The Occurrence of Matairesinol in Mountain Hemlock (*Tsuga mertensiana*), Western Hemlock (*Tsuga heterophylla*), and Balsam (*Abies amabilis*)[1]

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A colorless crystalline material, observed in the ring shake of mountain hemlock logs grown on Mt. Seymour near Vancouver, B.C., was collected and recrystallized from methanol-water, m.p. 66–67°. Paper chromatographic studies indicated purity; and comparative two-dimensional paper chromatography of methanol extracts of mountain hemlock, western hemlock, and balsam revealed that the substance was a normal component of the heartwood of these species. Similar examination of the sapwood extracts of these species indicated negligible amounts of this material.

Neither prolonged drying over phosphorus pentoxide nor recrystallization from glacial acetic acid changed the melting point appreciably. Negative tests for sugars after hydrolysis precluded the possibility of glycosides. An infrared spectrum of this material was characteristic of the lignans. Of known lignans with low melting points, proconidendrin[2] m.p. 88°, was excluded since a saturated aqueous solution had a *p*H of 5.0 (proconidendrin *p*H 3.0). Hinokinin, m.p. 64–65°, was also excluded since the isolated material failed to give a positive Gaebel test for methylenedioxy groups. However, matairesinol, m.p. 119°, was reported to crystallize with ethanol of crystallization[3] and melted at 74–76°. Because the infrared spectra of the two substances were very similar except in the 1725 and 1360 regions, a further comparison of properties was made.

Although recrystallization from glacial acetic acid failed to change the melting point appreciably, recrystallization from chloroform resulted in material melting at 119° (matairesinol m.p. 119°). Recrystallization from 30% aqueous acetic acid was equally effective in producing the higher melting material. On the basis of a mixed melting point, optical activity, and comparison of infrared and ultraviolet spectra this substance was identical with a reference sample of matairesinol.

The occurrence of matairesinol in hemlock wood should result in its presence in the spent sulfite pulping liquor from that species unless dehydrogenation to conindendrin occurs. This possibility was examined because in previous studies[4,5] the presence of matairesinol had not been detected and also Pearl had observed that the spent liquor apparently contained more conidendrin than the original wood. However, in test cooks with sodium bisulfite and sulfurous acid–bisulfite solutions, the matairesinol was recovered unchanged. Also, examination of the chloroform extract of the spent sulfite liquor from a commercial cook of hemlock-balsam (80:20) showed matairesinol to be present.

Current paper chromatographic studies on the heartwood extract of grand fir (*Abies grandis*) show matairesinol to be present. In view of the great similarity of the extractives of true firs found by Carlberg and Kurth[6] the occurrence of matairesinol in normal heartwood of *Abies concolor* and *Abies procera* may be expected.

EXPERIMENTAL

Preparation of the extracts. Samples of the three species were taken within a few days of felling. Bark was carefully removed and the sapwood separated from the heartwood. The wood (approximately 100 g.) was immediately cut into small pieces (not more than 2 in. in length and $^1/_8$ in. in width) and macerated with methanol in a Waring blendor. The resultant thin slurry was filtered and the filtrate evaporated to dryness at 50° under vacuum in a tared flask. Before weighing, the flask and its contents were evacuated an additional 2 hr. at room temperature under high vacuum. After weighing, enough methanol was added to adjust the concentration to 25 mg./ml. The extracts were stored at 4° until required for spotting chromatograms.

Two-dimensional chromatography. Two-dimensional chromatography, using butanol–water–acetic acid (60:25:15) against the machine direction of the paper and 2% acetic acid with the machine direction was standardized for the examination. Sheets of Whatman No. 1 were spotted with 25 λ of the 25 mg./ml. extract and run for 8 hr. in the butanol–acetic acid solvent at 20°. After drying they were run for 1.5 to 2 hr. with 2% acetic acid in the other direction. Four chromatograms were prepared for each extract. Detection was made by the use of ultraviolet light and one or more of the following detecting reagents: ferric-ferricyanide; diazotized sulfanilic acid; cinnamaldehyde–hydrochloric acid; phloroglucinol–hydrochloric acid; glycerol–methanol–hydrochloric acid (40:30:60); magnesium–hydrochloric acid and zinc–hydrochloric acid.

