

## Fiber Surface Modification

### Part III.<sup>1,2</sup> The Reaction of Lignin Model Compounds and Other Phenols with Cyanuric Chloride

F. J. ALLAN, G. G. ALLAN,\* T. MATTILA and P. MAURANEN \*\*

*Institute of Forest Products, College of Forest Resources, University of Washington, Seattle, Washington 98105, U.S.A.*

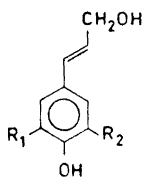
*Department of Chemistry, Paisley Technical College, Paisley, Scotland*

The structural environments of the phenolic hydroxyl groups in soft- and hard-wood lignins are discussed in terms of a proposed general system for their chemical modification without prior isolation from the aqueous pulping waste liquors in which they are generally available. The system depends on the reaction of phenolate anions with halogeno-*s*-triazines and this has been explored using lignin model compounds and a variety of substituted phenols. While the approach has broad applicability, bulky substituents adjacent to the phenolic hydroxyl group may inhibit reaction by steric or solubility effects.

Lignin is an abundant natural plant polymer which *in vivo* can be regarded as a three-dimensional phenolic network basically resulting from the nonspecific enzymatic oxidative copolymerization of coniferyl (Ia), sinapyl (Ib) and *p*-coumaryl (Ic) alcohols.<sup>3</sup> In softwood lignin approximately 95 % of the phenolic units originate from the coniferyl alcohol monomer with the remaining 5 % stemming mostly from the *p*-coumaryl alcohol and only traces from the sinapyl alcohol monomer.<sup>4</sup> In hardwood lignin, sinapyl alcohol plays a more important role and the corresponding figures for birch lignin,<sup>5</sup> for example, indicate that 42 % of the aromatic units are derived from coniferyl alcohol and 58 % from sinapyl alcohol. Other phenolic material within the locus of polymerization may also be incorporated into the lignin polymer by chain transfer or radical coupling.<sup>6</sup>

\* To whom inquiries should be addressed at the University of Washington.

\*\* Present address: Joutseno-Pulp, Lohja Mills, Lohja, Finland.

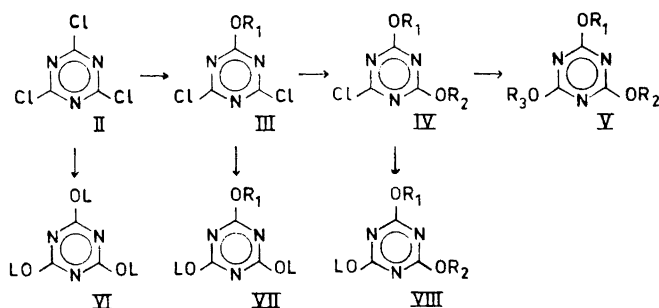


Ia	$R_1 = H; R_2 = OMe$
b	$R_1 = R_2 = OMe$
c	$R_1 = R_2 = H$

The various commercial chemical pulping techniques degrade this network in different ways<sup>7</sup> but in both acidic<sup>8</sup> and basic<sup>9</sup> processes the weakest bond of the lignin network is the  $\beta$ -O-4' ether linkage. Every  $\beta$ -O-4'-linkage hydrolyzed during the pulping yields one additional free phenolic hydroxyl group. Furthermore, in the kraft process, some of the methoxyl groups of the lignin are hydrolyzed producing free hydroxyl groups.<sup>10</sup> The resultant lignins therefore have in common a content of phenolic hydroxyl groups<sup>11</sup> which can range from about 7% for a kraft lignin<sup>11</sup> to 3% for a lignosulfonate.<sup>12</sup> The presence of these accessible and reactive functions offers the opportunity of modifying the structure of these waste polyanionic macromolecules which are, however, most readily available in their salt form as a component of pulping waste liquors. Generally the cost of isolating a metal-free lignin in a form suitable for further reaction has tended to diminish the economic attractiveness of lignin as a raw material. One general approach which offers promise of circumventing these problems would employ a chemical reagent, compatible with an aqueous environment to achieve the desired structural modification. It might then be anticipated that the lignin could be reattached to the surfaces of cellulosic or lignocellulosic fiber composites for interior or exterior reinforcement.<sup>1,2</sup> Among the alternatives available for lignin modification, cyanuric chloride (I) is considered to possess several significant advantages which include trifunctionality, reactivity and a low rate of hydrolysis in water below 10°C which, however, increases rather rapidly with pH elevations.<sup>13-15</sup>

The trifunctionality permits a stepwise replacement of the three active chlorine atoms as illustrated in the sequence II through V and suggests that the nucleophilic lignin macromolecule (LOH) in pulping waste liquor may be capable of displacing either  $R_1OH$ ,  $R_2OH$ , or indeed all three, as depicted in the reactions leading to (VI), (VII) and (VIII).

