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Studies on the Cleavage of β-Aryl Ether Bonds in Lignin Model Compounds Effected by Anthrone and its Derivatives *

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The β-ether cleavage reaction of the phenolic model compound *1*, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol, caused by anthrone or 10-methylanthrone in alkaline solution is compared with the degradation reactions of the anthrone adduct *2* and the 10-methylanthrone adduct *3*, 1-(4-hydroxy-3-methoxyphenyl)-1-(9-oxo-9,10-dihydro-10-anthryl)-2-(2-methoxyphenoxy)propane and 1-(4-hydroxy-3-methoxyphenyl)-1-(9-oxo-10-methyl-9,10-dihydro-10-anthryl)-2-(2-methoxyphenoxy)-propane, respectively. The amounts of the degradation products (guaiacol and *trans*-isoeugenol) indicate that there possibly is a pathway for the anthrone promoted β-ether cleavage not involving the formation of an adduct. 10,10′-Bianthrone, which was found among the reaction products, also has some ability to cleave β-ether bonds under the chosen conditions.

The catalytic effect of anthraquinone (AQ) on alkaline delignification has been studied in several laboratories and the mechanism is fairly well understood.[1–3] One important limiting factor in the practical application of this catalyst is the gradual disappearance of its effect during the course of the pulping reaction. Also, the catalyst cannot be recovered from the spent liquors.[4–7] The disappearance of the anthraquinone has been attributed to the reduction of the catalyst beyond the stage of anthrahydroquinone (AHQ).[8,9] The first of the reduction products is anthrone (AN), which is assumed[10] to form irreversible linkages with lignin and thus constitute a pathway for the disappearance of AQ in pulping reactions.[11]

Our observation[12] that AN cleaves the β-aryl ether bond in the phenolic model compound *1*, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol, in a reaction that resembles that of AHQ, indicates that the reaction between AN and lignin structural units may be more complex than previously thought.[11]

For instance, owing to the lack of a 10-hydroxyl group, AN adducts cannot be cleaved by the same mechanism as the corresponding AHQ adducts.[13]

The present work was undertaken to elucidate the mechanism of the anthrone-promoted β-ether cleavage in pulping conditions. The β-aryl ether cleavage reactions of *1* with anthrone, 10-methylanthrone and 10,10′-bianthrone were compared with the degradation reactions of the adducts *2* and *3*: 1-(4-hydroxy-3-methoxyphenyl)-1-(9-oxo-9,10-dihydro-10-anthryl)-2-(2-methoxyphenoxy)-propane and 1-(4-hydroxy-3-methoxyphenyl)-1-(9-oxo-10-methyl-9,10-dihydro-10-anthryl)-2-(2-methoxyphenoxy)propane.

RESULTS AND DISCUSSION

10-Methylanthrone adducts. When anthrone *4* reacts with different quinone methides in alkaline media it is alkylated at C-10.[13–15] An attempt[15] to obtain the corresponding adduct *3* having a methoxyl group (R=OCH_3) in the 10-position has failed. In order to investigate whether steric hindrance at C-10 would promote alkylation at the oxygen atom, the reactions of 10-methylanthrone *5* with two quinone methides were stu-

