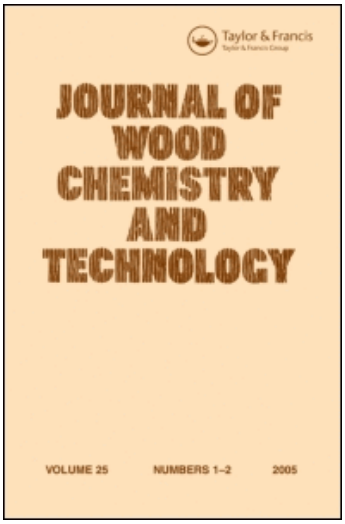

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The "Catalytic" Effect of Anthrone and Anthrahydroquinone in Cleaving β-Aryl Ether Bonds in Lignin Model Compounds

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THE "CATALYTIC" EFFECT OF ANTHRONE AND ANTHRAHYDROQUINONE IN CLEAVING β-ARYL ETHER BONDS IN LIGNIN MODEL COMPOUNDS.

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ABSTRACT

To elucidate the mechanism of anthrone-promoted β-ether cleavage reactions, the phenolic lignin model compound 1, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol, was heated with 0.1 mole of anthrone (AN) or anthrahydroquinone (AHQ) at 140 °C for 1/2, 1, 2, 3 and 5 hours in 1 M sodium hydroxide solution. The cleavage products [2-methoxyphenol and (2-methoxy-4-propenyl)phenol] were the same as in experiments with equimolar amounts or excess of AN and the yields increased as a function of reaction time to a maximum corresponding to the cleavage of four to five moles of 1 per one mole of AN. AHQ was found to react in a similar manner. This "catalytic" effect is tentatively attributed to sequential transformations of AN and AHQ to products capable of causing further reductive cleavages. GC-MS analysis of the reaction mixture showed the presence of by-products which indicate that some catalyst regeneration through oxidation of 1 or its hydrolysis products may have occured. 1-Hydroxyanthrone had a similar "catalytic" effect in cleaving β-ether bonds, but glucose did not.

INTRODUCTION

The accelerating effect of anthraquinone (AQ) in alkaline delignification reactions has been attributed[1-3] to its reduced

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form, mainly anthrahydroquinone (AHQ), which is able to form adducts with the reactive lignin quinone methides and cause the cleavage of β-ether bonds in lignin.

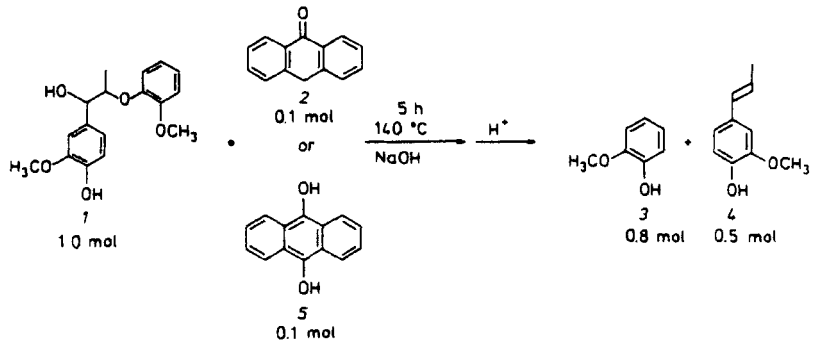
In the course of a study on the disappearance of AQ in pulping conditions, we found[4] that anthrone (AN), also formed from AQ in pulping conditions,[5,6] cleaves β-ether bonds in a reaction resembling that of AHQ. In a previous paper[7] we compared the amounts of cleavage products obtained on heating an adduct[8,9] of AN and the quinone methide from 1, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol, with those obtained on heating 1 with AN under the same conditions. The results suggested that there may be a pathway for the β-ether cleavage reaction that does not involve the formation of an adduct.

