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**ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VII):  
REACTIONS OF SYRINGYL ALCOHOL WITH TYPICAL PULPING REAGENTS**

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Portions of this work were used by D. A. Smith as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry.  
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ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VII):  
REACTIONS OF SYRINGYL ALCOHOL WITH TYPICAL PULPING REAGENTS

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ABSTRACT

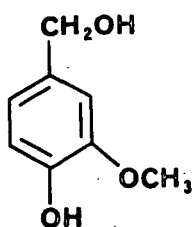
Syringyl alcohol (2) was heated at 135°C in 1M NaOH in the presence of anthrahydroquinone (AHQ), sodium hydrosulfide (NaSH), glucose, and mixtures of these. Quantification of 2 and reaction products 3-7 as a function of reaction time indicated that AHQ and glucose promoted radical reactions of the in situ quinonemethide (QM), derived from syringyl alcohol, while NaSH was mainly reacting as a nucleophile with the QM. Postulated radical product 4-methylsyringol (5) was produced in much greater amounts in the presence of AHQ and glucose. Bisyringyl (7), a QM radical anion coupling product, was observed in about 16% yield when 2 equiv. of AHQ were used. All the additives diverted the syringyl alcohol from its normal dimerization to disyringylmethane (3) by effectively capturing a large fraction of QM intermediates and producing adducts. The data indicate that adduct formation is irreversible and that electron transfer reactions, leading to QM<sup>-</sup> intermediates, account for some of the products.

INTRODUCTION

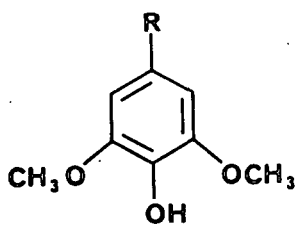
In order to remove as much lignin as possible during pulping, we need to control the extent of condensation reactions which occur with dissolved lignin fragments. Vanillyl and syringyl alcohols (1 and 2) undergo self-condensation reactions<sup>1,2</sup> that undoubtedly resemble lignin fragment condensation reactions. High temperature, alkaline vanillyl alcohol reactions produce a

complex mixture of monomer, dimer, trimer, oligomer, and polymer components.<sup>1</sup> The corresponding syringyl alcohol condensation reaction gives a relatively simple product mixture for which component quantification is possible.<sup>2</sup>

Previous studies with vanillyl alcohol have shown that anthrahydroquinone (AHQ) and sodium hydrosulfide (NaSH), the active agents in anthraquinone (AQ) and kraft pulping systems, respectively, cause a decrease in the extent of condensation reactions.<sup>1</sup> The intent of the study reported here is to determine how AHQ, NaSH, and a simple carbohydrate (glucose) affect the alkaline reactions of syringyl alcohol. The results could provide mechanistic information on condensation reactions and on the occurrence of electron transfer reactions in a pulpinglike environment.



1



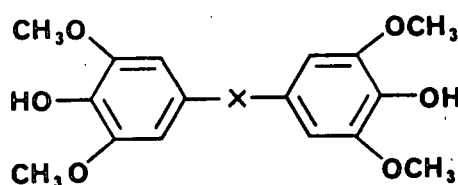
2, R = CH<sub>2</sub>OH

4, R = H

5, R = CH<sub>3</sub>

6, R = CHO

8, R = CH<sub>2</sub>SH



3, X = -CH<sub>2</sub>-

7, X = -CH<sub>2</sub>-CH<sub>2</sub>-

9, X = -CH<sub>2</sub>-S-CH<sub>2</sub>-

## RESULTS AND DISCUSSION

### **Anthrahydroquinone**

Anthrahydroquinone was selected for initial study for several reasons: the ability to pulp to lower residual lignin levels suggests less condensation reactions with an AQ process,<sup>4</sup> AHQ has shown a tendency for electron transfer reactions,<sup>5</sup> and AHQ appears to inhibit vanillyl alcohol condensation reactions.<sup>1</sup>

Syringyl alcohol (2) was heated at 135°C in 1M NaOH with different levels of AHQ and the reaction mixture sampled at numerous time intervals. The concentration of products and starting material are shown for three different time periods in Table 1. Complete time-concentration profiles are available.<sup>6</sup>

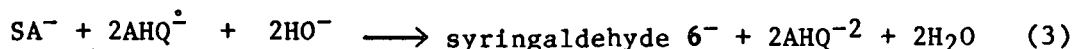
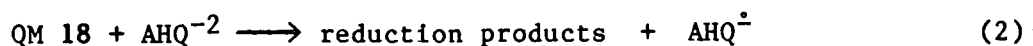
Except when large levels of AHQ (and other additives) were present, the material balances were good (ca. 80-95%). Apparently, with 2 equiv. of AHQ, extensive formation of adduct structures occurs between AHQ and the quinonemethide derived from syringyl alcohol. Analogous reactions between AHQ and other simple quinonemethides are known.<sup>7</sup> The expected adducts would have low volatility and, therefore, would not be observable by typical gas chromatography (GC) analysis. Methylation of the product mixture from the 2 equiv. AHQ reaction and analysis by GC-mass spectroscopy (GC-MS) indicated the presence of methylated adducts 11, 13, 15, and 17 (Scheme 1). Another unassigned methylated adduct product, having the same molecular weight as 17, was also observed.

