Studies on the Degradation of Phenolic Lignin Units of the β-Aryl Ether Type with Oxygen in Alkaline Media*

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The degradation of $p$-hydroxy-arylglycerol-$\beta$-aryl ether structures in lignins by oxygen in alkaline media has been studied using appropriate model compounds. Three pathways (A, B, C, Schemes 1 – 3), explaining the formation of the various degradation products under different conditions, have been elucidated. Pathways A and B involve oxidative elimination of the side chain by oxygen and hydrogen peroxide, respectively. Hydrogen peroxide may be generated by autoxidation of certain lignin structures and intermediates. Pathway C entails the oxidative cleavage of the C$_2$ – C$_3$ bond by oxygen.

The primary oxidation products (aliphatic and aromatic aldehydes and $p$-quiones) undergo further oxidative-alkaline degradation to give ultimately aliphatic acids.

It is also shown that the oxidative-alkaline degradation of certain enolizable phenacyl aryl ether structures follows similar routes.

In recent years, the treatment of wood and pulps with oxygen in alkaline media has become an attractive alternative to conventional delignification processes.1–8 Numerous studies have therefore been carried out to elucidate the breakdown of lignins by oxygen in alkali and plausible mechanisms have been proposed.3–8 These studies deal primarily with the oxidative attack on phenolic lignin nuclei and do not account for the reactions involving also lignin side chains.

The main subject of the present work is the degradation of structural elements of the $p$-hydroxy-arylglycerol-$\beta$-aryl ether and related types with oxygen in alkali. The reactions involved were studied using model compounds 1 – 6 representing “uncondensed”* (1 and 2) and “condensed”* (3 and 4) guaiacyl type units, as well as syringyl (5 and 6) type units.

Unless otherwise stated, the oxidative treatments were carried out under standard conditions. The term “standard conditions” refers here and in the following to an approximately 0.05 M concentration of the compound in 0.2 – 0.3 M sodium hydroxide, a reaction temperature of 40 °C and an oxygen pressure of 1 bar. The standard treatment was stopped when

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1.0—1.5 mol of oxygen per mol of compound had been consumed. The mild conditions and the length of the treatment were chosen to facilitate the isolation of intermediates.

RESULTS AND DISCUSSION

The results from the treatments of the model compounds with oxygen in alkali are summarized in Table 1 (see EXPERIMENTAL).

Table 1. Autoxidation of model compounds. Temperature: 40 °C. Alkalinity: 0.2—0.3 M NaOH. Oxygen consumption: 1—1.5 mol O₂/mol compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction time, h</th>
<th>Reaction products isolated and/or identified (Yield %)</th>
<th>Starting material %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48</td>
<td>G(8)</td>
<td>80</td>
</tr>
<tr>
<td>1-arom. methyl ether</td>
<td>48</td>
<td>G(8)</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>G(3), V(5), M₆</td>
<td>81</td>
</tr>
<tr>
<td>2a</td>
<td>1</td>
<td>acids: FA(4), AA(29.0), GA(15.0), OA(31.0), MA(4.2), SA (3.6), FuA(1)</td>
<td>9</td>
</tr>
<tr>
<td>2-triacetate</td>
<td>48</td>
<td>G(27), V(14), I(16), acids: VA(1), FA(64), other acids (5)</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>G(22), II(28)</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>G(5), I(15), I(5)</td>
<td>80</td>
</tr>
<tr>
<td>5,6-methyl ether</td>
<td>48</td>
<td>G(14), I(5)</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>G(14), I(5)</td>
<td>35</td>
</tr>
<tr>
<td>6-triacetate</td>
<td>3</td>
<td>G(52), syringaldehyde(4), I(5)</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>acids: FA(40), GA(15)</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>II (96)</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>1.5</td>
<td>acids: FA(3.8), AA(3.5), OA(7.9), MA(1.7)</td>
<td>0</td>
</tr>
<tr>
<td>Vanillin</td>
<td>40</td>
<td>acids: FA(103), AA(12), OA(5), MA(2), FuA(0.5), SA(3)</td>
<td>44</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>G(88)</td>
<td>0</td>
</tr>
<tr>
<td>(R¹ = H) Guaiacoxy-AA</td>
<td>18.5</td>
<td>acidic products (20); not identified</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>16</td>
<td>G(90), G(55), V(21)</td>
<td>6</td>
</tr>
<tr>
<td>(R = H, trans + cis)</td>
<td>22</td>
<td>G(55)</td>
<td>45</td>
</tr>
<tr>
<td>23</td>
<td>28</td>
<td>acid: Ver A (53)</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>G(trace)</td>
<td>89</td>
</tr>
<tr>
<td>25</td>
<td>28</td>
<td>dimerization products¹⁵</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>28</td>
<td>G(7)</td>
<td>0</td>
</tr>
<tr>
<td>27</td>
<td>28</td>
<td>acids: VA(2), guaiaxyo-AA(2)</td>
<td>90</td>
</tr>
</tbody>
</table>

