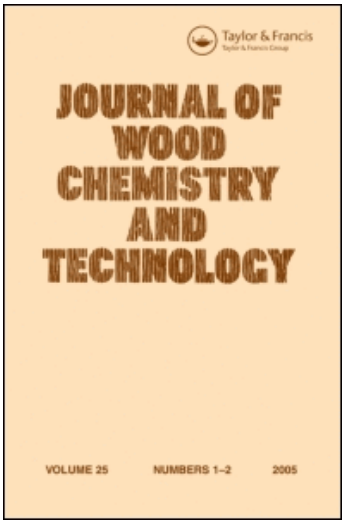

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Studies on the Ozonation of Structural Elements in Residual Kraft Lign Ins

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STUDIES ON THE OZONATION OF STRUCTURAL ELEMENTS IN RESIDUAL KRAFT LIGNINS*

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Dedicated to Professor Joe McCarthy on the occasion of his 70th birthday.

ABSTRACT

In order to elucidate the main reactions of ozone with residual lignins in softwood kraft pulps, model compounds representing conjugated structures (styrenes and stilbenes) and structures of the biaryl, diaryl ether and diarylmethane types have been treated with this oxidant.

The oxidation mixtures were analyzed using HPLC and GC techniques and the main components were identified by ^{1}H NMR and mass spectrometry. Formation of the degradation products is interpreted in terms of known mechanisms of ozonation.

A comparison between the reaction rates reveals that the structural types studied in this work can be arranged according to their ease of ozonation in the following order: stilbenes > styrenes > phenolic structures > muconic acid type intermediates (from the opening of aromatic rings) > non-phenolic structures >> aromatic aldehydes (from the degradation of conjugated structures).

The advantages connected with the use of ozone as delignifying reagent are briefly discussed in the light of the results obtained.

*A preliminary report on this work was given (by T.E.) at the International Symposium on Wood and Pulping Chemistry, Tsukuba Science City, Japan, May 23-27, 1983. Proceedings, Vol. 4, p. 94.

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INTRODUCTION

During the past decade, interest in using ozone as a bleaching reagent has considerably increased. This is due primarily to the general efforts aimed at substituting chlorine and chlorine-based bleaching chemicals by oxygen and oxygen-based reagents in order to meet the requirements of environmental protection, reduce overall energy consumption and lower investment costs.

Ozonation of lignin has been studied in a number of works using model compounds representing structural elements present in native softwood lignins[1-5] and the major reaction products have been identified. This report describes the ozonation of 14 compounds (Fig. 1) representative of important structural elements present in residual lignins of (unbleached) kraft pulps[6].

Compounds 1 - 3 serve as models of biaryl and diaryl ether structures, estimated to constitute 9.5 - 11 % and 3.5 - 4 % of the inter-unit linkages between arylpropane units in native softwood lignins[7] and known to survive kraft pulping[8]. The proportions quoted are likely to be considerably higher in residual lignins. Compounds 4 - 14 represent structural elements thought to arise during the pulping process. 4 and 5 reflect the behaviour of diarylmethane type structures formed by condensation of eliminated formaldehyde with phenolic structures[9,10]. Compounds 6 - 11 were used to study the ozonation of coniferyl alcohol (6 and 7), styrene aryl ether (8 and 9), and stilbene (10 and 11) structures, and compounds 12 - 14 that of simple aromatic nuclei bearing an α-desoxy (12) or an α-carbonyl (13 and 14) side chain. The occurrence of these types of structural elements in residual lignins seems likely in view of the results from extensive model studies[11] and the isolation from kraft spent liquors of monomeric[12,13] and dimeric[12] products representing these structural features.

The model compounds were ozonated in aqueous methanol* at room temperature and the main products separated by HPLC (reversed

* In some experiments pure methanol, water or aqueous acetone was used as solvent system (see Experimental).

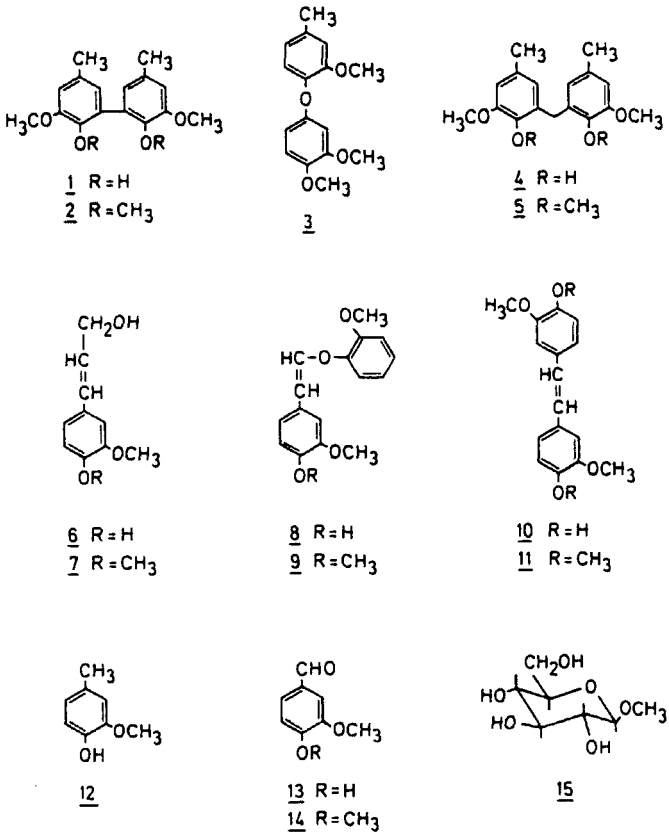


FIGURE 1. Model compounds used in the study of ozonation of residual lignin.

and straight phase) and identified by GC-MS and ^{1}H NMR. By treating mixtures containing equimolar amounts of model compounds with increasing amounts of the oxidant, the relative rates of ozonation of the various types of residual lignin structures were established.

RESULTS

Reaction Products from the Ozonation of Model Compounds

1) from the biaryl compounds 1 and 2

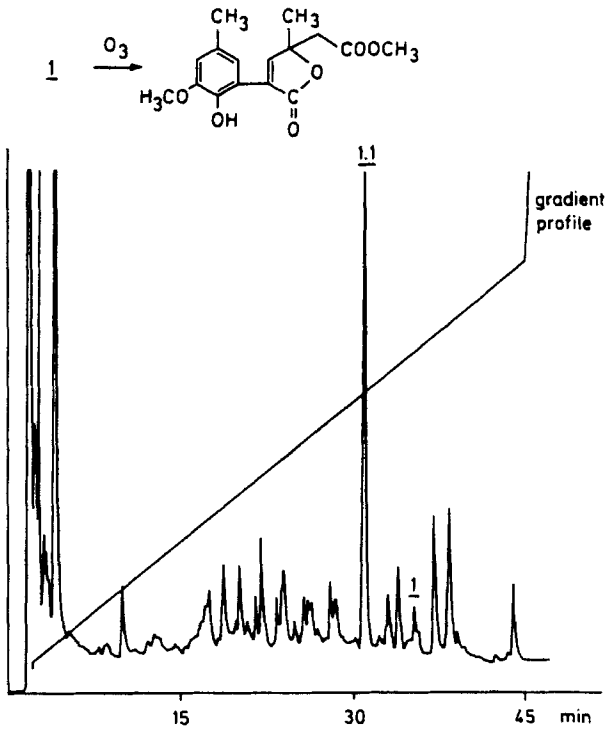


FIGURE 2. Ozonation of bicreosol (1).

Fig. 2 shows the HPLC-chromatogram of the complex reaction mixture obtained after ozonation of 1 with 2.5 equivalents ozone in acetone-water (4:1). The starting material was almost completely consumed and lactone 1.1 formed the major component. A large number of minor products so far unidentified were also found in the reaction mixture.

Results from the gas chromatographic separation following the treatment of 2 with 2.5 equivalents of ozone are given in Fig. 3. The main product was the muconic acid derivative 2.1 which underwent stepwise oxidative degradation yielding the keto esters 2.2 and 2.3, as well as the ester 2.4.