The present work was undertaken to gain further insight into the AN-accelerated β-ether cleavage reaction and to elucidate the obscure stoichiometry. The reaction was studied using only 0.1 mole of AN. In addition, the effects of AHQ, 1-hydroxyanthrone and glucose were studied. The main cleavage products were determined by GC. Most of the volatile by-products were identified by GC-MS.

RESULTS

"Catalytic" Effect of Anthrone.

Model compound 1 was heated at 140 °C with 0.1 mole of AN 2 in sodium hydroxide - dioxane solution for 1/2, 1, 2, 3 and 5 hours. It can be seen from Figure 1 that the liberated amounts of guaiacol (2-methoxyphenol) 3 and trans -isoeugenol [(2-methoxy-4-propenyl)-phenol] 4 (Scheme 1) increased as a function of reaction time. At all times the formation of 3 was faster than the formation of 4. After 2 hours reaction time the formation of both products became slower, and after 5 hours 3 was obtained in 76 % yield and 4 in 52 % yield. These yields are much higher than could be expected on the assumption that one mole of AN cleaves one mole of 1.



SCHEME 1

An additive level of 0.1 mole could only give a 10 % maximum yield increase of degradation products over that of the control if the stoichiometry is 1:1. Comparison with the amounts of 3 and 4 obtained in control experiments without any additive (Figure 1, 37 % and 2 %, respectively) reveals a difference of 40 % (76 % - 37 %) in the yield of 3 and a difference of 50 % (52 % - 2 %) in the yield of 4, indicating that one mole of AN cleaves 4-5 moles of 1.

"Catalytic" Effect of Anthrahydroquinone.

Although the mechanism of AHQ- accelerated β-ether cleavage reactions seems to be well understood,[2,3,10] it was of interest to determine if AHQ 5 has a similar "catalytic" effect to AN in cleaving β-ether bonds. Compound 1 was heated with 0.1 mole of AHQ under the same conditions as used for the reaction of 1 with AN. At the beginning of the reaction the released amounts of 3 and 4 were slightly lower than in the AN reaction, but after 5 hours reaction time they were the same (Figure 1). Similarly as in the case of AN, one mole of AHQ cleaved 4-5 moles of 1.

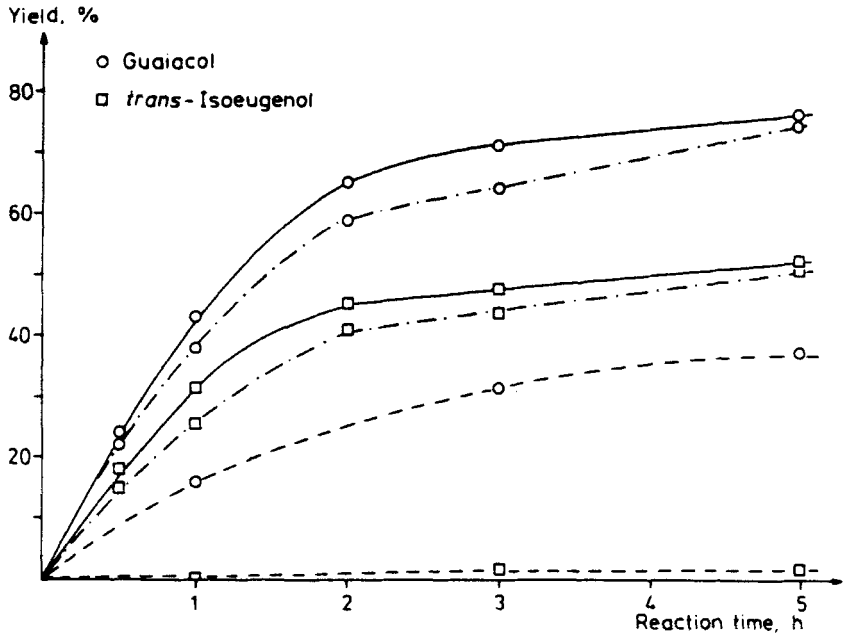


FIGURE 1. Yields of guaiacol and trans-isoeugenol on treatment of 1 in 1 M NaOH solution (10 % dioxane) with 0.1 mole of anthrone (————), anthrahydroquinone (—·—·—) and without any additive (– – – –) at 140 °C .

