ACTA CHEMICA SCANDINAVICA 27 (1973) 2597–2606

Acid Degradation of Lignin

Part VIII.* Low Molecular Weight Phenols from Acidolysis of Birch Lignin

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Refluxing of Björkman lignin from birch (*Betula verrucosa*) with 0.2 M hydrogen chloride in dioxan-water (9:1) for 4 h gives considerable amounts of phenols with one and two aromatic rings (about 30 % of the original lignin). A number of phenols has been identified. Most of them can be related to structural elements of the arylglycerol-β-aryl ether, 1,2-diaryl-1,3-propanediol, and syringaresinol types.

Acidolysis [refluxing with 0.2 M hydrogen chloride in dioxan-water (9:1)**] for 4 h of Björkman lignin gives considerable amounts of low molecular weight phenols.[1] The degradation proceeds mainly by cleavage of ether linkages, particularly those in arylglycerol-β-aryl ether structures.[2]

Phenols, carbonyl compounds, and, at least at an early stage of the acidolysis, benzyl alcohols are present in the lignin acidolysis mixture. It is very likely that condensation reactions occur in such a mixture. Experiments have been carried out which indicate that the formaldehyde liberated is partly consumed due to condensation.[3] Studies with model compounds of the arylglycerol-β-aryl ether type indicate that the benzyl alcohol groups present in such structures condense only to a limited extent during acidolysis.[1,2] As judged from studies of carboxylic acids formed on permanganate oxidation of acidolysed lignin condensation with aromatic rings occur to a minor extent only.[4] Coniferyl alcohol polymerizes under acidic conditions.[5] Since lignin contains minor amounts of cinnamyl alcohol end groups, this reaction should be of some importance in the acidolysis of lignin. The latter reaction and condensation reactions decrease the yield of low molecular weight phenols on acidolysis.

* Part VII, Ref. 2.

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

Upon acidolysis of aspen wood Pepper and co-workers [6] obtained evidence for the occurrence of condensation reactions by studying the yields of vanillin and syringaldehyde formed on alkaline nitrobenzene oxidation of the lignin samples isolated. In connection with the present studies it has been found that carbohydrates give 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde on acidolysis.[7,8] Due to the difference in carbohydrate content, considerably larger amounts of such aldehydes should be formed from wood than from Björkman lignin (concerning content of carbohydrates, see Refs. 8 and 9) on acidolysis. It seems possible that furaldehydes react with lignin in condensation reactions during acidolysis conditions. The difference in formation of such compounds may therefore explain why the results obtained on acidolysis of wood [6] (difficulties with the dissolution of the lignin, alkaline nitrobenzene oxidation studies) seem to indicate the importance of condensation reactions more than the results with Björkman lignin [1,2,4] do (gel filtration experiments, permanganate oxidation studies).

The major part of the work in this series deals with lignin from spruce (*Picea abies*), but results obtained with lignin from birch (*Betula verrucosa*) have been discussed to some extent. The present paper describes the identification of low molecular weight phenols from acidolysis of birch lignin. The relation of the compounds to structural elements in lignin is discussed. A study of the acidolysis products from bamboo and beech lignins has recently been published.[10] These lignins show structural resemblance to birch lignin and it is therefore of interest to compare these results with those obtained from the acidolysis of birch lignin.

As in the acidolysis experiments with spruce lignin,[1] the separation methods used included removal of the major part of the polymeric material on a silica gel column (the eluted material was 42 % of the original lignin) and division of the eluted material by gel filtration into fractions of monomers, dimers, and high molecular weight material (Fig. 1). The monomer fraction (20 % of

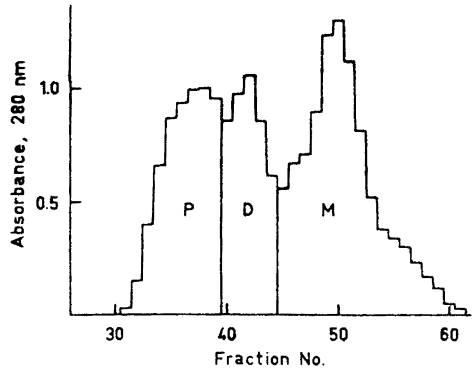
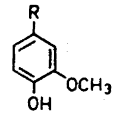
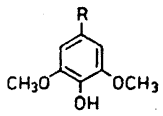


Fig. 1. Gel filtration of an essentially low molecular weight fraction separated by column chromatography from the reaction mixture obtained on 4 h acidolysis of Björkman lignin from birch [Sephadex G-25, eluent: dioxan-water (1:1)].

the original lignin) and the dimer fraction (10 % of the original lignin) were investigated to identify individual components. (The terms monomer and dimer in this paper refer to the number of aromatic rings present in the compounds.)

