated sulfuric acid at 120

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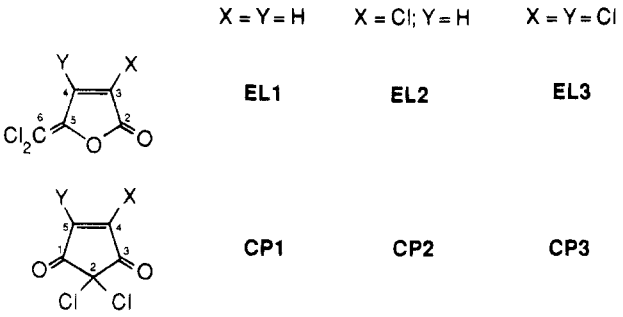

FIGURE 1. Structures of the studied compounds.

°C for 60 min. The reaction mixture was extracted with diethyl ether, and the product was purified by TLC (Merck silica gel 60 F_{254}). The plate was eluted with a mixture of *n*-hexane and diethyl ether (7:3) containing 1% acetic acid. The band at $R_f = 0.71$ was scraped out, and the compound was extracted from the silica gel by using ethyl acetate. Evaporation of the solvent gave EL2 as white crystals in 53% yield.

3,4-Dichloro-5-dichloromethylene-2-furanone (EL3) was obtained by treating 3,4-dichloro-5-(dichloromethyl)-5-hydroxy-2-furanone (*8*) with oleum (65% SO_3) at 120 °C for 40 min (*10*). The product was purified as EL2. $R_f = 0.85$; pale yellow crystals in 15% yield.

2,2-Dichlorocyclopentene-1,3-dione (CP1) and 2,2,4-trichlorocyclopentene-1,3-dione (CP2) were obtained by storing cyclopentene-1,3-dione in dichloromethane saturated with chlorine gas at room temperature for 5 days. The products were separated from each other by column chromatography on silica gel (200 mm × 10 mm i.d.). The column was eluted by the use of a stepwise gradient of diethyl ether in *n*-hexane. The proportions of diethyl ether were 2.5, 5, 10, 15, 20, 25, 30, 40, 60, 70, 80, and 100%. The fraction volumes were 10 mL. Compound CP2 eluted in the fractions containing 25–40% diethyl ether, and CP1 eluted in the fractions containing 70 and 80% diethyl ether. Final purification of the compounds was carried out by TLC at the same conditions as used for EL2. R_f, CP1 = 0.20; R_f, CP2 = 0.45. The yield of CP1 was 7%, and the yield of CP2 was 40%. Both compounds were yellow oils.

2,2,4,5-Tetrachlorocyclopentene-1,3-dione (CP3) was synthesized starting from hexachlorocyclopenta-1,3-diene as described previously (*10*). The compound was recrystallized from petroleum ether (boiling range 90–100 °C), the yield was 5%, and the melting point was 64–65 °C (lit. 64–65.5 °C, ref *10*).

The preparation of 3,4-dibromo-2(5*H*)-furanone (red-MBA) has been described previously (*13*). The NMR spectra were recorded with a Jeol GX 400 Fourier transform NMR spectrometer.

Full-scan mass spectra were obtained on a Hewlett-Packard 5971A mass selective detector coupled to a Hewlett-Packard 5890 gas chromatograph. The ionization mode was electron impact (70 eV). The mass range scanned was 30–400 amu, the scan rate was 1.5 scans/s. The GC was equipped with a HP-1 fused silica capillary column (25 m × 0.20 mm i.d., film thickness 0.33 μm).

Water Samples. The characteristics, chlorine dosage, and extraction procedures of the CBL sample, of the chlorine-treated natural humic water sample (HW), and of the three drinking water samples (DW1–3) have been described previously (refs *5*, *13*, and *7*, respectively).