By a suitable choice of a substituted alcohol,<sup>16</sup> phenol,<sup>17</sup> amine<sup>18</sup> or mercaptan<sup>19</sup> as a replacement for  $R_1OH$  and  $R_2OH$  in the formation of III and IV the functionality of the lignin should be susceptible to facile alteration without departure from an aqueous reaction system.



## RESULTS AND DISCUSSION

As a first step in the exploration of the foregoing ideas, the reactions of cyanuric chloride with phenolic groups in a variety of molecular environments has been investigated. Although relatively few triaryloxy-*s*-triazines have been described in the literature several distinct synthetic procedures have been evolved.<sup>17,20-23</sup> Of these, the most suitable for the system under investigation utilizes the reaction of the appropriate phenol as its sodium salt with cyanuric chloride in aqueous acetone or dioxan.<sup>17</sup> The function of the acetone or dioxan is solely to effect introduction of the cyanuric chloride into the aqueous reaction medium in a finely divided state. Using this approach, a number of compounds selected as models for phenolic units in lignin have been employed as the phenolic co-reactant.

The most common immediate environment of the phenolic group in lignin is that exemplified by a guaiacylpropane fragment<sup>4a</sup> in which the hydroxyl is potentially shielded by the adjacent methoxyl group in the *ortho* position (Ia). That this shielding was insignificant was demonstrated by reactions using guaiacol and vanillin as lignin models. The triaryloxy-*s*-triazines (Xj) and (Xg) were obtained in excellent yields. However, the steric shielding effect of the methoxyl group increases dramatically when reaction is attempted using models of the syringylpropane units which are major structural components of angiosperm lignins.<sup>4b</sup> Thus, the model 2,6-dimethoxyphenol failed to give a triaryloxy-*s*-triazine under the same reaction conditions and examination of both Dreiding and Stuart-Briegleb molecular models revealed that the flanking methoxyl groups enclose the phenolic hydroxyl group in a pincerlike embrace. This steric envelopment by methoxyls is not immediately obvious from conventional projection formulae and indeed does not seem to have been previously explicitly recognized. It is relevant to note that reaction of epichlorohydrin<sup>24</sup> with the hydroxyl groups of the guaiacyl and syringyl units in a lignin obtained from western red alder (*Alnus rubra*, Bong.)<sup>25</sup> by reductive pulping<sup>26-31</sup> afforded mobile oils unexpectedly low in oxirane content.

Moreover, molecular models further show that the aromatic rings in a diphenyl carrying 2,2'-dimethoxy substituents are not capable of free rotation around the intericyclic bond. This steric hindrance apparently originates in the size and angulation of the methoxyl group.

Surprisingly, 2,6-dimethylphenol also fails to react with cyanuric chloride to form a trisubstituted triazine. The presence of the two flanking methyl substituents although providing a lesser steric restriction than the corresponding methoxyls seemingly is still sufficient to block the free rotation in a 2,2'-disubstituted diphenyl and to require that the plane of the approaching phenolate anion be orthogonal to the plane of the heterocyclic ring. Both these *ortho*-disubstituted phenols therefore display appreciable steric shielding and the formation of the rather large intermediate required by the S<sub>N</sub>2 mechanism<sup>32</sup> is inhibited.

Nonetheless, *O*-derivatives of 2,6-dimethoxyphenol can be formed and the acetate<sup>33</sup> and benzoate<sup>34</sup> have been described. Furthermore, *O*-arylation is achieved in the synthesis of polyphenylene ethers from both 2,6-dimethyl- and 2,6-dimethoxy-phenol by oxidative coupling polymerization<sup>35-44</sup> which does not involve a bulky intermediate. The syringyl and other vicinally disubstituted hydroxyls in the lignin macromolecule therefore need not necessarily be regarded as unavailable as loci for the introduction of new functional groups although steric hurdles must be kept in mind.