"Catalytic" Effect of 1-Hydroxyanthrone.

To test if hydroxylated anthrones could enhance β-ether cleavage reactions, 1 was heated with 0.1 mole of 1-hydroxyanthrone 6 at 140 °C under the chosen conditions. 6 was chosen because it was easily prepared from the commercial 1-hydroxyanthraquinone. From the yields of 3 and 4 (Figure 2) it can be seen that 6, too, accelerated the β-ether cleavage reaction, though less so than AN or AHQ. One mole of 1-hydroxyanthrone cleaved approximately 2.5 moles of 1 (based on the yields of both 3 and 4) more than was cleaved in the control. The results show that hydroxylated anthrones have a "catalytic" effect in the cleavage of β-ether

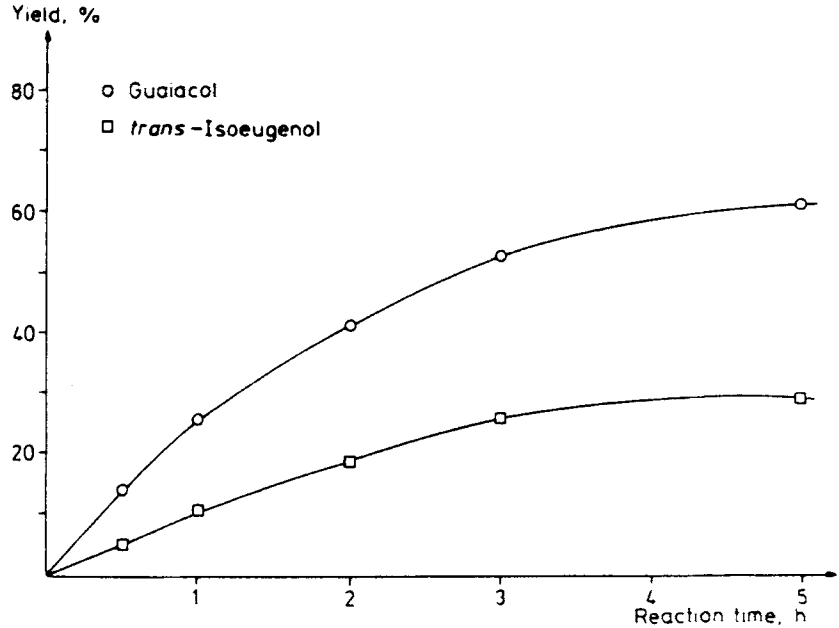
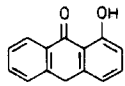


FIGURE 2. Yields of guaiacol and trans-isoeugenol on treatment of 1 in 1 M NaOH solution (10 % dioxane) with 0.1 mole of 1-hydroxyanthrone at 140 °C .

bonds and may play a role in AN- promoted β-ether cleavage reactions.



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Effect of Glucose.

Recent studies have shown that certain organometallic complexes[11] and reducing sugars,[12] structurally very different from AQ, can serve as catalysts for alkaline delignification. To