Determination of Compounds in Chlorine-Treated Waters. The studied compounds were analyzed in underivatized extracts by GC/MS in the selected ion monitoring (SIM) mode, and red-MBA was used as an internal standard. The analyses were carried out using a Dani 3800 capillary gas chromatograph interfaced to a VG 7070E mass spectrometer. The ionization mode was electron impact (70 eV), and the resolving power was 1000. The GC was equipped with a HP-1 fused silica capillary column (25 m × 0.20 mm i.d., film thickness 0.33 μm). The oven temperature program was initially held at 40 °C for 2 min and then programmed first at 20 °C/min to 120 °C and finally at 6 °C/min to 180 °C. The injection mode was splitless with the split valve closed for 1 min. The retention time of the air peak was 2 min. Helium was used as carrier gas at a flow rate of 0.40 mL/min. The retention times of the compounds were 8.4, 9.5, 9.8, 10.8, 11.3, 11.7, and 14.1 min for CP1, CP2, EL1, CP3, red-MBA, EL2, and EL3, respectively.

The ion peaks used for SIM quantitation were the $(M)^-$, $(M+2)^+$, and $(M+4)^-$ ions of EL2, EL3, CP2, and CP3. The $(M-CO)^+$, $(M)^+$, and $(M+2)^+$ ions were monitored in the determination of EL1 and CP1. The response factors of the most abundant selected ion vs red-MBA were calculated from the analyses of a standard mixture (single-point calibration). The identification of the compounds in the extracts was based on positive matching of retention times and relative ratios of ion peak areas, within an experimental error of 15%.

Stability Tests. Approximately 1 mg of each compound in ethyl acetate solutions (200–500 μL) was added to 60 mL of a 0.05 M phosphate buffer solution (pH 7.0). The solutions were stored at room temperature, and 10-mL aliquots were removed periodically for analysis. Decafluorobiphenyl (60 μg) was added to each aliquot as an internal standard; the aliquots were acidified and extracted twice with 5 mL of ethyl acetate. The ethyl acetate extracts were combined, evaporated to 50–100 μL, and then analyzed by GC (Varian 3700) equipped with a flame ionization detector (FID). The separation was performed on a HP-1 fused silica capillary column (25 m × 0.2 mm i.d., film thickness 0.33 μm). The GC oven temperature was held at 80 °C for 2 min and then programmed to 240 °C at a rate of 8 °C/min.

Mutagenicity Tests. Mutagenicity tests of the pure compounds were carried out according to the method described by Maron and Ames (*14*). *Salmonella typhimurium* tester strain TA100 was used without metabolic activation (S9 mix). The procedure was the same as previously described (*5*). The number of revertants induced by the positive control (0.5 μg of sodium azide) was 500–800, and the number of spontaneous revertants was 100–130. The compounds were assayed in dimethyl sulfoxide with the exception of compounds EL3 and CP1, which were assayed in ethyl acetate.

Results and Discussion

Structural Assignment of the Synthesized Compounds. The ^1H NMR data of the studied compounds are presented in Table 1. In accordance with the signal assignment of 5-hydroxy-5-methyl-2-furanones (5-MHFs) (*8*), the EL1 proton signals at δ 6.33 and 7.70 were assigned to H-3 and H-4, respectively.

In the ^{13}C NMR spectra of the enol lactones, the signals observed at δ 159.4–167.5 were assigned to the carbonyl

TABLE 1

^{1}H Chemical Shifts ($\delta_{H\text{-}i}$) in ppm[a] and ^{1}H–^{1}H Coupling Constants ($^nJ_{HH}$) (Hz) for Chlorinated Enol Lactones (EL1, EL2) and Cyclopentene-1,3-diones (CP1, CP2) in $CDCl_3$ Solution

compd	$\delta_{H\text{-}3}$	^3J	$\delta_{H\text{-}4}$	^3J	$\delta_{H\text{-}5}$
EL1	6.33 (d, 1 H)	5.49	7.70 (d, 1 H)	5.49	
EL2			7.63 (s, 1 H)		
CP1			7.40 (s, 1 H)		7.40 (s, 1 H)
CP2					7.38 (s, 1 H)

[a] Relative to TMS at δ = 0.00 ppm.

