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Acid Degradation of Lignin

Part VII.* The Cleavage of Ether Bonds

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Acidolysis (heating with 0.2 M hydrogen chloride in dioxane-water (9 : 1) at reflux temperature) of lignin for 4 h, extensively depolymerizes the lignin with the formation of substantial amounts of low molecular weight phenols. The importance of the hydrolysis of different types of ether bonds for the degradation is discussed. Most important for the degradation is cleavage of arylglycerol-β-aryl ethers. A detailed examination of the reaction mixtures obtained on 4 h acidolysis of some model compounds of this type has been made, and in this connection some aspects of the cleavage reaction are discussed. From a comparison of the results obtained with lignin and model compounds, the proportion of "uncondensed" guaiacyl units in spruce lignin carrying a glycerol side chain linked to an adjacent unit by a β-ether bond could be estimated to be 10–15 % (units linked to the lignin by diaryl ether bonds not included).

Acidolysis of lignin by heating with 0.2 M hydrogen chloride in dioxane-water (9 : 1) at reflux temperature ** for 4 h effects a degradation of the lignin with formation of considerable amounts of low molecular weight phenols.[1] This can readily be visualized in gel filtration experiments. The absorbance at 280 nm *versus* effluent volume on gel filtration (Sephadex) of a softwood lignin [Björkman lignin from spruce [2] (*Picea abies*)] and its 4 h acidolysis product is shown in Fig. 1. The curve obtained in the run carried out with the acidolysis product exhibits three peaks, P, D, and M. Calibration of the column with known compounds and experiments on a preparative scale indicate that these peaks correspond to polymers and oligomers (P), dimers (D), and monomers (M).*** As seen in Fig. 1, non-treated lignin contains no low molecular weight material.

* Part VI, see Ref. 7a.

** Throughout this paper the term "acidolysis" is used specifically for this treatment.

*** The terms monomer, dimer, oligomer, and polymer in this paper refer to the number of aromatic rings present in the compounds.

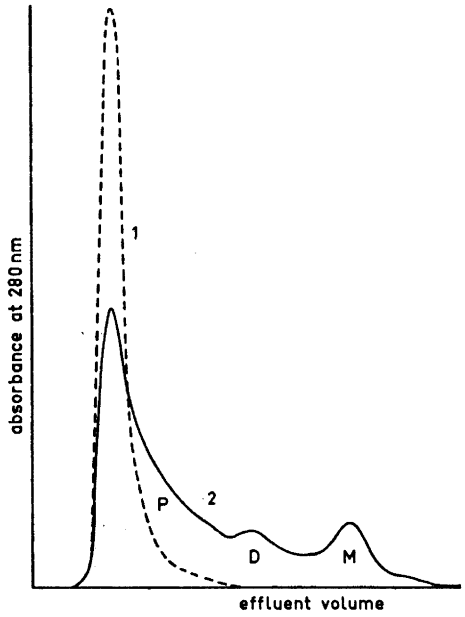
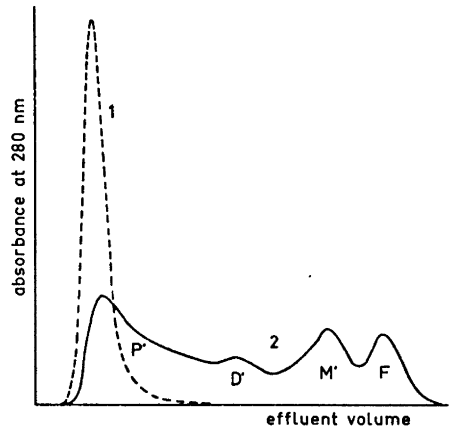


Fig. 1. Gel filtration of Björkman lignin from spruce (1) and its reaction product obtained on 4 h acidolysis (2) on Sephadex G-25 with dioxane – water (1 : 1) as eluting solvent.

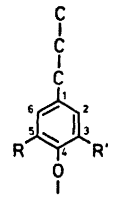


Fi.g 2. Gel filtration of Björkman lignin from birch (1) and its reaction product obtained on 4 h acidolysis (2) on Sephadex G-25 with dioxane – water (1 : 1) as eluting solvent.

The corresponding curves obtained in a similar investigation of a hardwood lignin [Björkman lignin from birch [3] (*Betula verrucosa*)] are shown in Fig. 2. The curve obtained in the experiment with the acidolysis product showed peaks P′, D′, and M′ which, as the corresponding peaks (P, D, and M) obtained in the experiment with spruce lignin (Fig. 1), can be attributed to polymers and oligomers (P′), dimers (D′), and monomers (M′). In addition, a fourth peak, denoted F, appeared. Peak F was found to be due to the presence of 2-furaldehyde, which obviously is produced during the acid treatment from minor amounts of xylan present in the lignin preparation (concerning the occurrence of carbohydrates in Björkman lignin preparations, see Refs. 2 and 3). As with spruce lignin (Fig. 1), non-treated birch lignin contains no low molecular weight material (Fig. 2).

It appears from the gel filtration experiments (Figs. 1 and 2) that birch lignin is more thoroughly degraded than spruce lignin on acidolysis. This is in accord with the fact that in preparative experiments considerably higher yields of monomers and dimers are obtained from birch lignin (30 % of the original lignin) than from spruce lignin (17 % of the original lignin).[1] Undoubtedly, this difference in formation of low molecular weight material is

closely related to the fact that a relatively large proportion of the phenylpropane units in birch lignin are of the syringyl type (III). In syringyl units the 3- as well as the 5-position is occupied by methoxyl groups; the 5-position and also the 3-position in case of units of type I play an important role for the connection of units of types I and II to adjacent units by acid-stable linkages (biphenyl and diaryl ether linkages). In addition, a greater frequency of acid-labile ether bonds in birch lignin[4] should also be of importance in accounting for the difference.



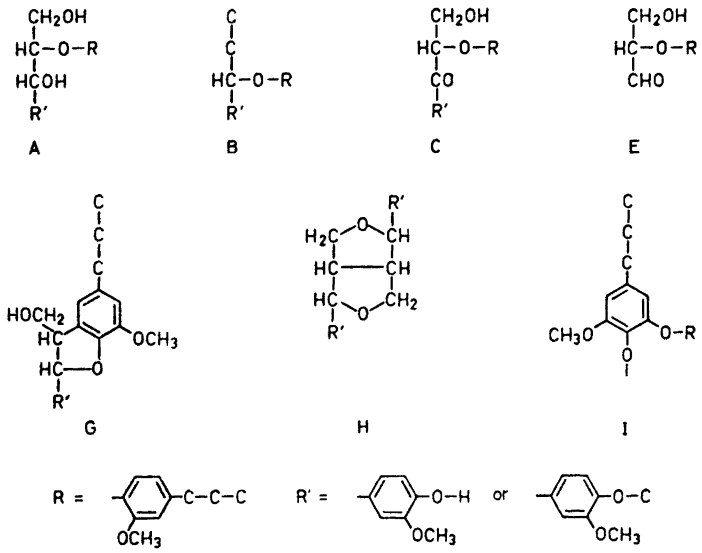
I R=R'=H
II R=H R'=OCH_3
III R=R'=OCH_3

The degradation of lignin on acidolysis can essentially be attributed to cleavage of various ether bonds. A degradation reaction which involves a rupture of a carbon–carbon bond represents the liberation of formaldehyde from terminal hydroxymethyl groups;[5] this reaction, however, is of minor importance for the depolymerization of the lignin (concerning the possible occurrence of a further reaction involving a cleavage of a carbon–carbon bond, see Ref. 6). Minor amounts of quinone ketals may be present in lignin;[7] their hydrolysis may also be of some minor importance for the acidolytic degradation of lignin. The hydrolysis of ester groupings present in lignin (see, *e.g.*, Ref. 8) should also contribute to the degradation on acidolysis.