Based on analogous reactions with structurally similar materials,<sup>7,8</sup> we believe that adduct 10 is the primary reaction product and the other adducts are secondary products (Scheme 1). The quinonemethide product 12 is simply a dehydration product of 10, and the other secondary products, 14 and its enol isomer 16, are reduction products of 10.

The data in Table 1 indicate that increasing the concentration of AHQ in the reaction mixture caused (a) the syringyl alcohol starting material to disappear more rapidly, (b) an increased production of 4-methylsyringol (5), a suspected radical derived product, and (c) a decrease in the level of disyringylmethane (3). The level of syringol (4) was fairly low in all runs and seemed not to be affected much by changes in AHQ levels. The production of syringaldehyde (6) was increased in the presence of AHQ and passed through a maximum at intermediate AHQ levels.

The different yields of syringaldehyde can be explained by the nature of the competing reactions indicated by equations 1-3. In

alkali at 135°C, syringyl alcohol (SA) is in equilibrium with a quinonemethide (QM 18) and hydroxide ion (eq. 1). Reactions of AHQ dianions with the quinonemethide can lead to an intermediate oxidized form of AHQ, i.e.,  $\text{AHQ}^{\cdot-}$  (eq. 2). The AHQ radical anion can then oxidize the benzylic alcohol group of SA to the aldehyde group of 6 (eq. 3).<sup>9,10</sup> At low levels of  $\text{AHQ}^{-2}$ , the concentration of  $\text{AHQ}^{\cdot-}$  will also be low and little oxidation should occur. At high levels of  $\text{AHQ}^{-2}$ , reduction of the QM by  $\text{AHQ}^{-2}$  (eq. 2) may dominate over oxidation reactions of  $\text{AHQ}^{\cdot-}$  with SA (eq. 3). At the 0.5 charge of  $\text{AHQ}^{-2}$ , the latter will be depleted (eq. 2) and reasonable levels of  $\text{AHQ}^{\cdot-}$  will be available for oxidation reactions which give rise to syringaldehyde.



The levels of bisyringyl (7) formed in the control and low addition AHQ experiments were quite low, generally in trace levels. However, as can be seen in Fig. 1, bisyringyl was formed rapidly when 2 equiv. of AHQ was employed. The bisyringyl yield rapidly reached 15-18% and then appeared to drop slightly after 30 min reaction time. This behavior suggests a radical dimerization process (to be discussed further later) which gives rise to 7, coupled to a slow secondary reaction which consumes 7 or a slow reversal of the dimerization reaction.

### Glucose

Carbohydrates are a common component of pulping liquors. The effect carbohydrates might have on lignin condensation reactions was determined by the addition of two molar equivalents of glucose to the alkaline reaction of syringyl alcohol. As can be seen in Table 1, the consumption rate of syringyl alcohol was increased from the control, and the production of disyringylmethane was less



Addition of sulfide also decreased the production of the other products; for example, the yield of 4-methylsyringol was less than a fourth of that produced in the control reaction. An analysis of the reaction solution by GC/MS led to the identification of two products unique to sulfide addition: 3,5-dimethoxy-4-hydroxybenzylthiol (8) and di-(3,5-dimethoxy-4-hydroxybenzyl)sulfide (9). Previous investigations with vanillyl alcohol and sulfide at temperatures of 75-95°C provided the analogous di-(3-methoxy-4-hydroxybenzyl)sulfide as the major product.<sup>17</sup>

As seen in Fig. 2, the production of the sulfur adducts was high initially but decreased thereafter. Crude calculations indicate that the missing material in the sulfide experiment (Table 1) can be accounted for by the sulfur adducts.<sup>5</sup> It is apparent that the sulfur adducts are reactive intermediates, which are in equilibrium with the starting SA. The adducts provide a steady source of SA, such that the amount of SA after 4 hours in the sulfide run is greater than that of the control run by almost a factor of two. Because SA is being regenerated from the adducts, disyringylmethane production starts out slow but builds to respectable levels after 4 hours.

The sulfide reactions can be best explained by the reactions shown in Scheme 2. Adducts 8 and 9 provide a holding place for QM 18 and appear to be less prone to condensation than SA, since the levels of products 3-6 decrease. However, the typical dimerization can still occur from the QM 18 released from the sulfur adducts. Gierer,<sup>18</sup> in studies with coniferyl alcohol, also concludes that "sulfidation constitutes only a temporary protection against condensation and degradation."

#### Additive Combinations

The additives that have been discussed already are often in the same pulping liquors; therefore, two additive combination reactions were examined. With 2 equiv. each of sodium hydrosulfide and glucose, the syringyl alcohol was quickly consumed and the

levels of disyringylmethane (3), syringol (4), and syringaldehyde (6) were significantly reduced relative to the control (Table 1). However, the formation of 4-methylsyringol (5) was high, roughly the same as that observed with 2 equiv. of AHQ. The level of 5 was greater than that observed for glucose or sodium hydrosulfide alone.