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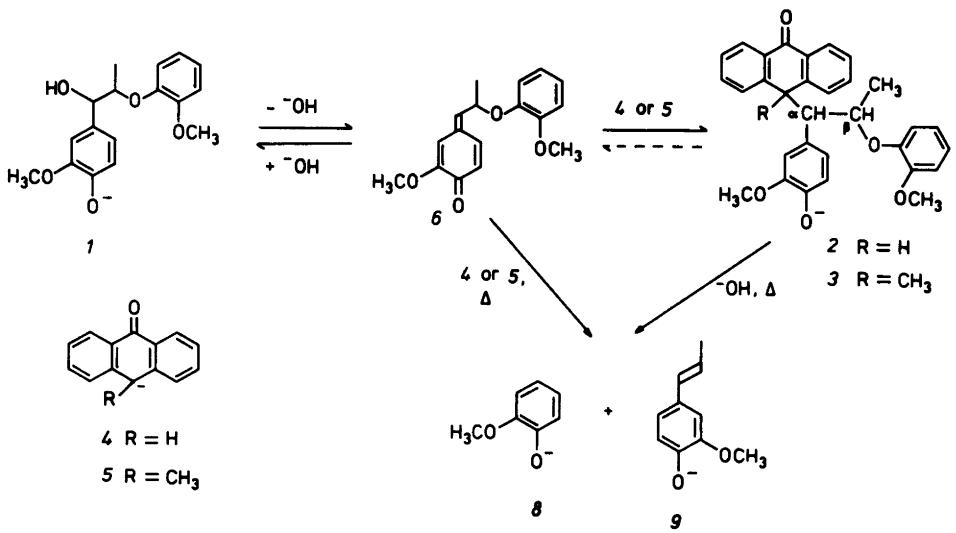
died. In reactions with the quinone methide derived from 1-(4-hydroxy-3-methoxyphenyl)-1-ethanol, and with the quinone methide *6* derived from *1*, mixtures of products were obtained. According to NMR, acetylation and separation on column chromatography gave the C-alkylated products *7*-Ac (acetylated *7*, 26 %) and *3*-Ac (acetylated *3*, 18 %), respectively, together with some unidentified products.

The ^{1}H NMR spectrum of *3*-Ac indicates that it is a *threo* isomer (for nomenclature see Ref. 15). The observed α,β coupling constant ($J_{\alpha\beta}$ 10 Hz, indicating a dihedral angle of 180 °) is similar to those reported for the *threo* isomers of other adducts of this type.[15,16] The highly shielded signals of the methoxyl group (δ 3.40) and protons (δ 6.53 and 5.43–5.73) in the α-aryl substituent are typical for such adducts.[2,15,17] Although there is no β-guaiacoxy group in the adduct *7*-Ac, the typical high field shifts of the substituents in the α-aryl ring were observed (Experimental), as earlier for the corresponding AHQ adduct.[15] It has been reported[15] that replacing the proton or the hydroxyl group at the 10-position in the adducts by a methoxyl or an acetoxy group causes an upfield shift of the methoxyl signal of the β-substituent. The methyl group at the 10-position did not have this effect. The methoxyl signal of the β-substituent of *3*-Ac prevailed at the position typical for an aromatic methoxyl group (δ 4.00). Comparing the chemical shifts of the 10-CH_3 group in the adducts *3*-Ac and *7*-Ac it can be seen that the 10-methyl protons of *3*-Ac are shifted to lower field (δ 2.20) relative to those in *7*-Ac (δ 1.97). This may be due to the ring current effect of the β-aroxy ring. The same trend can be observed in the carbon shifts (δ 28.1 for *3*-Ac and 24.4 for *7*-Ac).

Alkaline treatment of 1 in the presence of AN. In our previous article [12] we described the β-ether cleavage reaction in phenolic model compounds caused by anthrone when used in great excess in pulping conditions. Now we have observed that AN also cleaves the β-aryl ether bond when used in equimolar amounts in pulping conditions. When the model compound *1* was heated with 1.15 equivalents of AN in an alkaline solution at 140 °C for 5 h the β-ether bond was completely cleaved (Table 1 and Scheme 1).

a. The effect of dioxane. Previously [12] the AHQ and AN promoted β-ether cleavage reactions were carried out in an aqueous dioxane solution. Because in kraft and soda-AQ cooks water is the only solvent, we wanted to know if dioxane has any effect on the β-ether cleavage reaction in phenolic model compounds. *1* was heated with AN (1.15 eq.) for 3 h at 140 °C in an aqueous sodium hydroxide–dioxane solution and in pure aqueous sodium hydroxide solution. As can be seen (Table 1), the presence of dioxane did not have an obvious effect on the liberated amounts of guaiacol *8* (2-methoxyphenol) and *trans*-



Scheme 1. Phenolic compounds are depicted as anions and *4* and *5* in the enolate form.