a Reaction conditions: 100 °C, 7 bar. O₂. b Yield not determined.

AA = acetic acid, FA = formic acid, FuA = fumaric acid, G = guaiacol, GA = glycerol-β-aryl ethers, MA = malonic acid, OA = oxalic acid, SA = succinic acid, SM = starting material, V = vanillin, VA = vanillic acid, VerA = veratreric acid.

pressure of 7 bar, an extensive degradation took place within one hour. The reaction mixture contained small amounts of guaiacol and vanillin and a great number of aliphatic acids (GLC).

The oxidations of the t-butyl-substituted analogues 3 and 4 under standard conditions proceeded considerably faster than those of 1 and 2. Compound 3 yielded considerable amounts of guaiacol and of the p-benzoquinone derivative 11 after treatment for only 2 h. Compound 4 gave, in addition to guaiacol and 11, α-guaiacoxycrolein (15) after autoxidation for 1 h. No 5-t-butylnirrillin was detected in the reaction mixtures from 3 and 4 which contained large amounts of the starting compounds.

A still more rapid autoxidation under standard conditions was observed with the 2,6-dimethoxy-substituted phenols 5 and 6. After a reaction period of 1 h, the reaction mixture from compound 6 contained appreciable amounts of guaiacol and α-guaiacoxycrolein (15). No syringaldehyde was detected.

The different behaviour of the model compounds on treatment with oxygen in alkali and the formation, in varying yields, of the reaction products listed in Table 1 can be explained by suggesting three possible pathways of oxidative-alkaline degradation:

**Pathway A** involves elimination of the side chain by an alkali-promoted rearrangement of a cyclohexadienone hydroperoxide intermediate (1a–6a) and a further oxidative degradation of the quinoid and aldehydic fragments (Scheme 1). The first two steps in Scheme 1 have previously been proposed on the basis of results from the autoxidation of simple p-hydroxybenzyl alcohols. These steps have now been confirmed by the isolation of the appropriate fragmentation products from 4, viz. 11 and 14 (R1 = CH2OH). The first product was characterized as the pyrazoline derivative 13 formed by reaction with diazomethane and the second as

**Scheme 1.** Pathway A. (1) oxygenations, (2) alkaline rearrangements with fragmentation, (3) alkaline demethoxylation, (4) further oxidative degradation. Compounds 1–6 and 10–12 are depicted as anions.

the dehydration product 15 which arises in a reaction competing with the oxidative degradation of 14. Further support for the validity of oxidative side chain elimination according to Scheme 1 was supplied by the behaviour of methylated model compounds. Thus, the aromatic methyl ether of 1 and the α-methyl ether of 5 were found to be essentially stable towards treatment under standard conditions. Methylation of the phenolic hydroxyl group in 1 may be expected to block step (1) and methylation of the α-hydroxyl group in 5 should inhibit step (2). If it is assumed that the α-methyl ether of 5, like the parent compound, is oxygenated, its recovery after the oxidative treatment would indicate that the oxygenation step (1) is reversible.19