In the present paper, the cleavage on acidolysis of different types of ether bonds present or presumed to be present in lignin is discussed on the basis of studies with model compounds and lignin. Most important for the degradation of lignin on acidolysis is cleavage of arylglycerol-β-aryl ethers. A detailed examination of the reaction mixtures obtained on 4 h acidolysis of some model compounds of this type has therefore been made.

SUSCEPTIBILITY OF DIFFERENT TYPES OF ETHERS TO CLEAVAGE ON ACIDOLYSIS

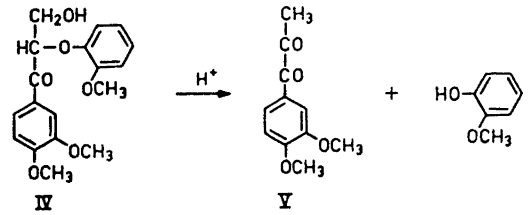
Arylglycerol-β-aryl ethers (type A). The cleavage of ethers of type A on acidolysis has been studied extensively by Adler and co-workers.[9–11] From these studies it can be concluded that cleavage of such ethers essentially accounts for the depolymerization of lignin on acidolysis. Some aspects of the cleavage reaction and an examination of the 4 h acidolysis mixtures of some model compounds representative of this type of structure are treated in a separate section of this paper.



For simplicity, units of type II have been used in the examples of ether structures shown above; alternatively, the units can be of type I or, when possible, of type III.

Noncyclic benzyl aryl ethers (type B). Ethers of type B are known to undergo cleavage on relatively mild acidic treatment.[12–14] It therefore can be assumed that ethers of type B are rapidly cleaved on acidolysis, and that this reaction contributes to the degradation of the lignin. However, the number of such units in lignin is considerably lower than the number of ether structures of type A and, therefore, their cleavage must be of limited importance for the degradation process.

Ketol ether structures of type C may be responsible for part of the ring-conjugated carbonyl groups present in lignin.[15] Acidolysis of a model compound representative of this type of structure, 3-hydroxy-2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1-propanone (IV), resulted in a cleavage of the ether bond with formation of 1-(3,4-dimethoxyphenyl)-1,2-propanedione (V) and guaiacol in high yield (Fig. 3); the reaction was relatively slow and traces of starting material could be detected (thin layer chromatography) in the reaction mixture even after 20 h acidolysis. Thus a cleavage of ethers of this type present in lignin can be expected on acidolysis. The formation of V and guaiacol on acid treatment (heating with 28 % sulphuric acid) of ketol ether IV has been encountered previously.[16] Minor amounts of ketone XIII are formed on acidolysis of spruce lignin; the presence of XIII in the acidolysis mixture can be explained as a result of the acidolytic action on ether structures of type A (see Discussion). However, a gas chromatographic examination, using trimethylsilyl derivatives, indicated that larger amounts of XIII were formed from lignin than from borohydride reduced lignin on 4 h acidolysis. Because it seems possible that the excess of XIII originates from ether structures of



IV V

Fig. 3. Acidolysis of 3-hydroxy-2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1-propanone (IV).

type C, this finding provides support for the occurrence of minor amounts of such structures in lignin.

Quinol ethers (type D). Lignin may contain small amounts of certain types of quinol ether structures.[7a] Experiments with model compounds indicate that such ether structures can be expected to undergo hydrolysis on acidolysis.[7a,17]

Glyceraldehyde-2-aryl ethers (type E). Evidence for the presence of minor amounts of ethers of type E in lignin has been obtained.[6,18,5,19] According to experiments with model compounds, such ethers are cleaved on acidolysis with formation of pyruvaldehyde and a unit with a free phenolic group.[6]

Methoxyl groups (type F). Minor amounts of methanol are formed on acidolysis of lignin; hydrolysis of methoxyl groups in quinone and quinonoid units may explain the major part of the methanol liberated.[7a] From experiments with model compounds it can be concluded that ethers of type F in units of types II and III are essentially stable to acidolysis.[7a]

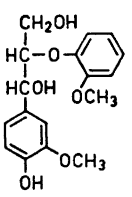
Cyclic benzyl aryl ethers (phenylcoumaran structures) (type G). According to experiments with model compounds, the benzyl aryl ethers in phenylcoumarane structures are cleaved on acidolysis to a minor extent with the formation of stilbene structures.[20] Because the two units in structures of type G still are connected in these stilbene structures, cleavage of the ether bond does not lead to any separation of phenylpropane units.

Dialkyl ethers of the type present in the pinoresinol type of structure (type H). The 4 h acidolysis mixture of (+)-pinoresinol has been found to consist of a mixture of (+)-pinoresinol and (+)-epipinoresinol;[1] thus, the acidic treatment did not result in a cleavage of the ether bonds. Similarly (±)-syringaresinol has been found to give a mixture of (±)-syringaresinol and (±)-episyringaresinol on 4 h acidolysis [21] (*cf.* Ref. 22).

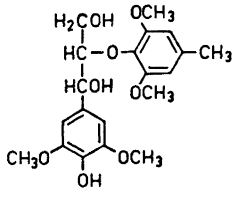
Diaryl ethers (type I). About the same yields of dicarboxylic acids derived from this type of structure have been obtained on permanganate oxidation (after methylation) of lignin samples subjected to acidolysis for various periods of time.[23] This indicates that ethers of type I are stable to acidolysis.

ACIDOLYSIS OF MODEL COMPOUNDS OF THE ARYLGLYCEROL-β-ARYL ETHER TYPE

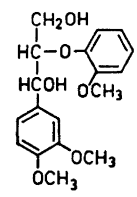
The reaction mixtures obtained on 4 h acidolysis of model compounds VI, VII, and VIII were examined. Cleavage of the β-aryl ether bond in compounds VI and VIII on acid treatment has been studied by Adler and coworkers (ethanolysis [24,25,9] and acidolysis [9–11]). Of particular interest for the present work are the findings that compounds VI and VIII give guaiacol in high yield on acidolysis, and that ketones IX, XI, XII, and XIII are formed on acidolysis of compound VI.[9–11] Ketol IX could be isolated from the reaction mixture obtained on brief acidolysis of compound VI.[11]



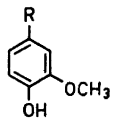
VI

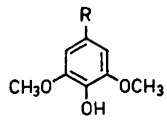


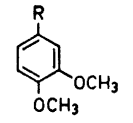
VII



VIII







IX R=CH_2COCH_2OH
X R=$CH(OH)COCH_3$
XI R=$COCH(OH)CH_3$
XII R=CH_2COCH_3
XIII R=$COCOCH_3$
XIV R=CHO
XV R=CH_2CHO

XVI R=CH_2COCH_2OH
XVII R=$COCH(OH)CH_3$

XVIII R=CH_2COCH_2OH
XIX R=$CH(OH)COCH_3$
XX R=$COCH(OH)CH_3$
XXI R=CHO

Fractionation of the acidolysis product of VI by column chromatography on silica gel gave, in addition to some starting material (3.5 %), guaiacol (73 – 74 %), ketol IX (53 %), a mixture of isomeric ketols X and XI (15 %), and an additional fraction which was 9 % of the starting material. Examination of this latter fraction by paper chromatography revealed the presence of vanillin (XIV) and traces of XII and XIII.