Composition of the monomer fraction. Compounds detected in the monomer fraction are shown in Fig. 2. Compounds *1*, *2*, *6*, *8*, *9*, and *11* were obtained in a crystalline state and identified with authentic samples by IR and mixed

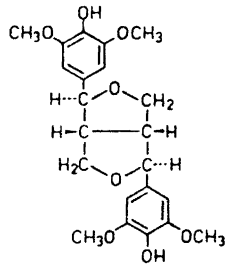



1 R = CH_2COCH_2OH
2 R = $COCH(OH)CH_3$
3 R = $CH(OH)COCH_3$
4 R = $COCOCH_3$
5 R = CHO
6 R = COOH
7 R = CH=CHCHO

8 R = CH_2COCH_2OH
9 R = $COCH(OH)CH_3$
10 R = $COCOCH_3$
11 R = CHO
12 R = CH=CHCHO

Fig. 2. Compounds detected in the monomer fraction.

m.p. For the identification of compounds *3–5*, *7*, *10*, and *12* paper chromatography was used. Ketols *1* and *8* were the most abundant constituents; their yields were 5 % and 2.6 % of the original lignin, respectively.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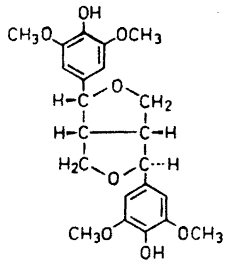
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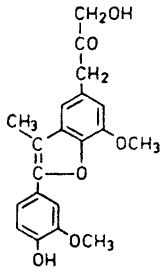
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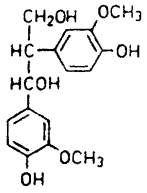
Composition of the dimer fraction. From two of the sub-fractions obtained by column chromatography crystalline compounds were obtained. These were (±)-syringaresinol (*13*) and a product, m.p. 185°, denoted compound Y in the following paragraph, which for reasons given below is proposed to be (±)-episyringaresinol (*14*). Each of the fractions was 0.9 % of the original lignin.

The IR spectrum of compound Y was identical with the IR spectrum reported for certain stereoisomers of syringaresinol (lirioresinol A and B [11]). Acidolysis (4 h) of (±)-syringaresinol gave a reaction product consisting of about equal amounts of compound *13* and compound Y. The fact that similar acidolysis of (+)-pinoresinol results in a mixture of (+)-pinoresinol and (+)-epipinoresinol [1] makes it likely that compound Y is identical with compound *14*. This is further supported by the fact that the dimethyl ether of (±)-syringaresinol on acid treatment gives a mixture of the dimethyl ethers of (±)-syringaresinol and (±)-episyringaresinol.[12] Additional work [13] on the structure of syringaresinol and its stereoisomers (including "lirioresinols" discussed in Ref. 11) can also be interpreted to indicate that compound Y is identical with compound *14*.

The remaining sub-fractions (constituting a total of 3.5 % of the original lignin) were reduced with sodium borohydride and acetylated; by this procedure carbonyl groups were replaced by $>CHOCOCH_3$ groups and hydroxy groups by acetoxy groups. The products were examined by GLC, GLC–MS, and thin layer chromatography. Proof for the presence of a number of derivatives of



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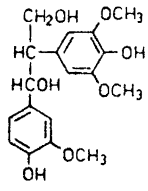

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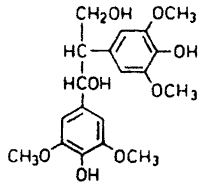

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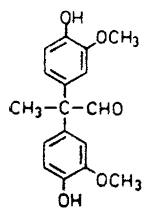
acidolysis products of 1,2-diaryl-1,3-propanediols *16*, *17*, and *18* was obtained by GLC and GLC-MS. Evidence for the presence of the derivative of phenylcoumarone *15* was obtained by gas chromatography and thin layer chromatography.