With 1 equiv. each of NaSH and AHQ, the syringyl alcohol concentration with time dropped at a rate intermediate between that expected for the individual additives (Table 1). Consequently, the two additives must be competing with each other in reactions with the SA quinonemethide. The low level of observed disyringylmethane (3) and high levels of 4-methylsyringol (5) and syringaldehyde (6) indicate that AHQ/AQ reactions eventually dominate. This may be because the adduct formation reactions are reversible, providing a constant source of QM which AHQ can divert to other products but NaSH can only add back to give more adduct. There is obviously much adduct formation, based on poor material balance.

#### CONCLUSIONS

Our results can best be explained by the sets of reactions shown in Scheme 3. In 1M NaOH at 135°C, syringyl alcohol is ionized and the phenolate ion is in equilibrium with a quinonemethide (18). It is apparent from the material balance for components 2-7 and extended product analyses that the QM 18 can be captured by carbohydrates,  $\text{AHQ}^{-2}$ , and  $\text{HS}^{-}$  to give adducts. Since glucose is unstable in alkali at 135°C,<sup>19</sup> it is not certain whether glucose or one of its carbohydrate fragments is reacting with the QM. Based on product composition data as a function of time, we believe that the adduct formation reactions are reversible, at least in the cases of AHQ and NaSH.

The sequence of events which appears to occur in the AHQ-syringyl alcohol case is as follows: (a) QMs are formed from SA rapidly at 135°C, (b)  $\text{AHQ}^{-2}$  efficiently converts many of these QMs

to  $QMs^{\dot{-}}$ , coproducing  $AHQ^{\dot{-}}$ , (c) coupling of a  $QM^{\dot{-}}$  with  $AHQ^{\dot{-}}$  within a solvent cage<sup>20,21</sup> may be a major pathway for adduct generation, (d) with large levels of  $AHQ^{-2}$  present, a good concentration of  $QMs^{\dot{-}}$  are produced simultaneously at early reaction times, (e) some of the  $QMs^{\dot{-}}$  escape the solvent cage and either (f) couple with another  $QM^{\dot{-}}$  or  $QM$  to give bisyringyl<sup>2</sup> or (g) are reduced by hydrogen atom transfer to give 4-methylsyringol. Later into the reaction,  $QMs$  are formed by breakdown of the  $QM-AHQ$  adduct structures and are converted to  $QMs^{\dot{-}}$  by electron transfer from  $AHQ^{-2}$ ; the concentration of  $QMs^{\dot{-}}$  and available  $QMs$  is low at this point so that the probability of coupling is low and hydrogen atom abstraction thus dominates.

In the glucose case, where electron transfer to  $QMs$  is known to be much slower than  $AHQ^{-2}$ ,<sup>5</sup> the first step appears to be ionic adduct formation. Reversal of the adduct formation gives a low steady state concentration of  $QMs$  and, by electron transfer,  $QMs^{\dot{-}}$ ; coupling will be rare, but reduction to 4-methylsyringol could occur.

In the hydrosulfide ion case, there appears to be an efficient, reversible production of sulfur adducts, probably via a simple ionic Michael addition of a sulfur ion to  $C_{\alpha}$  of the  $QM$ .<sup>22</sup> Reversal of the reaction provides a steady concentration of  $QM$  which, in the absence of electron transfer reagents, undergoes a normal<sup>2,22</sup> dimerization to disyringylmethane (3). In the presence of electron transfer reagents, such as in the mixed additive experiments with  $NaSH$  and  $AHQ$  or glucose, the  $QM$  released from sulfur adducts can be diverted via radical reactions to give some 4-methylsyringol (5).

The observation of relatively large levels of 4-methylsyringol (5) in the presence of  $AHQ$  and glucose and low levels in the presence of  $NaSH$  and no additives (other than  $1M$   $NaOH$ ) parallels observations made with regard to the abilities of these reagents to transfer electrons to quinonemethides.<sup>5</sup> The  $QM^{\dot{-}}$  produced by electron transfer from  $AHQ^{-2}$  or glucose to  $QM$  18 can give rise to

4-methylsyringol by abstraction of a hydrogen atom from a monoprotonated AHQ (i.e.,  $\text{AHQ-H}^-$ ), a carbo-hydrate fragment, a starting SA molecule, or other organic products in the mixture. Previous studies have established that the benzylic hydrogens of SA are the source of hydrogen atoms in a simple NaOH system<sup>2</sup> and that AHQ systems are better able to supply hydrogen atoms than glucose systems.<sup>5</sup> Hydrogen atom abstraction from SA may account for part of the observed syringaldehyde.<sup>2</sup>

### EXPERIMENTAL

The equipment, procedures, and most of the compound characterization are described in the previous paper.<sup>2</sup>

**Syringyl Alcohol Additive Reactions.** The additive reactions were run in a manner similar to the NaOH control case.<sup>2</sup> Some additives were placed in the reaction vessel with the NaOH before warming; these were sodium sulfide (0.4683 g, 2 equiv.) and AHQ (various levels). Glucose, because of its limited stability in alkali,<sup>19</sup> was added to the hot reaction vessel simultaneously with the syringyl alcohol; the quantities used were 1.0810 g (2 equiv.) in 5.00 g of water or 2.7024 g (5 equiv.) in 12.50 g of water. Additive combinations were performed in a similar way.

