

## Aromatic Keto- and Hydroxy-polyethers as Lignin Models. III \*

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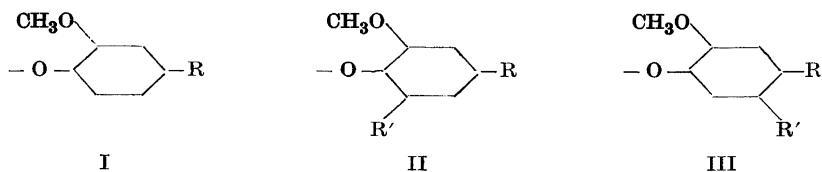
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A large number of methods have been employed for the direct oxidation of lignin, most of which, however, give poor yields of identifiable degradation products of any importance in relation to the structure of lignin.

About ten years ago Freudenberg *et al.*<sup>1, 2</sup> very successfully applied the method of oxidation with nitrobenzene and alkali to spruce lignin. With this lignin, *in situ* or in the form of "isolated lignin", for example lignin sulphonic acids, fairly high yields of vanillin and related compounds were obtained. In the following years this method was extensively used by v. Wacek and Kratzl<sup>3-7</sup> in their studies on the oxidation of various synthetic lignin models, mainly of the phenyl propane type. They investigated the influence of substituents on the course of the reaction and found that most phenyl propanes of type I furnished relatively large yields of identifiable oxidation products, especially if the side chain (R) carries several oxygen atoms or a double bond.

Much evidence can be brought forward in favour of the view that spruce lignin contains elements of types I—III<sup>8, 9</sup> \*\*.

Consequently it was of interest to study the oxidative degradation under comparable conditions of synthetic mononuclear compounds possessing these



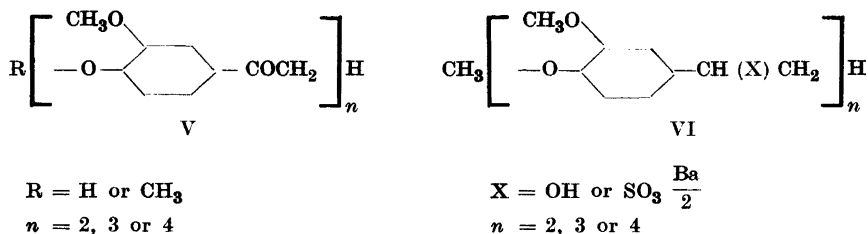
\* Part II. *Acta Chem. Scand.* 3 (1949) 1358.

\*\* Note added in proof: Richtzenhain<sup>30</sup> has recently shown that, in all probability, structures of type III do not exist as such in spruce lignin, but are formed during the isolation of the material.

general structures. (Tables 2 and 3.) Many of these compounds have been oxidized by v. Wacek and Kratzl and other workers. They, however, employed conditions not comparable to those chosen in this work.

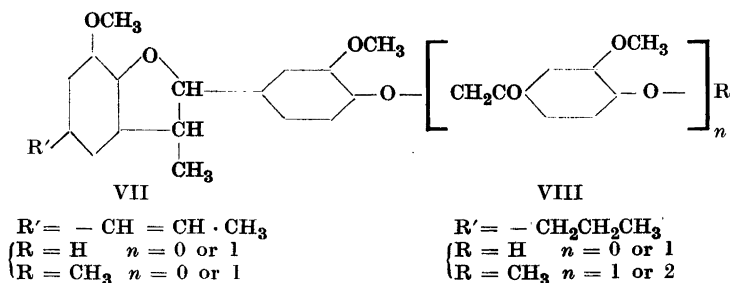
Special interest is attached to the degradation of synthetic chain molecules containing only "open elements" (I) or a combination of "open" and "condensed" (II or III) elements. This makes it possible to investigate whether an appreciable change in the yields of oxidation products is caused by the combination of the different elements into larger molecules. Furthermore, by comparing the yield of, for example, vanillin from lignin and from such model compounds one might be able to obtain valuable information regarding the relative frequency of open and condensed elements in lignin.

In Part II two series of compounds (V and VI), containing only elements of type I, were described.