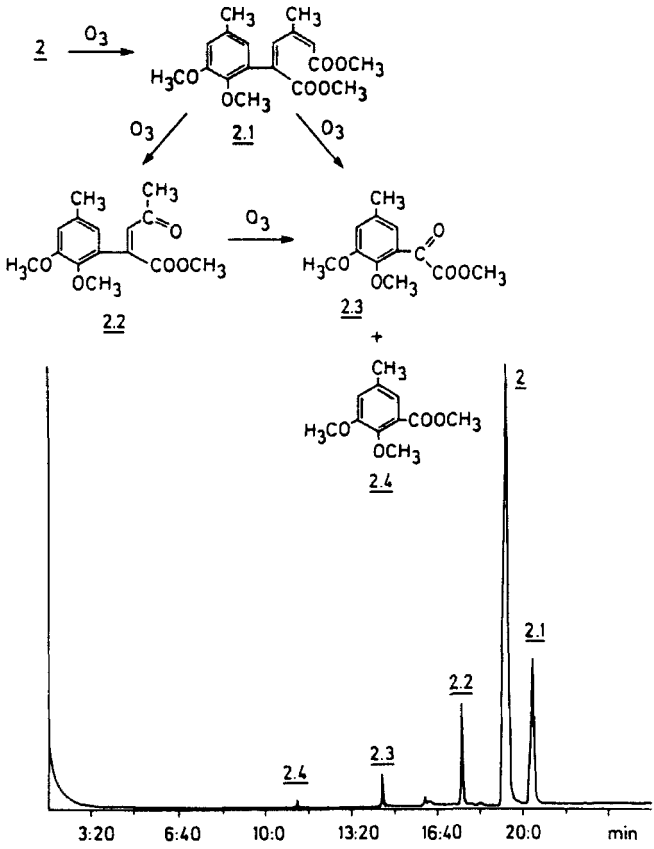


FIGURE 3. Ozonation of bicreosol dimethyl ether (2).

2) from the diaryl ether 3

Ozonation of 3 followed the course outlined in Fig. 4. Almost all of the starting material was rapidly consumed to give the aroxymuconic acid dimethyl ester 3.1. This was further degraded oxidatively to yield 3.2 (main product) and 3.3. A small amount of 3.1 underwent epoxidation, presumably by the action of hydrogen peroxide, formed during the decomposition of initial ozonation products, to give 3.4.

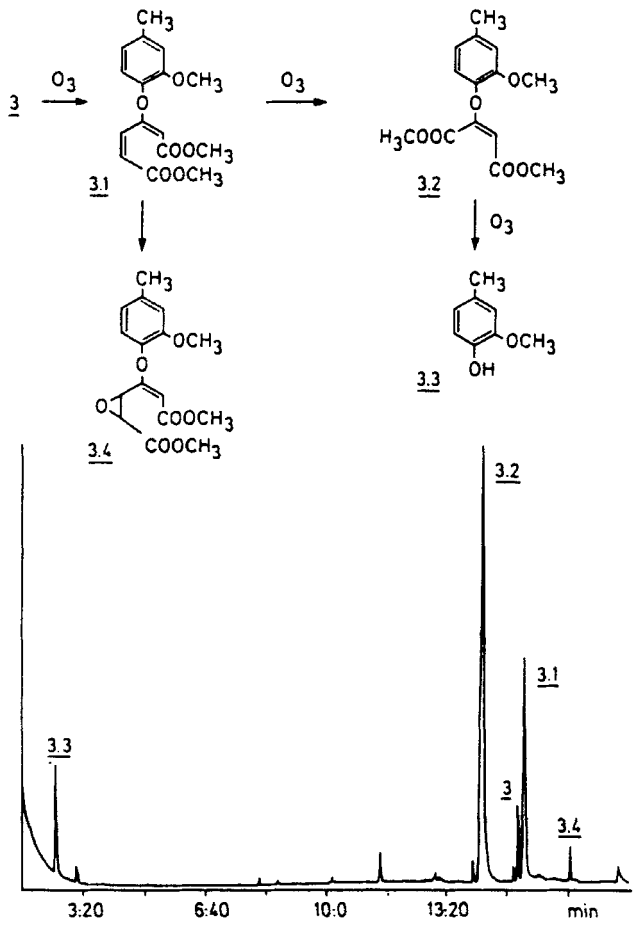


FIGURE 4. Ozonation of 4-methyl-2,3',4'-trimethoxydiphenyl ether (3).

3) from the diarylmethane 5

The behaviour of compound 5 (Fig. 5) was analogous to that of compound 2 (Fig. 3). Oxidative opening of one of the aromatic rings to give the corresponding muconic acid derivative (5.1) was again followed by stepwise oxidative degradation affording the keto esters 5.2 and 5.3, as well as small amounts of the ester 5.4.

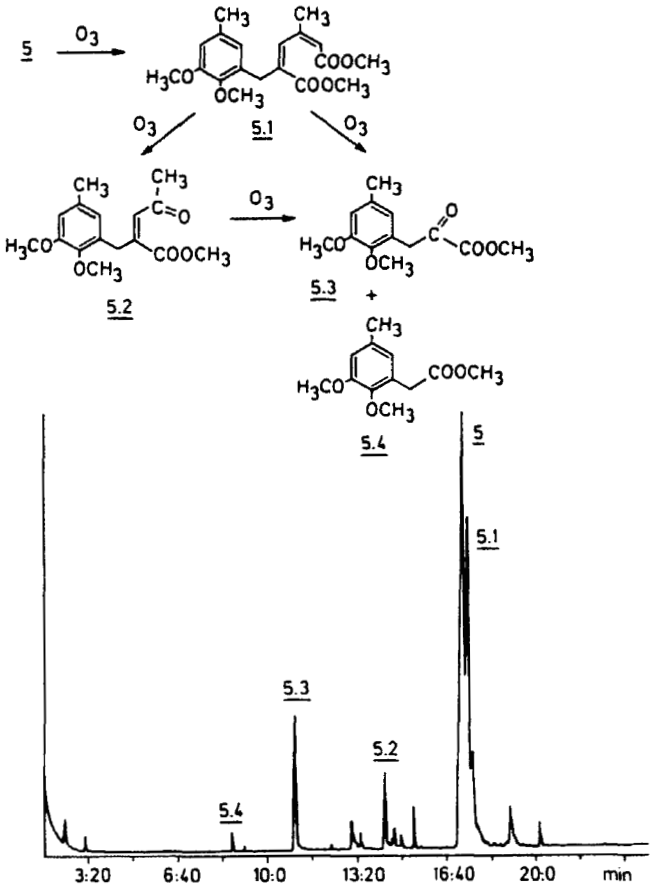


FIGURE 5. Ozonation of bis-(2,3-dimethoxy-5-methylphenyl) methane (5).

4) from coniferyl alcohol (6) and coniferyl alcohol methyl ether (7)

Compound 6 (used in the form of the diacetate) and the monomethyl ether 7 were attacked at the olefinic double bond to give the expected aromatic aldehydes and acids. The reaction mixture from 6-diacetate was found to contain also the corresponding aliphatic cleavage product 6.2 (glycolaldehyde acetate) (Fig. 6).

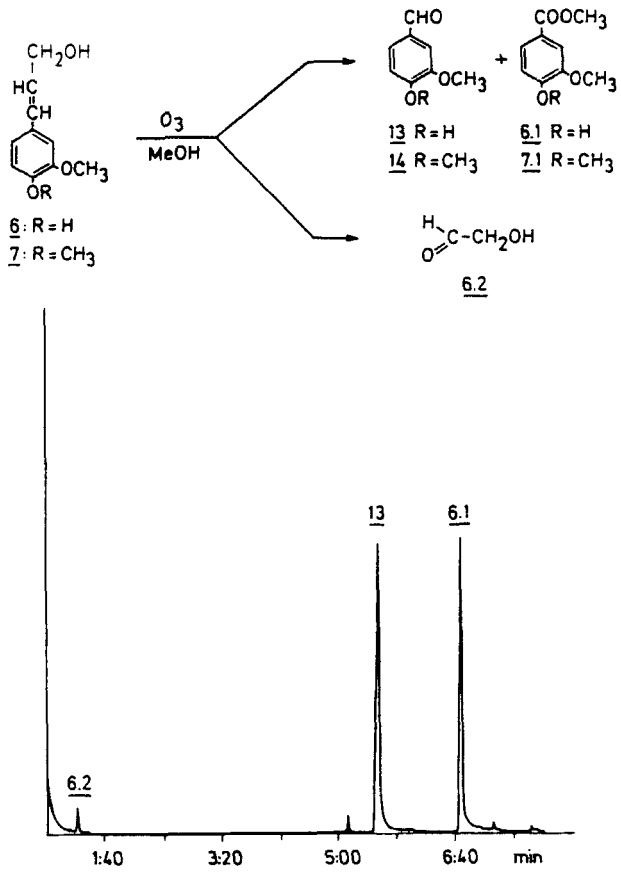


FIGURE 6. Ozonation of coniferyl alcohol (6) and its methyl ether (7).