Compounds found in the dimer fraction which have been found to be acidolysis products of compounds *16*, *17*, and *18* are shown in Fig. 3. The structures of several of the compounds are not fully proved. Acidolysis products from *16*, (*19*–*21*, and *22*) have previously been detected in acidolysis mixtures from spruce lignin,[14,1] and the identification of *19*, *21*, and *22*, *via*



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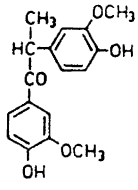

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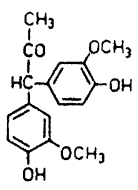

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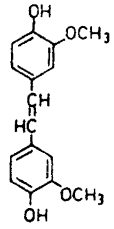

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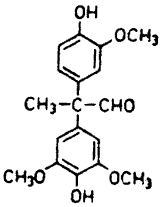

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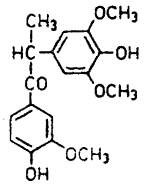

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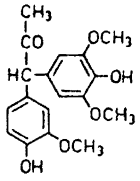

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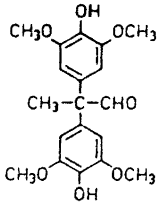

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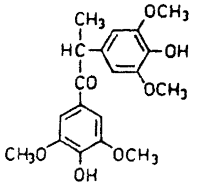

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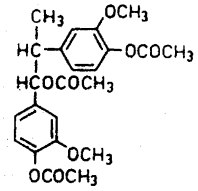
Fig. 3. Compounds in the dimer fraction which are formed on acidolysis of the 1,2-diaryl-1,3-propanediols *16-18*.

derivatives obtained on reduction-acetylation, by gas chromatography-mass spectrometry has been described in this connection.[1] (The structure of *19* is tentative, see Ref. 1.) In the present work gas chromatography-mass spectrometry was also used for the detection of compound *20 via* its derivative obtained on reduction-acetylation (*28*). The MS of the derivative was in accord with structure *28*, *e.g.* the molecular ion was *m/e* 430.

Structural evidence for compounds *23 – 25* comes from a striking analogy of the mass spectra of the derivatives with those of the corresponding derivatives of *19 – 21*. Similarly, evidence for the structure of compounds *26* and *27* was obtained from mass spectral data. The derivative of compound *27* was obtained in a crystalline state, m.p. 220°. This made it possible to obtain



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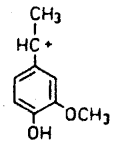

(m/e 151)

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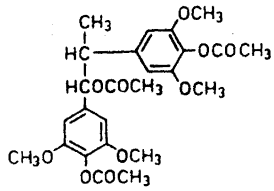

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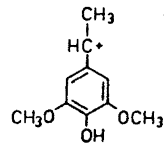

(m/e 181)

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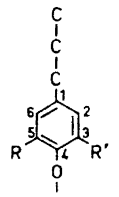
more conclusive structural evidence. Precise mass measurements of the molecular ion (*m/e* 490) gave the elemental composition $C_{25}H_{30}O_{10}$, which is in accord with structure *30*. The base peak was *m/e* 181 (fragment *31*); other peaks were less than 50 % of the base peak. Analogously, the base peak in the mass spectrum of derivative *28* was *m/e* 151 (fragment *29*), which strongly dominated the spectrum.

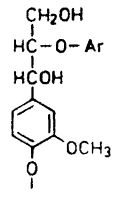
Acidolysis of the 1,2-diaryl-1,3-propanediols *16 – 18* followed by reduction-acetylation and subsequent examination of the mixtures by GLC supported the view that the lignin acidolysis products shown in Fig. 3 arise on acidolysis of compounds *16 – 18*.

DISCUSSION

The monomer fraction and the dimer fraction correspond to 30 % of the original lignin. The corresponding fractions obtained from spruce lignin constituted 17 % of the original lignin.[1] Thus considerably more low molecular weight material is formed from birch lignin than from spruce lignin on acidolysis. This difference should be essentially due to the fact that many of the units in birch lignin are of the syringyl type (*34*); in this type of units the 3- and the 5-positions are occupied by methoxyl groups and the aromatic rings are therefore linked to adjacent units by acid-stable biphenyl and diaryl ether linkages only to a small extent. Such a difference in formation of low molecular weight material has been encountered in several comparative degradations of softwood and hardwood lignins. Of particular interest in connection with this work is the observation that larger amounts of "Hibbert ketones" are formed from hardwoods.[15]



32 R = R' = H
33 R = H, R' = OCH_3
34 R = R' = OCH_3



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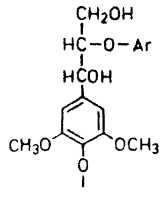

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Ar = aromatic ring in adjacent unit