Step (3) was shown by treating 5 under standard conditions and isolating 11 in high yield. The remarkable stability of 11 is obviously due to the t-butyl substituent and to hybridization between the para- and ortho-quinoid resonance structures of the anion. On prolonged treatment with alkali, the ortho-quinoid tautomer of 11 undergoes benzilic acid rearrangement followed by decarboxylation and various oxidation and addition reactions.11 When R = H or R = OCH₃, the quinoid intermediates (10 and 12) could not be isolated. It was shown in a separate experiment that the authentic compound 7, when exposed to standard conditions, gave among other products a mixture of aliphatic acids having the same qualitative composition as that of the mixture obtained from 2 after treatment under more drastic conditions (Table 1).

These results are in agreement with the assumption that para-quinones are intermediates in the oxidative degradation of phenolic nuclei in compounds of the β-aryl ether type (e.g. 2) according to Scheme 1. The reaction mixture from 7 also contained hydrophilic products not extractable with organic solvents. This fraction has not been investigated.

The further oxidative-alkaline degradation of the aldehydeic fragments (14, R¹ = H or CH₃OH) also includes oxygenation (1) and alkali-induced rearrangements (2) proceeding via hydroxy dioctetanes1,11 (cf. also Scheme 4)

Scheme 2. Pathway B. (1) quinone methide formation, (2) addition of hydrogen peroxide, (3) alkaline rearrangement with formation of a spiro epoxide, (4) alkali-promoted fragmentation. Compounds 1–6, 1c–6c, 10–12 and 16 are depicted as anions.

or via keto hydroperoxides in their hydrated or hemiacetal forms. The formation of the appropriate fragmentation products, guaiacol, formic acid and glycolic acid, was demonstrated by autoxidation of 2 and 6. The facile oxidative–alkaline degradation of α-aroxy aldehydes was confirmed by reacting guaiacoxacyacetaldheyde \( (14, \text{R}^1 = \text{H}) \) under standard conditions for 2 h and isolating guaiacol in 66% yield. Alkaline treatment of \( 14 (\text{R}^1 = \text{H}) \) in a nitrogen atmosphere under otherwise identical conditions did not afford any detectable amount of guaiacol which excludes purely alkaline degradation. As expected, guaiacoxacyacetaldheyde, which does not enolize, proved stable when exposed to standard autoxidation conditions.

**Pathway B.** Although pathway A (Scheme 1) satisfactorily explains the formation of the quinoid and aldehydeic intermediates, a further route of formation of these fragments, involving hydrogen peroxide as oxidant, must be considered (Scheme 2).

The possibility of the oxidative and alkali-promoted elimination of side chains following pathway B was indicated by the behaviour of \( \text{I-diacetate towards alkaline hydrogen peroxide} \) (Table 2). The sequence was illustrated by treating the \( \text{p-hydroxybenzyl alcohol} \) \( 17 \) with the same oxidant at room temperature and isolating the corresponding cyclohexadienone spiro epoxide \( 18 \) [steps (1) – (3), Schemes 2 and 3]. The elimination of the side chain from this intermediate by the action of alkali [step (4)] was demonstrated by treating compound \( 18 \) with a solution of sodium hydroxide in aqueous methanol at 60°C. The hydroquinone mono-methyl ether \( 19 \) thus expected was isolated in high yield. Compound \( 19 \) was also obtained when \( 17 \) was oxidized with hydrogen peroxide in the same solvent (Table 2).