TABLE 2

^{13}C Chemical Shifts ($\delta_{C\text{-}i}$) in ppm[a] for Chlorinated Enol Lactones (EL1–3) and Cyclopentene-1,3-diones (CP1–3) in $CDCl_3$ Solution

compd	$\delta_{C\text{-}1}$	$\delta_{C\text{-}2}$	$\delta_{C\text{-}3}$	$\delta_{C\text{-}4}$	$\delta_{C\text{-}5}$	$\delta_{C\text{-}6}$
EL1		167.5	121.5	139.9	147.5	111.4
EL2		162.7	126.8	133.3	144.6	112.2
EL3		159.4	124.6	139.5	141.5	115.0
CP1	189.0	69.1	189.0	145.8	145.8	
CP2	183.0	69.8	184.7	153.8	140.8	
CP3	179.5	70.3	179.5	148.7	148.7	

[a] Relative to TMS at δ = 0.0 ppm.

carbons (C-2) (Table 2). It is known that in nearly all α,β-unsaturated carbonyl compounds, the β-carbon has a higher δ_C value than the α-carbon (*15, 16*). The substitution of a hydrogen by a chlorine atom at the α- and β-carbons influences the chemical shifts of C-2, C-3, and C-4 of the enol lactones in the same way as observed for the 5-MHFs (*8*). In accordance with this, the signals at δ 121.5–126.8 and at δ 133.3–139.9 were assigned to the α- and β-carbons (C-3 and C-4), respectively. The shifts of C-5 and C-6 were assigned by recording a coupled ^{13}C NMR spectrum of EL1, whereby the signal at δ 147.5 was split into two doublets with small coupling constants (J = 9.2 and 7.6 Hz) and could be assigned as originating from C-5. Consequently, the singlet at δ 111.4 originated from C-6.

The ^{13}C NMR chemical shifts of 2,2,4,5-tetrachlorocyclopentene-1,3-dione (CP3) have been assigned previously (17). The shifts of C-4 and C-5 of CP2 were assigned by recording a coupled ^{13}C NMR spectrum, whereby the signal at δ 140.8 was split into a doublet (J = 183 Hz) and could be assigned as originating from C-5.

The mass spectra of enol lactones and cyclopentene-1,3-diones containing equal number of chlorine atoms are very similar (Figure 2). The major differences between the mass spectra of enol lactones and cyclopentenediones are that the cyclopentenediones fragment one chlorine atom more readily (*m/z* 129, 163, and 197 for the di-, tri-, and tetrachlorinated compounds, respectively) and that the fragments at *m/z* 82 and 110 have a higher relative abundance in the mass spectra of enol lactones than in the mass spectra of cyclopentenediones.

The fragments at $(M - 28)^+$ (*m/z* 136, 170, and 204 for the di-, tri-, and tetrachlorinated compounds, respectively) and at $(M - 56)^+$ (*m/z* 108, 142, and 176) are quite abundant.