5) from the styrene-β-aryl ether derivatives 8 and 9

The phenolic (8) and the non-phenolic (9) styrene-β-guaiacyl ethers (mixtures of cis- and trans-forms) were also attacked preferentially at the olefinic double bond affording mixtures consisting of the corresponding aromatic aldehydes and acids (Fig. 7). In the case of compound 9, production of veratric acid strongly dominated over that of veratraldehyde, whereas ozonation of 8 gave roughly equal amounts of vanillic acid and vanillin. In both ozonations, guaiacyl formiate (8.1) was formed as one of

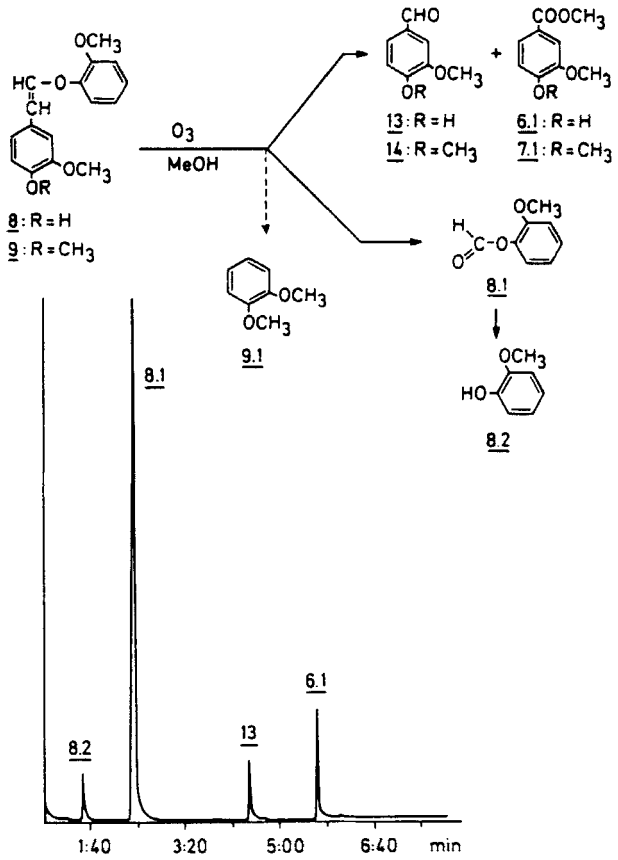


FIGURE 7. Ozonation of 4-hydroxy-3-methoxystyrene-β-guaiacyl ether (8) and 3,4-dimethoxystyrene-β-guaiacyl ether (9).

the main products arising from the guaiacyl ether moiety in 8 and 9. In addition, small amounts of guaiacol (from 8 and 9) and of veratrol (from 9) were found in the oxidation mixtures.

6) from the stilbene derivative 10

Analogously, ozonation of stilbene 10 gave vanillin as main product and small amounts of vanillic acid (Fig. 8). Traces of guaiacol, methoxyquinone and an unidentified product were also detected in the reaction mixture.

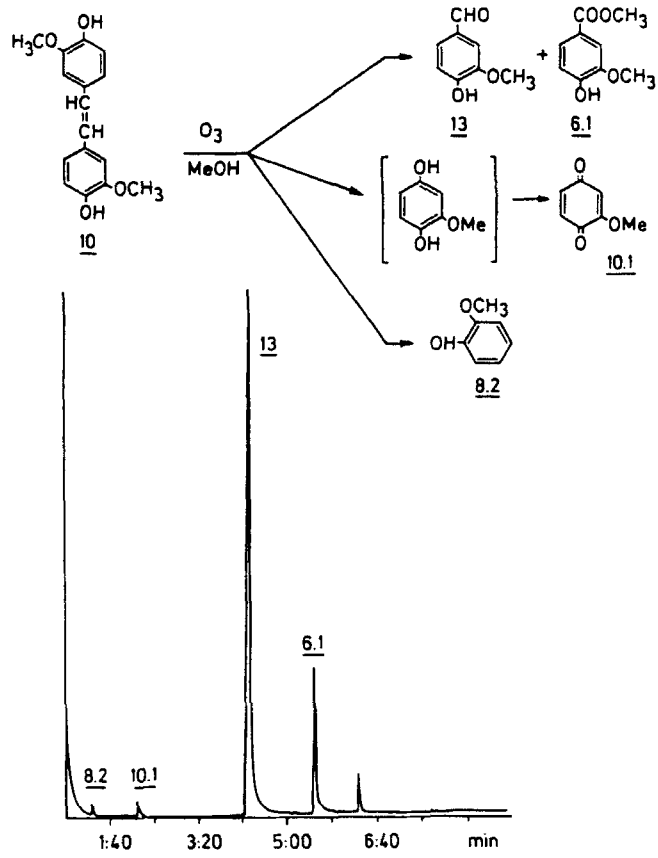


FIGURE 8. Ozonation of 4,4'-dihydroxy-3,3'-dimethoxystilbene (10).

7) from creosol (12)

Treatment of 12 in aqueous methanol yielded the corresponding muconic acid monomethyl ester derivative and its lactone as main products (Fig. 9).

In a separate experiment, compound 12, dissolved in water, was exposed to a stream of 4 % ozone in oxygen and the consumption of ozone was followed by iodometric titration of the unreacted oxidant (Fig. 10). It can be seen that 12 reacts rapidly with 1 mole of ozone. However, the rate of ozone consumption decreases rapidly

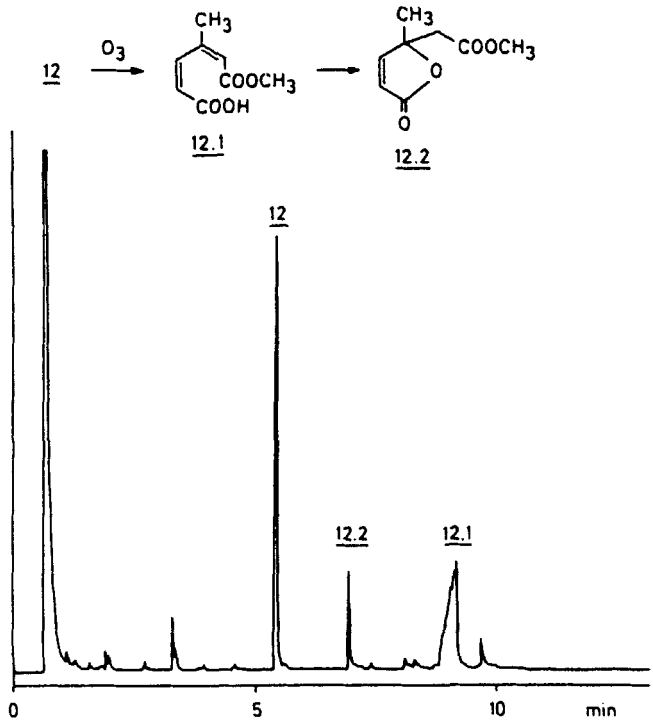


FIGURE 9. Ozonation of creosol (12).

when the amount of O_3 added exceeds 1 mole/mole 12. This is in agreement with the finding that the muconic acid structures formed initially are less reactive than the parent phenolic nuclei in the lignin model compounds used. The present work confirms the high yields of muconic acid-type products obtained after ozonation of phenolic structures reported previously by other authors[1-3,5].

