[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Studies on the Chemistry of Aspenwood. II.[1] Lignans from Aspen Spent Sulfite Liquor.[2,3]

IRWIN A. PEARL, DONALD L. BEYER, AND EDGAR E. DICKEY

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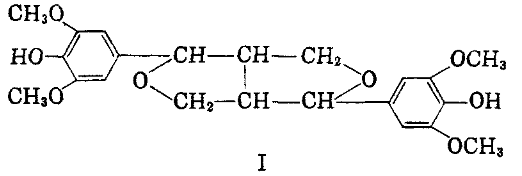
Three isomeric lignans having the structure, tetrahydro-1,4-bis(4-hydroxy-3,5-dimethoxyphenyl)furo[3,4-*c*]furan have been isolated from the spent sulfite liquor of aspenwood by means of chromatography and countercurrent distribution. Infrared absorption spectra indicate that two of these stereoisomers are forms of syringaresinol and lirioresinol, respectively.

In a recent paper[1] the ether extraction of a commercial spent sulfite liquor from the pulping of mixed aspens (*Populus tremuloides*, *P. grandidentata*, and *P. tacamahaca*) was described. This earlier paper included the fractionation of the ether extractives into bisulfite-, bicarbonate-, and alkali-soluble fractions and the isolation of *p*-hydroxybenzoic acid from the bicarbonate-soluble fraction. The present paper reports the fractionation of the alkali-soluble fraction and the isolation of several related crystalline lignans.

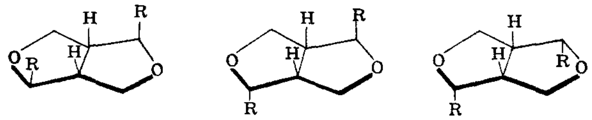
Paper chromatography of the alkali-soluble fraction[1] indicated *p*-hydroxybenzoic acid and materials with R_f values of 0.69 and 0.82 in butanol saturated with 2% aqueous ammonia. A 50:1 benzene-ethanol solution of this fraction was chromatographed on a column of acid-washed Magnesol[4] and developed with the same solvent as a flowing chromatogram. Fractions in the effluent were monitored by paper chromatography, and the fraction containing the largest amount of material was evaporated to dryness. The residue, now free of *p*-hydroxybenzoic acid, was submitted to countercurrent distribution in the Craig machine between both phases of a mixture of butanol and 2% aqueous ammonia at 20°. The tubes containing only the compound with R_f 0.69 were combined to yield a crystalline product (A) melting at 180–181° whose analysis and that of its acetate and ultraviolet and infrared absorption spectra matched those for lirioresinol (B), a lignan having the structure, 1*H*,3*H*-tetrahydro-1,4-bis(4-hydroxy-3,5-dimethoxyphenyl)furo[3,4-*c*]furan (I) recently isolated from the inner bark of *Liriodendron tulipifera*.[5]



I

In another experiment, the ether extract of the same commercial aspen spent sulfite liquor was fractionated in an acid system to yield chloroform-insoluble crystals (C) melting at 235–236° and chloroform-soluble crystals (D) melting at 169–172°. The analysis, infrared spectrum, and positive Mäule reaction indicated that (C) was probably a lignan with the tetrahydrofurofuran structure I, and that (D) as syringaresinol (E) a product having the structure I and obtained by an enzymatic synthesis from syringin.[6]

The probability that tetrahydrofurofuran structure I exists only in its *cis*-form has been discussed earlier.[5] Furthermore, it has been shown that three *d,l*-pairs of the *cis*-form of I are possible (II, III, and IV). Lirioresinol (B) and syringaresinol (E) must possess two of these stereoisomeric forms, and products A and D must possess the same two stereoisomeric forms respectively. The infrared curves of compounds B and E with identical structures, but different spatial configurations, are similar for the most part, but the specific differences are marked enough for differentiation. The similarity of the infrared curve of compound C with the curves of both B and E together with the analytical data and similarity or chemical reactions indicate that compound C may have the third possible stereoisomeric form of the tetrahydrofurofuran I.