In a second experiment, high molecular weight material (dimers and oligomers) was initially separated from the reaction mixture by gel filtration (Fig. 4). The high molecular weight fraction, which was 17 % of the starting material, consisted of starting material (3 %) and unidentified constituents (14 %). Minor amounts of coloured materials present in the original acidolysis mixture accumulated in the high molecular weight fraction. The material present in the high molecular weight fraction showed a UV maximum at 279 nm, and exhibited only a very slight absorption at higher wavelengths. Thus, appreciable amounts of dimeric products with strong absorption in the region above 279 nm of the types detected in lignin acidolysis mixtures [1]

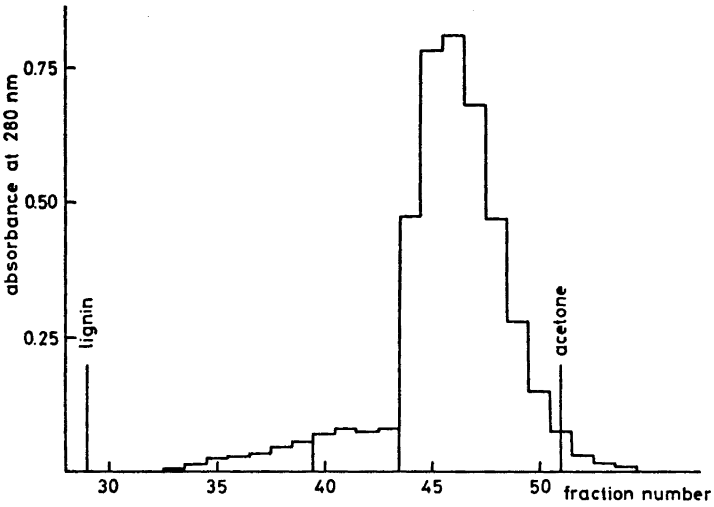


Fig. 4. Gel filtration of the reaction product obtained on 4 h acidolysis of compound VI [Sephadex G-25, eluting solvent, dioxane – water (1 : 1)]. Residual starting material was found in fractions 40 – 43. The location of the elution peaks of a polymer (lignin) and a small molecule (acetone) are shown.

were not formed on acidolysis of VI. The monomer fraction was subjected to column chromatography on silica gel. Yields of guaiacol, ketol IX, and mixture of isomeric ketols X and XI were 72 %, 53 %, and 14 %, respectively; these yields are essentially the same as the corresponding yields obtained in the experiment described above. Additional fractions, which comprised 4 % of the starting material, were found to contain vanillin (XIV), homovanillin (XV), XII and probably XIII. That clear evidence for the presence of XIII was not obtained can be explained by the fact that this compound is eluted from the gel filtration column somewhat prior to other detected monomers (*cf.* Ref. 26) and therefore, in part, is present in the high molecular weight fraction.

From the acidolysis product of VII, 2,6-dimethoxy-4-methylphenol could be separated in 63 % yield by column chromatography; in a second experiment a purer product was obtained in 52 % yield. In addition, ketol XVI was obtained in an impure fraction which corresponded to a yield of 30 %. The NMR spectrum indicated that the fraction consisted essentially of XVI, and gas chromatography, after silylation, showed one strong peak corresponding in retention time to the trimethylsilyl derivative of XVI. Crystalline XVI could be obtained from the fraction by purification by preparative thin layer chromatography followed by crystallization from chloroform/benzene. Examination of additional fractions revealed the presence of ketol XVII.

The reaction product obtained on 4 h acidolysis of VIII was fractionated by column chromatography on silica gel. Guaiacol (42 – 43 %), ketol XVIII (34 %), a mixture of ketols XIX and XX (5 %), VIII (42 %), and a further fraction (14 % of the starting material) in which 3,4-dimethoxybenzaldehyde

(XXI) was present (paper chromatography) were obtained. The fraction containing VIII consisted, according to an NMR examination, of a mixture of the *erythro* and *threo* forms of VIII. Crystals of the *erythro* form could be separated from the fraction. Since the *erythro* form of VIII was used as starting material, isomerization [*via* an intermediate benzylium ion (*cf.* Fig. 5)] must have occurred during the acid treatment. The fraction was contaminated with minor amounts of ketol XVIII (thin layer chromatography). The amount of ketol XVIII was found to correspond to < 3 % yield; an upper limit for the total yield of ketol XVIII would thus be 37 %.

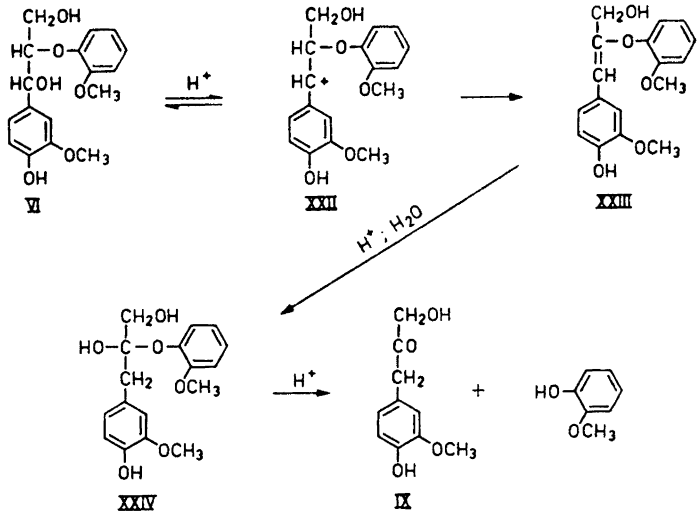
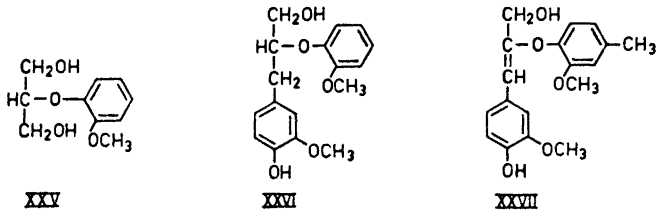


Fig. 5. Reaction route for the formation of ketol IX and guaiacol on acidolysis of compound VI.

Previous studies [9–11,27] indicated that ketol IX is formed from VI according to the reaction route shown in Fig. 5. In the first step enol ether XXIII is formed *via* an intermediate benzylium ion XXII, in a relatively slow reaction. The enol ether XXIII then rapidly undergoes hydrolysis, *via* hemiketal XXIV, with formation of ketol IX and guaiacol. According to the reaction route shown in Fig. 5, the presence of a benzyl alcoholic group (or other group, *e.g.* a benzyl aryl ether group, which would give rise to a benzylium ion on acidolysis) on the carbon atom adjacent to the β-ether bond is a prerequisite for the cleavage. The fact that no liberation of phenolic groups was observed ($\Delta\varepsilon$ for ionization [28]) on acidolysis of compounds XXV * and XXVI [14] is in accord with this assumption.

Support for an enol ether intermediate was obtained from the fact that an enol ether of type XXIII, compound XXVII, on acidolysis was rapidly hydrolysed with formation of ketol IX and 2-methoxy-4-methylphenol. In a preparative experiment enol ether XXVII was subjected to acidolysis

* The authors thank Dr. J. Gierer for a gift of this compound.



for 10 min. The yields of ketol IX and 2-methoxy-4-methylphenol were 74 % and 87 %, respectively. In addition, a fraction consisting of ketols X and XI, corresponding to a yield of 8.8 %, was obtained. It has been shown [29] that ketols IX, X, and XI, under acidolysis conditions, are interrelated in the following way: IX → X ⇌ XI. The conversion IX → X is a relatively slow reaction while the equilibrium X ⇌ XI is established relatively rapidly. Since formation of ketols X and XI from IX occurs relatively slowly, the presence of substantial amounts of X and XI in the 10 min acidolysis mixture obtained from XXVII is surprising. An explanation would be that a partial allylic rearrangement of XXVII occurs and that the isomeric enol ether formed is hydrolysed with formation of ketol X (and 2-methoxy-4-methylphenol). Applied to the suggested enol ether intermediate (XXIII) in the acidolysis of VI, this would imply that a partial isomerization occurs (possibly an equilibrium is established) and the isomeric enol ether (XXVIII) formed by allylic rearrangement is then hydrolysed with formation of ketol X and guaiacol (Fig. 6).