A comparison of the low molecular weight phenols from spruce lignin with those from birch lignin can roughly be interpreted to indicate that both lignins have similar structures with the exception of a different ratio of units *32 – 34* and differences due to the lack of condensation possibilities in syringyl units discussed above. However, other structural differences between birch and spruce lignin of interest for the formation of low molecular weight material on hydrolysis have been observed. Thus the frequency of hydrolysable ether bonds has been found to be higher in birch lignin.[4b] Similar results have been obtained in studies of beech lignin [16] which in all likelihood is closely related to birch lignin. NMR studies indicated that the guaiacyl units in birch lignin are condensed to a great extent.[17] This is not supported by the present study, since guaiacyl monomers constitute a rather large portion of the monomer fraction. Similarly, estimations made on the basis of the formation of aromatic acids on oxidative degradation suggest the presence of a considerable portion of noncondensed guaiacyl units in birch lignin.[4b]

The formation of ketols *1 – 3*, *8*, and *9* can be explained by the occurrence of structural elements of types *35* and *36* in the lignin.[2] Since the yield of ketols is rather high, birch lignin should contain a considerable number of units of these types. According to model experiments, compounds *4* and *5* originate – at least in part – from units of type *35*.[2] Analogously units of type *36* can be expected to give rise to compounds *10* and *11*.

Concerning the relation of acidolysis products *5 – 7* and the syringyl analogues of *5* and *7*, namely *11* and *12*, to lignin structures, *cf.* the discussion [1] of the origin of compounds *5 – 7* on acidolysis of spruce lignin.

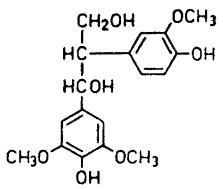
The formation of (±)-syringaresinol (*13*) and its acidolysis product, (±)-episyringaresinol (*14*), shows that birch lignin contains structural elements of the syringaresinol type. Evidence for this type of structural elements has been obtained by the fact that (±)-syringaresinol is formed on hydrolysis of pre-extracted wood from beech [18] (*Fagus silvatica*) and *Fraxinus mandshurica*.[19] However, compound *13* has also been found in an ethanol extract from wood of *Fraxinus mandshurica*.[20] Therefore, the formation of compounds *13* and *14* on acidolysis of isolated birch lignin complements the earlier evidence for the occurrence of structural elements of the syringaresinol type in lignin.

The yields of *13* and *14* were rather small, suggesting that birch lignin contains only a small percentage of syringaresinol structures. The total number of units involved in "resinol" structures (including syringaresinol, pinoresinol,

and analogous structures consisting of one unit of type *33* and one unit of type *34*) may be of the order of 10 % (yield of "dilactone" on oxidation [21]).

Sinapyl alcohol yields almost exclusively (±)-syringaresinol on oxidation.[22] The low yields of compounds *13* and *14*, as well as the formation of considerable amounts of other syringyl compounds on acidolysis, suggest that oxidative dimerization of sinapyl alcohol is very much suppressed in the formation of birch lignin. This can be explained by co-polymerization with coniferyl alcohol or reaction of sinapyl alcohol radicals with radicals of units containing a saturated side chain. The latter reaction is presumably the most important one. For a discussion of aspects of the biosynthesis of lignin of interest in this connection, see Ref. 23. Interestingly, it has been demonstrated that the oxidative dimerization of *p*-hydroxycinnamyl alcohols is suppressed when the oxidation is performed under suitable conditions in media containing a great excess of a phenol with a saturated side chain.[24]

Acidolysis products originating from 1,2-diaryl-1,3-propanediols *16 – 18* incorporated in the lignin constitute a rather large portion of the dimer fraction. The amount seems to agree fairly well with the amount of degradation products related to 1,2-diaryl-1,3-propanediols obtained on degradation of beech wood.[25]



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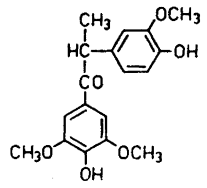

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In addition to compounds *16 – 18*, a fourth 1,2-diaryl-1,3-propanediol conceivably may be incorporated into the lignin, namely compound *37*. Compounds *23* and *25* can be expected to be formed from *17* as well as *37* on acidolysis. Compound *37* should, however, give rise to *38* rather than *24* on acidolysis. Mass spectral evidence (*e.g.* a large peak at *m/e* 181, fragment *31*) suggests that the compound detected in the birch acidolysis mixture is *24*. Thus evidence for the occurrence of structures related to compound *37* has not been obtained. Interestingly, only *16 – 18* have been obtained on hydrolysis of beech wood.[26]

The occurrence of phenylcoumarone *15* in the dimer fraction suggests the presence of phenylcoumaran structures in birch lignin of the same type as previously found in spruce lignin.[27] A degradation product which can be derived from phenylcoumaran structures containing a syringyl unit has recently been obtained in studies with beech wood.[25] Such structures are probably also present in birch lignin, but corresponding acidolysis products have not been detected. The failure to detect these and possibly other products may be due to decomposition of the derivatives during gas chromatography. Therefore the dimer fraction from birch lignin deserves further investigation.