Both matairesinol, which gave a distinctive red-purple spot with diazotized sulfanilic acid and conidendrin were detected in all the heartwood extracts. Another lignan hydroxy–matairesinol[7] and other unidentified components were also present. Matairesinol has an R_f of 0.94 in butanol–water–acetic acid and an R_f of 0.60 in 2% acetic acid.

Reversed phase chromatography. Additional chromatographic evidence of the presence of matairesinol in the three species was obtained by using the reversed phase system of Freudenberg and Knof.[8] Filter paper strips (SS #2043b) were saturated with formamide and after spotting with extract were run upwards in a developing solvent of acetal saturated with formamide. A vivid red-purple spot (D.S.A.), R_f 0.21 corresponding to matairesinol was present in the heartwood of the three species. Conidendrin (R_f 0.15), hydroxy-matairesinol[7] (R_f 0.05), and unidentified components were also present.

Spectral characteristics of matairesinol. Ultraviolet measure-

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[1] A contribution of the Vancouver Laboratory, Forest Products Research Branch, Department of Forestry of Canada. This paper was presented before the Division of Wood Chemistry, American Chemical Society, Portland, Oregon, June 16, 1961.

[2] August-Wilhelm Sohn, Patentschrift **1004176**.

[3] T. Easterfield and J. Bee, *J. Chem. Soc.*, **1028** (1910).

[4] H. Erdtman, *Svensk-Papperstidn.*, **47**, 155 (1944).

[5] I. Pearl, *J. Org. Chem.*, **10**, 219 (1945).

[6] G. L. Carlberg and E. F. Kurth, *TAPPI*, **43**, 982 (1960).

ments were made on a Beckman spectrophotometer Model DK2, using isopropyl alcohol as a solvent. Values are given for the crystalline material from mountain hemlock, m.p. 119° followed by those for a reference sample of matairesinol in brackets. λ_{max} 231 mμ (log ϵ 4.13) (log ϵ 3.84); λ_{min} 253–254 mμ (λ_{min} 255 mμ); λ_{max} 282 mμ, (log ϵ 3.84) (log ϵ 3.77).

Infrared measurements were made on a Baird atomic infrared recording spectrophotometer Model KM-1. Identical spectra were obtained using the potassium bromide pellet method from both the mountain hemlock crystals, m.p. 119°, and the reference sample of matairesinol. The following wave lengths are quoted in cm.$^{-1}$: 3400 s, 2925 m, 2000 w, 1870 w, 1770 s, 1610 m, 1520 s, 1460 m, 1440 w, 1380 m, 1355 w, 1272 s, 1240 w, 1208 w, 1150 w, 1125 w, 1080 w, 1020 s, 965 w, 940 w, 922 w, 890 w, 870 m, 850 w, 830 m, 792 w, 782 w, 750 m, 720 w, 680 w, 650 w. The lower melting point material, m.p. 66–67°, differed only in having broad peaks between 1725–1760 and 1360–1380 cm.$^{-1}$

Optical rotation. Optical rotation in acetone using the 4-decimeter tube gave the following: $[\alpha]_D^{25°}$ (m.p. 66–67°) = −42.2° (2.0 g./100 ml.); $[\alpha]_D^{25°}$ (m.p. 119°) = −45.0° (2.0 g./100 ml.); literature,[8] $[\alpha]_D^{25°}$ = −45.0° (4.2 g./100 ml.).

Stability of matairesinol to sulfite cooking. The stability of matairesinol to both neutral and acid sodium bisulfite was determined by three separate experiments:

(a) Matairesinol (80 mg.) was refluxed with 5 ml. of water containing 250 mg. of sodium bisulfite for 4 hr.

(b) Matairesinol (200 mg.) was cooked in a stainless steel bomb with 1.6 ml. of a 6% sodium bisulfite solution at 130° for 6 hr. Shaking was maintained during the heating.