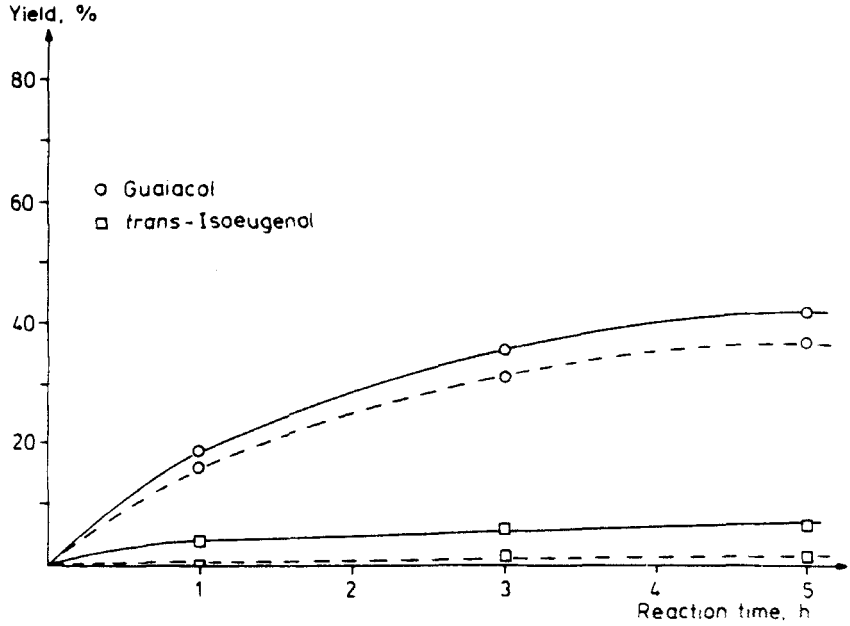
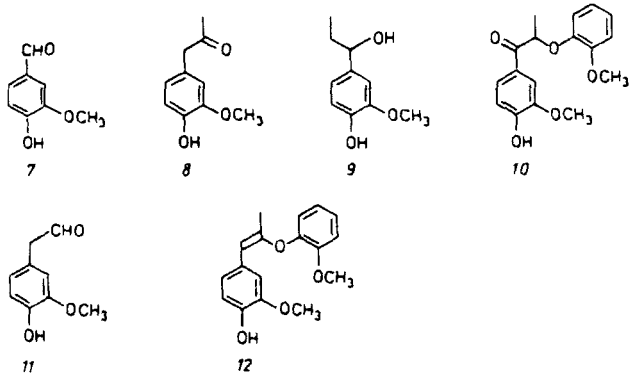


FIGURE 3. Yields of guaiacol and trans-isoeugenol on treatment of 1 in 1 M NaOH solution (10 % dioxane) with 1.15 mole of glucose (————) and without glucose (— — — —) at 140 °C .

compare the effect of glucose with that of AN and AHQ, 1 was heated with 0.1 mole of glucose at 140 °C for 1 and 3 hours in sodium hydroxide - dioxane solution under nitrogen. The obtained amounts of 3 and 4 were equal to those in control experiments. When 1 was heated with 1.15 mole of glucose at 140 °C for 1, 3 and 5 hours under the same conditions, the β-ether cleavage reaction was enhanced to some extent relative to the control (Figure 3). This is in agreement with Fullerton's observation.[12] However, as shown in Figure 3, the amounts of 3 and 4 liberated were very much lower than the amounts liberated by AHQ or AN when these were used in amounts of only 0.1 mole (Figure 1).

Product Analysis

In an effort to find products derived from AN, 1 was heated with larger amounts of AN (1.15 moles) at 140 °C in 1 M sodium hydroxide solution for 1 hour. It was observed that changing the AN level from 0.1 to 1.15 moles did not change the product distribution significantly (GC). Two gas chromatograms (obtained with two columns of different polarity) of the volatile components (as their acetates) of the reaction mixture are presented in Figure 4. Compounds 3 (78 %), 4 (57 %), vanillin (4-hydroxy-3-methoxybenzaldehyde) 7 (3 %), AQ (4 % of the original amount of AN) and AN (22 % left of the original amount of AN) were determined as their acetates. Guaiacylacetone [1-(4-hydroxy-3-methoxyphenyl)-2-propanone] 8, 1-(4-hydroxy-3-methoxyphenyl)-1-propanol 9 and 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone 10 were identified in the reaction mixture (as their acetates) by injecting the mixture and a reference sample at the same time and observing the overlapping of the peaks.



Mass spectra were also obtained of the peaks of the components and compared with spectra recorded for the reference compounds or with spectra reported in the literature. Compound 8 has been found also

in soda cooking conditions.[13] Compound 10 is an oxidation product of the starting material 1.