Anthrahydroquinone was prepared in a nitrogen atmosphere by the reduction of anthraquinone by dithionite. To a 250 mL Erlenmeyer flask was added 150 mL of oxygen-free water, enough 30% ultrapure NaOH to make at least a 1N NaOH solution, the preweighed anthraquinone (1.2492 g, 2 molar equivalents; 0.3123 g, 0.5 molar equivalents; or 0.0625 g, 0.1 molar equivalents), and an excess (~ 3 times) of  $\text{Na}_2\text{S}_2\text{O}_4$ . The solution was stirred for at least an hour after which 2M  $\text{H}_2\text{SO}_4$  was added until precipitation occurred. The solid was collected by filtration, washed twice with oxygen-free water, and placed in the reaction vessel.

**Bisyringyl (7) Analysis.** The concentration of SA (2) and reaction products 3-6 were determined by GC/MS selective ion monitoring (SIM) using deuterated analogs as internal standards.<sup>2</sup> A

deuterated analog of 7 was not available for use. Only trace levels of 7 were observed in all the experiments except the reaction of SA with 2 equiv. of AHQ. The quantity of bisyringyl present in the latter case was estimated by comparing the GC signal area of 7 to the GC signal area of 2 and 2-d<sub>2</sub>, which elute simultaneously, and by assuming that the response factors for 2 and 2-d<sub>2</sub> were identical.

The GC analysis employed a Hewlett-Packard 5890 with a flame ionization detector and a six foot OV-17 column with 30 mL/min of helium (carrier gas) and a temperature program of 210-285° at 15°/min holding at 285 for four min, 285-275° at 30°/min holding at 275 for 1.25 min, and finally, 275-300° at 30°/min holding at 300 for three min. The eight SIMS standard solutions,<sup>2</sup> which also contained bisyringyl of varying amounts, were used to obtain a response factor curve for bisyringyl relative to deuterium-enriched disyringylmethane. The GC signal area for bisyringyl in the reaction samples was then compared to the combined signal area of SA and SA-d<sub>2</sub>; since the amounts of the latter were known, or could be calculated for each sample, quantification of bisyringyl was possible.

**Syringyl Alcohol-AHQ Adducts.** The 135°C, 1M NaOH, 2 equiv. AHQ to SA experiment was repeated and 9 samples were collected over a 4-hour reaction time. Each sample (~ 3 mL) was methylated by adding, with stirring, 1 mL of dimethylsulfate. After 15 min, the excess dimethylsulfate was quenched with 4.5 mL of concentrated NH<sub>4</sub>OH and the methylated sample was then extracted with chloroform. The samples were qualitatively analyzed by the Hewlett Packard 5890 with an OV-17 column and the adducts were identified by GC/MS.<sup>25</sup> The components, in increasing elution order, gave the following m/z (%) values (the assignments for 17 and the unknown, ?, may be reversed):

11 404 (M+, 1), 223 (13), 181 (100).

15 374 (M+, 1), 193 (3), 181 (100).

17 388 (M+, 100), 373 (46), 345 (30), 221 (17), 202 (39),  
101 (35).

13 372 (M+, 100), 357 (30), 297 (31), 213 (20), 171 (26).  
? 388 (M+, 100), 373 (56), 311 (10), 255 (10), 221 (10),  
215 (12), 207 (12), 178 (24), 163 (18), 122 (12),  
119 (11), 133 (16).

**Sulfur Compounds.** The qualitative concentration analysis of the sulfur products formed from the addition of 2 molar equivalents of sodium sulfide to an alkaline reaction of syringyl alcohol was accomplished by obtaining GC chromatograms for the 18 reaction samples with the Hewlett Packard 5890 using the OV-17 column. As with the analysis of bisyringyl, the assumption was made that syringaldehyde and disyringylmethane and their deuterium-enriched analogs had the same response factors. This assumption allowed for the subtraction of the nondeuterated portion of the GC peaks; the amount of syringaldehyde and disyringylmethane in each sample was previously determined by SIMS. Thus, the GC areas of 8 and 9 were compared to the GC areas of deuterated syringaldehyde and deuterated disyringylmethane, respectively. This GC area ratio was then divided by the moles of deuterated compound contained in the sample and the volume of the sample. The mass spectra of the sulfur compounds gave the following  $m/z$  (%) values:

8 200 (M+, 26), 167 (100), 148 (34), 136 (21).  
9 366 (M+, 11), 332 (2), 200 (6), 168 (38), 167 (100),  
148 (20), 136 (13).

#### ACKNOWLEDGMENTS

Portions of this work were used by D. A. Smith as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry.