8) from vanillin (13)

Compound 13 in aqueous methanol reacted with ozone at a low rate yielding a main product to which structure 13.1 is tentatively assigned (Fig. 11). Analyses of the reaction mixture at different stages of the reaction period revealed that cleavage of the aromatic nuclei is preceeded by acetalization of the alde-

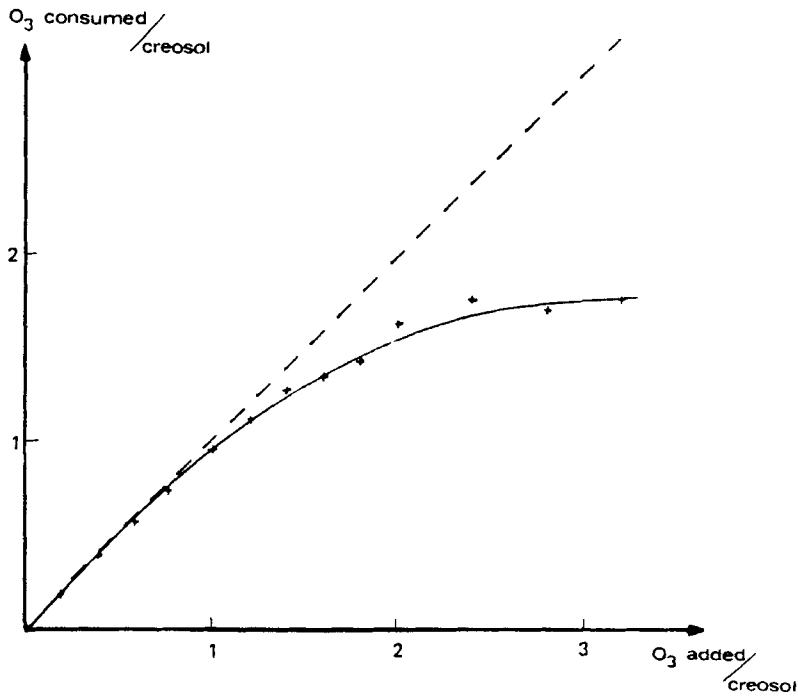


FIGURE 10. Course of ozonation of creosol (12).

hyde group. The cleavage product, the corresponding muconic acid monomethyl ester derivative then seems to undergo ring closure involving the carboxy and the acetal group. In non-protic solvents, e.g. in acetone, oxidation to vanillic acid via insertion of ozone into the C-H bond of the aldehyde group constitutes the main reaction.

Determination of Relative Reactivities (Competition Experiments)

1) Ozonation of a mixture of phenolic monomers and dimers

A mixture of equal amounts of the phenolic model compounds 1, 4, 10, 12 and 13 was dissolved in methanol and treated inter-

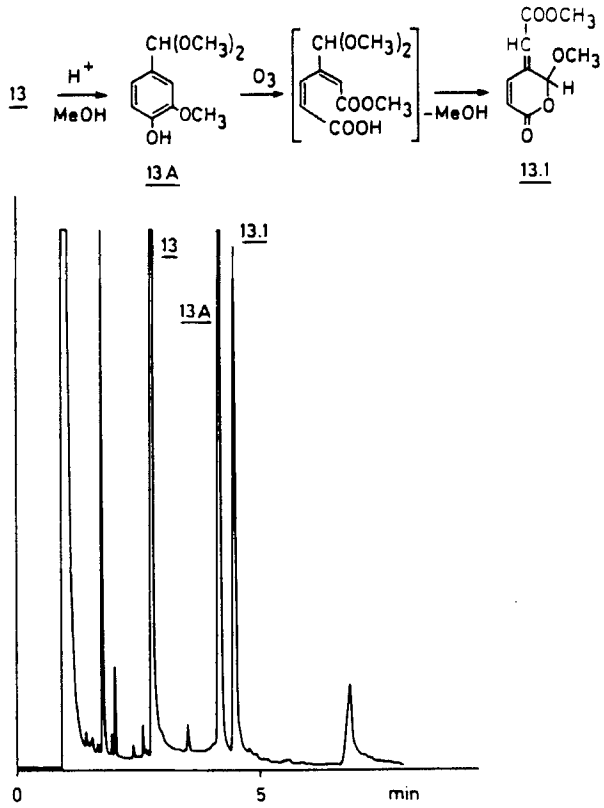


FIGURE 11. Ozonation of vanillin (13) via its dimethyl acetal (13A).

mittently with increasing amounts of ozone. Aliquots were withdrawn at certain intervals during the reaction period and analyzed using GC and HPLC techniques. Fig. 12 includes a series of HPLC (reversed phase) chromatograms of the reaction mixture after addition of increasing amounts of ozone. After addition of one equivalent, stilbene 10 was almost completely consumed, the other compounds remaining virtually unaffected. The second equivalent of ozone consumed substantial amounts of the biaryl compound 1 and the diarylmethane 4, whereas the monomers 12 and 13 remained essentially unaltered. After addition of 3 equivalents of the

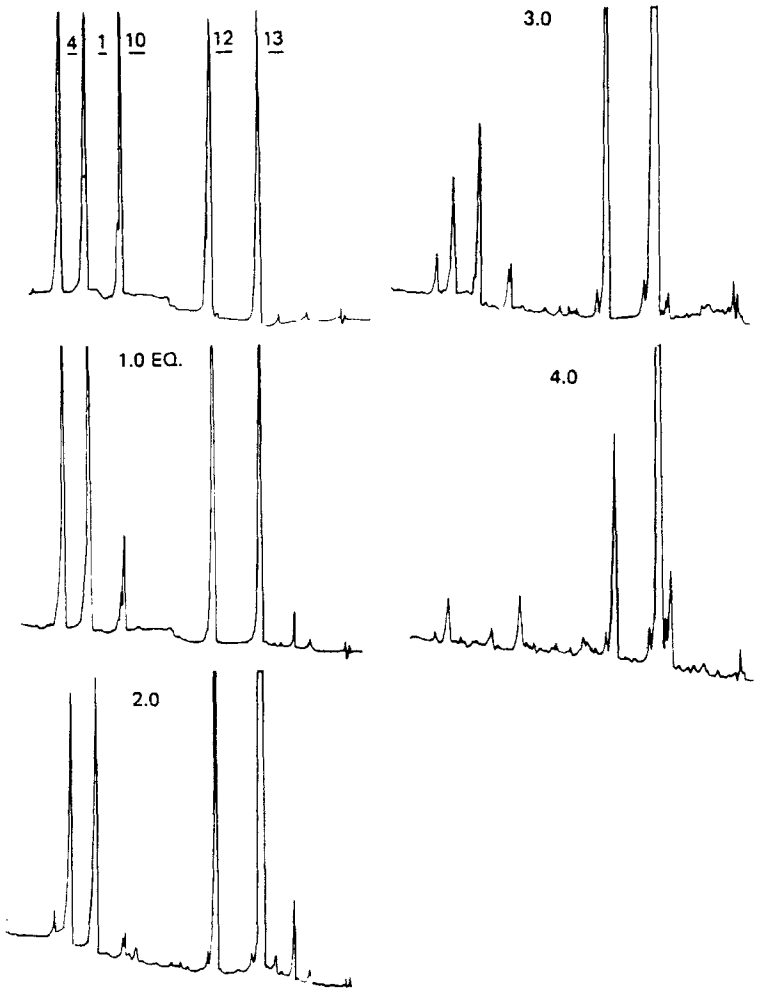


FIGURE 12. Ozonation of a mixture of phenolic monomers and dimers (1, 4, 10, 12 and 13).

oxidant only minor amounts of the dimers 1 and 4 survived, whereas the monomers 12 and 13 still resisted the treatment. A fourth equivalent of ozone removed the greater part of the creosol (12), while the α-carbonyl compound (vanillin, 13) originally present and formed from 10 remained intact.

2) Ozonation of a mixture of α-carbonyl compounds (13 and 14) and methyl β-D-glucopyranoside

The least reactive model compound of the preceding competition experiment (13), the corresponding methyl ether (14) and a model for non-reducing units in wood polysaccharides, methyl β-D-glucopyranoside, were similarly treated with increasing amounts of ozone. Fig. 13 contains a series of gas chromatograms of the acetylated reaction mixtures. Compounds 13 and 14, requiring a large excess of oxidant, were almost completely consumed, whereas the methylglucoside was virtually unaffected by the oxidative treatment under the conditions employed.

3) Ozonation of a mixture of phenolic and non-phenolic dimers

In a third competition experiment the course of ozonation of a mixture consisting of equivalent amounts of the dimeric compounds 1 - 5, 10 and 11 was followed in a similar manner (Fig. 14). As expected (cf. e.g. Ref. 14), stilbenes 10 and 11 were degraded first. After addition of 2.5 equivalents of ozone there remained only a small residue of the etherified compound (11) indicating a slight difference between the reactivities of these two stilbenes. 3.5 Equivalents of ozone reduced substantially the amounts of the phenolic dimers 1 and 4, the diarylmethane (4) reacting somewhat faster than the bicreosol (1). A total of 6 equivalents of the oxidant was required for the degradation of 10 and 11 (2) and for the cleavage of both rings in the phenolic dimers 1 and 4 (4). Three further equivalents were necessary to remove the non-phenolic diaryl ether (3) due to continued degradation of the muconic acid structure formed. The non-phenolic dimers 2 and 5 were even less reactive than 3. After addition of a total of 17.5 equivalents, the greater part of 5 had reacted while the etherified bicreosol 2 still remained essentially unaltered.

