

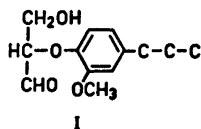
## Synthesis of Lignin Model Compounds for the Glyceraldehyde-2-aryl Ether Type of Structure

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The preparation of lignin model compounds for the glyceraldehyde-2-aryl ether type of structure (I) is described. The occurrence of structural elements in lignin of type I is discussed on the basis of results from studies of lignin degradation products.

The occurrence of glyceraldehyde-2-aryl ether structures (I) in lignin has been suggested on the basis of the formation of pyruvaldehyde on "acidolysis" of lignin and model compounds.<sup>1</sup> Later studies<sup>2-4</sup> have supported the presence of such structures in lignin and some additional evidence is given in the present paper. Moreover, recent results from studies on the enzymatic oxidation of lignin model compounds<sup>5</sup> have provided indirect support for the occurrence of lignin structures of type I. Structure I contains a "detached side chain". The



role of oxidative side chain detachment in lignin chemistry has been discussed extensively the past few years (see Refs. 6 and 7). In the present paper, the synthesis of model compounds for the glyceraldehyde-2-aryl ether type of structure is described. Some aspects concerning the occurrence of "detached side chains" in lignin are also discussed.

Model compound II (liquid) was obtained by heating the sodium salt of 2-methoxy-4-methylphenol with 2-bromo-1,1,3-trimethoxypropane

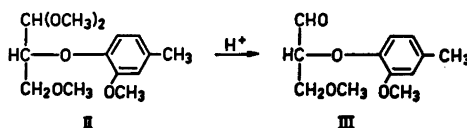
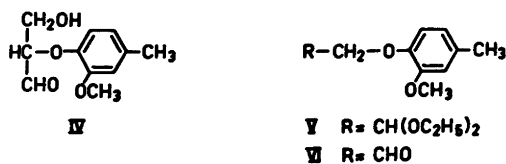


Fig. 1. Preparation of aldehyde III by hydrolysis of acetal II.

in ethanol solution. Although the yield was low, the product could be conveniently separated from the reaction mixture. Mild acidolysis of compound II gave aldehyde III (Fig. 1). This compound was obtained in a crystalline state (m.p. 44–46°). Aldehyde III is soluble in sulphite liquor and has been used as a model for structures of type I by Christofferson<sup>4</sup> in studies concerning the origin of pyruvaldehyde present in spent sulphite liquor (the formula given for the model compound in Ref. 4 is erroneous).

As reported previously,<sup>1</sup> attempts to prepare model compound IV by condensation of aldehyde VI with formaldehyde have been made. The product obtained gave 2-methoxy-4-methylphenol and pyruvaldehyde on "acidolysis", showed no infrared carbonyl absorption, and had a molecular weight which corresponded to a dimer of IV. On the basis of these properties, the product was suggested<sup>1</sup> to be a cyclic dimer of IV (in which the carbonyl groups take part in hemiacetal or acetal groups). The present paper describes experiments to prepare and characterize this product.

Starting material VI was prepared by hydrolysis of acetal V (obtained from the sodium



salt of 2-methoxy-4-methylphenol and 2-bromo-1,1-diethoxyethane; *cf.* Ref. 8). The compound was obtained as a crystalline monohydrate (VII; m.p. 74–75°) and this was used in the condensation experiments with formaldehyde (Fig. 2). Distillation *in vacuo* of hydrate VII gave aldehyde VI (m.p. 50–52°).

The above discussed product, suggested to be a dimer of IV (VIII) (Fig. 2), was separated from reaction mixtures obtained in condensation experiments and examined. The NMR spectrum revealed the presence of a 2-methoxy-4-methylphenoxy group, but otherwise showed no clearly discernible signals. Gel filtration properties were in accord with a dimer of IV. Additional structural evidence for compound VIII was provided by the fact that borohydride reduction gave glycerol ether X (TLC) (Fig. 3) (*cf.* Ref. 9). The conversion of VIII into compound X was demonstrated by acetylation of the reaction product and identification of the acetate derivative with the independently prepared diacetate XII. For the preparation of X and XII, see Experimental.

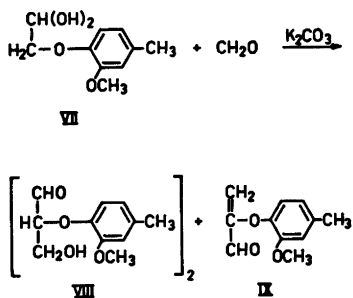


Fig. 2. Preparation of dimer VIII and aldehyde IX by condensation of compound VII with formaldehyde.