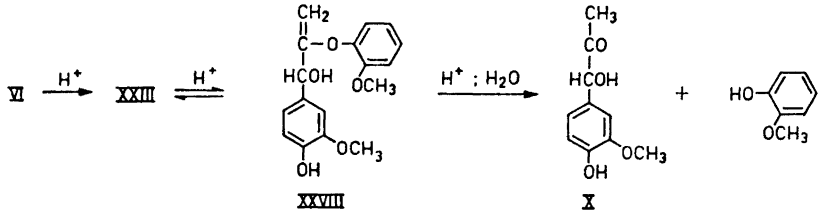


Fig. 6. Reaction route for the acidolytic cleavage of the β-aryl ether bond in compound VI with formation of ketol X and guaiacol.

Analysis of the 4 h acidolysis products from VI and IX by gas chromatography using trimethylsilyl derivatives showed that ketols XI and IX were present in the ratio 1 : 6 in case of VI (ketols XI and IX occur in about the same proportion in the 4 h acidolysis mixture of spruce lignin [30]), and that the corresponding ratio with IX was 1 : 12. With consideration of the interrelationships of ketols IX, X, and XI on acidolysis (see above), these findings provide support for the reaction route shown in Fig. 6 in the acidolysis of VI. According to the reaction routes shown in Figs. 5 and 6, and considering the interrelationships of compounds IX – XIII on acidolysis, the reactions involved in the formation of these products on acidolysis of VI can be summarized as in Fig. 7.

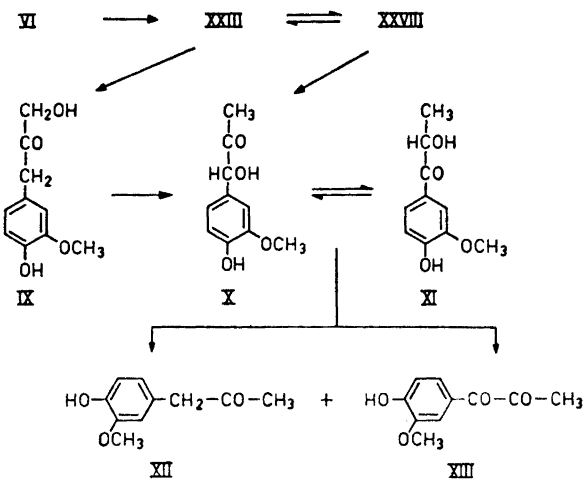


Fig. 7. Reaction scheme for the formation of ketones IX – XIII on acidolysis of compound VI.

A third reaction route for the acidolytic degradation of VI may be involved to a minor extent, *viz.* a fragmentation with formation of homovanillin (XV), guaiacol, and formaldehyde.[5]

It is presumed that the acidolytic cleavage of the β-aryl ether bonds in compounds VII and VIII with formation of ketols occurs in a manner analogous to the corresponding degradation of VI. The conversion of ketol XVIII into ketols XIX and XX on acidolysis has been demonstrated.[29] From a comparison of the 4 h acidolysis mixtures of compounds VI and VIII, and from earlier analytical studies with these two compounds,[9] it appears that VIII reacts more slowly than compound VI. Such a difference in reactivity between guaiacyl and 3,4-dimethoxyphenyl compounds has been observed in other acid-catalyzed reactions suggested to involve benzylium ions, *e.g.* the hydrolysis of benzyl aryl ethers.[14] Therefore, the difference in reaction rate between compounds VI and VIII provides support for a benzylium ion intermediate in the acidolytic degradation of these compounds. It is in this connection of some interest to note that ketol XVIII (half-life period ≈ 80 h) disappears more slowly than ketol IX (half-life period ≈ 30 h) on acidolysis; the reaction of both compounds follows roughly first order kinetics.[31]

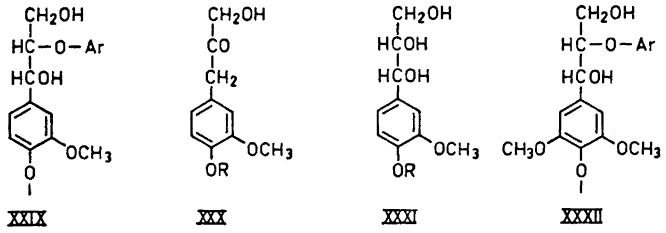
DISCUSSION

Among the different types of ether structures discussed above (types A – I), ethers of types A – G have been found to be cleaved to a greater or lesser extent on acidolysis. Cleavage of the benzyl aryl ether bond in phenylcoumaran structures (type G) results in a ring opening and does not contribute to the depolymerization of the lignin. Small amounts of ether structures of types C and D may be present in lignin; cleavage of such ethers may be of

some importance for the depolymerization of the lignin. Hydrolysis of glyceraldehyde-2-aryl ether structures (type E) and a small proportion of the methyl ethers (type F) contributes to the degradation to a small extent. The cleavage of the remaining two types of ethers (types A and B) is primarily responsible for the degradation of lignin on acidolysis.

Undoubtedly, the cleavage of arylglycerol-β-aryl ethers (type A) is the most important reaction for the degradation. Studies of the acid degradation of lignin and lignin model compounds (ethanolysis [24,25,32,9,33] and acidolysis [9–11,1]) as well as numerous other investigations (see, *e.g.*, Refs. 34, 35, 33), provide strong evidence for the occurrence of ethers of type A as an important structure in lignin. The presence of β-aryl ether structures in lignin was originally suggested by Erdtman [36] on the basis of biogenetic considerations.

In addition to the predominating constituent, ketol IX, and other products, compounds X – XV occur in the monomer fraction obtained from the 4 h acidolysis product of spruce lignin.[1] As mentioned above, compounds IX – XV are also present in the 4 h acidolysis product of compound VI. In both cases the relative abundance of the compounds is similar. (The formation of relatively larger amounts of vanillin from lignin has been discussed in Ref. 1. More of compound XIII seems to be formed from lignin; this may be due to a formation of XIII from ether structures of type C in lignin, see above.) This similarity in formation of compounds IX – XV can be explained by the occurrence of β-ether units of type XXIX in the lignin.



XXIX XXX XXXI XXXII

Ar = aromatic ring in adjacent unit
R = adjacent unit

Comparison of the yield of ketol IX from lignin and model compound VI suggests that about 10 % of the units in the lignin are of type XXIX. A calculation based on the yield of ketol XVIII from compound VIII, which is representative of units of type XXIX with an etherified phenol group, and on the yield of ketol IX from lignin indicates that the proportion of units of type XXIX is about 15 %. Thus, the results indicate that in spruce lignin, 10 – 15 % of the units are of type XXIX*. The total number of units carrying a glycerol side chain linked to an adjacent unit by a β-aryl ether bond (including "uncondensed units" (XXIX) as well as "condensed units") has been estimated to be about twice as many.[9,10,31] This is in accord with the fact

* Acidolysis will not liberate ketol IX from units of this type linked to the lignin by acid-stable ether bonds (diaryl ether linkages, type I) and such units are therefore not included in this estimation.

that about equal amounts of "uncondensed" and "condensed" units are present in spruce lignin.[10,37]

Units of types XXX and XXXI, the presence in lignin of which has been discussed, could also be expected to give rise to formation of ketol IX (and its conversion products X – XIII) on acidolysis. Thus hydrolysis of ether bonds would liberate IX and XXXIII; the latter was found to be rapidly (< 20 min) converted to ketol IX on acidolysis (Fig. 8). In a preparative experiment ketol IX was isolated in 68 % yield from the reaction product obtained on 2 h acidolysis of XXXIII. The fact that arylglycerol XXXIV, *i.e.* compound XXXIII with etherified (methylated) phenol group, gave ketol XVIII on acidolysis (Fig. 8), suggests that units of type XXXI can be converted to units of type XXX on acidolysis. In an analogous manner, a third arylglycerol, compound XXXV gave ketol XVI on brief acidolysis (Fig. 8). On acidolysis, compound XXXIV as well as compound XXXV disappears rapidly (< 20 min).