II III IV

Fig. 1. Possible Stereoisomers

The differences in melting points recorded for compound A and lirioresinol[5] and for compound D and syringaresinol[6] are probably due to differences

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[1] For paper I of this series, see I. A. Pearl and D. L. Beyer, *Tappi*, **40**, 45 (1957).

[2] Presented before the Division of Cellulose Chemistry at the 132nd meeting of the American Chemical Society, New York, New York, September 8-13, 1957.

[3] This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

[4] I. A. Pearl and E. E. Dickey, *J. Am. Chem. Soc.* **73**, 863 (1951).

[5] E. E. Dickey, *J. Org. Chem.*, **23**, 179 (1958).

[6] K. Freudenberg and H. Dietrich, *Chem. Ber.*, **86**, 4 (1953).

in ratios of optical antipodes present in the crystalline products. Larger scale studies on the optical properties of these lignans are in progress. In addition, studies on the extractives of aspen spent sulfite liquor and on the wood and bark extractives of authentic samples of *Populus tremuloides* and *P. grandidentata* are in progress in an attempt to determine the natural occurrence of these lignans in aspen.

EXPERIMENTAL[7]

Isolation of lirioresinol (*compound A*). An ether solution containing 2.0 g. of the alkali-soluble fraction from the preliminary fractionation of the ether extractives of a commercial aspen spent sulfite liquor[1] was filtered, and evaporated to dryness in a rotating evaporator at 20°. The residue was taken up in 50:1 benzene-ethanol and adsorbed on a column of acid-washed Magnesol[4] 35 mm. in diameter and 4 ft. in length. The column was developed as a flowing chromatogram with 50:1 benzene-ethanol. A total of 78 30-ml. samples were collected in the effluent. These were monitored by means of paper chromatography employing butanol–2% aqueous ammonia as the developer. At this point traces of materials not present in the original fraction[1] were indicated by the chromatograms. The fraction comprising samples 20–41 and containing 1.40 g. of solids was evaporated to dryness and taken up in a little butanol saturated with 2% aqueous ammonia. The sample was distributed between the two phases of a mixture of butanol and 2% aqueous ammonia at 20° in a 10 ml./10 ml. Craig countercurrent distribution machine. After 60 transfers the tubes were monitored by means of paper chromatography and tubes 12–30 contained only the product with butanol–2% aqueous ammonia R_f 0.69. The combined fraction was evaporated to dryness in a rotating evaporator (total yield, 0.51 g.), and the residue was covered with anhydrous ethanol and allowed to stand at 20° for 24 hr. The crystals were filtered and washed with cold ethanol to yield 0.4 g. compound A melting at 180–181°, giving a strong Mäule test, and having the following maxima in its ultraviolet absorption spectrum: λ_{max} 213 mμ, ϵ 43850; $\lambda_{shoulder}$ 237 mμ, ϵ 14600; λ_{max} 273 mμ, ϵ 2870.

Anal. Calcd. for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26. Found: C, 63.46; H, 6.25.

Lirioresinol obtained from the inner bark of *Liriodendron tulipifera*[5] melted at 210–211°. The R_f values on paper at 20° for lirioresinol[5] and for compound A were identical in the following three solvent systems: butanol saturated with 2% aqueous ammonia, 10:3:3 butanol-pyridine-water, and benzene saturated with formic acid. Spots were located by means of the Mäule spray reagents.

Acetylation of compound A with acetic anhydride and pyridine and recrystallization from ethanol yielded colorless crystals of its diacetate melting at 188° and having the following maxima in its ultraviolet absorption spectrum: λ_{max} 210 mμ, ϵ 47600; λ_{max} 230 mμ, ϵ 15870; λ_{max} 272 mμ, ϵ 2310.

Anal. Calcd. for $C_{26}H_{30}O_{10}$: C, 62.14; H, 6.02. Found: C, 62.00; H, 6.04.