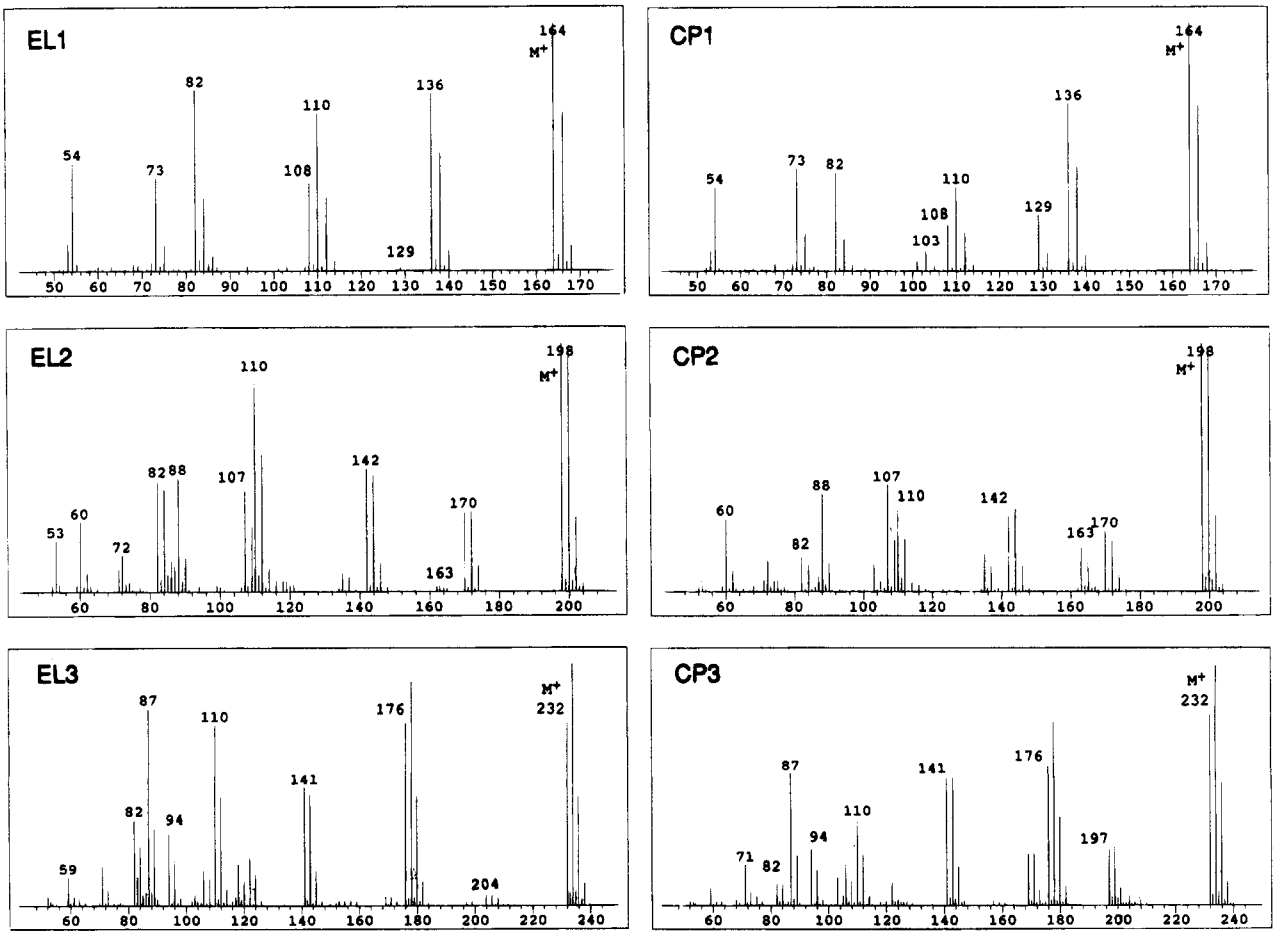

FIGURE 2. Full-scan mass spectra of chlorinated enol lactones (EL1–3) and cyclopentene-1,3-diones (CP1–3).