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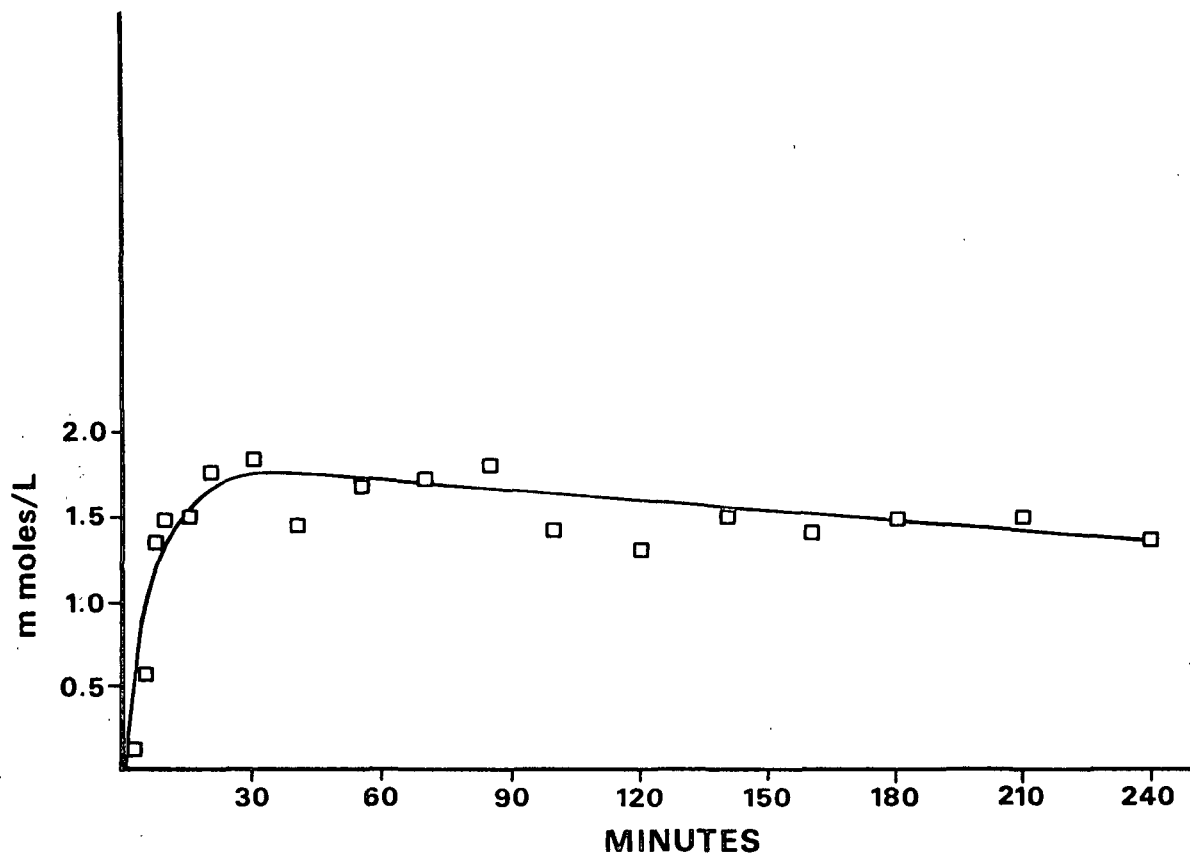


Figure 1. The concentration profile of bisyringyl when 20 mmoles/L of syringyl alcohol was heated at 135°C with 1M NaOH containing 2 equivalents of AHQ.