Table 1. Yields of guaiacol and *trans*-isoeugenol on treatment of *1* (1.00 mmol) with anthrone *4* (1.15 mmol), 10-methylanthrone *5* or 10,10′-bianthrone *12* and on heating the adduct *3*-Ac. Temp. 140 °C, nitrogen atmosphere. Results are not corrected for recovery or for possible unreacted *1*. The amounts of consumed *4* and unreacted *1* are shown for some reactions.

	Heating time h	Solution	Guaiacol %	*trans*-Isoeugenol %	*erythro-1* %	*4*[a] mmol
1	3	NaOH-dioxane	21	2		
1+4	5	NaOH-dioxane	92	69	3	0.89
1+4	3	NaOH-dioxane	77	63	15	0.75
1+4	3	NaOH	83	58		0.76
1+12	3	NaOH-dioxane	38	20		
1+5	3	NaOH-dioxane	49	32		
3-Ac	3	NaOH-dioxane	28	11		

[a] Consumed in the reaction.

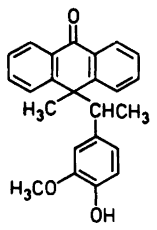
Table 2. Yields of guaiacol *8* and *trans*-isoeugenol *9* on treatment of *1* with anthrone *4* (1.15 eq.) and on heating of the adduct *2* in 1 M sodium hydroxide (40 % dioxane) solution. Temp. 140 °C, reaction time 3 h, nitrogen atmosphere. The losses of *8* (4 %) and *9* (7 %) (determined by recovery tests) in cooking, acetylation and extraction processes were taken into account when calculating the results.

	Yield/% Guaiacol	*trans*-Isoeugenol
1+4[a]	95	79
2	64	42

[a] 15 % of the original amount of *1* was detected by GLC. The yields of *8* and *9* were calculated for every consumed mole of *1*.

isoeugenol *9* (2-methoxy-4-(1-propenyl)phenol). On the other hand, in the alkaline cleavage reactions of non-phenolic model compounds, dioxane has been found to supress the rate of alkaline cleavage.[18] Also, phase separations[19,20] have been observed at high temperatures for some sodium hydroxide concentrations in dioxane.

b. Product analysis. The reaction mixtures were immediately acetylated subjecting them to only minimal exposure to air. Calculated from the amounts of recovered AN, about one mole of AN was consumed for each mole of guaiacol formed in the reaction (Table 1). The fate of the consumed AN is still under investigation. Among the oxidation products of AN, AQ and 10,10′-bianthrol *10* (in its acetate form) were identified by liquid chromatography, but no 10,10′-bianthronylidene *11*, which has been reported in an earlier work.[11] The sum of the amounts of AQ (traces by GLC) and *10* (by ^{1}H NMR) did not correspond to the amounts of AN consumed in the reaction. TLC analysis revealed some unidentified components among the products.



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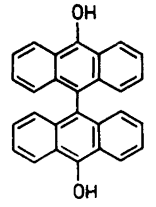

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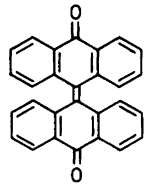

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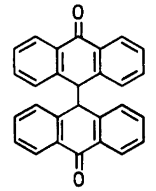

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After 3 h cooking 15 % of the original amount of *1* was detected by GLC. The yields of guaiacol and *trans*-isoeugenol in Table 2 are calculated assuming total consumption of *1*.

Alkaline treatment of 1 in the presence of 10-methylanthrone or 10,10'-bianthrone. 10-Methylanthrone has been found in the spent liquors of soda-AQ pulping.[7] The carbohydrate fraction of the wood is the probable source of the methyl group.[9] Both 10-methylanthrone and 10,10'-bianthrone *12*, which in cooking conditions is converted to *10*, also had the ability to cleave the β-ether bond in the phenolic model compound *1* when heated in the chosen conditions. The amounts of liberated guaiacol and *trans*-isoeugenol were lower compared with anthrone-promoted β-ether cleavage (Table 1), though much higher compared with the control.