4) Ozonation of mixtures of trans-stilbene and creosol, and trans-stilbene and stilbene 10

Equimolar amounts of the title compounds were ozonized in a similar manner and their consumption followed by GC. Stilbene 10

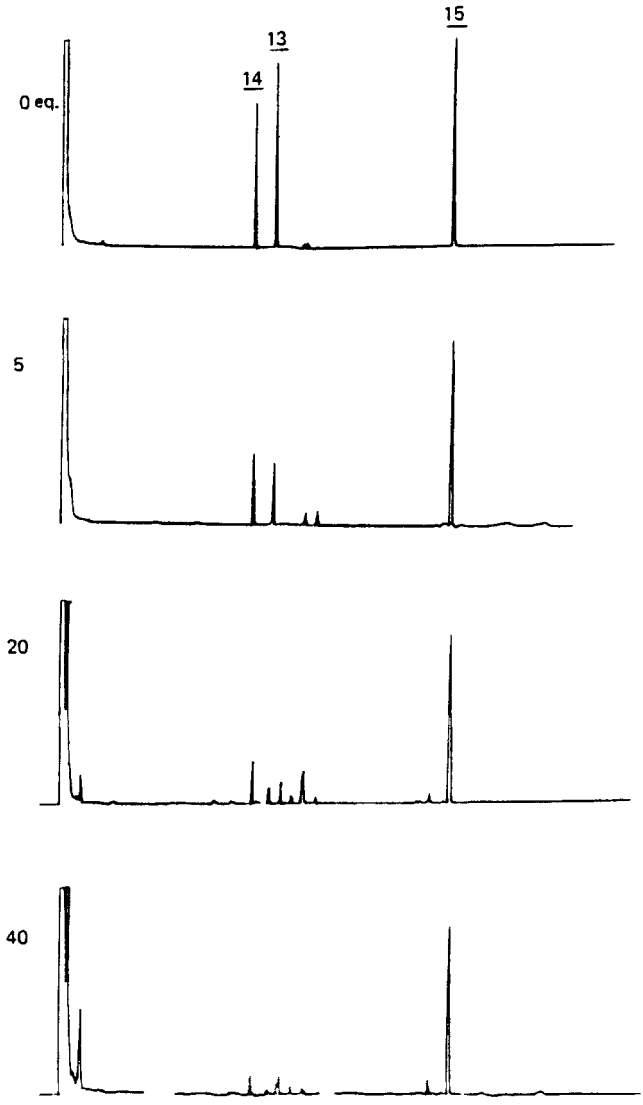


FIGURE 13. Ozonation of a mixture of α-carbonyl compounds (13 and 14) and methyl β-D-glucopyranoside (15).

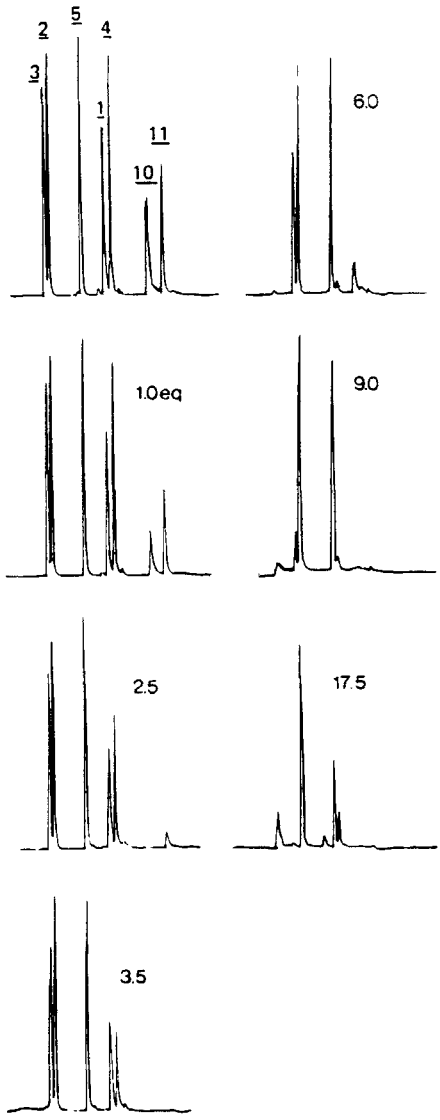


FIGURE 14. Ozonation of a mixture of phenolic and non-phenolic dimers (1 - 5, 10 and 11).

was consumed before trans-stilbene reacted, and trans-stilbene was degraded before creosol was attacked.

DISCUSSION

The reaction between ozone and model compounds representing aromatic and olefinic moieties in residual kraft lignins from softwoods can be interpreted in terms of the Criegee mechanism outlined in Scheme 1 (for a review, see refs. 15 and 16). According to this mechanism, the initial 1,3-dipolar cycloaddition of the oxidant across the aromatic or aliphatic double bond to give a primary ozonide (1,2,3-trioxolane) (1) is followed by a reverse 1,3-dipolar cycloaddition (a 1,3-dipolar reversion) yielding a carbonyl compound and a carbonyl oxide (zwitter ion) (2). The latter constitutes the key intermediate of ozonolysis. In participating (i.e. protic, nucleophilic) solvents (R^1OH) this intermediate gives the corresponding α-hydroxy (R^1 = H) or α-alkoxy (R^1 = alkyl) hydroperoxide (3). Alternatively, these hydroperoxides can arise by direct attack of the participating solvent on the primary ozonide (4). In non-participating solvents one of the principal competitive routes for the carbonyl oxide intermediate is 1,3-dipolar cycloaddition of a carbonyl compound to give a secondary ozonide (1,2,4-trioxolane) (5). Acid- or base-catalyzed decomposition of this trioxolane again affords the corresponding aldehyde (or ketone) and the α-hydroxy- or α-alkoxy hydroperoxide (6). The latter is then hydrolyzed to hydrogen peroxide and the corresponding carbonyl compound (aldehyde, ketone or acid) (7), or loses water to yield the corresponding acid (or ester) (8).

Ozonation of Aromatic Compounds 1 - 5 and 12 - 14 in Aqueous Methanol

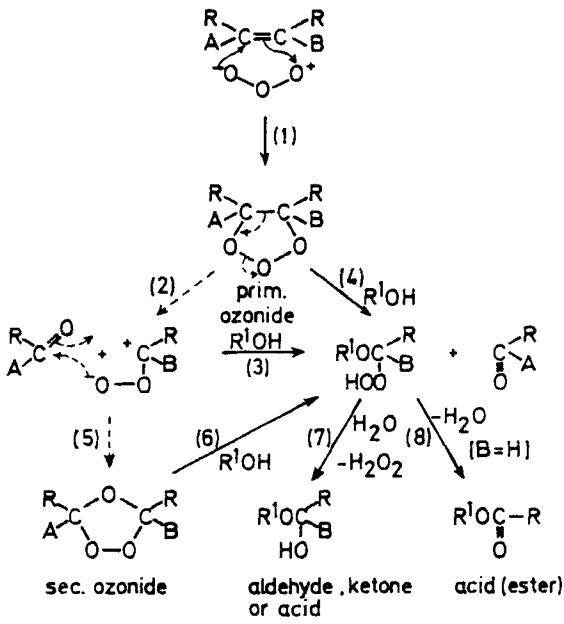
These reactions, resulting in the cleavage of an aromatic ring between the methoxyl and hydroxyl group-bearing carbon atoms, are likely to follow routes (1) - (4) - (7) or (1) - (2) - (3) - (7)

(Scheme 1). Initial 1,3-cycloaddition of ozone (1), followed by decomposition of the primary ozonide (4), (2) - (3) or (2) - (5) - (6), is supported by retention of the methoxyl groups as methyl esters (1.1, 2.1, 3.1, 5.1, 12.1 and 13.1). This excludes a pathway proceeding *via* substitution by ozone, elimination of oxygen and methanol, and formation of intermediates of the *ortho*--quinone type. The latter course of events would also be unlikely in view of the electrophilic character of ozone[17]. The supposition that the initial attack by ozone is electrophilic in nature is strongly supported by the greater ease of reaction of aromatic nuclei substituted by electron-donating moieties as compared to unsubstituted ones (*cf.* *e.g.* rate of consumption of 1 and 4 compared to that of 12, Fig. 12). The greatest increase in the reaction rate is observed with aroxyl (3) groups, followed by benzyl (4 and 5) and aryl (1 and 2) groups. In general, phenolic compounds, *e.g.* compounds of the guaiacyl type (1 and 4), react faster than the corresponding methylated compounds, e.g. those of the veratryl type (2 and 5) (Fig. 14).