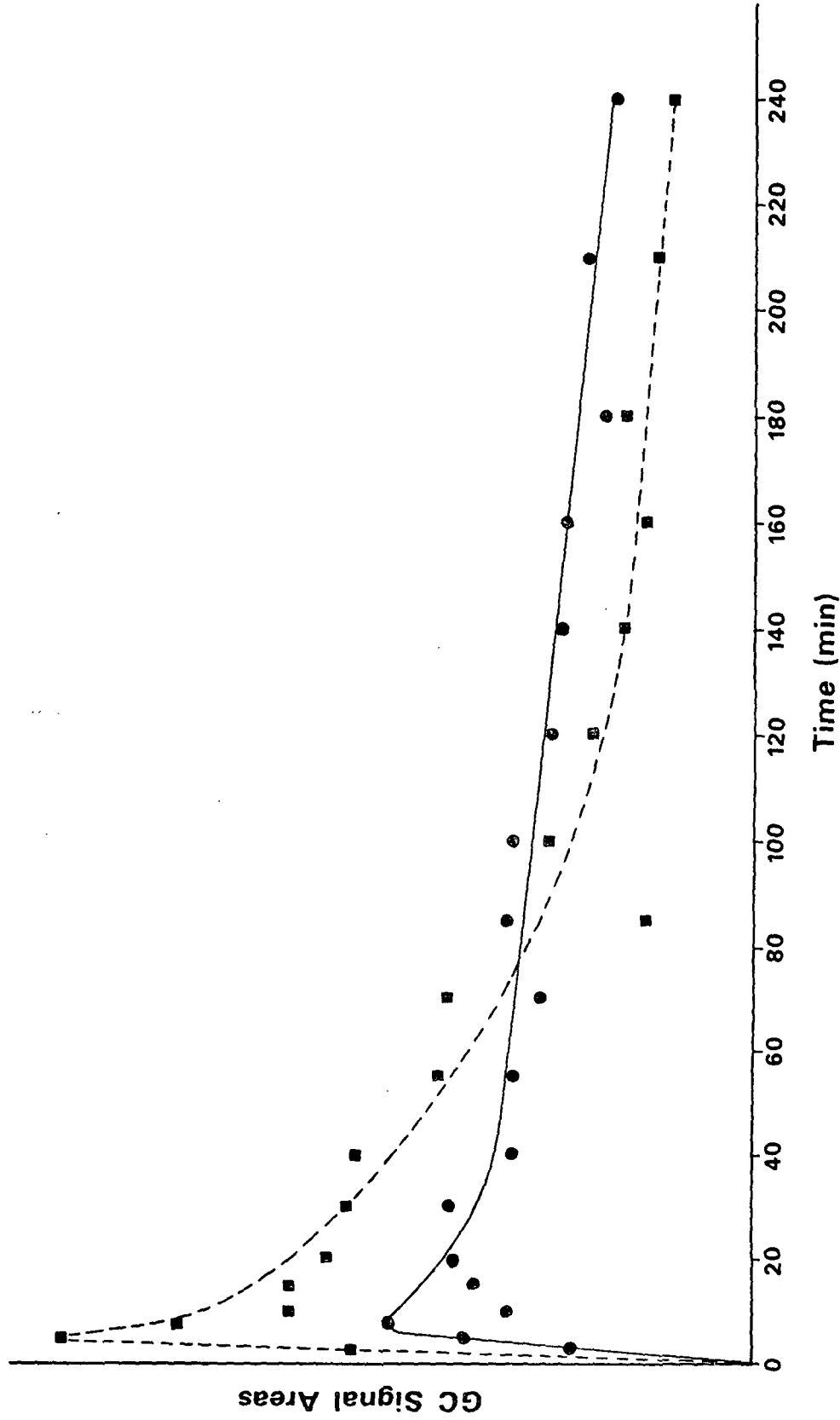
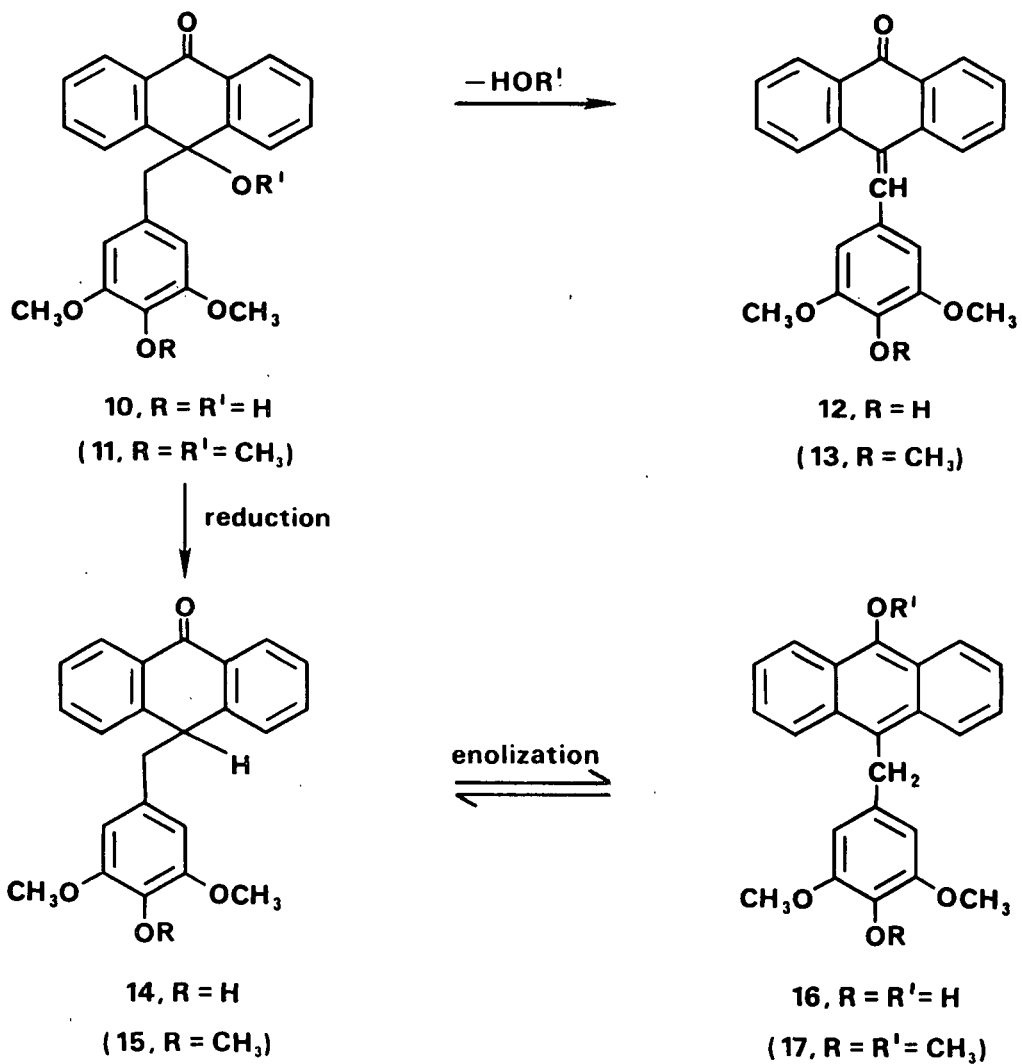