Instead of rearranging to give spiro epoxides \( (1d – 6d) \), the intermediates of the \( \text{p-hydroxybenzyl hydroperoxide type in } \beta\text{-aryl ether structures} \ (1c – 6c, \text{Scheme 2}) \) could also be thought to form dioxetanes by neighbouring group participation with concomitant elimination of the \( \beta\text{-aroxy} \) substituent. This reaction would be reminiscent of the cleavage of \( \beta\text{-aryl ether bonds involving the formation of oxirane}^{13} \) or thirane \(^{14}\) intermediates. However, treatment of the diacetylated compound \( 1 \) with alkaline hydrogen peroxide in a nitrogen atmosphere resulted in a large amount of guaiacol \( \text{(Table 2)} \) but no vanillin \( \text{(TLC). In a separate experiment it was shown that vanillin survives a similar oxidative treatment. The absence of vanillin in the reaction mixture from 1-diacetate is in accordance with steps (3) and (4) and excludes the other fragmentation alternative in Scheme 2.} \)

The initial oxidative steps of the degradation following routes A and B are due to oxygen and hydrogen peroxide, respectively. Both routes involve cleavage of the \( \text{C}_2\text{-aryl bond and lead to the same aldehydeic and quinoid intermediates. The further degradation of these intermediates may be common for both pathways.} \)

**Pathway C,** presented in Scheme 4, accounts for the formation of aromatic aldehydes by cleavage of the \( \text{C}_2\text{-C}_3 \) bond. Like pathway B, this route is initiated by alkaline conversion of the starting compound into the corresponding quinone methide which then gives the corresponding \( \beta\text{-aroxy styrene intermediate.}^{14} \) In contrast to pathway B, however, the subsequent oxidative degradation is brought about by oxygen rather than by hydrogen peroxide.

The proposed oxidative-alkaline degradation of \( \text{β-guaiacoxystyrene intermediates (e.g. 20, R = H), formed from quinone methide intermediates (7b – 6b), follows a route analogous to that for the degradation of the aldehydic fragments 14 (Scheme 1).} \) This analogy in the

![Scheme 3](https://via.placeholder.com/150)

Scheme 3. (1) quinone methide formation, (2) addition of hydrogen peroxide, (3) formation of a spiro epoxide, (4) opening of the spiro epoxide ring with rearomatization and elimination of the side chain. Compounds 17 and 19 are depicted as anions.

mechanism of degradation may be ascribed to the fact that styrene derivatives 20 in the carbanion form constitute conjugated analogues to the carbanions derived from the aldehydic fragments 14. As in the case of the aldehydic intermediates (14), the fragmentation of β-guaiacyloxy styrenes could also proceed via addition of hydroxide ions, followed by rearrangement of the resulting α-hydroxy hydroperoxides.

The suggested formation of β-aroxystyrene derivatives prior to the oxidative degradation was supported by treating a mixture of the trans- and cis-forms of 20 (R = H) (approximate ratio 2:1) under standard autoxidation conditions for 16 h. Guaiacol and vanillin were isolated as main reaction products. The starting material recovered (6%) was a mixture of the trans- and cis-forms in an approximate ratio of 1:3.

The more facile degradation of the β-guaiacyloxy styrene derivative 20 (R = H) compared to that of the parent β-guaiacyl ethers 1 or 2 shows that the formation of either the quinone methide intermediates [step (1)] or the styrene intermediates [step (2)] is the rate-determining step in the over-all reaction. When 2-triacetate was treated under standard conditions (Scheme 8), considerable amounts of guaiacol, vanillin and the 1,3-dioxane derivative 21 were formed (Table 1). The extensive reaction may be attributed to the cleavage of the group in the α-position which constitutes a better leaving group than the α-hydroxyl group in 2. In this way, the conversion into 2b, i.e. quinone methide formation [step (2)] is facilitated. Compound 21 arises from 2b by an alkali-promoted condensation with liberated formaldehyde (4).\textsuperscript{15} Reaction (4) competes with reaction (3) (formation of the β-aroxystyrene intermediate 20, R = H).