As can be seen from the chromatograms (Figure 4) there are only minor unidentified volatile components in the mixture. Tentatively peak g (M^+ 208) could be homovanillin 11 and peak k (M^+ 328) could be enol ether 12 (both as their acetates). In soda cooking conditions[13] the amounts of enol ether exceeds the β-ether cleavage products. Homovanillin and 12 were not available as reference materials. Besides AQ, the only volatile oxidation product of AN found was anthrahydroquinone. This was eluted from the columns either with acetylated 1 (Chromatogram A) or with acetylated 10 (Chromatogram B). The identification of AHQ in the reaction mixture was based on the molecular ion (M^+ 294) of its acetate, found together with the molecular ion of the acetate of 10 (M^+ 344) in the mass spectrum of peak 1. However, the amounts of AHQ are negligible as estimated from peak 1.

TLC revealed there to be several nonvolatile components in the reaction mixture. The mixture was chromatographed several times on silica dry column and by thick-layer chromatography. Apart from 10,10'-bianthrol, no further AN-derived products were obtained in pure form and in such amounts that they could be identified. No product that would explain the "catalytic" effect of AN was found.

DISCUSSION

The simple adduct mechanism proposed[2,3] for the β-ether cleavage caused by reduced AQ species such as AHQ and AN does not explain the stoichiometry of the reactions observed in these experiments. In the case of AHQ this mechanism assumes a complete oxidation of AHQ to AQ. This AQ, by oxidizing benzylic alcohol groups to the corresponding ketones, is known to accelerate the cleavage of β-ether bonds.[14,15] This type of reaction does not explain the formation of 4 which is the product of a reductive

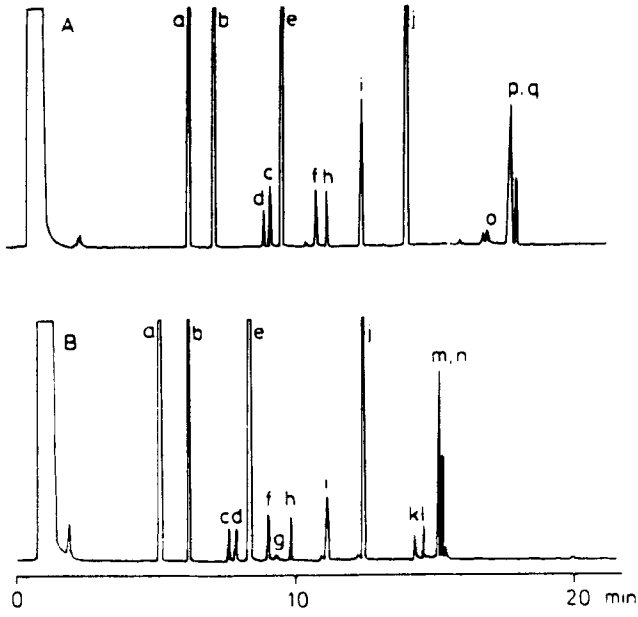


FIGURE 4. Gas chromatograms (A: column OV-1701, B: column SE-54) of the acetylated products obtained on heating 1 in 1 M NaOH solution with 1.15 mole of anthrone at 140° C for 1 h under nitrogen. Peak assignments: a (3) ; b (internal standard, methyl anisate); c (7); d (cis-4); e (trans-4); f (8); g (11); h (9); i (AQ); j (AN); k (12); l (AHQ + 10); m,n (erythro-1 + threo-1); o (10); p,q (erythro-1 + threo-1 + AHQ).

splitting. The origin of the electrons needed for the reductive splitting is not known at present. The "catalytic" effect observed points to a combination of mechanisms. It could be attributed to successive cleavage reactions caused by oxidation or other reaction products of AN and AHQ to products capable of cleaving further β-ether bonds. The results show that hydroxylated anthrones also have "catalytic" effect in the cleavage of β-ether bonds and may play a role in AN-promoted β-ether cleavage reactions. However, the levels of oxidation products of AN were found to be low or nonexistant in the product mixture. Another explanation is that AN^{-} and $AN\cdot$[16,17] forms (anion and radical forms of AN) are interconverting through reactions with dioxane used as solvent.