As reported in Part II, the compounds V ( $\text{R} = \text{COC}_6\text{H}_5$ ) could not be properly reduced to the corresponding benzyl alcohols owing to deacylation and other complications. A new attempt to synthesize such alcohols containing a free phenolic hydroxyl group has now been made, starting from the benzyl ethers ( $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ ) instead of the corresponding benzoates. The method, however, failed as the subsequent cleavage of the benzyl ethers with sodium and alcohol (*cf.* Richtzenhain<sup>10</sup>) only resulted in unidentifiable amorphous products.

Another series of compounds (VII and VIII), containing elements of both type I and II, have also been synthesized.



The syntheses were accomplished by reacting dehydrodi-*isoeugenol*<sup>11</sup> (VII, R = H,  $n = 0$ ) or dihydrodehydrodi-*isoeugenol*<sup>12</sup> (VIII, R = H,  $n = 0$ ) with an appropriate bromo derivative in a manner closely analogous to the syntheses of the members of series V. (*Cf.* experimental part.)

The members of the series V, VI, VII, and VIII were subjected to oxidation with nitrobenzene and alkali. (Tables 4—7.) Some of the compounds were also heated with alkali alone. (Table 1.) The results of the latter experiments possess considerable interest in relation to the probable mechanism of the nitrobenzene oxidation process.

## RESULTS

## Heating with alkali

Table 1 summarizes the results obtained. All experiments were carried out by heating 2 g of the substance at 180° C for two hours with 60 ml of 2 *N* sodium hydroxide solution. The yields are calculated on the basis of the theoretically possible figures.

Table 1.

Compound	Veratric acid %	Other compounds %	Undissolved material %
V, R = CH <sub>3</sub> , $n = 2$	14	Acetoguaiacone (IX) * 75	0
V, R = CH <sub>3</sub> , $n = 3$	18	{ Acetoguaiacone 75 Vanillic acid 12	2
VI, X = OH, $n = 2$	3	Vinyl guaiacol (XI) * 18	7
VI, X = OH, $n = 3$	trace	Vinyl guaiacol 23	0

\* See Table 2, p. 1527.

## Oxidation with nitrobenzene and alkali

Very little has been reported in the literature on the conditions required for obtaining optimal vanillin yields<sup>2, 13</sup>. Therefore, the vanillin yields from a number of compounds were first studied as functions of temperature and time. All substances investigated behaved closely alike in this respect as is shown in Figs. 1 and 2.

A temperature of 180° and a reaction time of two hours is evidently sufficiently near the optimal experimental conditions.

The influence of the alkali concentration and the amounts of nitrobenzene and alkali was also studied.

Fig. 3 shows that in general 2 *N* sodium hydroxide gives the best results, but in the case of series VI (chain molecules containing benzyl alcoholic groupings) the use of stronger alkali greatly increases the vanillin yield. As seen from Figs. 4 and 5, the amounts of nitrobenzene and alkali seem to have little influence, provided they exceed a minimum value.

Even though only some of the compounds recorded in Tables 2—7 have been studied under varying conditions, it may safely be assumed that in general the optimum conditions are those described on p. 1527.

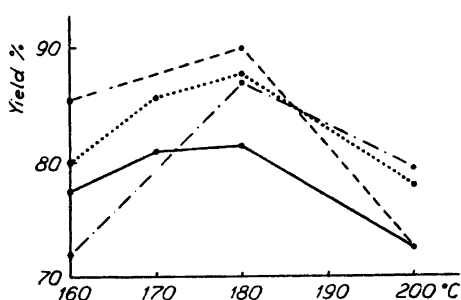


Fig. 1. Vanillin yield as function of reaction temperature (at optimal time). 60 ml/g of NaOH and 8 ml/g of nitrobenzene.

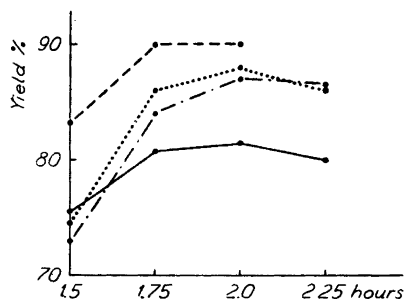


Fig. 2. Vanillin yield as function of reaction time at 180°. 60 ml/g of NaOH and 8 ml/g of nitrobenzene.