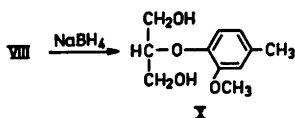
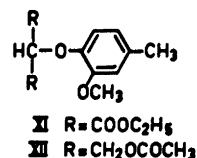


Fig. 3. Formation of glycerol ether X on reduction of dimer VIII with sodium borohydride.

In the preparation of dimer VIII an additional product was obtained, namely aldehyde IX. This compound is a likely intermediate in the acidolytic degradation<sup>1</sup> of compounds II–IV. In accord with expectations, it was found that compound IX gave pyruvaldehyde and 2-



methoxy-4-methylphenol in high yields on brief “acidolysis”. The fact that compound VI was stable during “acidolysis”<sup>1</sup> is also in accord with the assumption that an enol ether of type IX is an intermediate in the acidolytic cleavage of glyceraldehyde-2-aryl ethers.

In connection with studies of the formation of pyruvaldehyde on acidolysis of lignin, it was found that negligible amounts were formed from borohydride-reduced lignin (Ref. 3 and unpublished data). This is in accord with the proposal that the pyruvaldehyde originates from glyceraldehyde-2-aryl ethers, since such structures should be converted into glycerol-2-aryl ether structures on reduction with borohydride (*cf.* above and Ref. 9). The latter type of structure can be expected to give glycerol on “soda cooking”.<sup>10</sup> In fact, borohydride treated lignin (but not nontreated lignin) gave glycerol on “soda cooking” (2 M NaOH, 170°, 2 h). The amount was somewhat smaller than expected from the studies of the pyruvaldehyde formation from nontreated lignin. Rather unexpectedly, it was found that glycerol was destroyed to a great extent during “soda cooking”; this makes quantitative evaluations of the results uncertain.

Comparison of the yields of pyruvaldehyde on “acidolysis” of lignin and model compounds suggests that about 2% of the units in lignin are linked to glyceraldehyde with a 2-aryl ether bond. Calculations based on results from sulphite cooking studies<sup>4</sup> suggest a somewhat higher value.

During sulphite cooking structures of type I may be formed from arylglycerol- $\beta$ -aryl ether structures in electrophilic displacement reactions.<sup>10b</sup> To what extent such or originally present structures of type I give rise to the pyruvaldehyde formed on sulphite cooking might be elucidated by sulphite cooking experiments with model compounds of the arylglycerol- $\beta$ -aryl ether type and borohydride reduced lignin. In any case, it seems very likely that pyruvaldehyde (and pyruvic acid) present in sulphite liquor<sup>4</sup> arises from cleavage of glyceraldehyde-2-aryl ether groups.

Recent studies on lignin degradation products have demonstrated the occurrence of several types of structural elements containing units lacking propyl side chains (Refs. 7 and 11, see also Ref. 12). Based on yields of degradation products,<sup>13,14</sup> it seems that one of these types, namely the 1,2-diaryl-1,3-propanediol structure, is rather frequent in lignin. The figure obtained in the above-mentioned estimation of the frequency of "detached side chains" of the glyceraldehyde-2-aryl ether type therefore seems to be too low to fit with the number of units lacking side chains.

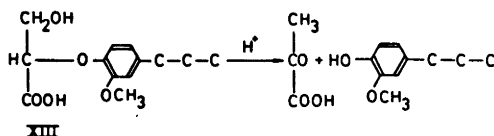


Fig. 4. Acidolytic cleavage of the proposed lignin structure XIII.

One explanation could be the occurrence of "detached side chains" of the glyceric acid-2-aryl ether type (XIII) (possibly with an esterified carboxylic group).<sup>15</sup> In connection with attempts to detect such structures in lignin the reaction shown in Fig. 4 was investigated. Model studies showed that ethers of type XIII were stable during "acidolysis". As expected, no pyruvic acid was formed on "acidolysis" of lignin. Additional model experiments showed that the reaction in Fig. 4 occurred to some extent on "acidolysis" at elevated temperature (140°) as indicated by the formation of pyruvic acid.