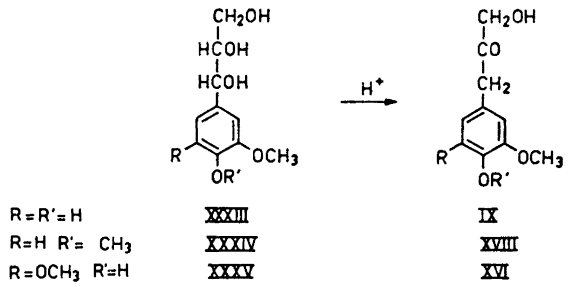


Fig. 8. Formation of ketols IX, XVIII, and XVI on acidolysis of arylglycerols XXXIII, XXXIV, and XXXV, respectively.

No direct evidence for the occurrence of units of type XXX in lignin has been obtained, but it has been considered conceivable that such units, in part, are responsible for the presence of unconjugated carbonyl groups in lignin (Ref. 15, see also the schematic model of the constitution of spruce lignin in Ref. 35c). Support for the occurrence of units with glycerol side chains (XXXI) has been achieved recently.[38] In this connection, it is worth mentioning that guaiacylglycerol (XXXIII) has been detected in extractives from a conifer [39] and that glucosides of guaiacylglycerol, isolated from pine needles,[40a] also have been detected in the cambial sap of pine.[40]

On oxidation with periodate, the terminal hydroxymethyl groups in units of type XXX, as well as XXXI, would be released as formaldehyde. Only small amounts of formaldehyde are formed on oxidation of lignin with periodate (Refs. 41 and 42; it has recently been found that on oxidation of Björkman lignin from spruce, as well as from birch, with periodate, the amount of formaldehyde formed was 0.029 (spruce) and 0.012 (birch) mol/OCH_3 [31]), thus implying that only small amounts of such groupings can be present in lignin, and consequently, that such structures are of minor importance for the formation of IX – XIII on acidolysis. The observations that "Hibbert

ketones" are obtained on ethanolysis of "periodate lignin" [43] and that the yield of IX – XIII on acidolysis of borohydride reduced lignin and non-reduced lignin is about the same (see Ref. 1), are in accord with the view that ketones formed originate from ethers of type A rather than units of types XXX and XXXI.

As mentioned previously,[1] fractions of monomers and dimers have been separated from the reaction mixture obtained on 4 h acidolysis of a hardwood lignin [Björkman lignin from birch (*Betula verrucosa*)]. From the monomer fraction (20 % of the original lignin), ketols IX and XVI, in addition to a number of other compounds, have been isolated in a crystalline state. Ketol XVI melting at 102° (lit.[44] 106.5 – 107.5°), was obtained in a fraction which was 5 % of the original lignin. According to a gas chromatographic examination using trimethylsilyl derivatives, ketols IX and XVI were found to be the predominating constituents of the monomer fraction.[30] It is assumed that ketol XVI is produced from structural elements of type XXXII. The fact that a relatively large amount of ketol XVI was obtained from the lignin while the yield of ketol XVI obtained on 4 h acidolysis of model compound VII, which is representative of structures of type XXXII, was rather low suggests that a relatively large proportion of structural elements of type XXXII are present in birch lignin. This is in accord with a recent appraisal of the composition of birch lignin.[4] The yield of ketol IX, which would originate from units of type XXIX, was 2 – 3 % of the original lignin.

Prominent constituents of the dimer fraction (10 % of the original lignin) were (±)-syringaresinol, (±)-episyringaresinol, and acidolysis products from 1,2-diaryl-1,3-propanediols.

Quantitatively important products among the low molecular weight phenols formed on degradation of a hardwood (beech, *Fagus silvatica*) by "mild hydrolysis" are (±)-syringaresinol, syringylglycerol (XXXV), and 1,2-diaryl-1,3-propanediols.[45,46] It appears, from what has been said in this paper, that acidolysis of these products will give rise to prominent constituents in the acidolysis mixture obtained from birch lignin. Thus there seems to be a similarity with respect to origin of low molecular weight phenols formed on "mild hydrolysis" of beech wood and on the more complete degradation of isolated birch lignin on acidolysis.

EXPERIMENTAL

Materials. Dioxane and ethyl acetate were purified according to Ref. 47. Silica gel for column chromatography was Mallinckrodt analytical reagent, 100 mesh, dried at 110° overnight.

IR spectra were recorded using KBr pellets (solids) or NaCl prisms (liquids), with a Beckman IR 9 instrument. *NMR spectra* were recorded on a Varian A-60 instrument with TMS as internal standard and chloroform-*d* as solvent. *UV spectra* were recorded on a Beckman DK-2A instrument.

Paper chromatography. For the detection of compounds X, XI, XII, XIII, XIV, XVIII, XIX, and XX by paper chromatography using the solvent system ligroin – water – chloroform – methanol (7 : 5 : 2 : 1), [48] see Refs. 29 and 1. In the present work, compound VI (R_F 0.04, orange) and 3,4-dimethoxybenzaldehyde (XXI) (R_F 0.84, purple) were also detected using this solvent system (for detection agents, see Ref. 29). An additional solvent system [butanol – ethanol – ammonia – water (40 : 10 : 1 : 49) [49]] was used for the detection of VI (R_F 0.83). For the detection of ketol XVII the solvent

system toluene – acetic acid – water (4 : 1 : 5) (descending, upper layer moving phase) was used (R_F 0.24). As detecting agents diazotized sulphanilic acid in 10 % aqueous Na_2CO_3 (light pink) and 2,4-dinitrophenylhydrazine in dilute hydrochloric acid (orange) were used.

Thin layer chromatography was carried out on plates coated with a 0.3 mm thick layer of silica gel (Merck HF_{254}). Unless otherwise specified, benzene – ethyl acetate (1 : 1) was used as eluting agent and the compounds were made visible by exposure to iodine vapour (brown spots). R_F values: VI, 0.12; VIII, 0.15; XVI, 0.17; IV, 0.22; XVIII, 0.26; XXVII, 0.44; V, 0.50; guaiacol, 0.64; 2-methoxy-4-methylphenol, 0.65.

Preparative thin layer chromatography was performed on plates similar to those used for analytical purposes. The zones of silica gel containing the materials of interest, detected by UV light, were scratched off and the compounds eluted with acetone.

Analytical gel filtration experiments were performed as described in Ref. 30. The presence of 2-furaldehyde in the eluate corresponding to peak F in Fig. 2 was demonstrated by UV examinations and thin layer chromatography (R_F 0.50; yellow spot with 2-methylindol in hydrochloric acid/ethanol).

Standard procedure for column chromatography on silica gel using gradient elution, see Ref. 1.

2-(2-Methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol (VIII) (*erythro* form) was prepared by catalytic hydrogenation of 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1-propanone (IV) instead of by reduction with $NaBH_4$ of the same compound as described by Adler *et al.*[24] Compound IV (2.0 g) was hydrogenated at room temperature in 50 ml dioxane with 0.20 g 10 % Pd/C as catalyst. After 90 min the calculated amount of hydrogen had been consumed and uptake had ceased. The catalyst was filtered off and the solvent removed by film evaporation. Crystallization from ether gave 1.1 g product of m.p. 94 – 96°. Recrystallization from benzene gave 0.9 g VIII of m.p. 98 – 99° (lit.[50] 97.5 – 98.5°).