Steric factors may also intervene disadvantageously if one *ortho* substituent is bulky enough, as typified by 2-*t*-butyl-, 2-benzoyl-4-dodecyloxy-, 2-methoxy-4-formyl-6-nitro- and 4-*t*-butyl-2-phenyl-phenol, and in these examples the hydroxyl groups are effectively and completely screened by

Table 1. Characteristics

No.	Compound	Structure	Crystalline form
1	2,4,6-Tri(4- <i>sec</i> -amylphenoxy)- <i>s</i> -triazine	Xa	blades <sup>ac</sup>
2	2,4,6-Tri(3-benzoxyphenoxy)- <i>s</i> -triazine	Xb	felted needles <sup>a</sup>
3	2,4,6-Tri(2-benzyl-4-chlorophenoxy)- <i>s</i> -triazine	Xc	fine nodules <sup>e</sup>
4	2,4,6-Tri(4-bromophenoxy)- <i>s</i> -triazine *	Xd	thin strands <sup>a</sup>
5	2,4,6-Tri(4- <i>t</i> -butylphenoxy)- <i>s</i> -triazine	Xe	spiky needles <sup>ac</sup>
6	2,4,6-Tri(5-chloro-2-formylphenoxy)- <i>s</i> -triazine	Xf	soft needles <sup>d</sup>
7	2,4,6-Tri(4-formyl-2-methoxyphenoxy)- <i>s</i> -triazine	Xg	hard nodules <sup>b</sup>
8	2,4,6-Tri(2-isopropyl-5-methylphenoxy)- <i>s</i> -triazine **	Xh	rhombohedrons <sup>a</sup>
9	2,4,6-Tri(3-isopropylphenoxy)- <i>s</i> -triazine	Xi	fine needles <sup>a</sup>
10	2,4,6-Tri(2-methoxyphenoxy)- <i>s</i> -triazine	Xj	rhombohedrons <sup>a</sup>
11	2,4,6-Tri(4-methoxyphenoxy)- <i>s</i> -triazine	Xk	felted needles <sup>a</sup>
12	2,4,6-Tri(4-methylthio-3-methylphenoxy)- <i>s</i> -triazine	Xl	blades <sup>f</sup>
13	2,4,6-Tri(4-methylthiophenoxy)- <i>s</i> -triazine	Xm	felted needles <sup>a</sup>
14	2,4,6-Tri(4-phenoxyphenoxy)- <i>s</i> -triazine	Xn	fine needles <sup>a</sup>
15	2,4,6-Tri(8-quinolinoxy)- <i>s</i> -triazine	IXf	fine prisms <sup>ab</sup>
16	2-Chloro-4,6-di(4-aceto-2-methoxyphenoxy)- <i>s</i> -triazine <sup>#2</sup>	IXb	hard nodules <sup>f</sup>
17	2-Chloro-4,6-di(2-chloro-4-phenylphenoxy)- <i>s</i> -triazine <sup>#1</sup>	IXc	hard nodules <sup>a</sup>
18	2-Chloro-4,6-di(2,6-dimethoxyphenoxy)- <i>s</i> -triazine <sup>#3</sup>	IXd	prisms <sup>a</sup>
19	2-Chloro-4,6-di(2,6-dimethylphenoxy)- <i>s</i> -triazine <sup>#4</sup>	IXe	fine needles <sup>g</sup>

Crystallization solvents: <sup>a</sup> ethyl acetate, <sup>b</sup> dimethylformamide, <sup>c</sup> methanol, <sup>d</sup> hexane, <sup>e</sup> acetone, <sup>f</sup> dioxan, <sup>g</sup> ethanol.

\* Bromine content; calc. 40.26 %, found 39.8 %.

their vicinal substituents. However, a wide range of substituted phenols can participate in reactions with cyanuric chloride. Thus the superficially highly hindered 4-*t*-butyl-2-benzylphenol can react to yield a triaryloxy compound and again by using molecular models it seems that the benzyl group in this phenol leaves sufficient space for the formation of the necessary intermediate in contrast to a benzoyl group in the same position. It can therefore be anticipated that neither the more spacious  $\beta$ -5' intermonomeric linkages of native lignin nor the diphenylmethane units formed by condensation reactions during pulping<sup>45</sup> are likely to sterically block an *ortho* phenolic hydroxyl group. In addition, previous work has shown that several phenols including *o*-cresol,<sup>13,46</sup>  $\alpha$ -naphthol<sup>13</sup> and salicylaldehyde<sup>17</sup> afford the corresponding triaryloxy-*s*-triazines. In this research 4-aceto-2-methoxy-, 4-*sec*-amyl-, 3-benzyloxy-, 2-benzyl-4-chloro-, 4-bromo-, 4-*t*-butyl-, 5-chloro-2-formyl-, 2-chloro-4-phenyl-, 2,6-dimethoxy-, 2,6-dimethyl-, 4-formyl-2-methoxy-, 2-isopropyl-5-methyl-, 3-isopropyl-, 2-methoxy-, 4-methoxy-, 3-methyl-4-methylthio-, 4-methylthio-, 4-phenoxy-phenol, and 8-hydroxyquinoline have been employed as the phenolic component. Under these conditions the aryloxy-*s*-triazine products (IXb-f, Xa-n) characterized in Table 1 were obtained.