## EXPERIMENTAL

IR spectra were recorded using KBr pellets (solids) or NaCl discs (liquids), with a Beckman IR 9 instrument. NMR spectra were recorded

on a Varian A-60 instrument with TMS as internal standard. Mass spectra were taken on an AEI model MS 902 instrument. This equipment was also used for precise mass measurements of molecular ions. Elemental compositions were determined from these measurements using the tables of Beynon-Williams.<sup>16</sup>

Thin layer chromatography (TLC) was performed on silica gel plates. Eluents were benzene-ethyl acetate (1:1) ( $R_F$  values: X, 0.12; VIII, 0.17; 2-methoxy-4-methylphenol, 0.47; IX, 0.48; XII, 0.51) and benzene-ethyl acetate (4:1) ( $R_F$  values: III, 0.28; II, 0.36; 2-methoxy-4-methylphenol, 0.44). As developing agents iodine vapour (brown spots) and formalin- $H_2SO_4$  (1:9) were used (black spots after heating). Compounds VIII and IX were also made visible as purple spots by spraying with 2-methylindole in hydrochloric acid/ethanol and subsequent heating.

1,1,3-Trimethoxy-2-(2-methoxy-4-methylphenoxy)propane (II). 2-Methoxy-4-methylphenol (18.5 g) and 2-bromo-1,1,3-trimethoxypropane<sup>17</sup> (26.7 g) were added to a solution of 2.6 g Na in 50 ml ethanol and the mixture was heated in a steel autoclave at 150° for 5 h. After the NaBr which had formed was filtered off, the reaction mixture was diluted with dichloromethane, washed with 1 M NaOH and water, and dried over  $Na_2SO_4$ . Removal of the solvent by film evaporation gave an oil weighing 24.5 g. The product was chromatographed on a silica gel column (5 × 40 cm, 300 g  $SiO_2$ ) with benzene-ethyl acetate (3:1) as eluent. The eluate fraction 700–950 ml contained compound II (TLC). The eluted material dissolved in ether was washed with 1 M NaOH and an essentially pure product (TLC) weighing 2.0 g was obtained. Final purification was made by distillation *in vacuo* (0.05 torr = 7 Pa) at 90°.

Precise mass measurements of the molecular ion gave  $m/e$  270.14738. Calc. for  $C_{14}H_{22}O_5^+$ :  $m/e$  270.146713. The molecular ion was 34% of the base peak,  $m/e$  75, which is attributed to the fragment ion  $(CH_3O)_2CH^+$ .

NMR spectrum ( $\delta$  units; solvent,  $CCl_4$ ): 2.24 (3 H, singlet; Ar- $CH_3$ ), 3.30 (3 H, singlet) and 3.33 (3 H, singlet) [ $-CH(OCH_3)_2$ ], 3.41 (3 H, singlet;  $-CH_2-O-CH_3$ ), 3.71 (1 H, doublet,  $J=4.8$  Hz) and 3.73 (1 H, doublet,  $J=3.4$  Hz) ( $-CH_2-$ ), 3.78 (3 H, singlet; Ar-O- $CH_3$ ), 4.12 (1 H, doublet of triplets,  $J=3.4$  Hz and about 5 Hz; Ar-O- $CH_2$ ), 4.42 (1 H, doublet,  $J=5.1$ ;  $-CH(OCH_3)_2$ ), 6.49–6.91 (3 H, multiplet; aromatic protons).

3-Methoxy-2-(2-methoxy-4-methylphenoxy)propanal (III). Acetal II (0.33 g) was refluxed with 10 ml 0.2 M HCl in dioxan-water (9:1) for 10 min. The reaction mixture was neutralized with 10 ml 0.2 M  $NaHCO_3$  and extracted with chloroform (20 + 2 × 10 ml). The extract was dried over  $Na_2SO_4$ . The amount of solvent was reduced to 10 ml by film evaporation. TLC showed one predominating spot. The solution was chromatographed on a silica gel column

(32 × 2 cm; 50 g SiO<sub>2</sub>) with benzene-ethyl acetate (4:1) as eluent. From the eluate fraction 140–195 ml 0.21 g of an oil was obtained. Distillation (60–70°, 0.05 torr = 7 Pa) gave 0.12 g of an oil which crystallized on cooling (m.p. 44–46°). The IR spectrum showed a strong band at 1725 cm<sup>-1</sup> (C=O). The molecular ion (*m/e* 224) was the base peak in the mass spectrum. Precise mass measurements of the molecular ion gave *m/e* 224.1038. Calc. for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub><sup>+</sup>: *m/e* 224.104851.