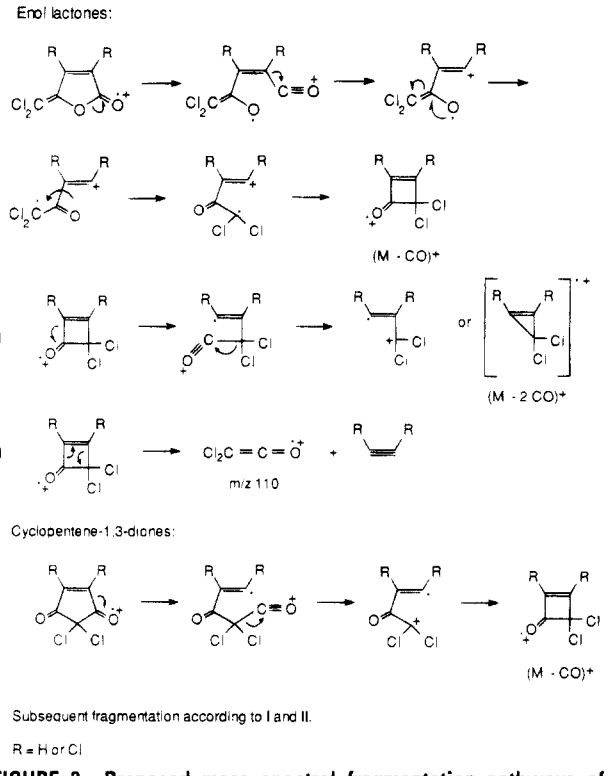

FIGURE 3. Proposed mass spectral fragmentation pathways of chlorinated enol lactones and cyclopentene-1,3-diones.

They are most probably formed by the elimination of one molecule $(M - 28)^+$ and two molecules $(M - 56)^+$ of carbon monoxide from the molecular ion (Figure 3). The abundant fragment at *m/z* 110 (dichloroketene) is probably formed by the elimination of carbon monoxide, acetylene, mono-, and dichloroacetylene from the molecular ions. The fragment representing mono- and dichloroacetylene can be observed in the spectra of the tri- and tetrachlorinated compounds at *m/z* 60 and 94, respectively. The fragment at $(M - 91)^+$ (*m/z* 73, 107, and 141 for the di-, tri-, and tetrachlorinated compounds, respectively) is also quite abundant. It may be formed by the loss of one chlorine atom from the fragment formed by the loss of two molecules of carbon monoxide from the molecular ion.

Transformation Reactions. On the basis of previous studies (*6*, *10*) and of observations made in the current study, we propose that enol lactones, cyclopentene-1,3-diones, 5-dcMHFs, and 5-methoxy-5-dcMFs are related to each other according to Figure 4.

Roedig and Märkl (*10*) found that EL3 was formed when CP3, tetrachlorinated 5-dcMHF, and tetrachlorinated 5-methoxy-5-dcMF were treated with strong acid (oleum). Strömberg et al. (*6*) and Roedig and Märkl (*10*) obtained tetrachlorinated 5-dcMHF by storage of CP3 for a few minutes in slightly alkaline solutions. Furthermore, in the work of Roedig and Märkl (*10*), it was demonstrated that EL3 could be converted to tetrachlorinated 5-methoxy-5-dcMF by boiling the compound in methanol. In our work, we have observed that when enol lactones are heated with methanol under acid conditions, 5-methoxy-5-dcMFs are formed. However, we found that at the conditions (1 h, 70 °C) at which 5-dcMHFs are quantitatively converted to the methoxy derivatives, only about 3% of EL1 and about 18% of EL2 is transformed to the corresponding 5-methoxy-5-dcMF. Franzén and Kronberg (*8*), showed that only after methylation for 5 h at 70 °C, EL1 was quantitatively (>90%) converted to the methoxy derivative of 5-dcMHF.

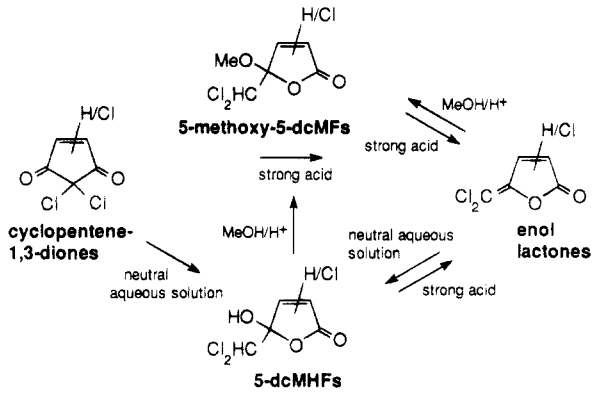

FIGURE 4. Transformation reactions of 5-(dichloromethyl)-5-hydroxy-2-furanones (5-dcMHFs), methyl ethers of 5-dcMHFs (5-methoxy-5-dcMFs), chlorinated enol lactones, and cyclopentene-1,3-diones.