The degradation of the adducts. When the *threo* adduct *2*, formed in the reaction of the quinone methide *6* with anthrone by Landucci's method,[15] was heated under the same conditions as a mixture of *1* and anthrone (NaOH, dioxane, 140 °C, 3 h), it decomposed completely (NMR). The yields of guaiacol and *trans*-isoeugenol were significantly lower than in the case of the mixture (Table 2). The reaction mixture contained both the *threo-1* (11 %) and *erythro-1* (5 %), indicating that the cleavage of the C-10–C-α bond occurred to a quinone methide intermediate. When the adduct *3*-Ac was heated under the same conditions the results were similar. The liberated amounts of guaiacol and *trans*-isoeugenol were considerably lower (Table 1) than for the mixture of *1* and 10-methylanthrone. At present we do not know the mechanistic explanation for the lower yields of cleavage products *8* and *9* from the adducts *2* and *3*. It is possible that there is a pathway for the β-ether cleavage which does not involve the formation of an adduct. Adducts such as *2* and *3* have been assumed to be intermediates in the AQ accelerated β-ether cleavage reactions in pulping conditions,[2,3] though radical and electron transfer mechanisms have also been suggested.[21]

EXPERIMENTAL

General. Melting points, determined in open capillary tubes with an electrothermal apparatus, are uncorrected. ^{1}H NMR spectra were recorded on a Jeol JNM-PMX 60 spectrometer and ^{13}C NMR spectra on a Jeol JNM PFT 100 spectrometer. Mass spectra were obtained with Jeol JMS-01SG-2 and Varian MAT 112-S instruments. The samples were introduced by direct inlet probe or through a gas chromatograph. High performance liquid chromatography (HPLC) was carried out on a Pye Unicam LC 20 apparatus, column ODS, 5 μm, solvent methanol–water (3:1), UV detection at 254 nm. All acetylations were performed with a mixture of dry acetic anhydride and pyridine (1:1).

Gas Chromatography (GLC). 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 the liquid phases SE-52 (25 m, film thickness 0.25 μm), SE-54 (25 m, film thickness 0.15 μm) and OV-1701 (23 m, film thickness 0.15 μm). 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 250–300 °C; detector 250–270 °C; temperature program 50–250 °C, 15 °C/min, and isothermic at 250 °C. The instrument was microcomputer controlled with two-channel integration and printing software.

Starting materials and reference compounds. 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol 1[22] was obtained as a mixture of *erythro* and *threo* isomers (9:1).[23]

threo-*1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-acetoxypropane 1-diAc* (acetylated *1*) MS [70 eV; *m/e* (% rel. int.)]: 388 (8, M), 265 (32), 223 (25), 181 (31), 180 (33), 151 (100), 124 (83); *erythro-1-diAc* 388 (8, M), 265 (58), 223 (48), 181 (41), 180 (38), 151 (100), 124 (90).

10-Methylanthrone 5 was synthesized by the reported method.[24] M.p. 64–66 °C (lit.,[24] 64.5–65.5 °C). ^{1}H NMR data agreed with the literature values.[7] MS [75 eV; *m/e* (% rel. int.)]: 208 (89.2, M), 194 (19.4), 193 (100.0), 178 (24.2), 165 (71.0), 164 (17.2), 163 (20.5).

10,10'-Bianthrone 12 was obtained by oxidizing anthrone (Koch-Light) with $FeCl_3$.[25] M.p. 250 °C (darkened) (lit.,[25] 230–235 °C, lit.,[26] 245–250 °C). ^{1}H NMR data were in agreement with the literature values.[27] No molecular ion was obtained in mass spectra obtained with electron impact mode.