Conversely, electron-attracting groups, such as α-carbonyl groups, virtually eliminate the attack on the aromatic ring unless they are "masked" by acetalization (*cf.* reaction of 13, Fig. 11). Instead, aromatic aldehydes in non-protic solvents such as acetone tend to undergo oxidation to give the corresponding carboxylic acids *via* insertion of the oxidant into the C-H bond of the aldehydic group[18].

The electrophilic character of the initial ozone attack and the concerted 1,3-dipolar cycloaddition can be reconciled if it is assumed that the electrophilic oxygen of the ozone molecule becomes more strongly bonded in the transition state than its nucleophilic counterpart[19].

Muconic acid monomethyl ester derivatives arising from the cleavage of aromatic rings of the 3-methoxy-4-hydroxyphenyl type tend to undergo ring closure to give the corresponding lactones (*cf.* formation of 1.1, 12.2 and 13.1 in Figs. 2, 9 and 11, respectively). Apparently the remaining phenolic ring in lactone 1.1



R = aliphatic or aromatic residue
A,B = H, alkyl, aryl or aroxy (olefinic systems)
A,B = hydroxy or methoxy (aromatic systems)
R^1 = H, alkyl or acyl

SCHEME 1. General scheme of ozonolysis of olefinic and aromatic systems.

is oxidatively degraded before or together with the muconic acid (lactone) moiety (Fig. 2). The higher rate of attack on a phenolic nucleus compared to subsequent oxidative degradation of the resulting muconic acid derivative is also reflected in the course of ozone consumption during ozonation of the monomeric compound 12 (Fig. 10).

On the other hand, muconic acid dimethyl ester derivatives (2.1, 3.1, 5.1), formed by the opening of aromatic rings of the 3,4-dimethoxyphenyl type, undergo stepwise oxidative degradation affording 2.2 - 2.4, 3.2 and 5.2 - 5.4, respectively, the second

aromatic ring remaining essentially intact. Thus, oxidation at the olefinic double bonds in muconic acid-type structures proceeds more readily than oxidative cleavage of aromatic rings in non-phenolic structures.

Irrespective of whether the oxidative cleavage of the aromatic rings in 1 - 5 and 12 - 14 follows route (1) - (4), (1) - (2) - (3) or (1) - (2) -(5) - (6) (Scheme 1), a peroxidic intermediate is formed which is converted into the corresponding muconic acid mono- or dimethyl ester derivative and hydrogen peroxide. Formation of the latter product has not been demonstrated in this study. Hydrogen peroxide generation might be indicated by the presence of oxiranes in the reaction mixture; e.g. compound 3.4 could arise from the reaction of 3.1 with the oxidant. However, oxirane 3.4 could also be formed by "partial" cleavage of one of the olefinic double bonds in 3.1[20].

Ozonation of Olefinic Compounds 6 - 11

Cleavage of olefinic double bonds by ozone in participating (i.e. protic, nucleophilic) solvents (R^1OH) generally leads to α-hydroxy (R^1 = H), α-alkoxy (R^1 = alkyl) or α-acetoxy (R^1 = acyl) hydroperoxides (see above). The reaction is considered to proceed via steps (1) - (2) - (3). However, direct attack of the participating solvent on the primary ozonide (4), or 1,3-dipolar cycloaddition of the carbonyl oxide intermediate to a carbonyl compound (5) followed by attack of the participating solvent on the secondary ozonide (6), represent alternative pathways (Scheme 1)[15].

In general, ozonations of olefinic compounds proceed considerably faster than those of aromatic compounds[16]. This also holds true for representatives containing electron-donating hydroxy and/or methoxy-substituted aryl (6 - 11) or aroxyl (8 and 9) groups adjacent to the double bond (Figs. 12 and 14). Such groups promote dipolarophilic activity of the olefinic double bond and thereby facilitate cycloaddition of the oxidant. A

similar beneficial effect of hydroxy- and/or methoxy-substituted aryl and aroxyl groups on the rate of cleavage of olefinic double bonds is also indicated by the facile oxidation of the muconic acid derivatives 2.1, 3.1 and 5.1 to give 2.2, 3.2 and 5.2, respectively (Figs. 3-5). Compound 3.2, being an enol aryl ether, in part undergoes acidic hydrolysis affording creosol (12) and keto succinic acid (not identified).

All possible routes of total cleavage of olefinic double bonds lead to the formation of an aldehydic (or ketonic) and a hydroperoxy fragment (Scheme 1). The latter may be hydrolyzed yielding hydrogen peroxide and another aldehydic (or ketonic) fragment (7) or may rearrange with elimination of water affording the corresponding acid (8).

Ozonation of the olefinic model compounds 6 - 11 afforded expected aromatic aldehydes (13, 14) and acids (esters, 6.1, 7.1) as well as the appropriate aliphatic aldehydes (6.2 and 8.1) (Figs. 6-8). No aliphatic acids (esters) were detected in the reaction mixture. From these product patterns it can be concluded that the nucleophilic attack by the protic solvent takes place preferentially, if not exclusively, at the carbon atom adjacent to the aromatic ring in primary ozonides (4), secondary ozonides (6) or carbonyl oxides (3). No clear trend could be discerned as to the conditions determining the ratio aromatic aldehyde/aromatic acid, i.e. route (7)/route (8).

In addition to the compounds expected on the basis of Scheme 1, some anomalous ozonolysis products (cf. ref. 21) were found in the reaction mixtures obtained from olefinic models[22]. The formation of these products will be described in a forthcoming communication.

CONCLUSIONS

The formation of the described reaction products from the model compounds representing structural elements in residual lignins is consistent with the general pathways of ozonolysis. In both categories, i.e. aromatic and olefinic structures, the

reaction is greatly facilitated by the presence of electron-donating groups, confirming the electrophilic nature of the initial attack by ozone.

Comparative ozonations illustrated by the competition experiments in Figs. 12-14 showed distinct differences in the ease of reaction between the different types of model compounds. These can be arranged according to their relative reaction rates in the following order: stilbenes > styrenes > phenolic structures > muconic acid intermediates > non-phenolic structures >> α-carbonyl structures > carbohydrates.

The different rates of ozonation suggest that differential determination of particular lignin and residual lignin structures may be a possibility. This is currently being studied.

The results presented here reveal that ozone may be expected to be most effective in the degradation of olefinic (conjugated) and aromatic (particularly phenolic) structures. Chlorine/chlorine dioxide and oxygen attack preferentially the same types of structure but require more drastic conditions.

Native carbohydrates either do not react, or react only to a negligible extent, under the conditions of conventional ozonolysis. However, during technical bleaching with ozone, hydrogen peroxide is formed by hydrolysis of peroxidic intermediates from lignin as indicated in the present study (Scheme 1). Part of this oxidant, and of ozone itself, may decompose to give highly reactive hydroxy and hydroperoxy radicals capable of attacking carbohydrate constituents. Thus, in order to take full advantage of the high selectivity of ozone as a delignifying reagent, care must be exercised to avoid, or at least minimize, the generation of these radicals by stabilisation of the reagent and the hydrogen peroxide formed.

EXPERIMENTAL

Materials

Chemicals and solvents were of p.a. grade or purified by distillation before use. Ozone was produced using a Welsbach Model T-23 ozonator.

The model compounds employed were prepared as previously described: 1[23]; 2 by methylation of 1 with dimethylsulfate-alkali; 3(according to ref. 24 but using creosol (12) instead of vanillic acid as reaction partner); 4 by alkaline condensation of creosol (12) with formaldehyde and purification of the condensation product by column chromatography (silica gel, light petroleum-ethyl acetate (4:1), m.p. 130-131°C[25]; 5 by methylation of 4 with dimethylsulfate-alkali; 6-diacetate[26]; 7 (according to ref. 26 but using veratraldehyde (14) instead of acetylvanillin as condensation partner); 8[27]; 9 by methylation of 8 with diazomethane; 10[28]; 11 by repeated methylation of 10 with diazomethane. Compounds 12, 13 and methyl-β-D-glucopyranoside were purchased from Eastman, Merck and Sigma Chem, respectively. Compound 14 was obtained by methylation of 13 with dimethylsulfate-alkali.