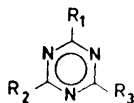
The formation of the tris-derivative (Xb) from 3-benzyloxyphenol (resorcinol monobenzoate) is noteworthy because Schaefer, Thurston and Dudley in

of aryloxy-*s*-triazines.

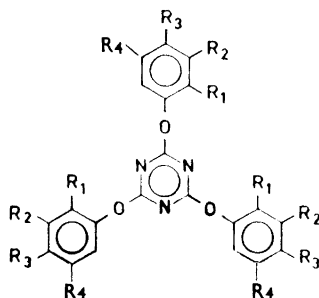
M.p. °C	Yield		Formula	M.W.	Carbon %		Hydrogen %		Nitrogen %	
	Wt.	%			Calc.	Found	Calc.	Found	Calc.	Found
183-184	6.7 g	59	C <sub>36</sub> H <sub>45</sub> N <sub>3</sub> O <sub>3</sub>	567.8	76.15	75.96	7.99	7.8	7.40	7.9
187-189	10.5	75	C <sub>42</sub> H <sub>27</sub> N <sub>3</sub> O <sub>9</sub>	717.7	70.28	70.33	3.79	4.0	5.85	5.9
144-145	4.0	55	C <sub>42</sub> H <sub>30</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub>	731.1					5.75	6.0
130-131	5.0	84	C <sub>21</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> Br <sub>3</sub>	594.1	42.44	42.71	2.04	2.0	7.07	7.3
191-193	4.1	40	C <sub>33</sub> H <sub>39</sub> N <sub>3</sub> O <sub>3</sub>	525.7	75.39	75.36	7.48	7.7	7.99	8.1
176-177	1.8	30	C <sub>24</sub> H <sub>12</sub> N <sub>3</sub> O <sub>6</sub> Cl <sub>3</sub>	544.7	52.90	52.75	2.22	2.4	7.71	7.9
208-210	7.5	70	C <sub>27</sub> H <sub>21</sub> N <sub>3</sub> O <sub>9</sub>	531.5					7.91	7.9
158-160	3.8	36	C <sub>33</sub> H <sub>39</sub> N <sub>3</sub> O <sub>3</sub>	525.7					7.99	8.0
130-132	5.0	52	C <sub>30</sub> H <sub>33</sub> N <sub>3</sub> O <sub>3</sub>	483.6					8.69	8.9
164-166	4.2	94	C <sub>24</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub>	447.5	64.43	63.83	4.73	4.9	9.39	9.3
199-200	4.2	94	C <sub>24</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub>	447.5	64.43	64.21	4.73	4.8	9.39	9.4
237-238	5.5	51	C <sub>27</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	537.7					7.81	7.5
216-217	8.1	81	C <sub>24</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	495.7					8.48	8.4
219-221	2.5	40	C <sub>38</sub> H <sub>27</sub> N <sub>3</sub> O <sub>6</sub>	633.7	73.93	73.66	4.30	4.2	6.63	6.6
260-262	2.8	55	C <sub>30</sub> H <sub>18</sub> N <sub>6</sub> O <sub>3</sub>	510.5	70.58	70.71	3.55	3.8	16.46	16.7
204-205	5.3	61	C <sub>21</sub> H <sub>18</sub> N <sub>3</sub> O <sub>6</sub> Cl	443.9					9.47	9.3
188-190	2.8	41	C <sub>27</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub>	520.8	62.26	62.31	3.10	3.1	8.07	8.2
195-197	8.0	93	C <sub>19</sub> H <sub>18</sub> N <sub>3</sub> O <sub>6</sub> Cl	419.8					10.02	9.9
163-165	6.8	94	C <sub>19</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> Cl	355.8					11.81	11.8

(#1,2,3,4.) Chlorine content: (1) calc. 20.4 %, found 19.7 %; (2) calc. 8.0 %, found 7.8 %; (3) calc. 8.4 %, found 8.2 %; (4) calc. 10.0 %, found 10.5 %.

\*\* Otto<sup>21</sup> gives m.p. 151° for this compound prepared by the fusion of cyanuric chloride and thymol.