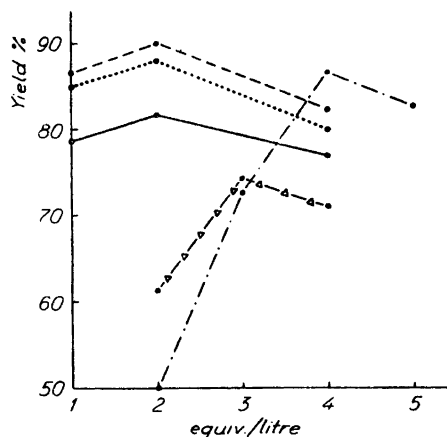


Fig. 3. Vanillin yield as function of alkali concentration. Reaction temp. 180°; time 2 hours. 60 ml/g of NaOH and 8 ml/g of nitrobenzene.

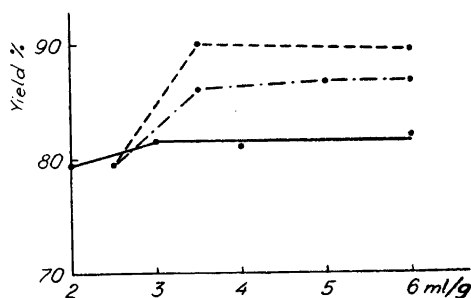


Fig. 4. Vanillin yield as function of the amount of nitrobenzene. Reaction temp. 180°; time 2 hours. 60 ml/g of NaOH.

————— *Acetoguaiacone*  
 - - - - - *Isoeugenol*  
 ..... *V*, *R* =  $\text{CH}_3$ , *n* = 2  
 - · - · - · *VI*, *X* = *OH* *n* = 2  
 Δ-Δ-Δ-Δ-Δ *VI*, *X* = *OH* *n* = 3

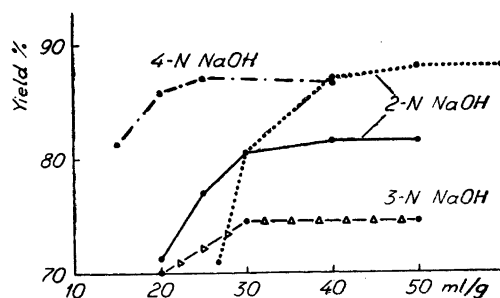


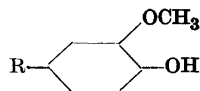
Fig. 5. Vanillin yield as function of the amount of alkali. Reaction temp.  $180^\circ$ ; time 2 hours. 8 ml/g of nitrobenzene.

The following tables give the results of the oxidation experiments. The yields are calculated on the basis of the theoretically possible figures.

“Total yield” is the sum of the yields of vanillin and vanillic acid.

In all experiments 0.5–2 g of substance were employed. The reaction was carried out at  $180^\circ$  with a reaction time of two hours. 2 *N* sodium hydroxide solution (60 ml per g of substance) was used unless otherwise stated. The amount of nitrobenzene was 8 ml per g of substance.

Table 2. Oxidation of compounds of the general structure:



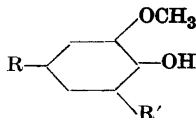
No.	R	Vanillin %	Vanillic acid %	Total yield %	Yields reported by other authors %
IX*	— $\text{CH}_2\text{OH}$	82 <sup>+</sup>	3	85	“very high” <sup>17</sup>
X*	— $\text{CH}_2\text{SO}_3 \frac{\text{Ba}}{2}$	80	—	—	—
XI <sup>14</sup>	— $\text{CH} = \text{CH}_2$	80	6	86	—
XII	— $\text{COCH}_3$	81	4	85	93 <sup>4</sup> , 83 <sup>18</sup>
XIII <sup>15</sup>	— $\text{COCH}_2\text{OH}$	66	10	76	—
XIV	— $\text{CH}_2\text{CH}_2\text{CH}_3$	17	—	—	6 <sup>5</sup>
XV	— $\text{COCH}_2\text{CH}_3$	30	—	—	11 <sup>4</sup>
XVI <sup>16</sup>	— $\text{COCH}(\text{OH})\text{CH}_3$	33	20	53	45 <sup>4</sup>
XVII	— $\text{CH}_2 - \text{CH} = \text{CH}_2$	88	—	—	—
XVIII	— $\text{CH} = \text{CH} - \text{CH}_3$	90	trace	90	89 <sup>19</sup>
XIX**	— $\text{CH} = \text{CHCHO}$	86	4	90	—

\* Kindly supplied by Dr. B. Lindgren.