Further oxidation of the aromatic aldehydes (e.g. vanillin) gives, in addition to formic acid, a mixture of other aliphatic acids which were also obtained after a similar treatment of the corresponding methoxy-p-quinones (e.g. 7). This result is consistent with the view that the oxidative-alkaline degradation of aromatic aldehydes proceeds via a Dakin type of reaction to give the appropriate p-quinones.\textsuperscript{4}

Some of the products listed in Table 1 can be considered to indicate the actual degradation route for the side chain of a phenolic arylglycerol-β-guaiacyl ether model compound. Thus, glycolic acid and α-guaiacyloxyacrolein (15) should be generated by pathway A or B.
(Schemes 1 or 2) whereas aromatic aldehydes (e.g. vanillin) should only arise through pathway C. p-Quinones (e.g. 7-9), on the other hand, could be produced both directly (pathways A and B) and via aromatic aldehydes (pathway C). However, quantitative estimates of the significance of the different pathways based on the amounts of products isolated cannot be made because of the instability of some of these products under the conditions used. Furthermore, alkali-promoted non-oxidative reactions may contribute to the over-all degradation of phenolic β-aryl ether structures, provided that the formation of quinone methide intermediates is possible.\textsuperscript{15,16}

Treatment of phenacyl aryl ethers with oxygen in alkaline media

When compound 22 was treated under standard conditions, extensive oxidation took place. Guaiacol and veratic acid were isolated from the reaction mixture in high yields. The methyl derivative of 22 (23) was not oxidatively degraded to any appreciable extent and was recovered in high yield.

The hydroxy derivative of 23 (24) also resisted oxygenation during the standard treatment but underwent alkali-promoted dimerization.\textsuperscript{14} Compound 25 lost one molecule of formaldehyde upon treatment under standard conditions.

Scheme 6. Reactions of phenacyl aryl ethers: (1) oxygenation, (2) rearrangement with fragmentation, (3) dimerization.

Scheme 7. Compounds 26–28 are depicted as anions.

conditions and was converted quantitatively into 23 (cf. also Ref. 15).

The phenolic counterparts of 22 and 24 (26 and 27, respectively) exhibited considerable stability towards oxygen under standard conditions. After a 48 h treatment of 26, the starting material was thus recovered in high yield. Only small amounts of guaiacol, guaiacoxycetic acid and vanillic acid were formed. Similar treatment of compound 27 afforded the unsaturated carbonyl compound 28 (cf. also formation of 15, Scheme 1) in a high yield.

No detectable amounts of dimerization or oxidation products were found.

The behaviour of compounds 22–28 towards oxygen-alkali can be interpreted as follows: 22 is degraded following a route [steps (1) and (2), Scheme 6] analogous to the degradations of the aldehydic fragmentation products (Schemes 1 and 2) and of the aroxystyrene intermediates (Scheme 4). The slight oxygenation of 23 is due to a low degree of enolization while the stability of 25 towards oxygen is a result of its inability to enolize. Compound 24 does enolize but the carbanion formed is consumed by a competitive addition to an enone system [step (3)] arising from 24 by dehydration.16 The phenolic phenacyl aryl ethers 26 and 27 have a greatly impaired ability to enolize due to the efficient stabilization of their phenolate anions by resonance. The small amounts of guaiacoxycetic acid and vanillic acid obtained from 26 are indicative of pathway A (or B) and pathway C, respectively. Subsequent to enolization, 27 undergoes dehydration to give 28 rather than oxygenation.

Scheme 8. Oxidation of phenacyl aryl ethers by hydrogen peroxide: (1) dehydration, (2) epoxidation by hydrogen peroxide, (3) alkaline opening of the epoxide ring, (4) cleavage of the hemiketal, (5) oxidative cleavage of the 1,2-diketone (cleavage of the original C₈–C₉ bond).

or dimerization. 28 remains unchanged when exposed to the standard autoxidation conditions.

In alkaline solution the unsaturated phenolic keto compound 28 exhibits strong absorption at 370 nm (ε = 18,440 1 mol⁻¹ cm⁻¹) due to the extended conjugation. This chromophoric system is reminiscent of the chromophore formed from coniferaldehyde in alkaline solutions.