Isolation of compound C. A 30-g. sample of total ether extract of aspen spent sulfite liquor[1] was substantially freed from *p*-hydroxybenzoic acid by distribution between both phases of a 2:2:1 mixture of benzene, acetic acid, and water[8] at 20° in a 40 ml./40 ml. Craig countercurrent distribution machine. After 172 transfers, the contents of tubes 28–40 were combined to yield a crude fraction with the desired components. The operation was repeated four times until 150 g. of ether extractives had been processed to yield a crude fraction containing 15.9 g. of solids. This combined fraction was then distributed between both phases of a 4:1:5 mixture of toluene, acetic acid, and water[9] in the last noted Craig machine containing 100 tubes. The upper phase overflow from transfers 203 through 300 was concentrated as one sample to give 0.83 g. crystalline solids. The solid was suspended in chloroform at 20° and filtered. The chloroform-insoluble crystals melted at 234–237°. They were recrystallized from 1:1 chloroform-ethanol to yield 43.5 mg. small granular, Mäule-positive, colorless crystals melting at 235–236°. The purified product had R_f's of 0.58 and 0.85 at 20° in butanol–2% aqueous ammonia and 10:3:3 butanol-pyridine-water, respectively.

Anal. Calcd. for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26; Mol. wt., 418. Found: C, 63.14; H, 6.28; Mol. wt., 418 (Rast, in camphor).

Isolation of syringaresinol (*compound D*). The chloroform filtrate above was evaporated to dryness, and the residue was recrystallized first from chloroform–petroleum ether (b.p. 65–110°) and then twice from 95% ethanol to yield 272 mg. of almost colorless crystals giving a positive Mäule reaction, melting at 168–172°, and having a rotation $[\alpha]_D^{28}$ 3.93° (*c* 3.9 in chloroform). The purified compound had R_f's of 0.60 and 0.85 at 20° in butanol–2% aqueous ammonia and 10:3:3 butanol-pyridine-water, respectively. These were identical with those of authentic syringaresinol.[6]

Anal. Calcd. for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26 Mol. wt., 418. Found: C, 63.18; H, 6.23; Mol. wt., 399 (Rast, in camphor).

Synthetic syringaresinol prepared according to Freudenberg and Dietrich[6] melted at 170–173°.

Spectra. Ultraviolet absorption spectra were determined in 95% ethanol with a Beckman model DU spectrophotometer. Concentrations were approximately 0.02 g. per liter. Infrared absorption spectra of Figure 2 were obtained with a Perkin-Elmer model 21 recording spectrophotometer using a sodium chloride prism and potassium bromide pellets prepared by hand grinding with sample before pressing.

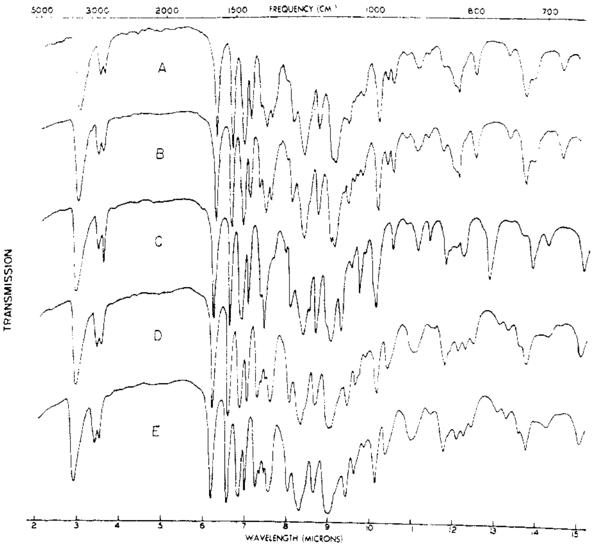

Fig. 2. Infrared absorption curves: A, lirioresinol from aspen spent liquor; B, lirioresinol from *Liriodendron tulipifera;* C, compound C; D, syringaresinol from aspen spent liquor; E, enzymatically synthesized syringaresinol

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[7] All melting points are uncorrected. Analyses were performed by the Analytical Department of The Institute of Paper Chemistry and by Huffman Microanalytical Laboratories, Wheatridge, Colorado. Infrared spectra were determined by Mr. Lowell Sell.

[8] H. Bray, K. White, and W. Thorpe, *Biochem. J.*, **47**, 271 (1950).

[9] E. C. Bate-Smith, *Chem. & Ind.* (*London*), 1457 (1954).