EXPERIMENTAL

GLC was accomplished with a Varian Aerograph 1200 instrument. Column dimensions: 100 × 0.3 cm o.d. stainless steel tubing. Solid support: Chromosorb G, acid-washed and treated with dimethyldichlorosilane, 80 – 100 mesh. Stationary phase OV-1 (2 %). Temperatures: Injector 290°, detector 250°, and column 240° (in a few experiments 250°). Carrier gas: N_2, 25 ml/min. Detector: FID. Internal standard: Retention times are given relative that of dotriacontane. For *GLC–MS* an LKB 9000 instrument was used.

For *paper chromatography* (PC) the solvent system employed by Kratzl and Schweers [28] was used. For the detection of *3 – 5*, and *7* with this system, see Refs. 29 and 1. Compounds *10* (R_F 0.55), *11* (R_F 0.30), and *12* (R_F 0.20) were also detected by PC. Compound *10* is yellow and the spot could therefore be seen on the paper. On spraying with diazotised sulphanilic acid in 2 % aqueous Na_2CO_3, *10* and *11* gave pink spots. Compound *12* appeared as a purple spot on spraying with phloroglucinol in hydrochloric acid/ethanol.

Thin layer chromatography (TLC) was performed on plates covered with a 0.3 mm thick layer of silica gel (Merck HF_{254}). Eluent, benzene-ethyl acetate (1:1). Spots were made visible by exposing them to iodine vapour and by spraying with formalin-H_2SO_4 (1:9).

Preparative TLC was performed on plates similar to those used in analytical experiments. Eluent, ethyl acetate. The zones of silica gel containing the materials of interest, detected by UV light, were scratched off and eluted with acetone.

Standard procedure for column chromatography on silica gel using gradient elution. The procedure described in Ref. 1 was followed, but with ethyl acetate instead of benzene-ethyl acetate (2:3) in the reservoir.

Acidolysis of syringaresinol (13). (±)-Syringaresinol (*13*) [prepared by oxidation of sinapyl alcohol with peroxidase, m.p. 170° (lit.[22] 169.5°)] was refluxed for 4 h with 0.2 M hydrochloric acid in dioxan-water (9:1). The reaction product, extracted with chloroform was chromatographed according to the standard procedure. Two fractions of about equal weight were obtained. These were starting material and a compound, m.p. 183°, proposed to be (±)-episyringaresinol (*14*), *cf.* p. 2599.

Acidolysis of birch lignin

Björkman lignin (4.1 g, OCH_3 = 21.1 %) from birch (*Betula verrucosa*) was acidolysed according to the procedures described for the examination of acidolysis mixtures from spruce lignin.[1] Work-up procedures were also essentially the same. Polymeric material was removed by chromatography on silica gel (40 g SiO_2) with benzene-dioxane (3:1) as eluent. Elution was continued until the absence of material with $R_F < 0.05$ was shown by TLC. Gel filtration on a Sephadex G-25 (fine) column (180 g) with dioxan-water (1:1) as solvent (see Fig. 1) gave a monomer fraction (0.82 g) and a dimer fraction (0.38 g).

Examination of the monomer fraction

The monomer fraction was chromatographed on silica gel according to the standard procedure, but initially (315 ml eluate) with benzene-ethyl acetate (2:3) in the reservoir. Crystalline compounds were identified by IR and mixed m.p. *Tubes 19 – 23* gave 10 mg of an oil. PC revealed the presence of *1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione (4)*. *Tubes 24 – 32* gave 66 mg of an oil. PC indicated the presence of *vanillin (5)*, *coniferaldehyde (7)*, and *1-(4-hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione (10)*. *Tubes 33 – 41* gave 12 mg of an oil. From dichloromethane a small amount of crystals were obtained with m.p. about 200°, identified as *vanillic acid (6)* (m.p. 210° [30]). *Tubes 36 – 41* gave 47 mg of a partially crystalline product. PC indicated the presence of syringaldehyde. Preparative TLC gave a fraction from which impure crystals were obtained from benzene. After washing with ether, a product of m.p. 108° was obtained. This was identified as *syringaldehyde (11)* (m.p. 113° [31]). *Tubes 42 – 47* gave 69 mg of an oil. The presence of *sinapaldehyde (12)* was demonstrated by PC. From benzene crystals were obtained with m.p. 106°, identified as *2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (2)* (m.p. 109 – 110° [32]). *Tubes 48 – 54* gave *32* mg of an oil. The presence of *1-hydroxy-1-(4-*