Streicher (*11*) proposed that 5dc-MHFs are transformed to enol lactones by the elimination of water in the GC injector. We could verify this suggestion as we could occasionally observe small amounts of enol lactones when underivatized dc5-MHFs were injected to the GC.

It should be noted that Roedig and Märkl (*10*) suggested CP3 to be transformed in slightly alkaline solutions to the open-chain keto acid instead of the hydroxylactone tautomer. However, the 5-MHFs do probably not exist in the open-chain form. We found that GC and NMR analyses of 5-dcMHFs stored at neutral pH showed no evidence for formation of neither the E- nor the Z-isomer of the keto acid tautomers. Also, on the basis of IR spectra, it has been shown that the lactone structure of 5-MHFs rather than the keto acid tautomer is greatly favored (*8*, *18*).

Concentrations of Enol Lactones and Cyclopentenediones in Water. The studied compounds could be observed in each extract. However, EL3 could not be detected in DW1, and EL1 could not be quantified in the samples because of interference of peaks from a compound with almost the same retention time as EL1 (Figure 5). In CBL, the dominating compound was CP3, which was found at a concentration of 171 μg/L (2 g/ton of pulp). The concentrations of the other compounds ranged from 2 to 18 μg/L (0.02–0.2 g/ton of pulp). Previously, McKague et al. (*9*) reported CP3, EL2, and EL3 to be produced in the amount of 72, 4.9, and 0.3 g/ton of pulp, respectively. The higher amounts of the compounds found in the study of McKague et al. can in part be explained by the 2-fold higher lignin content of the unbleached pulp than in the pulp used in our work. The presence of EL1, CP1, and CP2 in CBL has not been reported previously.

In the HW extract, the dominating compound was CP1. The concentrations of the compounds ranged from 7 to 65 ng/L.

In DW1–3, the compounds were observed at concentration ranges from a few to less than 1 ng/L. The highest amounts of the compounds were found in DW1, which had been disinfected with chlorine only, but the compounds could also be detected in DW3, which had been disinfected with a combination of ozone and chloramine.

Considering that the concentration levels of the corresponding 5-dcMHFs are higher than those of the enol lactones and cyclopentenediones (*7*) and that enol lactones and cyclopentenediones are only to a small extent converted to 5-methoxy-5-dcMFs under the conditions used for derivatization of 5-MHFs, it can be concluded that enol