NMR spectrum ( $\delta$  units; solvent, chloroform-*d*): 2.30 (3 H, singlet; Ar-CH<sub>3</sub>), 3.39 (3 H, singlet; -CH<sub>2</sub>-O-CH<sub>3</sub>), 3.82 (3 H, singlet; Ar-O-CH<sub>3</sub>), 3.82 (2 H, doublet, *J* = 4.3 Hz; -CH<sub>2</sub>-), 4.45 (1 H, doublet of triplets, *J* = 4.3 and 1.5 Hz; Ar-O-CH<sub>2</sub>), 6.54–6.98 (3 H, multiplet; aromatic protons), 9.88 (1 H, doublet, *J* = 1.5 Hz; -CHO).

*1,1-Diethoxy-2-(2-methoxy-4-methylphenoxy)-ethane (V)* was prepared from 2-bromo-1,1-diethoxyethane and 2-methoxy-4-methylphenol according to a procedure (method B) described by Julia and Tchernoff<sup>8</sup> for the synthesis of similar compounds. The product was purified by distillation (4 torr = 500 Pa, bath temperature 147°). Yield: 59%. (Found: C 66.51; H 8.89. Calc. for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>: C 66.12; H 8.72.) NMR spectrum ( $\delta$  units; solvent, chloroform-*d*): 1.21 (6 H, triplet, *J* = 7.0; -CH<sub>2</sub>-CH<sub>3</sub>), 2.26 (3 H, singlet; Ar-CH<sub>3</sub>), 3.66 (2 H, quartet, *J* = 7.0) and 3.70 (2 H, quartet, *J* = 7.1) (-CH<sub>2</sub>-CH<sub>2</sub>), 3.80 (3 H, singlet; -O-CH<sub>3</sub>), 4.01 (2 H, doublet, *J* = 5.2; Ar-O-CH<sub>2</sub>-), 4.84 (1 H, triplet, *J* = 5.2 Hz; >CH-), 6.53–6.91 (3 H, multiplet; aromatic protons).

*1,1-Dihydroxy-2-(2-methoxy-4-methylphenoxy)-ethane (VII)*. Acetal V (8.0 g) was refluxed with 100 ml 0.2 M HCl in dioxan-water (4:1) for 10 min. The reaction mixture was neutralized with 0.4 M NaHCO<sub>3</sub> to pH 6 and extracted with a total of 200 ml chloroform. The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed by film evaporation. The residual oil weighed 6.35 g. From ether saturated with water, 4.9 g crystals (m.p. 74–75°) was obtained. (Found: C 60.70; H 7.07; OCH<sub>3</sub> 15.79. Calc. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>: C 60.59; H 7.12; OCH<sub>3</sub> 15.66.)

NMR spectrum ( $\delta$  units, 20°; solvent, DMSO-*d*<sub>6</sub>): 2.24 (3 H, singlet; Ar-CH<sub>3</sub>), 3.75 (3 H, singlet; -O-CH<sub>3</sub>), 3.88 (2 H, doublet, *J* = 5.2 Hz; -CH<sub>2</sub>-), 5.13 (1 H, approximately quintet, *J* = 6.3 and 5.2 Hz), 5.97 (2 H, doublet, *J* = 6.3 Hz; -OH), 6.43–6.91 (3 H, multiplet, aromatic protons). When the spectrum was recorded at higher temperatures, the presence of aldehyde VI was indicated.

*2-(2-Methoxy-4-methylphenoxy)acetaldehyde (VI)* was obtained upon distillation (0.04 torr = 5 Pa, 50–60°) of compound VII. The product melted at 51–52°. (Found: C 66.28; H 6.59; OCH<sub>3</sub> 17.33. Calc. for C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>: C 66.65; H 6.71; OCH<sub>3</sub> 17.22.) The IR spectrum showed a strong band at 1735 cm<sup>-1</sup> (C=O). NMR spectrum ( $\delta$  units; solvent chloroform-*d*): 2.29 (3 H, singlet;

Ar-CH<sub>3</sub>), 3.83 (3 H, singlet; -O-CH<sub>3</sub>), 4.50 (2 H, doublet, *J* = 1.3 Hz; -CH<sub>2</sub>-), 6.66–6.73 (3 H, multiplet; aromatic protons), 9.84 (1 H, triplet, *J* = 1.3 Hz; -CHO).

The compound gave a semicarbazone melting at 174–176° after recrystallization from ethanol-water. (Found: C 55.89; H 6.29; O 20.74; N 17.85; OCH<sub>3</sub> 13.15. Calc. for C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>-N<sub>3</sub>(OCH<sub>3</sub>): C 55.69; H 6.37; O 20.23; N 17.71; OCH<sub>3</sub> 13.08.)