General Ozonation Procedure

a) Product analysis experiments

The model compound (50 mg) was dissolved in 90 % aqueous methanol (25 ml) in a glass reaction vessel equipped with a septum screwcap and gas inlet and outlet parts. A stream of oxygen containing 4 % ozone was passed through the solution at room temperature. The gas flow was measured using a flowmeter and equipped with a valve (Aalborg Instruments) and the amount of ozone produced per time unit was determined before and after the ozone treatment by iodometric titration of a three minute's ozone-oxygen stream. The average value of three such determinations was used for calculating the time needed for the addition of the desired number of equivalents of ozone. The course of ozonation was followed by withdrawing samples (1 ml) after each addition of 0.5 equivalents of ozone and the treatment was terminated after addition of a total of 2.5 equivalents by passing a stream of nitrogen through the solution. Correction was made for any unreacted ozone which was trapped in a solution of potassium iodide and determined by iodometric titration.

Sample components were separated both by reversed phase (RP) HPLC using direct injection and, after replacing methanol--water by dichloromethane, by silica gel-HPLC (see below). In the case of non-phenolic substrates, the two types of chromatograms contained the same major peaks indicating that no substantial amounts of acids were formed during the treatment. The same samples in dichloromethane were then analyzed by GC-MS.

Sufficient quantities of the main components of the ozonation mixtures were separated by preparative HPLC (silica gel or RP) and analyzed by ^{1}H NMR (also by ^{13}C NMR in case of 4.2 and 13.1).

b) Competition experiments

The model compounds (40 µmole of each) were dissolved in methanol (50 ml) and a stream of oxygen/ozone containing 20 µmole O_3/min passed through the solution. Aliquots (0.5 ml) were withdrawn at certain intervals during the ozone addition and analyzed either by RP-HPLC or, after replacing the solvent by dichloromethane, by GC.

Chromatographic Methods

The data of the chromatographic equipment and the conditions used are listed in the following:

Gas chromatography

Hewlett-Packard instrument, model 5790A with FID. SE-30 fused silica capillary column, length 25 m.

Silica gel HPLC

Spectraphysics instrument model SP 8000 with a ACS 750-11 UV detector (280 nm). Nucleosil Si (5 µm) column, length 250 mm, width 4.6 mm. Eluent: ethyl acetate-light petroleum, linear gradient: usually 10 % → 50 %.

Reversed phase HPLC

Altex pumps, model 110A with Altex microprocessor equipped with a Beckman variable wavelength detector, model 165. Nucleosil C-8 (5 µm) column, length 250 mm, width 4.6 mm. Eluent: actonitrile-water (both containing 0.1 % acetic acid), linear gradient: 10 % → 70 %.

Spectroscopy

^{1}H and ^{13}C NMR spectra were obtained on a Bruker 200 MHz instrument, model WP 200, using deuteriochloroform as solvent.

Mass spectra were performed at 70 eV using a Finnigan instrument with a SE-30 fused silica capillary column, length 15 m. (The Finnigan instrument was connected to a Data General Nova 3 computer with an INCO:s data system for MS-data evaluation.)

Product identification

α-(2-Hydroxy-3-methoxy-5-methylphenyl)-γ-methoxycarbonylmethyl--γ-methyl-α-butenolide (1.1).

M.s. m/e (rel. int.): 306 (M, 42), 291 (M-15, 10), 247 (M-59, 2), 233 (M-73, 100), 232 (M-74, 6), 205 (M-73-28, 8), 189 (M-73-44, 20)

^{1}H NMR: δ 1.54 [s, 3 H, non-$ArCH_3$], 2.32 [s, 3 H, $ArCH_3$], 2.78 [d, 1 H, CH_2, J_{gem} 15.6], 2.96 [d, 1 H, CH_2, J_{gem} 15.6], 3.70 [s, 3 H, $COOCH_3$], 3.90 [s, 3 H, $ArOCH_3$], approx. 6.73 [m, 2 H, Ar], 7.50 [s, 1 H, olefinic]

1-(2,3-Dimethoxy-5-methylphenyl)-3-methyl-1,3-butadiene-1,4-dicarbolyxic acid dimethyl ester (2.1)

M.s. m/e (rel. int.): 334 (M, 18), 319 (M-15, 1), 303 (M-31, 14), 275 (M-59, 57), 271 (M-31-32, 24), 243 (M-59-32, 100), 228 (30), 200 (10), 137 (10), 130 (20), 115 (10)

^{1}H NMR: δ 2.09 [dd, 3 H, non-ArCH_3], 2.33 [s, 3 H, ArCH_3], 3.67 [s, 3 H, $COOCH_3$], 3.71 [s, 3 H, $COOCH_3$], 3.74 [s, 3 H, ArOCH_3], 3.85 [s, 3 H, ArOCH_3], 5.83 [m, 1 H, C<u>H</u>$COOCH_3$, J ~ 1], 6.64 - 6.74 [m, 2 H, Ar], 6.80 [m, 1 H, -CH=C<u>H</u>-, J ~ 1]

1-(2,3-Dimethoxy-5-methylphenyl)-3-oxo-1-butene-1-carboxylic acid methyl ester (<u>2.2</u>)

M.s. m/e (rel. int.): 278 (M, 18), 247 (M-31, 100), 232 (M-31-15, 5), 219 (M-59- 4), 189 (5), 161 (5), 131 (5), 77 (4), 59 (3), 43 (28)

^{1}H NMR: δ 2.17 [s, 3 H, non-ArCH_3], 2.33 [s, 3 H, ArCH_3], 3.74 [s, 3 H, $COOCH_3$], 3.85 [s, 3 H. ArOCH_3], 3.86 [s, 3 H, ArOCH_3], 6.65 [s, 1 H, olefinic], 6.74 [m, 2 H, Ar]

2,3-Dimethoxy-5-methylphenylglyoxylic acid methyl ester (<u>2.3</u>)

M.s. m/e (rel. int): 238 (M, 14), 207 (M-31, 1), 179 (M-59, 100), 164 (12), 136 (30), 121 (5), 91 (15), 77 (5), 65 (8), 39 (7)

2,3-Dimethoxy-5-methylbenzoic acid methyl ester (<u>2.4</u>)

M.s. m/e (rel. int.): 210 (M, 100), 195 (M-15, 4), 179 (M-31, 63), 177 (M-33, 80), 167 (M-15-28, 8), 149 (20), 136 (35), 121 (18), 91 (15), 79 (8), 77 (10), 65 (17), 59 (4), 53 (6), 45 (23), 39 (18)

2-(2-Methoxy-4-methylphenoxy)-1,3-butadiene-1,4-dicarboxylic acid dimethyl ester (<u>3.1</u>)

M.s. m/e (rel. int.): 306 (M, 24), 275 (M-31, 14), 247 (M-59, 100), 215 (M-59-32, 14), 193 (12), 169 (24), 138 (25), 137 (36), 123 (30), 109 (12), 91 (18), 79 (25), 77 (18), 59 (18)

^{1}H NMR: δ 2.35 [s, 3 H, ArCH_3], 3.63 [s, 3 H, $COOCH_3$], 3.72 [s, 3 H, $COOCH_3$], 3.80 [s, 3 H, ArOCH_3], 4.95 [m, 1 H, O-C=C<u>H</u>-], 6.19 [dd, 1 H, -CH=C<u>H</u>$COOCH_3$, J = 12.4 and ~1], 6.72 - 7.02 [m, 3 H, Ar], 7.40 [dd, 1 H, -C<u>H</u>=CH$COOCH_3$, J = 12.4 and ~1]

2-Methoxy-4-methylphenoxyethene-1,2-dicarboxylic acid dimethyl ester (3.2)

M.s m/e (rel. int.): 280 (M, 3), 249 (M-31, 2), 221 (M-59, 1), 206 (1), 152 (2), 143 (M-137, 100), 115 (30), 91 (3), 77 (4), 69 (14), 59 (6), 47 (8)

^{1}H NMR: δ 2.33 [s, 3 H, $ArCH_3$], 3.81 [s, 3 H, $ArOCH_3$], 3.83 [s, 3 H, $COOCH_3$], 3.84 [s, 3 H, $COOCH_3$], 5.47 [s, 1 H, olefinic], 6.72 - 6.96 [m, 3 H, aromatic]