Phenacylaryl ethers, which give enones by an alkali-promoted reaction, are extensively degraded when alkaline hydrogen peroxide is used as oxidant instead of oxygen (Scheme 8). Compound 24 yielded guaiacol and veratric acid in varying yields depending on the amount of oxidant employed. Treatment with an equimolar amount afforded, in addition to guaiacol and veratric acid, the enone 29 and a dimerization product, both of which are formed merely by the action of alkali.

The oxidative fragmentation of 24 by alkaline hydrogen peroxide may be explained by the reaction route outlined in Scheme 8.

CONCLUSIONS

The results listed in Table 1 suggest that pathway A is the dominant process under standard conditions. Phenols carrying sub-


stituents in both the 2 and 6-positions (e.g., 3–6) react with particular ease probably due to their relatively low acidity. The inverse correlation of oxidizability with acidity seems reasonable since weak acids give relatively unstable carbanions which are more sensitive to the electrophilic attack by oxygen.14

Extensive oxidative degradation of mono-o-substituted phenols (e.g. 1 and 2) requires more drastic conditions. Under such conditions, quinone methide intermediates may be formed which can initiate also pathways B and C. The competition between B and C will be primarily determined by the alkalinity of the solution and the availability of hydrogen peroxide during the oxidative treatment.

All three pathways, outlined in Schemes 1, 2 and 4 and summarized in Scheme 9, lead ultimately to the formation of aliphatic degradation products arising from eliminated side chains and to aliphatic acids and hydrophilic polymerization products arising from intermediates of the para-quino and aromatic aldehyde types. The alkaline-oxidative degradations of β-aryl ether structures also result in the liberation of the β-aroxyl substituent as a phenolate ion. The stability of the latter (e.g. the guaiacolate ion liberated from 1–6) towards oxygen in alkali under the conditions used shows that the oxidative degradation of phenolic units containing side chain structures of the benzyl alcohol type (e.g. 1–6) starts with the oxidative elimination (pathways A and B) or fragmentation (pathway C) of the side chain rather than with the oxidative cleavage of the phenolic nucleus.

Once the aroxyl substituent is liberated by one of the routes A–C, the degradation process may be repeated, provided the liberated phenolic unit has the same or a similar type of β-aryl ether structure. The oxidative lignin fragmentation (“oxidative lignin peeling”) may thus continue until it reaches a unit containing a side chain which does not meet the structural requirements for at least one of the three pathways.

The degradation of phenacyl-aryl ethers by oxygen-alkali (Scheme 6) exhibits many formal analogies to that of the aldehydic fragments (Scheme 1) and the β-quinacoxystyrene intermediates (Scheme 4). The degradation is restricted to structures having an easily

enolizable keto group and lacking the ability to form an enone system for conjugate addition.15

The oxidative-alkaline degradation processes are accompanied and, in part, counteracted by oxidative coupling reactions13 and alkali-promoted conjugated additions (condensations and polymerizations).15

EXPERIMENTAL

Materials

Syntheses of model compounds. The following compounds were prepared as previously described: 11,13 5 (analogous to 1), 7,20 8,21 9,23 14 (R1 = H),23 17,28 20 (R = H, cis and trans),12 22,36 23,36 24,28 25,27 26 (analogous to 27), 27.13

The β-aryl ethers 3–6 were prepared from the appropriate acetophenones as described for 1 and 2.

All analyses agree within ±0.3 % units with the calculated values.

4-Acetoxy-5-t-butyl-3-methoxyacetophenone. 6-t-Butylguaiacol 26 (50 g) dissolved in acetyl chloride (100 ml) was added to a cooled solution (10 °C) of aluminium chloride (50 g) in acetyl chloride (200 ml). The temperature of the reaction mixture was kept below 15 °C. After the addition had been completed, the reaction mixture was stirred for 30 min, treated with cooled 0.5 M hydrochloric acid and extracted with chloroform. The excess of 6-t-butyguaiacol acetate was distilled off (142–146 °C/19 mmHg). Crystallization of the distillation residue from light petroleum yielded the pure compound (17 %), m.p. 83–85 °C. (Found: C 68.47; H 7.32; O 24.19. C18H15O4 requires: C 68.18; H 7.58; O 24.24.)