*Dimer (VIII) of 3-hydroxy-2-(2-methoxy-4-methylphenoxy)propanal (IV)*. Compound VII (5.0 g) was dissolved in 20 ml DMSO and 100 mg K<sub>2</sub>CO<sub>3</sub> and 10 ml 37% formaldehyde solution were added. The mixture was stirred for 20 min at room temperature. After the addition of 170 ml 0.1 M KH<sub>2</sub>PO<sub>4</sub>, the reaction mixture was extracted with chloroform (100 + 3 × 75 ml). The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and solvent removed by film evaporation. The residue, according to TLC, contained two components which gave purple spots with 2-methylindole in hydrochloric acid/ethanol, *i.e.* liberated pyruvaldehyde on acid treatment, *cf.* Ref. 1. The components were separated by chromatography on a silica gel column (2.5 × 40 cm; 170 g SiO<sub>2</sub>) with benzene-ethyl acetate (1:1) as eluent. It may be noted that DMSO present in the residue was adsorbed at the top of the column. Eluate fraction 120–150 ml gave 0.78 g product (*fraction A*). Eluate fraction 190–260 ml gave 0.95 g product (*fraction B*).

Fraction A consisted essentially of 2-(2-methoxy-4-methylphenoxy)acrolein (IX). This was separated by chromatography on silica gel with dichloromethane as eluent. A product weighing 0.57 g was obtained. Purification by distillation (0.01 torr = 1 Pa, 55–63°) gave 0.40 g of an oil.

Mass measurements of the molecular ion gave *m/e* 192.077100. Calc. for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub><sup>+</sup>: *m/e* 192.078638.

The IR spectrum showed a strong band at 1705 cm<sup>-1</sup> (C=O).

NMR spectrum ( $\delta$  units; solvent, chloroform-*d*): 2.39 (3 H, singlet, Ar-CH<sub>3</sub>), 3.93 (3 H, singlet; -O-CH<sub>3</sub>), 5.03 (1 H, doublet, *J* = 2.6 Hz) and 5.21 (1 H, doublet, *J* = 2.6 Hz) (=CH<sub>2</sub>), 6.61–6.98 (3 H, multiplet, aromatic protons), 9.43 (1 H, singlet, -CHO).

Fraction B was subjected to column chromatography on silica gel using gradient elution according to the previously described standard procedure<sup>14a</sup> to isolate the major component, which was subsequently purified by distillation (80–110°, 0.05 torr = 7 Pa). It has previously been suggested<sup>1</sup> that the product obtained in this way is a dimer of IV, in this paper denoted VIII. This was derived from the facts that no carbonyl band appeared in the IR, the molecular weight determined by osmometry fitted very well with a dimer of IV, and pyruvaldehyde and 2-methoxy-4-methylphenol were formed on "acidolysis".<sup>1</sup> We have made further studies which support the assumption that the product

is a dimer of IV. Thus gel filtration on Sephadex G-25 with dioxan-water (1:1) as eluent<sup>18</sup> supported a dimeric structure ( $K_d = 0.4$ ;  $K_d'$  values for compounds III and X were about 0.7). Furthermore, reduction with  $\text{NaBH}_4$  gave glycerol ether X (see below). The NMR spectrum showed the presence of a 2-methoxy-4-methylphenoxy group, but was otherwise too complex to permit interpretation; possibly the product is a mixture of isomeric dimers. The mass spectrum corresponded to monomer IV. Mass measurements of the molecular ion gave  $m/e$  210.091. Calc. for  $\text{C}_{11}\text{H}_{14}\text{O}_4^+$ ;  $m/e$  210.089 202. The molecular ion was 84% of the base peak,  $m/e$  138, which is proposed to be due to fragment ion (2-methoxy-4-methylphenol)<sup>+</sup>.

*Diethyl 2-(2-methoxy-4-methylphenoxy)-malonate (XI)*. Diethyl chloromalonate (35 g) was refluxed with the sodium salt of 2-methoxy-4-methylphenol (29 g) in 100 ml ethanol for 6 h (cf. Ref. 10a). The reaction mixture was poured into water and extracted with ether. The ether layer was dried over  $\text{Na}_2\text{SO}_4$  and the ether removed by film evaporation. The residual oil was distilled (b.p. 116–120°/1 torr = 100 Pa). Yield: 24.5 g (46%).