^{13}C NMR: δ 21,47 [$Ar\underline{C}H_3$], 53.00 [$COO\underline{C}H_3$], 56.03 [$ArO\underline{C}H_3$], 57.14 [$COO\underline{C}H_3$], 92.8 [$-\underline{C}(=\underline{C}H)-$], 113.67 [ArC3], 121.34 [ArC5], 122.70 [ArC6], 136.99 [$-\underline{C}(=CH)-$], 137.46 [ArC4], 144.3 [ArC2], 151.02 [ArC1], 163.73 [$\underline{C}OOCH_3$], 164.10 [$\underline{C}OOCH_3$]

2-(2-Methoxy-4-methylphenoxy)-3,4-epoxy-1,3-butadiene-1,4-dicarboxylic acid dimethyl ester (3.4)

M.s. m/e (rel. int.): 322 (M, 19), 306 (M-16, 3), 263 (M-59, 1), 247 (M-16-59), 234 (17), 221 (17), 193 (12), 175 (10), 138 (46). 123 (27), 113 (61), 111 (100), 105 (15), 91 (85), 77 (40), 69 (25), 65 (20), 59 (70)

^{1}H NMR: δ 2.34 [s, 3 H, $ArCH_3$], 3.64 [s, 3 H, $COOCH_3$], 3.76 [s, 3 H, $COOCH_3$], 3.80 [s, 3 H, $ArOCH_3$], 3.90 [dd, 1 H, $-\underline{CH}(O)-\underline{CH}COOCH_3$, J = 4.6 and ~1], 4.75 [dd, 1 H, $-\underline{CH}(O)-\underline{CH}COOCH_3$, J = 4.6 and ~1], 4.98 [d, 1 H, olefinic, J ~1], 6.76 - 6.92 [m, 3 H, Ar]

1-(2,3-Dimethoxy-5-methylbenzyl)-3-methyl-1,3-butadiene-1,4-dicarboxylic acid dimethyl ester (5.1)

M.s. m/e (rel. int.): 348 (M, 12), 316 (M-32, 13), 289 (M-59, 24), 285 (M-32-31, 12), 274 (12), 257 (11), 183 (M-165, 100), 165 (M-183, 1), 152 (22), 137 (15), 128 (6), 115 (4), 91 (5), 77 (4), 59 (3)

^{1}H NMR: δ 1.99 [dd, 3 H, non-$ArCH_3$], 2.29 [s, 3 H, $ArCH_3$], 3.65

[s, 3 H, $COOCH_3$], 3.67 [s, 3 H, $COOCH_3$], 3.69 [d, 2 H, $ArCH_2$-, J ~1], 3.79 [s, 3 H, $ArOCH_3$], 3.84 [s, 3 H, $ArOCH_3$], 5.70 [m, 1 H, $-C=\underline{CH}-COOCH_3$, J ~1], 6.63 - 6.68 [m, 2 H, Ar], 6.80 [m, 1 H, $-\underline{CH}=C-COOCH_3$]

1-(2,3-Dimethoxy-5-methylbenzyl)-3-oxo-1-butene-1-carboxylic acid methyl ester (5.2)

M.s. m/e (rel. int.): 292 (M, 60), 261 (M-31, 5), 260 (M-32, 10), 249 (M-43, 13), 229 (30), 218 (35), 217 (45), 189 (60), 175 (45), 159 (30), 150 (49), 131 (14), 115 (12), 91 (18), 77 (16), 43 (100)

^1H NMR: δ 2.19 [s, 3 H, non-$ArCH_3$], 2.29 [s, 3 H, $ArCH_3$], 3.61 [d, 2 H, $ArCH_2$-, J = 1.6], 3.77 [s, 3 H, $ArOCH_3$], 3.78 [s, 3 H, $ArOCH_3$], 3.86 [s, 3 H, $COOCH_3$], 5.94 [tr, 1 H, olefinic, J = 1.6], 6.6 - 6.7 [m, 2 H, Ar]

2,3-Dimethoxy-5-methylphenyl pyruvic acid methyl ester (5.3)

M.s. m/e (rel. int.): 252 (M, 40), 192 (M-60, 8), 177 (8), 165 (M-59-28), 75), 150 (M-102, 100), 120 (8), 105 (25), 91 (15), 77 (15), 59 (5), 39 (6)

2,3-Dimethoxy-5-methylphenylacetic acid methyl ester 5.4)

M.s. m/e (rel. int.): 224 (M, 90), 209 (M-15, 15), 177 (5), 165 (M-59, 30), 150 (M-74, 100), 120 (5), 105 (22), 91 (17), 77 (19), 59 (6), 39 (8)

Glycolaldehyde acetate (6.2)

M.s. m/e (rel. int.): 102 (M, 3), 101 (M-1, 2), 74 (M-28, 2), 73 (M-29, 9), 60(M-42, 6), 43 (100)

Formic acid guaiacyl ester (8.1)

M.s. m/e (rel. int.): 152 (M, 20), 124 (M-28, 100), 109 (M-28-15, 80), 81 (M-28-15-28, 75), 53 (20), 52 (24)

Methoxy-p-benzoquinone (10.1)

M.s. m/e (rel. int.): 140 (M + 2, 20), 138 (M, 66), 125 (10), 110 (M-28, 15), 108 (M-30, 25), 82 (42), 69 (100), 54 (80), 53 (45), 52 (30), 41 (18)

2-Methyl-1,3-butadiene-4-carboxylic acid-1-carboxylic acid methyl ester (12.1)

M.s. m/e (rel. int.): 170 (M, 1), 155 (M-15, 1), 139 (M-31, 9), 138 (M-32, 2), 125 (M-45, 55), 121 (16), 111 (M-59, 100), 97 (30), 93 (13), 83 (18), 69 (16), 65 (6), 59 (10)

γ-Methoxycarbonylmetyl-γ-methyl-α-butenolide (12.2)

M.s. m/e (rel. int.): 170 (M, 2), 155 (M-15, 2), 139 (M-31, 5), 138 (M-32, 4), 127 (30), 113 (15), 110 (M-60, 4), 97 (M-73, 100), 69 (M-73-28, 31), 59 (25), 43 (45)

Vanillin dimethyl acetal (13A)

M.s. m/e (rel. int.): 198 (M, 12),167 (M-31, 100), 152 (M-46, 28), 151 (M-46-1, 26), 137 (M-46-15, 4), 123 (M-46-1-28, 2), 109 (M-46-15-28, 3), 81 (5), 79 (5), 77 (3), 75 (5), 65 (3), 39 (4)

γ-Methoxycarbonylmethylene-δ-methoxy-α-pentenolide (13.1)

M.s. m/e (rel. int.): 198 (M, 2), 197 (M-1, 1), 167 (M-31, 35), 166 (23), 154 (M-44, 42), 139 (M-59, 100), 123 (8), 111 (35), 95 (10), 79 (49), 75 (10), 69 (12), 59 (27), 51 (49), 39 (20)

^{1}H NMR: δ 3.63 [s, 3 H, $COOCH_3$], 3.80 [s, 3 H, $H-\underset{|}{\overset{|}{C}}-OCH_3$], 5.59 [tr, 1 H, $H-\underset{|}{\overset{|}{C}}-OCH_3$, J ~0.9], 6.13 [m, 1 H, $-\underset{|}{C}=CH-COOCH_3$, J = 0.9 and 1.8], 6.20 [d + d, 1 H, -CH=CHCOO-, J = 10 and 1.8], 8.22 [d + tr, 1 H, -CH=CHCOO-, J = 10 and 0.9]

^{13}C NMR: δ 52.1 [$COOCH_3$], 56.9 [$H-\underset{|}{\overset{|}{C}}-OCH_3$], 102 [$H-\underset{|}{\overset{|}{C}}-OCH_3$], 122 and 123 [$=CH-COOCH_3$ and $=CH-COO-$], 136 [$-CH=CHCOO-$], 141

[-CH=C-], 161 [COOCH$_3$], 165 [-COOCH-]

IR: cm^{-1} 3083 (w), 3004 (w), 2954 (m), 2841 (w), 1740-20 (vs), 1646 (m), 1589 (m), 1436 (m), 1263 (s), 1173 (s), 1127 (m), 1085 (m), 1027 (m), 989 (m)

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