\*\* Kindly supplied by Dr. E. Adler.

+ Alkali concentration 4 equiv./litre.

Table 3. Oxidation of compounds of the general structure:



No.	R	R'	Vanillin %	XXIII % (R = R' = CHO)	XXIV % (R = CHO, R' = COOH)
XX <sup>20</sup>	- CH <sub>2</sub> OH	- CH <sub>2</sub> OH	0.8	13	6
XXI <sup>21</sup>	- CH <sub>2</sub> -CH=CH <sub>2</sub>	- CH <sub>2</sub> OH	2.2	9	11
XXII <sup>22</sup>	- CHO	- CH <sub>2</sub> CH=CH <sub>2</sub>	1.6	20	6
XXIII <sup>23</sup>	- CHO	- CHO	1.5	12	26
XXIV *	- CHO	- COOH	2	—	—

\* This experiment is quoted from Freudenberg <sup>24</sup>.

In Tables 4—7 the yields are calculated on the following assumptions:

a) Elements with the para hydroxyl groups methylated yield no vanillin. This seems to be justified by the fact that neither acetoveratrone nor dehydrodi-*isoeugenol* methyl ether (VII, R = CH<sub>3</sub>, n = 0) gives any vanillin.

b) Elements of type II yield no vanillin. This is justified by the results summarized in Table 3.

Table 4. Oxidation of the members of series V (see p. 1524).

Compound	Vanillin %	Vanillic acid %	Total yield %
R = H, n = 2	63	11	74
R = H, n = 3	60	12	72
R = H, n = 4	60	—	—
R = CH <sub>3</sub> , n = 2 *	88	0	88
R = CH <sub>3</sub> , n = 3	71	4	75
R = CH <sub>3</sub> , n = 4	73	—	—

\* A similar compound containing bromine has been oxidized by Kratzl <sup>6</sup>.

Table 5. Oxidation of the members of series VI (see p. 1524).

Compound	Vanillin %	Vanillic acid %	Total yield %	Alkali concentration equiv./litre
X=OH, $n = 2$	87	0	87	4
X=OH, $n = 3$	74	4	78	3
X=OH, $n = 4$	72	—	—	3
X=SO <sub>3</sub> <sup>Ba</sup> / <sub>2</sub> , $n = 2$	83	0	83	4
X=SO <sub>3</sub> <sup>Ba</sup> / <sub>2</sub> , $n = 3$	70	—	—	3
X=SO <sub>3</sub> <sup>Ba</sup> / <sub>2</sub> , $n = 4$	71	—	—	3

Table 6. Oxidation of the members of series VII (see p. 1524).

Compound	Vanillin %	Vanillic acid %	Total yield %	XXIII %	XXIV %
R = H, $n = 0$	69	6	75	1	11
R = H, $n = 1$	66	8	74	trace	9
R = CH <sub>3</sub> , $n = 0$ <sup>11</sup>	0	0	—	—	—
R = CH <sub>3</sub> , $n = 1$	70	3	73	2	12

Table 7. Oxidation of the members of series VIII (see p. 1524).

Compound	Vanillin %	Vanillic acid %	Total yield %
R = H, $n = 0$	60	6	66
R = H, $n = 1$	67	—	—
R = CH <sub>3</sub> , $n = 1$	67	5	72
R = CH <sub>3</sub> , $n = 2$	62	—	—

## DISCUSSION

The results from the heating with alkali alone (Table 1) show that under the conditions employed the ether linkages are split by alkali, since the compounds were completely dissolved and degradation products corresponding to the "elements" were isolated. The yields in the last two experiments were low, probably due to polymerizations and condensations.

These results strongly support the view, first expressed by Lautsch<sup>25</sup>, that the oxidation is preceded by a fission of ether linkages and subsequent dehydration. The vinyl guaiacol formed from the members of series VI is evidently a dehydration product.

The oxidation of "condensed" compounds of type II (Table 3), containing side chains (R') of varying structure, clearly shows that no appreciable amounts of vanillin are formed from such elements. Yields amounting to 20—40 % of 5-formyl vanillin (XXIII) and 5-vanillin carboxylic acid (XXIV) were however obtained. The rest was amorphous and could not be identified.

Finally, Tables 4—7 show that with a few exceptions (the first members of series V, R = CH<sub>3</sub>, VI, and VIII) the total yields from the "open" elements vary only slightly, ranging from 72 to 78 %. The yields conform approximately with those obtained from the corresponding mononuclear compounds.