3,5-Dimethoxy-4-hydroxyacetophenone. This compound was prepared using a modification of a method previously described. The acetate of 1,3-dimethoxyphenol (39 g) was treated with aluminium chloride (32 g) in nitrobenzene (200 ml) at 50 °C for 1 h. After addition of cooled 0.5 M hydrochloric acid, the reaction mixture was extracted with 2 M sodium hydroxide. The aqueous layer was acidified and extracted with methylene chloride. Evaporation of this extract and crystallization of the residue from ethanol gave the pure compound (20 %), m.p. 123–126 °C (lit. 110–120 °C).

Analytical data of β-aryl ethers.

1-(4-Acetoxy-5-t-butyl-3-methoxyphenyl)-2-O-(2-methoxyphenyl)ethyleneglycol (3-acetate), m.p. 97–99 °C (ligrom). (Found: C 68.03; H 6.91; O 24.99. C24H20O6 requires: C 68.02; H 7.26; O 24.71).

1-(4-Acetoxy-5-t-butyl-3-methoxyphenyl)-2-O-(2-methoxyphenyl)-1,3,5-diacytelylglycerol (4-triacetate), amorphous. The 1H NMR spectrum

Table 2. Oxidation of model compounds with alkaline hydrogen peroxide. Alkalinity: 0.2—0.3 M NaOH, nitrogen atmosphere. Temperature: 40 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Reaction time, h</th>
<th>Equiv. of H₂O₂</th>
<th>Reaction products isolated and/or identified (yield % of theoretical)</th>
<th>Starting material, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Diacetate</td>
<td>d-w (2:3)</td>
<td>1</td>
<td>1</td>
<td>G (60)</td>
<td>0</td>
</tr>
<tr>
<td>Vanillin</td>
<td>d-w (2:1)</td>
<td>1</td>
<td>1.5</td>
<td>18 (25)</td>
<td>100</td>
</tr>
<tr>
<td>17</td>
<td>d-w (2:1)</td>
<td>0.5</td>
<td>1.5</td>
<td>19 (26)</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>m-w (3:1)</td>
<td>2.5</td>
<td>1.2</td>
<td>29 (19) G (35), Ver A (31), 0</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>e-w (3:1)</td>
<td>2.5</td>
<td>3</td>
<td>Dimeric product (12)¹⁴</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>e-w (3:1)</td>
<td>24</td>
<td>G (88), Ver A (80)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>e-w (3:1)</td>
<td>3</td>
<td>G (88), Ver A (80)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>e-w (3:1)</td>
<td>1</td>
<td>1</td>
<td>G (88), Ver A (80)</td>
<td>90</td>
</tr>
</tbody>
</table>

d-w dioxane-water, m-w methanol-water, e-w ethanol-water, G = guaiacol, Ver A = veratric acid.

indicated a 1:1 mixture of the *erythro* and *threo-* forms. (Found: 64.60; H 7.00; O 28.40. C₁₇₋₁₈H₂₀O₅ requires: C 64.52; H 6.81; O 28.60.)

1-(3,5-Dimethoxy-4-hydroxyphenyl)-2-O-(2-methoxyphenyl)-glyceral (6), m.p. 162—164 °C (chloroform). The ¹H NMR spectrum of the synthetic compound indicated the *threo-* configuration. The coupling constant of the α and β-protons in the side chain was 3Jα,β = 7.0 cps.²² Anal. C₁₇₋₁₈H₂₀O₅: C, H, O.

Methods

Autoxidation of model compounds. The reaction conditions and results are given in Table 1. Autoxidation with oxygen under pressure was carried out in a 1 l stainless steel autoclave. The yields of the low molecular weight acids were determined by an ion-pair benzylolation or methylation technique in combination with GC analysis. The work-up procedure and preparative separation of the reaction mixtures were carried out as previously described.³

Oxidation of model compounds with alkaline hydrogen peroxide. The reaction conditions and results are given in Table 2.