NMR spectrum ( $\delta$  units, chloroform-*d*): 1.26 (6 H, triplet,  $J = 7.1$ ;  $-\text{CH}_2\text{CH}_3$ ), 2.26 (3 H, singlet; Ar- $\text{CH}_3$ ), 3.78 (3 H, singlet; Ar-O- $\text{CH}_3$ ), 4.26 (4 H, quartet,  $J = 7.1$ ;  $-\text{CH}_2-$ ), 5.16 (1 H, singlet,  $-\text{CH} <$ ), 6.52–7.01 (3 H, multiplet; aromatic protons).

*2-(2-Methoxy-4-methylphenoxy)-1,3-propanediol (X)* was prepared by reduction of ester XI with  $\text{LiAlH}_4$  (cf. Ref. 10a). The crude product was purified by chromatography on a silica gel column with ethyl acetate as eluent followed by distillation (110°, 0.02 torr = 3 Pa). The product was obtained as a colorless oil.

Precise mass measurements of the molecular ion gave  $m/e$  212.101946. Calc. for  $\text{C}_{11}\text{H}_{16}\text{O}_4^+$ ;  $m/e$  212.104851.

NMR spectrum ( $\delta$  units; solvent, chloroform-*d*): 2.27 (3 H, singlet; Ar- $\text{CH}_3$ ), 3.54 (2 H, singlet;  $-\text{OH}$ ), 3.78 (3 H, singlet;  $-\text{O}-\text{CH}_3$ ), 3.76 (4 H, doublet,  $J = 4$  Hz;  $-\text{CH}_2-$ ), 3.99 (1 H, multiplet;  $-\text{CH} <$ ), 6.47–7.01 (3 H, multiplet; aromatic protons).

*Diacetate (XII) of compound X*. Compound X was acetylated with acetic anhydride-pyridine. Excess reagent was removed by distillation and the residual product purified by distillation *in vacuo*. (Found: C 61.10; H 6.63. Calc. for  $\text{C}_{15}\text{H}_{20}\text{O}_6$ ; C 60.80; H 6.80.) The IR spectrum showed a strong band at 1745  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ). NMR spectrum ( $\delta$  units; solvent, chloroform-*d*): 2.03 (6 H, singlet;  $-\text{CO}-\text{CH}_3$ ), 2.28 (3 H, singlet; Ar- $\text{CH}_3$ ), 3.79 (3 H, singlet;  $-\text{O}-\text{CH}_3$ ), 4.3 (5 H, multiplet;  $-\text{CH}_2-\text{CH}(\text{OAr})-\text{CH}_2-$ ), 6.55–6.95 (3 H, multiplet; aromatic protons).

*Reduction of compound VIII (dimer of IV)*. Compound VIII (100 mg) was dissolved in 5 ml dioxan and 2–3 ml  $\text{NaBH}_4$  solution was added (2 g  $\text{NaBH}_4$  in 100 ml 0.25 M NaOH). After 1 h

the solution was extracted with chloroform. The extract was dried over  $\text{Na}_2\text{SO}_4$  and the solvent evaporated. Examination by TLC indicated that the product was compound X (small amounts of contaminants were present). The product was acetylated with acetic anhydride-pyridine and the resulting acetate was purified by chromatography on silica gel with benzene-ethyl acetate (4:1) as eluent. A pure product (TLC) weighing 105 mg was obtained. This was shown to be identical with authentic diacetate XII by IR and NMR analyses.

*Acidolysis of aldehyde IX*. Aldehyde IX (6.0 mg) was acidolysed for 5 min in 10 ml 0.2 M HCl in dioxan-water (9:1). Five ml 0.4 M  $\text{NaHCO}_3$  was added and the mixture extracted with chloroform (10+2×5 ml). It was demonstrated that the major part of the pyruvaldehyde remains in the aqueous layer during this work up procedure. To the aqueous layer 50 ml 2,4-dinitrophenylhydrazine solution was added (3 g 2,4-dinitrophenylhydrazine was dissolved in 100 ml 72%  $\text{HClO}_4$  and 100 ml  $\text{H}_2\text{O}$  added). After 1 h the precipitate was filtered off and washed with 12%  $\text{HClO}_4$ , water, and ethanol. The precipitate (11.6 mg) was identified as the bis[(2,4-dinitrophenyl)hydrazone] of pyruvaldehyde. The formation of 2-methoxy-4-methylphenol was demonstrated by examination of the organic layer with TLC.

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