The sulphonic acids listed in Table 5 give approximately the same yields as the corresponding alcohols.

It is interesting to note that the main product obtained from the condensed elements in Table 6, 5-vanillin carboxylic acid (XXIV), has actually been isolated by Freudenberg<sup>1</sup> from the products obtained by oxidizing wood.

From the results discussed above it is evident that the vanillin yield obtained from simple mononuclear elements of type I is substantially the same as that obtained from chain molecules containing these elements connected by ether linkages (series V and VI). On the other hand, little or no vanillin is formed from elements of type II. Chains containing both types of elements connected by ether linkages will furnish vanillin in a yield corresponding to the amount of elements of type I present in the starting material. Consequently it appears to be possible to estimate the relative amounts of elements of the types I and II (or III?) in lignin preparations. This question will be discussed in a forthcoming paper on the oxidation of various lignin preparations and derivatives.



## EXPERIMENTAL

Dehydrodi-*isoeugenol*. (VII, R = H,  $n = 0$ )

This compound was prepared by a modification of the method described by Erdtman<sup>11</sup>: 50 g of *isoeugenol* (freshly distilled) were dissolved in 450 ml of alcohol (95 %) and 200 ml of water. Then 70 g of ferric chloride (crystallized) in 200 ml of water were added. The solution turned dark green and cloudy. A few crystals of dehydrodi-*isoeugenol* were added. After 24 hours in the refrigerator, a reddish white crystalline mass had separated and the solution was reddish yellow. The crystals were collected by filtration and washed with 45 % alcohol. Recrystallization from a small amount of alcohol yielded 15 g (30 %) of a colourless product. M. p. 132–133°.

Acetoguaiacyl-dehydrodi-*isoeugenol* methyl ether(VII, R = CH<sub>3</sub>,  $n = 1$ )

5 g of  $\omega$ -bromoacetoveratrone (see Part II), 6.3 g of dehydrodi-*isoeugenol* and 10 g of anhydrous potassium carbonate in 100 ml of absolute methyl ethyl ketone were refluxed under anhydrous conditions for 30 minutes. The mixture was washed with water, the methyl ethyl ketone layer dried over anhydrous sodium sulphate and concentrated *in vacuo*. An oil was obtained, which crystallized on cooling and trituration with alcohol. Yield 7.95 g (82 %). M. p. 112–120°. Repeated recrystallizations from alcohol yielded flat crystals of m. p. 123–124°.

C <sub>26</sub> H <sub>20</sub> O <sub>3</sub> (OCH <sub>3</sub> ) <sub>4</sub>	Calc.	C 71.4	H 6.40	OCH <sub>3</sub> 24.6
	Found	» 71.8	» 6.46	» 24.7

Acetoguaiacyl-dehydrodi-*isoeugenol* benzoate(VII, R = C<sub>6</sub>H<sub>5</sub>CO,  $n = 1$ )

4.2 g of  $\omega$ -bromobenzoylacetoguaiacone (see Part II), 4 g of dehydrodi-*isoeugenol* and 10 g of potassium carbonate in 100 ml of methyl ethyl ketone were reacted as described above. Yield 3.7 g (51 %). Recrystallization from alcohol yielded needles of m. p. 124–125°.

C <sub>33</sub> H <sub>25</sub> O <sub>5</sub> (OCH <sub>3</sub> ) <sub>3</sub>	Calc.	OCH <sub>3</sub> 15.7	Found	OCH <sub>3</sub> 15.9
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Acetoguaiacyl-dehydrodi-*isoeugenol*(VII, R = H,  $n = 1$ )

2.7 g of the above compound were refluxed with 2 ml of piperidine in 75 ml of alcohol for 30 minutes. The mixture was poured into water and acidified. An amorphous powder separated, which crystallized on treatment with alcohol. Yield 1.6 g (73 %). The crystals were dissolved in chloroform, the solution filtered through aluminium oxide and the

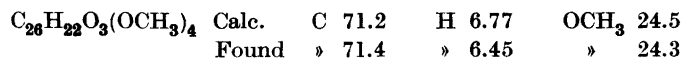
chloroform evaporated. The residue was recrystallized from dilute alcohol. Repeated recrystallizations yielded almost colourless crystals of m. p. 129–130°.