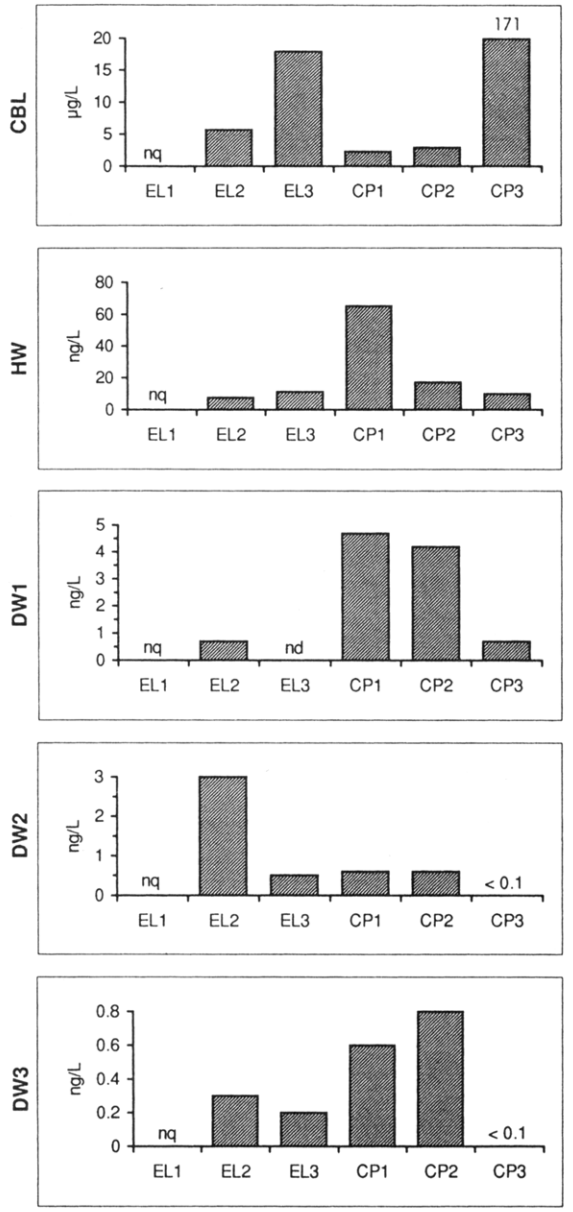

FIGURE 5. Concentrations of chlorinated enol lactones (EL1−3) and cyclopentene-1,3-diones (CP1−3) in pulp bleaching liquor from the chlorination stage (CBL), in chlorine treated natural humic water (HW), and in three samples of drinking water (DW1−3). nd = not detected; nq = not quantified.

lactones and cyclopentenediones do not interfere with the quantitation of 5-dcMHFs.

Chemical Stability. The most stable compound was EL1, which was found to have a chemical half-life of 17 h at pH 7.0 and room temperature (Figure 6a). The half-lives of EL2 and EL3 were determined to 3.5 and 1.5 h, respectively. After storage of EL1 for 48 h, 12% of the compound was still present, while after 24 h of storage 2% of the original amount of EL2 and no EL3 could be detected. These results are well in accordance with results obtained previously by McKague et al. (*9*).

The cyclopentenediones were very unstable at pH 7. The compounds CP1 and CP2 were found to have half-lives of 6.5 and 0.5 min, respectively (Figure 6b). CP3 was even more unstable than CP1 and CP2. After 45 s, only 5% of the original amount could be detected, and after 1 min, no CP3 could be detected.

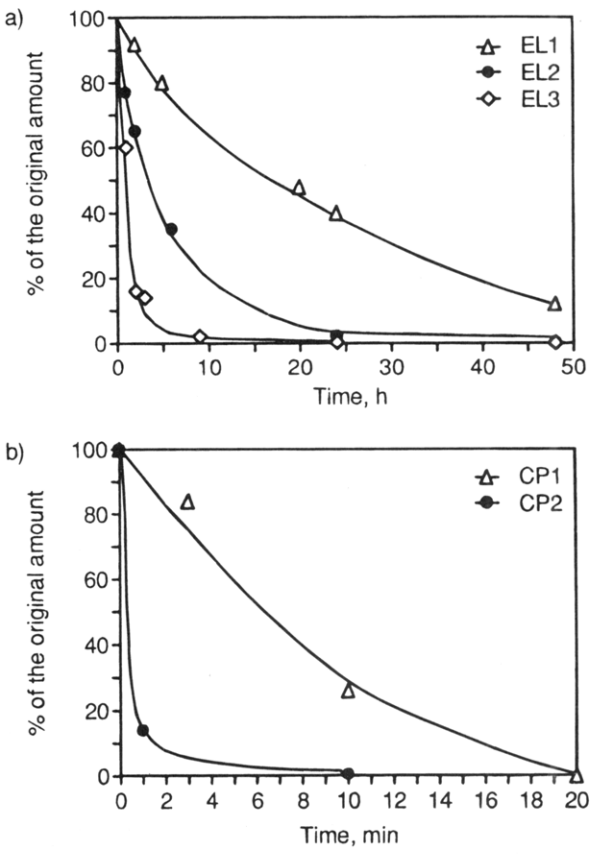

FIGURE 6. Degradation of (a) the enol lactones EL1, EL2, and EL3 and (b) the cyclopentene-1,3-diones CP1 and CP2 upon storage at pH 7 and room temperature.