3-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxy-5-methylphenoxy)-2-propene-1-ol (XXVII) was prepared from the acetate of the methyl ester of α-(2-methoxy-p-tolyloxy)-ferulic acid [51] by reduction with $LiAlH_4$ according to a procedure which differed somewhat from that used by Freudenberg and Müller.[51] A solution of 2.45 g of the starting material in 150 ml ether was added dropwise, during a 40 min period, to a refluxing solution of 0.9 g $LiAlH_4$ in 200 ml ether. The reaction mixture was refluxed for an additional 80 min. Excess reagent was decomposed by addition of ether saturated with water. Subsequently, 100 ml of water was added and the reaction mixture was carefully neutralized with dilute H_2SO_4. The ether layer was separated and the aqueous layer extracted with an additional amount of ether. The combined ether layers were dried over Na_2SO_4 and the solvent was removed by film evaporation. The residue was dissolved in glacial acetic acid and water was added. A crystalline product with an unsharp m.p. (60 – 90°), weighing 1.3 g, was obtained. Recrystallization twice from acetic acid/water and subsequently, once from dichloromethane/hexane did not change the m.p. The product gave only one spot on examination by thin layer chromatography. On the basis of spectral properties, elemental analysis, and weight loss on drying at 45°/0.01 mmHg (found 5.3 %, calc. 5.4 %), the product was characterized as a monohydrate of XXVII. (Found: C 64.29; H 6.53; OCH_3 18.36. Calc. for $C_{16}H_{16}O_4(OCH_3)_2$: C 64.67; H 6.63; OCH_3 18.57.)

Acidolysis procedures

Preparative acidolysis experiments. Method A. The samples were refluxed with 50 ml 0.2 M HCl in dioxane – water (9 : 1) for the desired periods of time. In experiments carried out for longer periods of time (> 15 min), nitrogen was bubbled through the solutions during the heating. After cooling, the reaction mixtures were neutralized with 50 ml 0.2 M aqueous $NaHCO_3$ and extracted with 100 ml chloroform, and then extracted three times with 25 ml chloroform. The extracts were dried over Na_2SO_4 and the solvent was removed by film evaporation.

Method B differed from method A only in the fact that dichloromethane instead of chloroform was used for the extraction of the reaction mixtures.

Method C. The acidity of the acidolysis mixtures was reduced to about pH 3 with 0.4 M $NaHCO_3$ and subsequent extraction was done once with a volume of chloroform

equal to the amount of acidolysis reagent and then four times with a volume of chloroform equal to one half of the acidolysis reagent; in other respects the experiments were performed according to method A.

Analytical acidolysis experiments. a. The samples were heated with the acidolysis reagent in sealed glass ampoules as described in Refs. 5 and 30. Preparation of lignin acidolysis mixtures for gel filtration was made according to Ref. 30. For UV spectroscopic examinations, the acidolysis mixtures were diluted with ethanol – water (1 : 1) and alkaline solutions were made 0.2 M with respect to NaOH. The separation of the acidolysis products from the reaction mixtures for gas chromatographic examinations using trimethylsilyl derivatives was made as described in Ref. 30, but the gel filtration step was omitted. b. A few experiments were made according to procedures used for experiments made on a preparative scale, but with smaller amounts of acidolysis reagent.

Preparative acidolysis experiments

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (VI). [52, 34, 53] a. Compound VI (0.60 g) was subjected to acidolysis according to method A. Time of acidolysis, 4 h. The starting material was prepared according to Kratzl *et al.*,[34] and was purified by chromatography on a silica gel column using benzene – ethyl acetate (1 : 1) as eluting agent; the purified product can be expected to consist essentially of the *erythro* form of VI.[50,53] The acidolysis product was subjected to column chromatography according to the standard procedure.

Tubes 15 – 20 gave 170 mg of an oil identified as guaiacol by IR and thin layer chromatography. To avoid losses of guaiacol the product was dried only for a brief period of time prior to weighing. UV spectrophotometric determination (solvent, ethanol), made prior to drying of the fraction, indicated that 173 mg guaiacol was present in the fraction.

Tubes 22 – 44 gave 54 mg of an oil. Paper chromatography showed the presence of vanillin (XIV) and traces of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (XII) and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione (XIII).

Tubes 45 – 56 gave 54 mg of an oil. According to paper chromatography the product was a mixture of 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (XI) and 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (X).

Tubes 58 – 75 gave 196 mg of a crystalline product, m.p. 79 – 81°, identified by IR and mixed m.p. as 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone (IX) (m.p. 81 – 82° [54]).

Tubes 85 – 90 gave 21 mg of an oil which, according to paper chromatography, was starting material.

b. Compound VI [0.62 g of the *erythro* form, m.p. 90 – 92° (lit.[53] 90 – 92°)] was subjected to acidolysis according to method C. Time of acidolysis, 4 h. *Gel filtration* of the acidolysis product was performed essentially according to the procedure previously described [1] for the separation of low molecular weight lignin acidolysis products. A column packed with 170 g Sephadex G-25 (fine) was used. After dilution (from each fraction 0.07 ml was taken by a microsyringe and 20 ml ethanol was added), the UV spectra of the fractions were recorded. Fractions 33 – 56 showed a maximum at about 280 nm. Examination of the fractions by thin layer chromatography showed the presence of starting material in fractions 40 – 43 [detection of VI was made by exposure to iodine vapour, and also by spraying with an ethanolic solution of 2,6-dibromo-*N*-chloroquinonimine followed by dilute aqueous NaOH (blue spot, *cf.* Ref. 55)]. Based on this examination and on the investigation of the fractions by UV, the fractions containing material absorbing at 280 nm were divided into three groups (33 – 39, 40 – 43, and 44 – 54). The fraction groups were worked up as in the previously described experiment with lignin,[1] with the exception that the material obtained from fractions 44 – 54 was not dried to avoid losses of guaiacol. The material in fractions 33 – 39 and 40 – 43 weighed 49 and 58 mg, respectively. From fractions 40 – 43, 19 mg of starting material was separated by preparative thin layer chromatography [eluting agent, benzene – ethyl acetate (1 : 1)]. It should be noted that minor amounts of coloured material present in the acidolysis product accumulated in fractions 33 – 43. *The material in fractions 44 – 54* was subjected to column chromatography according to the standard procedure. The major components were guaiacol

(172 mg, tubes 14 – 20) and ketol IX (200 mg, tubes 65 – 85). The material eluted between these two compounds was studied in more detail than in the experiment with VI described above.

Tubes 21 – 25 gave 2 mg of a light yellow oil. Paper chromatography provided some evidence for the occurrence of XIII, but the presence of this compound was not clearly demonstrated.

Tubes 26 – 35 gave 19 mg of an oil. The detection of vanillin and homovanillin (XV) in a corresponding fraction separated from a 4 h acidolysis mixture of VI has been reported previously.[5] In this experiment vanillin was separated by preparative thin layer chromatography [eluting agent, benzene – ethyl acetate (1 : 1)] and crystallized from benzene/petroleum ether. The product melted at 80° and was identified as vanillin (m.p. 81° [47]) by IR and mixed m.p.

Tubes 36 – 46 gave 4 mg of an oil. The presence of XII was demonstrated by paper chromatography.

Tubes 46 – 52 gave 27 mg of crystals of m.p. 106°. These were identified as ketol XI (m.p. 109 – 110° [56]) by IR and mixed m.p.

Tubes 53 – 64 gave 28 mg of an oil. According to paper chromatography the fraction consisted of a mixture of ketols X and XI.