Methylation with diazomethane in ether furnished a methyl ether identical with VII, R = CH<sub>3</sub>, *n* = 1 (m. p. 123–124°).

Acetoguaiacyl-dihydrodehydrodi-*isoeugenol* methyl ether  
(VIII, R = CH<sub>3</sub>, *n* = 1)

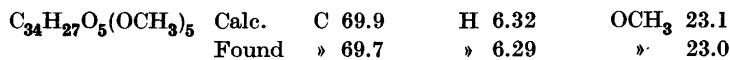
4 g of *ω*-bromoacetoveratrone, 5 g of dihydrodehydrodi-*isoeugenol*<sup>12</sup> and 10 g of potassium carbonate in 100 ml of methyl ethyl ketone were reacted as described above. Yield 6 g (78 %). Three recrystallizations from alcohol yielded flat crystals of m. p. 99–100°.



Di-(acetoguaiacyl)-dihydrodehydrodi-*isoeugenol* methyl ether

(VIII, R = CH<sub>3</sub>, *n* = 2)

5 g of *ω*-bromoacetoguaiacyl-acetoguaiacone methyl ether (see Part II), 3.88 g of dihydrodehydrodi-*isoeugenol* and 7.5 g of potassium carbonate in 75 ml of methyl ethyl ketone were reacted as described above. Yield 6.25 g (79 %). On recrystallization from methanol and then from acetone almost colourless crystals of m. p. 114–115° were obtained.



Acetoguaiacyl-dihydrodehydrodi-*isoeugenol* benzoate

(VIII, R = C<sub>6</sub>H<sub>5</sub>CO, *n* = 1)

5.3 g of *ω*-bromobenzoylacetoguaiacone, 5 g of dihydrodehydrodi-*isoeugenol* and 10 g of potassium carbonate in 100 ml of methyl ethyl ketone were reacted as described above. Yield 4.9 g (54 %). Two recrystallizations from methanol yielded needles of m. p. 98–99°.



Acetoguaiacyl-dihydrodehydrodi-*isoeugenol*

(VIII, R = H, *n* = 1)

The above compound was debenzoylated with piperidine as described for VII, R = H, *n* = 1 (p. 1531). Yield 73 %. Repeated recrystallizations from methanol yielded crystals of m. p. 82–83°.



Methylation with diazomethane in ether furnished a methyl ether identical with VIII,  $R = CH_3$ ,  $n = 1$  (m. p. 100–101°).

Acetoguaiacone benzyl ether

10 g of acetoguaiacone and 15 ml of benzyl chloride were dissolved in 150 ml of alcohol and 3.7 g of sodium hydroxide were added. After refluxing for 1.5 hours, the mixture was poured into water and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate and evaporated. An oil was obtained which crystallized on cooling. Yield 13.3 g (86 %). M. p. 81–84°. Two recrystallizations from petroleum (b. p. 40–60°) yielded needles of m. p. 86–86.5°.

$C_{15}H_{13}O_2(OCH_3)$	Calc. $OCH_3$ 12.1	Found $OCH_3$ 12.1
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$\omega$ -Bromoacetoguaiacone benzyl ether

10 g of acetoguaiacone benzyl ether were dissolved in 100 ml of chloroform. A solution of 6.25 g of bromine in 50 ml of chloroform was added in small portions. When all the bromine had reacted, the mixture was washed with bicarbonate solution and then with water. The chloroform solution was dried over anhydrous sodium sulphate and evaporated. An oil was obtained which crystallized on cooling. Yield 9.7 g (75 %). Three recrystallizations from benzene-petroleum (b. p. 120–140°) yielded needles of m. p. 102.5–103°.

$C_{15}H_{12}O_2Br(OCH_3)$	Calc. $OCH_3$ 9.3	Br 23.9
	Found » 9.2	» 23.8

3-Methoxy-4-benzyl oxyphenacyl coerulignol ether

5 g of  $\omega$ -bromoacetoguaiacone benzyl ether, 2.55 g of coerulignol and 5 g of anhydrous potassium carbonate in 50 ml of absolute methyl ethyl ketone were reacted as described on p. 1531. The resulting oil solidified to a yellowish mass. Yield 5.5 g (90 %). Recrystallization from a small amount of ether yielded colourless needles of m. p. 86.5–87.5°.