It can be concluded that enol lactones are more stable than cyclopentenediones and that the chemical stability decreases with an increasing number of chlorine atoms in the compounds. This order of stability is opposite to the one observed for 5-dcMHFs and 5-trichloroMHFs—the stability of these compounds increases with an increasing number of chlorine atoms in the molecules (*7*).

GC analyses of the methylated ethyl acetate extracts of the aqueous solutions of CP1, CP2, and CP3 stored for 20, 10, and 1 min, respectively, and of EL1, EL2, and EL3 stored for 43, 48, and 24 h, respectively, showed that all these compounds had at least partially been transformed to the corresponding 5-dcMHFs. No other degradation products could be observed by GC analysis. Thus, both the enol lactones and the cyclopentene-1,3-diones can be considered as precursors for 5-dcMHFs in neutral aqueous solutions (Figure 4).

As all the studied compounds are unstable under neutral conditions, it is remarkable that they can be found in chlorine-treated humic water and in drinking water (chlorination stage bleaching liquors are strongly acidic). Probably the compounds are continuously formed in reactions between residual chlorine and organic material in the water. Phenolic subunits of humic material and lignin have been suggested as precursors for these compounds (*12*, *19*).

Mutagenicity. All the studied compounds except CP3 were found to generate mutagenicity in Ames tester strain TA100 (Figure 7). The mutagenic activity ranged from 0.7 to 24 net revertants/nmol, the most active compound being CP1. The compounds EL2 and EL3 generated an activity of 2.7 and 1.0 net revertants/nmol, respectively. McKague

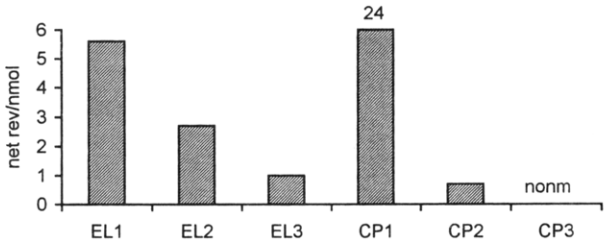

FIGURE 7. Mutagenic activity of chlorinated enol lactones (EL1–3) and cyclopentene-1,3-diones (CP1–3) in Ames tester strain TA100 without metabolic activation. nonm = nonmutagenic.

et al. (*9*) reported a much higher activity for these compounds: 25 and 36 net revertants/nmol for EL2 and EL3, respectively.

Like the chemical stability, the mutagenic activity seems to decrease with an increasing number of chlorine atomes in the molecules. In comparison to the mutagenicity of the 5-dcMHFs (*7*), EL1, EL2, and especially CP1 are more potent mutagens.

The TA100 mutagenicity recorded for the CBL, HW, DW1, DW2, and DW3 samples was 1000, 21, 3, 1.5, and 0.5 net revertants/mL, respectively (*5*, *13*, *7*). Based on the determined specific mutagenicities of the enol lactones and cyclopentenediones and their concentration in the samples, it is apparent that the compounds are not important mutagens in the studied samples, as they altogether contribute for at most 0.1% of the total mutagenicity.

Conclusions

Chlorinated enol lactones and cyclopentene-1,3-diones are formed during chlorination of softwood kraft pulp and of water containing humic material. In chlorination stage liquors, the amounts formed are probably dependent on the κ number of the unbleached pulp and on the chlorine dose. Due to the environmental concerns of organically bound chlorine in the effluents of pulp and paper mills, the chlorine usage has been reduced remarkably during the past few years. Therefore, it is expected that the formation of compounds like these will be even more reduced in the near future. Considering the chemical instability of these compounds, they are very unlikely to constitute any environmental hazard in the receiving waters.

This work demonstrated that chlorinated enol lactones and cyclopentene-1,3-diones can also be detected in drinking water derived from surface water, although in trace amounts. As the compounds show a relatively weak mutagenic activity in the Ames assay, they cannot be considered as important mutagens in drinking water.

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