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(2,6-dimethoxy-4-methylphenoxy)-1,3-propanediol (VII).* (Synthesis.[57]) Compound VII (0.38 g of the *threo* form, m.p. 145 – 147°) was subjected to acidolysis according to method C. Time of acidolysis, 4 h. The acidolysis product was subjected to column chromatography according to the standard procedure but with ethyl acetate instead of benzene – ethyl acetate (2 : 3) in the reservoir.

Tubes 22 – 27 gave 102 mg of oily crystals identified as 2,6-dimethoxy-4-methylphenol by IR (KBr). In a second experiment 111 mg of the phenol melting at 39 – 41° (lit.[58] 41°) was obtained with 0.50 g VII as starting material.

Tubes 28 – 55 gave 126 mg of an oil. This fraction was not examined for individual components.

Tubes 56 – 65 gave 25 mg of an oil. Paper chromatography revealed the presence of 2-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone (XVII).

Tubes 66 – 74 gave 16 mg of an oil. Paper chromatography showed the presence of ketol XVII and unidentified constituents.

Tubes 75 – 98 gave 65 mg of an oil. Purification by preparative thin layer chromatography (eluting agent, ethyl acetate) followed by crystallization from chloroform/benzene gave a product of m.p. 104.5 – 106°. The product was identified (IR and mixed m.p.) as 1-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone** (XVI) (m.p. 106.5 – 107.5° [44]). Examination of the total fraction by NMR spectroscopy indicated that the fraction consisted essentially of XVI. This is in accord with the observation that gas chromatography after silylation gave a chromatogram showing only one strong peak, corresponding in retention time to the trimethylsilyl derivative of XVI.

2-(2-Methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol (VIII). Compound VIII [0.54 g of the *erythro* form with m.p. 98 – 99° (lit.[50] 97.5 – 98.5°)] was subjected to acidolysis according to method A. Time of acidolysis, 4 h. The product obtained was subjected to column chromatography according to the standard procedure.

Tubes 15 – 19 gave 84 mg of an oil identified as guaiacol by IR and thin layer chromatography. To avoid losses of guaiacol, the product was dried only for a brief period of time prior to weighing. According to UV spectroscopic measurements (solvent, ethanol), made prior to drying of the product, the amount of guaiacol present in the fraction was 87 mg.

Tubes 25 – 58 gave 75 mg of an oil. The presence of 3,4-dimethoxybenzaldehyde (XXI) was demonstrated by paper chromatography.

Tubes 59 – 63 gave 16 mg of an oil. According to paper chromatography the oil consisted of a mixture of 1-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (XIX) and 2-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone (XX).

Tubes 65 – 80 gave 114 mg of an oil which, according to IR and paper chromatography, consisted of 1-hydroxy-3-(3,4-dimethoxyphenyl)-2-propanone (XVIII). Proof for the

* The authors thank fil. lic. G. E. Miksche for a gift of this compound.

** The authors thank Prof. J. M. Pepper for a gift of this compound.

identity of this compound was obtained by preparing an acetate (m.p. 52 – 53°) and identifying this compound with the acetate (m.p. 55 – 56° [59]) prepared from synthetic XVIII [59b] (IR and mixed m.p.). In some of the subsequent tubes (81 – 87), minor amounts of ketol XVIII were present. The amount of XVIII present in these tubes was estimated to be < 10 mg (thin layer chromatography); an upper limit for the total amount of ketol XVIII formed would thus be 124 mg.

Tubes 81 – 113 gave 228 mg of an oil. Thin layer chromatography indicated that the fraction consisted essentially of VIII. As pointed out above, minor amounts of ketol XVIII were present in tubes 81 – 87. On addition of ether, a partial crystallization occurred; the crystalline product was identified as starting material. Comparison of the NMR spectrum of the fraction with the NMR spectra of the *erythro* and *threo* forms of VIII* (to get simplified NMR spectra the solutions were shaken with D_2O to exchange hydroxyl protons prior to the recording of the spectra) showed that the fraction consisted essentially of a mixture of these two compounds.

1-(4-Hydroxy-3-methoxyphenyl)-1,2,3-propanetriol (XXXIII). Compound XXXIII [0.52 g of the monohydrate of the *erythro* form melting at 82 – 83° (lit.[60] 83 – 84°)] was subjected to acidolysis according to method B. Time of acidolysis, 2 h. By column chromatography according to the standard procedure a fraction consisting of 0.30 g of 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone (IX) [m.p. 79 – 80° (lit.[54] 81 – 82°)] could be separated from the acidolysis product. Yield, 68 %.

1-(4-Hydroxy-3,5-dimethoxyphenyl)-1,2,3-propanetriol (XXXV).[61,45] Compound XXXV [51 mg of the *erythro* form[45,57] melting at 126° (lit.[45] 127°)] was subjected to acidolysis according to method C, with the exception that the amount of acidolysis reagent used was 5 ml. Time of acidolysis, 15 min. The acidolysis product weighed 41 mg after drying at 20 mmHg over KOH and P_2O_5. The major component was XVI (TLC). Separation was accomplished by column chromatography on a silica gel column (1.5 × 60 cm; 25 g SiO_2) with benzene – ethyl acetate (2 : 3) as eluting agent. Compound XVI (34 mg) with m.p. 104 – 107° was obtained (yield 67 %). Recrystallization from chloroform/benzene raised the m.p. to 106 – 108°. The product was identified as 1-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (XVI) (m.p. 106.5 – 107.5° [44]) by IR and mixed m.p.

1-(3,4-Dimethoxyphenyl)-1,2,3-propanetriol (XXXIV). Compound XXXIV [0.40 g of the *threo* form with m.p. 109° (lit.[60] 109 – 110°)] was subjected to acidolysis according to method B. Time of acidolysis, 20 min. The acidolysis product (0.32 g) was chromatographed on a silica gel column (20 g SiO_2) with benzene – ethyl acetate (3 : 2) as eluting agent. Those fractions which, according to a thin layer chromatographic examination, contained XVIII were combined and the solvent was removed by film evaporation. The resulting residue weighed 0.22 g after being dried at 20 mmHg over KOH and P_2O_5 overnight. The product was identified as 1-hydroxy-3-(3,4-dimethoxyphenyl)-2-propanone (XVIII) by comparison with a synthetic sample [59b] (IR and paper chromatography). Yield, 60 %.

3-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenyl)-2-propene-1-ol (XXVIII). Compound XXVIII (0.60 g of the monohydrate, see p. 2018) was subjected to acidolysis according to method B. Time of acidolysis, 10 min. The acidolysis product was subjected to column chromatography according to the standard procedure.

Tubes 16 – 23 gave 215 mg of an oil identified as 2-methoxy-4-methylphenol by IR and thin layer chromatography.

Tubes 57 – 74 gave 31 mg of an oil. According to paper chromatography, this fraction consisted of a mixture of 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (X) and 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (XI).

Tubes 75 – 98 gave 259 mg crystals of m.p. 81 – 82°. The product was identified as 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone (IX) (m.p. 81 – 82° [54]) by IR and mixed m.p.

3-Hydroxy-2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1-propanone (IV). Compound IV [0.40 g of m.p. 115 – 117° (lit.[24] 114 – 116°)] was subjected to acidolysis according to method B, with the exception that nitrogen was not bubbled through the solution during the heating. Time of acidolysis, 25 h.

* The authors thank Dr. J. Gierer for a gift of the *threo* form of VIII.