This possibility is excluded, because the yields of 3 and 4 were the same in experiments with dioxane and without dioxane (Experimental). Oxidation level of the by-products (7, 8, 10 and 11) indicate that some catalyst regeneration through oxidation of 1 or its hydrolysis products may have occured, although the amounts are insufficient to account for the observed "catalysis".

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Jeol JNM-PMX 60 spectrometer. Mass spectra were obtained with a Jeol JMS-01SG-2 instrument. The samples were introduced by direct inlet probe or through a gas chromatograph. All acetylations were performed with a mixture of dry acetic anhydride and pyridine (1:1).

Gas Chromatography (GC). The gas chromatographic studies were carried out on a Micromat HRGC 412 instrument equipped with two flame ionization detectors. The fused silica columns (Orion Analytica) were coated with liquid phases SE-54 (25 m, film thickness 0.15 μm or 25 m, film thickness 0.25 μm) and OV-1701 (23 m or 25 m, film thickness 0.15 μm and 0.25 μm, respectively). Diameter of all columns was 0.32/0.44 mm. Columns were connected in pairs to the same injector and to separate detectors. Carrier gas: nitrogen, splitless time 30 s. Injector 270 °C; detector 280 °C; temperature program 50-270 °C or 100-270 °C, 15 °C/min and 7 min at 270 °C. The instrument was microcomputer-controlled with two-channel integration and printing software.

Starting materials and reference compounds. For preparation and spectral data of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol 1, its diacetate and anthrol acetate see ref. 7 and references therein.

1-Hydroxyanthrone [1-Hydroxy-9(10H)anthracenone] 6 was obtained by refluxing 1-hydroxyanthraquinone (Aldrich Chemical Co.) with $SnCl_2$

in conc. HCl.[18] ^{1}H NMR ($CDCl_3$): δ 4.26 (2 H, s, CH_2), 6.77-7.00 (2 H, m, ArH), 7.31-7.80 (4 H, m, ArH), 8.20-8.46 (1 H, m, ArH), 13.00 (1 H, bs, OH, hydrogen bonding). MS [75 eV; m/e (% rel. int.)]: 210 (M^+, 88.5), 182 (17.5), 181 (39.1), 153 (17.5), 152 (44.5), 105 (20.2), 92 (21.6), 77 (23.6), 76 (100.0).

1-(4-Hydroxy-3-methoxyphenyl)-2-propanone 8.[19] The mass spectrum was in accordance with literature values.[20] ^{1}H NMR of the acetate of 8 ($CDCl_3$): δ 2.14 (3 H, s, CH_3), 2.30 (3 H, s, $COCH_3$), 3.64 (2 H, s, CH_2), 3.80 (3 H, s, OCH_3), 6.70-7.13 (3 H, m, ArH).

1-(4-Hydroxy-3-methoxyphenyl)-1-propanol 9.[21] MS [75 eV (% rel. int.)]: 182 (M^+, 22.3), 164 (43.5), 153 (100.0), 149 (20.1), 125 (24.5), 93 (58.6), 77 (12.4), 65 (21.4).

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone 10 was obtained by debenzylating[22] 1-(4-benzyloxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone obtained by an earlier described method.[23] The ^{1}H NMR and MS spectra were in accordance with the literature values.[24]

Cooking of 1 with 0.1 moles of anthrone, anthrahydroquinone or 1-hydroxyanthrone. Anthrahydroquinone was generated from the stable diacetate[25] in the reaction mixture. The cookings were run with 1 (25.0 mg, 0.0822 mmol), anthrone (1.6 mg, 0.00824 mmol) or anthrahydroquinone diacetate (2.4 mg, 0.00816 mmol) or 1-hydroxyanthrone (1.7 mg, 0.00810 mmol) dissolved in peroxide-free dioxane (1.0 ml), 2 M sodium hydroxide (5.0 ml) and water (4.0 ml) in Pyrex glass ampoules. Only 10 % of dioxane was used in order to prevent phase separations.[26,27] Before being sealed, the ampoules were evacuated and flushed with oxygen-free nitrogen three times.