10,10'-Bianthrol diacetate 10-diAc (acetylated *10*) m.p. 284–286 °C (lit.,[28] 275 °C, lit.,[29] 279–282 °C). ^{1}H NMR ($CDCl_3$): δ 2.71 (6 H, s), 7.08–7.27 (8 H, m), 7.27–7.65 (4 H, m), 8.00–8.28 (4 H, m).

Anthrol acetate 4-Ac (*4* acetylated at oxygen

atom) m.p. 134–135 °C (lit.,[30] 133 °C). ^{1}H NMR ($CDCl_3$): δ 2.63 (3 H, s), 7.36–7.63 (4 H, m), 7.77–8.13 (4 H, m), 8.37 (1 H, s). MS [75 eV; *m/e* (% rel. int.)]: 236 (12.4, M), 195 (15.8), 194 (97.3), 193 (32.0), 165 (100.0), 164 (19.9), 163 (32.5).

Adducts. 1-(4-Hydroxy-3-methoxyphenyl)-1-(9-oxo-9,10-dihydro-10-anthryl)-2-(2-methoxyphenoxy)propane 2 was synthesized using the published procedure.[15] Purification on a silica dry-column (Woelm Pharma GmbH & Co; acetone-light petroleum, 40–60 °C, 1:3) gave light yellow crystals (67 %), m.p. 160–162 °C. The molecular ion (480, M) observed in the mass spectra (22 eV, EI mode) was very weak. The main fragmentation was that of the C-10 – benzyl bond, main fragments at *m/e* 288, 287, 286, 195, 194, 165, 164, 163, 149, 124. The ^{1}H NMR spectrum was in accordance with that published for the corresponding acetate.[15]

1-(4-Acetoxy-3-methoxyphenyl)-1-(9-oxo-10-methyl-9,10-dihydro-10-anthryl)-ethane 7-Ac (acetylated *7*) was prepared by allowing the quinone methide of 1-(4-hydroxy-3-methoxyphenyl)-1-ethanol[31] (168.0 mg, 1.0 mmol) to react with 10-methylanthrone (187.2 mg, 0.9 mmol) according to the published method.[15] After acetylation and upon silica dry-column chromatography (Woelm Pharma GmbH & Co; hexane–chloroform 1:4) the crude product gave an unidentified product (62.1 mg), m.p. 103–104 °C, and *7*-Ac in 26 % yield (92.5 mg, without optimizing) as a light yellow solid, m.p. 106–110 °C. ^{1}H NMR ($CDCl_3$): δ 1.00 (3 H, d, *J* 7 Hz), 1.97 (3 H, s), 2.26 (3 H, s), 3.15 (1 H, q, *J* 7 Hz), 3.43 (3 H, s), 5.80 (1 H, d, *J*~1.5 Hz), 6.06 (1 H, dd, *J* 8 Hz and ~1.5 Hz), 6.73 (1 H, d, *J* 8 Hz), 7.36–7.86 (6 H, m), 8.13–8.44 (2 H, m). ^{13}C NMR (25.15 MHz, $CDCl_3$): δ 16.6 (C-β), 20.5 (acetate CH_3), 24.4 (CH_3), 46.0 (C-10), 54.8 (C-α), 55.6 (OCH_3), 113.7–149.7 (aromatic carbons), 168.7 (acetate CO), 183.7 (CO). MS (75 eV, the molecular ion was very weak in EI mode (400, M), main fragments at *m/e* 209, 208, 207, 193, 178, 152, 151, 150). Mol. wt., obs. 400.1675, calc. for $C_{26}H_{24}O_4$ 400.1674.