- IX a  $R_1 = R_2 = R_3 = \text{Cl}$   
 b  $R_1 = \text{Cl}; R_2 = R_3 = 4\text{-aceto-2-methoxyphenoxy}$   
 c  $R_1 = \text{Cl}; R_2 = R_3 = 2\text{-chloro-4-phenylphenoxy}$   
 d  $R_1 = \text{Cl}; R_2 = R_3 = 2,6\text{-dimethoxyphenoxy}$   
 e  $R_1 = \text{Cl}; R_2 = R_3 = 2,6\text{-dimethylphenoxy}$   
 f  $R_1 = R_2 = R_3 = 8\text{-quinolinoxy}$



- |     |   |   |   |
|-----|---|---|---|
| X a | $R_3 = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ | h | $R_1 = \text{CH}(\text{CH}_3)_2; R_4 = \text{Me}$ |
| b   | $R_3 = \text{OOCPh}$  | i | $R_2 = \text{CH}(\text{CH}_3)_2$                  |
| c   | $R_1 = \text{CH}_2\text{Ph}; R_3 = \text{Cl}$                   | j | $R_1 = \text{OMe}$                                |
| d   | $R_3 = \text{Br}$   | k | $R_3 = \text{OMe}$                                |
| e   | $R_3 = \text{C}(\text{CH}_3)_3$                                 | l | $R_2 = \text{Me}; R_3 = \text{SMe}$               |
| f   | $R_1 = \text{CHO}; R_2 = \text{Cl}$                             | m | $R_3 = \text{SMe}$                                |
| g   | $R_1 = \text{OMe}; R_3 = \text{CHO}$                            | n | $R_3 = \text{OPh}$                                |

quest of hydroxyphenoxy-*s*-triazines were unable to obtain the corresponding *s*-triazine from resorcinol monoacetate.<sup>22</sup> This was ascribed to the gummy nature of the intermediate aryloxychloro-*s*-triazines and the ease of hydrolysis of a phenyl acetate relative to a phenyl benzoate may also have been a complicating factor.

Though no attempts were made to optimize yields, reaction at 25° as originally recommended<sup>22</sup> tended to give difficultly separable mixtures and superior results were again obtained, as with aldehydophenols,<sup>17</sup> at somewhat lower reaction temperatures. However, these reaction conditions were not uniformly successful when applied to the phenols listed above. Thus, 2-chloro-4-phenylphenol did not afford the corresponding triaryloxy-*s*-triazine but instead yielded the diaryloxy-monochloro-*s*-triazine (IXc) in which only two of the three chlorine atoms of the cyanuric chloride (IXa) had been replaced.

The failure to obtain the triaryloxy derivative probably cannot be ascribed to the steric effect of the chlorine atom flanking the hydroxyl reaction site since pentachlorophenol, with two flanking chlorine atoms, condenses with

(IXa) under very similar reaction conditions.<sup>22</sup> However, the condensation product was monochlorodiaryloxy-*s*-triazine which could not be further converted into the *tris*-pentachlorophenoxy-*s*-triazine; this inactivity being attributed to the very low solubility of the intermediate triazine. Presumably the low solubility of the pentacyclic diaryloxychloro-*s*-triazine (IXc) likewise prevents complete replacement of the chloro-functions in this case.

Solubility and not steric difficulties must also be responsible for the failure of acetovanillone to afford a triaryloxy-*s*-triazine since both vanillin and guaiacol yielded *tris*-derivatives under the same reaction conditions. In particular, the *pK* values of vanillin (7.4)<sup>47</sup> and acetovanillone should be very similar since both have carbonyl groups in the 4-position exercising negative inductive and mesomeric effects of the same magnitude.

The solubility characteristics were also disadvantageous in the reaction involving 4-(1-indanyl)phenol which afforded ill-defined mixtures of chloro-compounds which could not be separated by crystallization.

#### EXPERIMENTAL

*2,4,6-Tri-(4-sec-amyloxy)-s-triazine (Xa)*. A solution of cyanuric chloride (3.69 g, 0.02 moles) in acetone (100 ml) or dioxan (50 ml) was added with vigorous stirring to ice-water (200 ml). The resultant finely divided suspension, maintained at 0–5°, was then treated dropwise with a sodium hydroxide (2.4 g, 0.06 moles) solution (200 ml) of 4-*sec*-amyloxyphenol (9.85 g, 0.06 moles) added over 15 min. The mixture was stirred for 2 h at the same temperature and then for a further hour at room temperature. The crystalline solid which had separated was collected, well washed with water and then with methanol. Subsequent crystallization from methanol-ethyl acetate yielded the product characterized in Table I. The other eighteen compounds listed in Table I were similarly prepared. Chlorine and nitrogen analyses were carried out as previously described.<sup>1</sup>

Melting points were determined with Fisher-Johns Hot Stage Apparatus and are uncorrected.

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