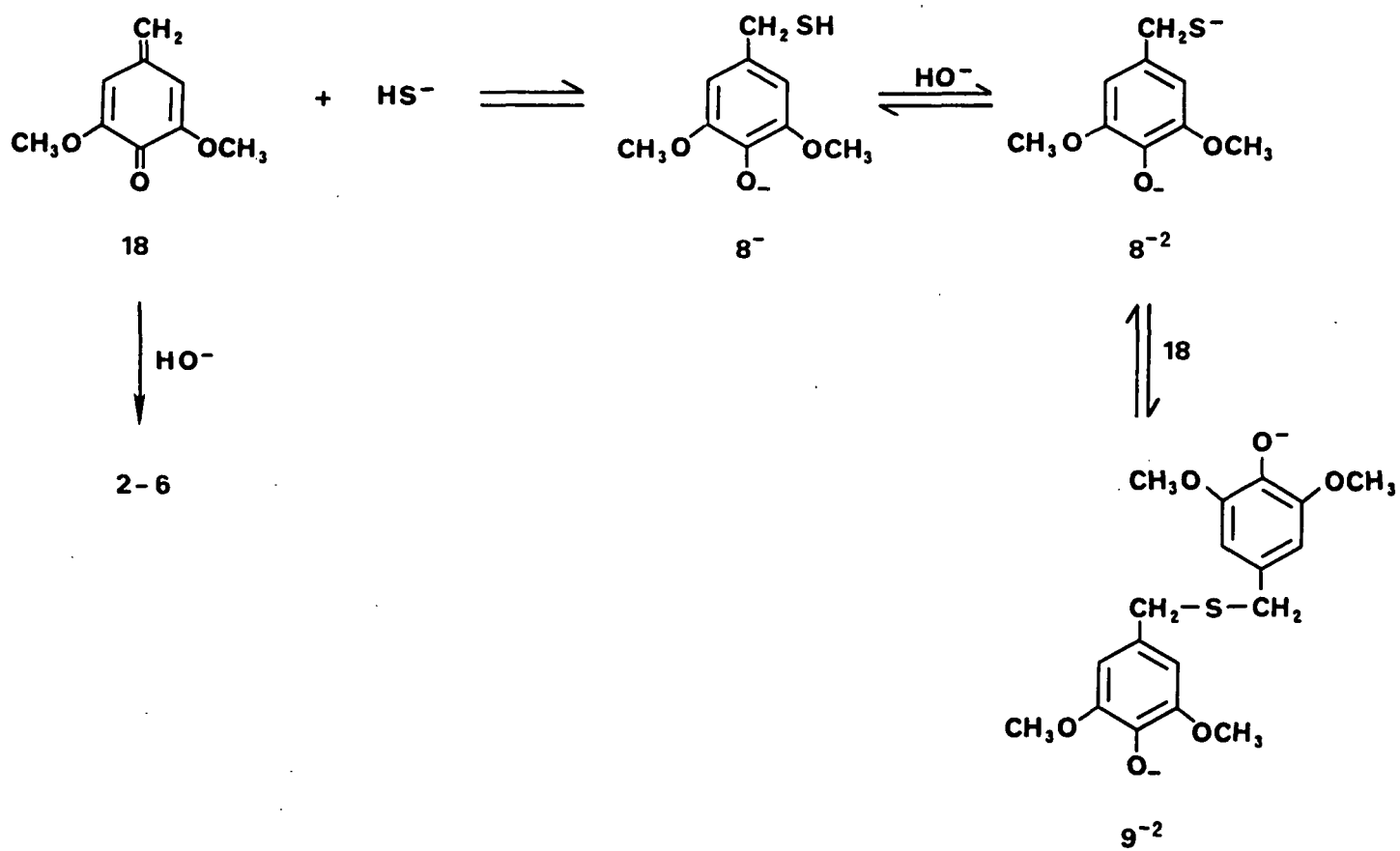