Examination of the acidolysis product by thin layer chromatography (eluting agent, dichloromethane) indicated that the product consisted of a mixture of guaiacol (R_F 0.50) and compound V (R_F 0.30). Separation was accomplished by chromatography on a silica gel column (2 × 48 cm; 66 g silica gel). Dichloromethane was used as eluting agent until the guaiacol had been eluted (TLC). Elution was then continued with dichloromethane – ethyl acetate (4 : 1) applied to the column. From the effluent between 250 – 380 ml 106 mg of guaiacol (IR and TLC) was obtained (yield 71 %). From the effluent between 590 – 670 ml, 220 mg 1-(3,4-dimethoxyphenyl)-1,2-propanedione (V) (IR and mixed m.p.) of m.p. 67 – 68° was obtained; recrystallization from ether – petroleum ether gave 185 mg V melting at 68 – 69° (lit.[59a] 69 – 70°). Yield, 74 %.

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REFERENCES

1. Lundquist, K. *Acta Chem. Scand.* **24** (1970) 889.
2. Björkman, A. *Svensk Papperstid.* **59** (1956) 477.
3. Björkman, A. and Person, B. *Svensk Papperstid.* **60** (1957) 158.
4. Larsson, S. and Miksche, G. E. *Acta Chem. Scand.* **25** (1971) 647.
5. Lundquist, K. and Ericsson, L. *Acta Chem. Scand.* **24** (1970) 3681.
6. Lundquist, K., Miksche, G. E., Ericsson, L. and Berndtson, L. *Tetrahedron Letters* **1967** 4587.

7a. Lundquist, K. and Ericsson, L. *Acta Chem. Scand.* **25** (1971) 756. b. Larsson, S. and Miksche, G. E. *Acta Chem. Scand. In press.*

8. Shimada, M., Fukuzuka, T. and Higuchi, T. *Tappi* **54** (1971) 72.
9. Adler, E., Pepper, J. M. and Eriksoo, E. *Ind. Eng. Chem.* **49** (1957) 1391.
10. Adler, E. *Paperi Puu* **43** (1961) 634.
11. Lundgren, R. *Paperi Puu* **43** (1961) 670.
12. Freudenberg, K., Harkin, J. M. and Werner, H.-K. *Chem. Ber.* **97** (1964) 909.
13. Adler, E., Miksche, G. E. and Johansson, B. *Holzforschung* **22** (1968) 171.
14. Johansson, B. and Miksche, G. E. *Acta Chem. Scand.* **26** (1972) 289.
15. Adler, E. and Marton, J. *Acta Chem. Scand.* **13** (1959) 75.
16. Adler, E. and Yllner, S. *Svensk Papperstid.* **55** (1952) 238.
17. Hemrå, L. and Lundquist, K. *Unpublished results.*
18. Klemola, A. and Pepper, J. M. *Chem. Commun.* **1969** 1048.
19. Christofferson, K. *Svensk Papperstid.* **73** (1970) 566.
20. Lundquist, K. and Hedlund, K. *Acta Chem. Scand.* **25** (1971) 2199.
21. Lundquist, K. *Unpublished results.*
22. Weinges, K. *Chem. Ber.* **94** (1961) 2522.
23. Larsson, S. and Miksche, G. E. *Acta Chem. Scand.* **21** (1967) 1970 and *unpublished results.*
24. Adler, E., Lindgren, B. O. and Saedén, U. *Svensk Papperstid.* **55** (1952) 245.
25. Adler, E. and Lindgren, B. O. *Svensk Papperstid.* **55** (1952) 563.
26. Lundquist, K. and Wesslén, B. *Acta Chem. Scand.* **25** (1971) 1920.
27. Adler, E. *Svensk Kem. Tidskr.* **80** (1968) 279.
28. Aulin-Erdtman, G. *Chem. Ind. (London)* **1955** 581; *Svensk Kem. Tidskr.* **70** (1958) 145.
29. Lundquist, K. and Hedlund, K. *Acta Chem. Scand.* **21** (1967) 1750.
30. Lundquist, K. and Kirk, T. K. *Acta Chem. Scand.* **25** (1971) 889.
31. Adler, E., Carlsson, B. and Lundquist, K. *Unpublished results.*
32. Sarkanen, K. and Schuerch, C. *J. Am. Chem. Soc.* **79** (1957) 4203.
33. Kratzl, K. and Paszner, L. *Cellulose Chem. Technol.* **4** (1970) 293.
34. Kratzl, K., Kisser, W., Gratzl, J. and Silbernagel, H. *Monatsh.* **90** (1959) 779.
35. a. Ashorn, T. *Soc. Sci. Fennica, Commentationes Phy. Math.* **25** (1961); Enkvist, T., Ashorn, T. and Hästbacka, K. *Paperi Puu* **44** (1962) 395. b. Gierer, J. and Lenz, B.

Svensk Papperstid. **68** (1965) 334. c. Freudenberg, K. In Freudenberg, K. and Neish, A. C. *Constitution and Biosynthesis of Lignin*, Springer, Berlin 1968, p. 45.
36. Erdtman, H. *Research* **3** (1950) 63.
37. Freudenberg, K., Jovanović, V. and Topfmeier, F. *Chem. Ber.* **94** (1961) 3227; Ludwig, C. H., Nist, B. J. and McCarthy, J. L. *J. Am Chem. Soc.* **86** (1964) 1186; Lenz, B. L. *Tappi* **51** (1968) 511.
38. Nimz, H. *Chem. Ber.* **100** (1967) 181.
39. von Rudloff, E. *Chem. Ind. (London)* **1965** 180.
40. Theander, O. a. *Acta Chem. Scand.* **19** (1965) 1792. b. *Private communication.*
41. Lindgren, B. O. and Saedén, U. *Acta Chem. Scand.* **6** (1952) 963.
42. Adler, E. and Hernestam, S. Cited in Adler, E. and Yllner, S. *Svensk Papperstid.* **57** (1954) 78.
43. Gardner, J. A. F. *Can. J. Chem.* **32** (1954) 532.
44. Gorecki, E. W. and Pepper, J. M. *Can. J. Chem.* **37** (1959) 2089.
45. Nimz, H. *Chem. Ber.* **98** (1965) 3153.
46. Nimz, H. and Gaber, H. *Chem. Ber.* **98** (1965) 538; Nimz, H. *Chem. Ber.* **98** (1965) 3160; **99** (1966) 469.
47. Vogel, A. I. *Practical Organic Chemistry*, 3rd Ed., Wiley, New York 1966.
48. Kratzl, K. and Schweers, W. *Monatsh.* **85** (1954) 1046.
49. Gardner, J. A. F., Henderson, D. W. and MacLean, H. *Can. J. Chem.* **40** (1962) 1672.
50. Gierer, J. and Norén, I. *Acta Chem. Scand.* **16** (1962) 1976.
51. Freudenberg, K. and Müller, H. G. *Ann.* **584** (1953) 40.
52. Adler, E. and Eriksoo, E. *Acta Chem. Scand.* **9** (1955) 341.
53. Miksche, G. E., Gratzl, J. and Fried-Matzka, M. *Acta Chem. Scand.* **20** (1966) 1038.
54. Fisher, H. E. and Hibbert, H. *J. Am. Chem. Soc.* **69** (1947) 1208.
55. Gierer, J. *Acta Chem. Scand.* **8** (1954) 1319.
56. Cramer, A. B. and Hibbert, H. *J. Am. Chem. Soc.* **61** (1939) 2204.
57. Miksche, G. E. *Unpublished results.*
58. Freudenberg, K. and Hübner, H. H. *Chem. Ber.* **82** (1952) 1181.
59. a. Eastham, A. M., Fisher, H. E., Kulka, M. and Hibbert, H. *J. Am. Chem. Soc.* **66** (1944) 26. b. Fisher, H. E., Kulka, M. and Hibbert, H. *J. Am. Chem. Soc.* **66** (1944) 598.
60. Adler, E. and Gustafsson, B. *Acta Chem. Scand.* **17** (1963) 27.
61. Pearl, I. A. and Gratzl, J. *J. Org. Chem.* **27** (1962) 2111.

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