$C_{24}H_{22}O_3(OCH_3)_2$	Calc. C 74.3	H 6.72	$OCH_3$ 14.8
	Found » 74.0	» 6.50	» 14.9

Dihydro-3-methoxy-4-benzyl oxyphenacyl coerulignol ether

4 g of the above compound were reduced with 4 g of aluminium isopropoxide in 30 ml of absolute isopropyl alcohol following the procedure described in Part II. Yield 3.5 g (88 %). Recrystallization from ether yielded colourless plates of m. p. 55–57°.

$C_{24}H_{24}O_3(OCH_3)_2 + H_2O$	Calc. $OCH_3$ 14.1	$H_2O$ 4.1
	Found » 14.2	» 4.0

On drying the compound *in vacuo* at 70° a decrease in weight corresponding to one mole of water of crystallization was observed. The anhydrous substance had a m. p. of 62–63°.

$C_{24}H_{24}O_3(OCH_3)_2$     Calc.  $OCH_3$  14.7    Found  $OCH_3$  14.8

### Oxidation experiments

#### Apparatus

The oxidations were carried out in 100 ml autoclaves of stainless steel, rotating in an electrically heated oil bath. The temperature could be controlled with an accuracy of  $\pm 1^\circ$ .

A preliminary determination was made of the time taken for the contents of the autoclaves to attain the temperature of the oil-bath after immersion in it. This was done by placing in the autoclaves, each containing 50 ml of water, capillary tubes charged with substances of melting points ranging from 80 to 180° and immersing the autoclaves in the oil bath, which was maintained at 180°, for different lengths of time. From subsequent examination of the materials in the capillary tubes it was concluded that 8–9 minutes were required for the contents of the autoclaves to reach oil-bath temperature and this time is included in the reaction times reported in this paper.

#### Procedure

The autoclaves were charged, heated in the oil bath and then cooled with running water. The contents were subjected to steam distillation to remove nitrogenous compounds. After acidification, the residues were continuously extracted with benzene for about 24 hours.

#### Examination of the products

The benzene extracts were shaken with bisulphite, bicarbonate and sodium hydroxide in the usual manner. The various fractions were then investigated in the following way:

##### a) Bisulphite fraction.

(The procedure for the separation of all three of the aldehydic compounds isolated is given. In most cases, however, this fraction contained only vanillin.)

After acidification, the solution was freed from sulphur dioxide by passing a stream of carbon dioxide through the mixture at about 90° for 15–30 minutes. On cooling, a precipitate was obtained in some cases. This was removed by filtration, the filtrate extracted with ether and the ether solution dried over anhydrous sodium sulphate and evaporated. The residue was washed with small amounts of ether (A). The undissolved material together with the precipitate referred to above were triturated with a little acetone to remove coloured impurities. On recrystallization from water almost colourless needles of m. p. 252–254° were obtained. (Freudenberg and Klink<sup>28</sup> reported 255° for *5-vanillin carboxylic acid*, XXIV.)

$C_8H_8O_4(OCH_3)$     Calc.     $OCH_3$  15.8    eq.wt. 196  
                          Found    »    15.8    » » 195

The ether solution (A) was evaporated and the residue stirred with hot petroleum (b. p. 120–140°) (B). The undissolved residue was recrystallized from water, yielding yellowish crystals of m. p. 119–120°. The compound gave no depression with an authentic sample of *5-formyl vanillin* (XXIII).

From the petroleum solution (B) yellowish *vanillin* crystals separated. The final purification was effected by filtering an ether solution of this material through a column of aluminium oxide. On evaporation almost colourless vanillin, m. p. 79–81°, was obtained.

The analytical determination of vanillin was carried out using a modification of the method recommended by Mr. J. R. Salvesen of Marathon Corporation, Wisconsin, U. S. A., and kindly put at our disposal by him.