hydroxy-3-methoxyphenyl)-2-propanone (*3*) was indicated by PC. *Tubes 55 – 65* gave 182 mg of an oil. Preliminary examinations indicated the presence of compound *1*. Extraction with 15 % hydrogen sulphite solution from a solution of the fraction in ether-dichloromethane (2:1) and recovery of the extracted material (acidification, extraction by chloroform) gave 105 mg crystals with m.p. 71 – 75°, identified as *1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone* (*1*) (m.p. 81 – 82° [33]). The residue obtained from the organic layer gave crystals from benzene melting at 118 – 120°, identified as *2-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone* (*9*) (m.p. 126 – 127° [34]). *Tubes 66 – 75* gave 48 mg of an oil containing unidentified products. *Tubes 76 – 86* gave 202 mg crystals of m.p. 102 – 103°. From chloroform-benzene, 146 mg of product melting at about 105° was obtained. Repeated recrystallisation raised the m.p. to 106 – 107°. The product was identified as *1-hydroxy-3-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone* (*8*) (m.p. 106.5 – 107.5° [35]). *Tubes 87 – 94* gave 31 mg of an oil. TLC indicated that compound *8* may be present in the fraction.

Examination of the dimer fraction

The dimer fraction was chromatographed on silica gel according to the standard procedure.

Sub-fractions obtained from tubes 19 – 23 (10 mg), tubes 24 – 31 (30 mg), 32 – 39 (43 mg), 40 – 44 (31 mg), and 45 – 50 (30 mg) were reduced and acetylated as described for fractions of dimers from spruce lignin [1] and, subsequently, examined by GLC and GLC–MS. No prominent peaks other than those discussed below appeared. Concerning the identification of compounds *19 – 27*, see p. 2600.

Tubes *19 – 23* showed peaks with rel. ret. times 0.43 (the derivative of *stilbene 22*) and 0.38 (the derivative of *aldehyde 19*). *Tubes 24 – 31* showed peaks with rel. ret. times 0.27 (the derivatives of *ketones 20* and *21*) and 0.40 (the derivative of *aldehyde 23*). *Tubes 32 – 39* showed a peak with rel. ret. time 0.36 (the derivatives of *ketones 24* and *25*) and a stronger peak with rel. ret. time 0.50 (the derivative of *aldehyde 26*). An additional peak (rel. ret. time 2.11, in this run the temperature of the column was 250° instead of 240°) corresponded to the derivative of *phenylcoumarone 15*. Confirmation by GLC–MS failed due to decomposition in the molecule separator. However, according to TLC the derivative of *15* was present in the fraction. *Tubes 40 – 44* showed a peak with rel. ret. time 0.47 (the derivative of *ketone 27*). From acetone, crystals (m.p. 220°) were obtained; this product was identical with the major component of the fraction. The elemental composition was determined as $C_{25}H_{30}O_{10}$ by mass measurements of the molecular ion (measured: 490.1865, calculated: 490.1839); an AEI model MS 902 was used. This is in accord with structure *30*. *Tubes 45 – 50* showed a peak with rel. ret. time 0.47 (the derivative of *27*?).

Further sub-fractions were obtained from tubes 51 – 56 (36 mg) and tubes 58 – 63 (36 mg). The material in *tubes 51 – 56* gave crystals from methanol, m.p. 185°. The product is proposed to be (±)-*episyringaresinol* (*14*), see p. 2599.

Crystalline (±)-*syringaresinol* (*13*) (m.p. 166 – 170°, lit.[22] 169.5°) was obtained from the material in *tubes 58 – 63*. The product was identified with an authentic sample by IR and mixed m.p.

Acknowledgements. The author thanks Prof. E. Adler and Prof. M. Nilsson for their interest and for valuable criticism. Dr. H. Nimz, Karlsruhe, is thanked for gifts of compounds *17* and *18*.

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Received February 28, 1973.