Treatment of guaiacylglycerol with alkali. Guaiacylglycerol (14, R²=H) (2 mmol) was treated with a 0.3 M sodium hydroxide solution in ethanol-water (4:1) at 40 °C for 2 h (nitrogen atmosphere). No guaiacol could be detected in the reaction mixture (TLC).

Treatment of syring epoxide with alkali. Compound 18 (0.18 mmol) was treated with a 0.2 M sodium hydroxide solution in methanol-water (4:1) (10 ml) at 60 °C for 6 h (nitrogen atmosphere). 2,6-Di-t-butyl-4-methoxyphenol (19) was isolated in 91 % yield.

Product identification

6-t-Butyl-2-hydroxy-p-quinone (11), yellow crystals from ethanol, m.p. 135—138 °C (Lit.¹¹ 138—139.5 °C).

7a-t-Butyl-6-methoxy-3a,7a-dihydro-3H-inda- zolquinone (4,7) (13), pale yellow crystals from ether. Decomposes between 155 and 162 °C. Anal. C₁₇₋₁₈H₂₀N₂: C, H, O, N. IR (KBr): 1690 (s, C=O), 1650 (s, C=O), 1505 (s, C=C–C=O). UV [MeOH (ε)]: 268 (9150), 1H NMR (60 MHz, CDCl₃): δ 1.10 (s, 9 H, t-Bu), 3.80 (s, 3 H, OMe), 5.03 (A) and 4.39 (B) [CH₂], 3.06 (X) [CH]; ABX; JAB 18.3; JAX 11.1; JBX 7.5; 5.88 (s, 1 H, ol).

α-(2-Methoxyphenoxo)-acrolein (15), GC-MS analysis (fragments having m/e>100 and intensities > 10 % of base peak are given): 178 (M, 100), 149 (M—29, 14), 135 (M—43, 13), 124 (M—44, 12), 123 (M—55, 30), 121 (M—57, 25), 109 (35), 108 (50). 1H NMR (60 MHz, CDCl₃) of the crude fraction (90 % 15) obtained by autoxidation of 6 and ether extraction of the alkaline reaction mixture: δ 3.79 (s, 3 H, OMe), 5.02 (d, 1 H, ol, Jε,ε 2.7 Hz), 5.22 (d, 3 H, ol, Jε,ε 2.7 Hz), 7.00 (m, 3 H, ar), 9.45 (s, 1 H, CHO).

5,7,11,15,15-pentamethoxy-3-oxa-pentacone (16), white crystals, m.p. 95—97 °C (ether). Anal. C₁₇₋₁₈H₂₀O₅: C, H, O. UV [MeOH (ε)]: 258 (15 200). 1H NMR (60 MHz, CDCl₃): 1.23 (s, 18 H, 2×t-Bu), 1.47 (d, 3 H, CH₃, JCH₃,CH₃ 5.3 Hz), 3.44 (q, 1 H, CH₃, JCH₃,CH₃ 5.3 Hz), 6.08 (d, 1 H, ol, Jε,ε 2.7 Hz), 6.33 (d, 1 H, ol, Jε,ε 2.7 Hz).

2,6-Di-t-butyl-4-methoxyphenol (19), white crystals, m.p. 102—104 °C (light petroleum) (lit.¹² 105—106 °C). GC-MS analysis (fragments having m/e>100 and relative intensities > 10 % of base peak are given): 236 (M, 32), 222 (M—14, 15), 221 (M—15, 100), 220 (M—16, 10), 205 (M—31, 10), 193 (M—43, 10), 179 (M—57, 17), 177 (20), 165 (10), 163 (10), 161 (11), 151 (10), 149 (13), 135 (10). 1H NMR (60 MHz, CDCl₃): 1.40 (s, 18 H, 2×t-Bu), 3.73 (s, 3 H, OMe), 4.70 (s, 1 H, OH), 6.74 (s, 2 H, ar).
Compounds 21 and 28 were identified as previously described.

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REFERENCES


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