An aliquot of the original benzene extract (equivalent to about 50 mg of vanillin) is filtered through a column of aluminium oxide, previously treated with hydrochloric acid. The column is then thoroughly washed with ether and in this way the aldehydes XXIII and XXIV are adsorbed and only vanillin passes through. (If, as in most cases, vanillin is the only aldehyde present, this step is of course omitted.) The solution is then placed in a distilling flask together with 50 ml of water containing 0.4 g of sodium bisulphite and the solvent removed by distillation. The residual aqueous solution is filtered into a stoppered 300 ml Erlenmeyer flask. When the solution has attained room temperature, another 0.4 g of sodium bisulphite, a few drops of starch solution, and 2 ml of 10 % potassium iodide solution are added. After standing for 20 minutes the mixture is cooled to 0°. At this temperature 5 % potassium iodate solution is added from a burette until the equivalence point is almost reached. The mixture is then titrated with 0.05 *N* iodine solution to a faintly blue colour. Then 20 ml of 0.05 *N* iodine solution are added with a pipette. The mixture is heated on the water bath to 20°, 10 ml of concentrated hydrochloric acid added, and the solution heated to 35°. Then the flask is stoppered and allowed to stand at room temperature for five minutes, and the excess of iodine estimated by titration with 0.05 *N* sodium thiosulphate solution. One ml of 0.05 *N* iodine solution corresponds to 3.8 mg of vanillin.

The results obtained by this method were occasionally checked by gravimetric analyses employing 2,4-dinitrophenyl hydrazine (according to Pearl<sup>27</sup>) or 3-nitrobenzoyl hydrazine (according to Tomlinson and Hibbert<sup>28</sup>). These control experiments showed that the titration method gives results which are 2–3 % low. This was confirmed by model experiments with pure vanillin. All vanillin yields reported, therefore, have been corrected.

#### b) Bicarbonate fraction.

From this fraction only *vanillic acid* (m. p. 207–208°) and *veratric acid* (m. p. 175–176°) could be isolated. These compounds could easily be purified by vacuum sublimation and recrystallization from water or benzene-petroleum (b. p. 40–60°). When the two acids occurred together, however, it was very difficult to accomplish a quantitative separation. Several attempts to effect a separation by chromatographic adsorption on different media were unsuccessful. However, by fractional vacuum sublimation essentially as described by Hibbert *et al.*<sup>29</sup> for the separation of vanillin and syringic aldehyde, a fairly good separation could be achieved. The first fraction was collected at 120° (1 mm) and had a melting point ranging between 160 and 190° (veratric acid containing vanillic acid). The second fraction was collected at 150°. M. p. 204–207°. (Almost pure

vanillic acid.) On resublimation, the first fraction yielded further amounts of vanillic acid. This method is of course somewhat inaccurate and the reported yields of vanillic acid are probably not quantitative.

c) *Sodium hydroxide fraction.*

After filtering the ether extract through a column of aluminium oxide and evaporating the ether, these fractions generally yielded brown, sticky residues. In most cases orange red crystals of *p*-hydroxy azobenzene<sup>1</sup> (m. p. 150–151°) soon appeared. As a rule, no other crystalline compounds could be isolated, but a distinct smell of *guaiacol* was generally observed.

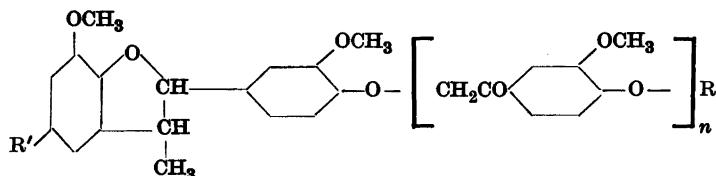
Only in the case of products of alkali fission experiments (see Table 1) could appreciable amounts of phenols be isolated from this fraction.

*Vinyl guaiacol* (XI) was isolated from the acidified solutions by steam distillation. The distillate was extracted with ether, the ether evaporated and the residue distilled *in vacuo*. A colourless oil, boiling at about 100° (5 mm), was obtained. The oil was benzoylated with benzoyl chloride in pyridine, yielding colourless crystals (from alcohol) of m. p. 109–111°. No depression was observed with an authentic sample of vinyl guaiacol benzoate<sup>14</sup>.

*Acetoguaiacone* (IX) was purified by vacuum sublimation and recrystallization from water. M. p. 114–115°.

#### SUMMARY

A series of lignin models of the general formula



have been synthesized. The members of this series and of two series described in Part II, containing only ether linked elements, have been subjected to oxidation with nitrobenzene and alkali. In addition some of the compounds have been heated with alkali alone.

The results show that the oxidation is preceded by alkaline fission of the ether linkages. Elements connected only by ether linkages give high yields of vanillin and vanillic acid; elements connected by carbon-carbon linkages give neither of these products.

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