The ampoules were heated in an oil bath at 140 °C for 1/2, 1, 2, 3 and 5 h. A warm-up time of 2 min was not included in the time at temperature. After cooling for 3 min at room temperature and then in cold water, the alkaline mixture was quickly neutralized

with dilute acetic acid and extracted with methylene chloride (5 x 2 ml) avoiding all but minimal exposure to air. The combined methylene chloride layers were immediately transferred to the acetylation mixture (acetic anhydride - pyridine, in excess). The internal standard, methyl anisate, was added and GC analysis was performed directly from the acetylation mixture.

Cooking of 1 with 0.1 mole of anthrone in 1 M sodium hydroxide solution (without dioxane) was carried out at 140 °C for 3 h.

Cookings of 1 with glucose. Compound 1 (25.0 mg, 0.0822 mmol) was heated at 140 °C with glucose (17.0 mg, 0.0944 mmol or 1.5 mg, 0.00833 mmol) in peroxide-free dioxane (1.0 ml), 2 M sodium hydroxide (5.0 ml) and water (4.0 ml) under nitrogen atmosphere. The reaction times were 1, 3 and 5 h with 1.15 moles of glucose and 1 and 3 h with 0.1 mole of glucose.

Cookings without any additives (controls) were carried out at 140 °C for 1, 3 and 5 h.

Recovery tests were run[7] with 1.15 moles of AN. The losses of guaiacol (4.0 %) and trans-isoeugenol (6.8 %) in cooking and acetylation processes were not taken into account when calculating the results.

Product analysis. Compound 1 (1.0 g, 3.289×10^{-3} mol) was heated at 140 °C for 1 h with anthrone (0.734 g, 3.783×10^{-3} mol) in 1 M sodium hydroxide (70 ml) under nitrogen atmosphere. Before it was closed, the stainless steel autoclave had been alternatively evacuated and flushed with oxygen-free nitrogen three times. After cooling in cold water, the alkaline mixture was quickly neutralized with dilute acetic acid and extracted with methylene chloride (6 x 25 ml) under nitrogen atmosphere. Acetylation of the products was carried out immediately, in the methylene chloride solution, under nitrogen. After the usual work-up, the methylene chloride

solution of the products was made up to 100 ml, an appropriate aliquot was withdrawn, the internal standard was added and the products forming volatile acetates were analyzed by GC and GC-MS.

From the rest of the methylene chloride solution of the products, the solvents were removed in vacuo. The oily, reddish brown residual (2.205 g) was chromatographed on a silica dry column (Woelm Pharma GmbH & Co; hexane-chloroform, 1:3). In all 44 fractions were collected. According to TLC and GC, fractions 1-19 (A, 1.452 g) consisted of AQ and the acetates of AN, 3, 4 and 10,10'-bianthrol (identified by TLC and ^{1}H NMR). According to GC, fractions 20-44 (B, 0.549 g) consisted of the acetates of 1, 7, 8, 9, 10 and possibly of AHQ. In addition, TLC revealed several unidentified components. Fraction C (0.181 g), obviously polymeric, was obtained with methanol. When fraction B (0.409 g) was rechromatographed on a silica dry column (cyclohexane - ethyl acetate - chloroform, 4:1:2), 32 fractions were collected, each of them consisting of several components, unknown components as well as the identified ones. Each of the fractions was further chromatographed by thick-layer chromatography, but none of the unidentified components could be obtained in pure form and in an amount sufficient to be identified.

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