Figure 2. Relative GC signal areas in arbitrary units for 3,5-dimethoxy-4-hydroxybenzylthiol (8),  $\bullet$ , versus a deuterated syringaldehyde standard and for di-(3,5-dimethoxy-4-hydroxybenzyl) sulfide (9),  $\blacksquare$ ; versus deuterated disyringylmethane standard.

Scheme 1



Scheme 2



Scheme 3

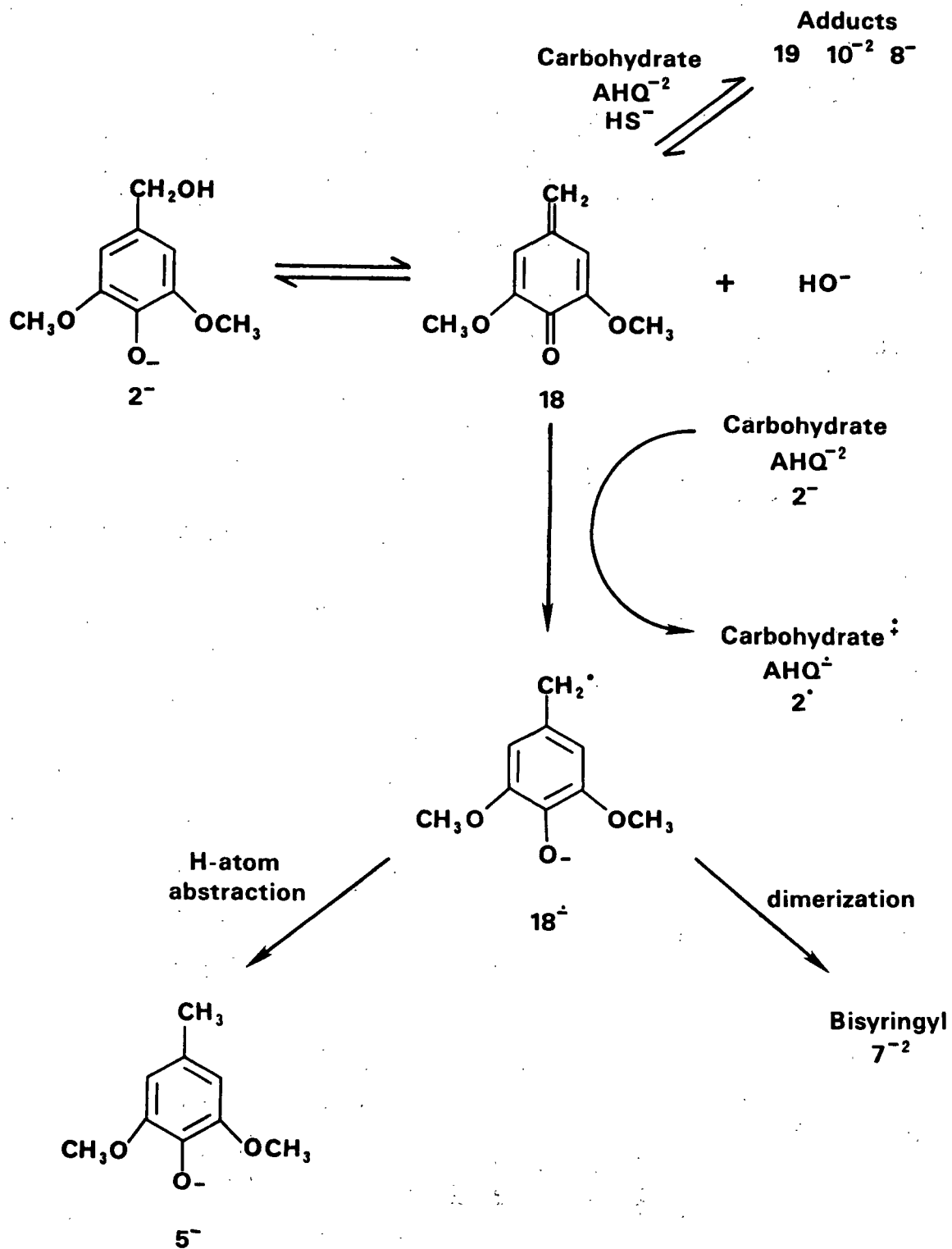


Table 1. Component yields associated with heating syringyl alcohol (SA) at 135°C in 1M NaOH with different additives and different additive levels.

Additive (equiv.)	Component yields (% of starting SA) as a function of time (min)																	
	2		3 <sup>c</sup>		4		5		6		Total							
	30	120	240	30	120	240	30	120	240	30	120	240	30	120	240			
None <sup>a</sup>	64	27	12	22	47	58	1	2	3	1	2	2	2	5	12	89	83	87
AHQ (0.1)	60	22	7	23	44	53	2	3	4	2	6	8	8	14	16	95	89	88
AHQ (0.5)	60	3	0	17	26	29	2	3	4	5	11	12	11	31	36	95	74	81
AHQ (2) <sup>a,b</sup>	14	6	8	2	3	4	1	1	2	8	10	11	5	8	11	29	28	36
Glucose (2) <sup>a</sup>	34	10	4	9	18	23	1	1	2	4	7	10	0	1	1	48	37	40
Glucose (5)	0	0	0	2	3	3	1	1	1	4	5	5	1	1	1	8	10	10
NaSH (2)	39	27	24	9	27	43	1	1	2	0	1	1	0	1	2	49	57	72
NaSH (2)/glucose (2)	12	2	0	6	12	12	1	1	1	7	11	12	0	1	2	26	27	27
NaSH (1)/AHQ (1)	32	14	9	3	7	8	1	1	1	4	6	7	4	10	14	44	38	39

<sup>a</sup>Average of three runs.  
<sup>b</sup>Bisyringyl (7) was observed at a level of 16 ± 2% from 7.5-240 min (Fig. 1); its presence in the other experiments was only at trace levels.  
<sup>c</sup>2 Moles of SA are required to make 1 mole of 3; yields are based accordingly.