1-(4-Acetoxy-3-methoxyphenyl)-1-(9-oxo-10-methyl-9,10-dihydro-10-anthryl)-2-(2-methoxyphenoxy)propane 3-Ac (acetylated *3*) was prepared by allowing the quinone methide of *1* (304.0 mg, 1.0 mmol) to react with 10-methylanthrone (187.2 mg, 0.9 mmol) according to the published method.[15] The crude product was acetylated at 50 °C. Purification of the crude acetate twice on a silica dry-column (Woelm Pharma GmbH & Co; chloroform; cyclohexane–ethyl acetate–chloroform 4:1:2) gave an unidentified product (67.4 mg) and *3*-Ac as white crystals, yield 87.8 mg (18 % without optimizing), m.p. 176–178 °C. ^{1}H NMR ($CDCl_3$): δ 0.97 (3 H, d, *J* 6 Hz), 2.20 (3 H, s), 2.30 (3 H, s), 3.40 (3 H, s), 3.62 (1 H, d, *J* 10 Hz), 4.00 (3 H, s), 4.63–5.26 (1 H, m), 5.43–5.73 (2 H, overlapping), 6.53 (1 H, d, *J* 8 Hz), 7.00–7.16 (4 H, m), 7.46–8.50 (8 H, m). ^{13}C NMR (25.15 MHz, $CDCl_3$): δ 19.5 (C-γ), 20.5 (acetate CH_3), 28.1 (CH_3), 46.3 (C-10), 55.3 and 55.9 (OCH_3), 64.9 (C-α), 74.4 (C-β), 112.2–150.1 (aromatic carbons), 168.5 (acetate CO), 182.9 (CO). MS (75 eV, the molecular ion was weak in EI mode (536, M), main fragments at *m/e* 329, 287, 286, 208, 207, 206, 193, 164, 163, 124, 123). Mol. wt., obs. 536.2204, calc. for $C_{34}H_{32}O_6$ 536.2198.

Cooking with anthrone, 10-methylanthrone or 10,10'-bianthrone. Compound *1* (500.0 mg, 1.645 mmol) was heated at 140 °C with anthrone (370.0 mg, 1.907 mmol) for 3 and 5 h (no pre-heating) or with 10-methylanthrone (396.7 mg, 1.907 mmol) for 3 h, and *1* (212.8 mg, 0.700 mmol) was similarly heated with 10,10'-bianthrone (300.0 mg, 0.777 mmol) for 3 h in peroxide-free dioxane (40 ml), 2 M sodium hydroxide (50 ml) and water (10 ml). 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 chloroform (4×25 ml) subjecting it to only minimal exposure to air. The combined chloroform layers were immediately transferred into the acetylation mixture (acetanhydride-pyridine, in excess, nitrogen atmosphere). After the usual work up, the solvents were removed *in vacuo* for recording of the ^{1}H NMR spectrum of the mixture. The mixture of products was thereafter dissolved in chloroform (100.0 ml, *pa.*), an appropriate aliquot was withdrawn, the internal standards (methyl anisate, Fluka, *purum*; 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol[32] for the quantitative determination of *1*-diAc) were added and GLC analysis was made.

Cooking without any additive was carried out as above.

Cooking without dioxane was performed as above using 1 M sodium hydroxide (100 ml).

Recovery tests were run in nitrogen atmosphere with guaiacol (123.4 mg, 0.995 mmol or 124.7 mg, 1.006 mmol), *trans*-isoeugenol acetate (169.4 mg, 0.822 mmol) and anthrone (370.0 mg, 1.907 mmol) in peroxide-free dioxane (40 ml), 2 M sodium hydroxide (50 ml) and water (10 ml). The reaction time was 3 h and temperature 140 °C (no pre-heating). The alkaline reaction mixtures were worked up and acetylated as above. The recovery in the cooking, acetylation and extrac-

tion processes for guaiacol was 96 %, for *trans*-isoeugenol 93 % and for anthrone 89 % (of which 5 % as AQ).

Degradation of the adducts. Adduct *2* (82.6 mg, 0.172 mmol or 90.0 mg, 0.188 mmol) or adduct *3*-Ac (17.4 mg, 0.0325 mmol), peroxide-free dioxane (20 ml), 2 M sodium hydroxide (25 ml) and water (5 ml) were heated in nitrogen atmosphere at 140 °C for 3 h (no pre-heating). The work up of the alkaline mixtures, the acetylations and the GLC analysis were carried out as described for the cooking of *1*.

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