(c) Matairesinol (200 mg.) was cooked in a stainless steel bomb with 2.0 ml. of 6% sodium bisulfite saturated with sulfur dioxide at 130° for 6 hr. Shaking was maintained during the heating.

Chloroform extracts of each cook as well as of commercial waste sulfite liquor were examined by means of reversed phase paper chromatography. In the case of the three cooks only unchanged matairesinol was detected. No other lignan was found to be present. In the case of waste sulfite liquor extract, matairesinol, conidendrin, and some unknowns were clearly present.

Acknowledgment. We are indebted to Dr. K. Freudenberg for the reference sample of matairesinol and to MacMillan, Bloedel, and Powell River Company for a sample of commercial waste sulfite liquor.

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(7) H. Hergert and O. Goldschmidt, private communication.

(8) K. Freudenberg and L. Knof, *Chem. Ber.*, **90**, 2857 (1957).

Reaction of the Cyclic Chloride of o-Benzoylbenzoic Acid with Diethyl Ethoxymagnesiomethylmalonate

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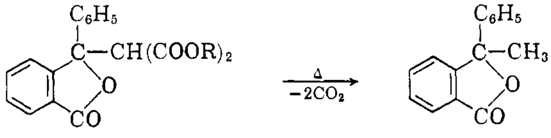
During a study of the reaction of methyl *o*-benzoylbenzoate with diethyl sodiomalonate, a compound, m.p. 100–101°, was isolated.[2] This compound was proved to be diethyl 3-phenylphthalidylmalonate, I_A, by hydrolysis to the malonic acid, I_B, followed by decarboxylation of the latter to 3-methyl-3-phenylphthalide, II.



I_A ($R = C_2H_5$)
$_B$ ($R = H$)

II

A compound, III, m.p. 77–79°, claimed to have the structure I_A, had been prepared by reaction of the pseudo acid chloride of *o*-benzoylbenzoic acid with diethyl ethoxymagnesiomalonate.[3] However, Koelsch[4] proposed that this compound is the enol form of ethyl *o*-benzoylmalonate, III_A,[5] since authentic I_A, m.p. 100–102°, was prepared by reaction of diethyl sodiomalonate with ethyl *o*-benzoylbenzoate.[4]

Before Koelsch's publication,[4] we had attempted to prepare the compound described by Yost and Burger.[3] However, due to a mislabeled reagent bottle, diethyl methylmalonate was used instead of diethyl malonate. A compound, m.p. 106–107°, was obtained to which the structure IV was assigned since it absorbs strongly at 5.65 μ (five-membered lactone) and 5.80 μ (ester). Furthermore the NMR

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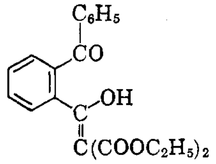
[2] A small amount of the same compound was obtained when pseudo methyl *o*-benzoylbenzoate, H. Meyer, *Monatsh.*, **25**, 475 (1904), was treated with diethyl sodiomalonate.

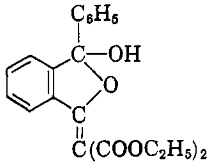
[3] W. L. Yost and A. Burger, *J. Org. Chem.*, **15**, 1113 (1950).

[4] C. F. Koelsch, *J. Org. Chem.*, **25**, 642 (1960).

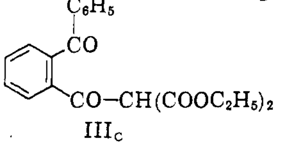
[5] In our hands, different preparations of III melt unsharply over about 10° ranges. For example, a sample of III sent by Professor Koelsch melted over the range 80–88°. Recrystallization from benzene–petroleum ether afforded samples which melted over ranges from 80–90° to 92–102°. These samples gave essentially identical infrared spectra in potassium bromide pellets. Probably III is a mixture of the forms $III_{A,B,C}$ whose composition varies with the crystallization media.



III_A



III_B



III_C

As none of the fractions had a band in the 5.6–5.7-μ region, lactonic structures are ruled out. We are not doing further work with III.