[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

THE OCCURRENCE OF CONIDENDRIN IN WESTERN HEMLOCK (*TSUGA HETEROPHYLLA*)[1]

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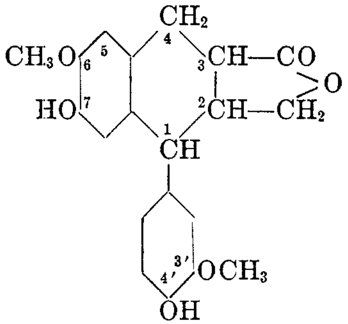
Conidendrin or sulfite liquor lactone was first obtained by Lindsey and Tollens (1) on extraction of the sulfite waste liquor from sprucewood with ether, and Holmberg (2) in 1920 proved its lactone structure. Erdtman (3) showed that conidendrin is identical with the lactone of 6-methoxy-7-hydroxy-1-(3′-methoxy-4′-hydroxyphenyl)-2-hydroxymethyl-1, 2, 3, 4-tetrahydronaphthalene-3-carboxylic acid and this phenyltetralin structure was confirmed by synthesis (4). The original opinion that conidendrin is formed first in the sulfite pulping of wood was disproved when Kawamura (5) isolated conidendrin from *Tsuga sieboldii* Carr, and Emde (6) extracted it from Norwegian spruce (*Picea excelsa*). Briggs and Peak (7) isolated conidendrin from the resinous exudates ("matai") of *Podocarpus spicatus*. In a qualitative investigation, Erdtman (8) found conidendrin in the sulfite waste liquors of seven out of fourteen *Picea* species, of four out of four *Tsuga* species, and of only one out of seven *Abies* species.



In the preparation of native lignin from western hemlock (*Tsuga heterophylla*) (9), a considerable amount of a crystalline compound was isolated which was identified as conidendrin. It crystallized partially from the dioxane solution of the resinous material obtained by alcohol extraction of the wood. It was identified by its melting point and its rotation, and by its acetate and methyl derivative. The preparation of the latter by means of diazomethane failed, probably on account of steric hindrance. In addition to these derivatives, the benzoyl and *p*-toluenesulfonyl derivatives were prepared. The former, obtained in good yield, is only very slightly soluble in acetone, in contrast to the other conidendrin derivatives. The ultraviolet absorption spectrum of conidendrin shows a maximum at 284 mmu and a comparison of the absorption curve

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with that of the native hemlock lignin (Figure 1) shows the close structural relationship between conidendrin or the lignans in general and lignin, and furnishes further proof for Freudenberg's theory (10) that lignin is built up by phenylpropane derivative building stones.

EXPERIMENTAL

Isolation of conidendrin. The dioxane-ether mother liquors obtained in the purification of native hemlock lignin (9) were evaporated to dryness. The residual resin, when allowed to stand for several days, crystallized and formed a mixture of conidendrin and resins. It was mixed with the minimum amount of dioxane or absolute alcohol and the conidendrin was separated from the resinous solution by filtration. The conidendrin was purified by crystallizations from 95% alcohol until a constant melting point was obtained. The yield was 25–30 grams or about 0.15% of the wood. Conidendrin crystallizes either in needles or in polyhedral crystals. Both forms melt at 254–255°, $[\alpha]_D^{20}$ −54.4° (c = 3.984 in acetone) [Holmberg (2) reported 254° and −54.5°].

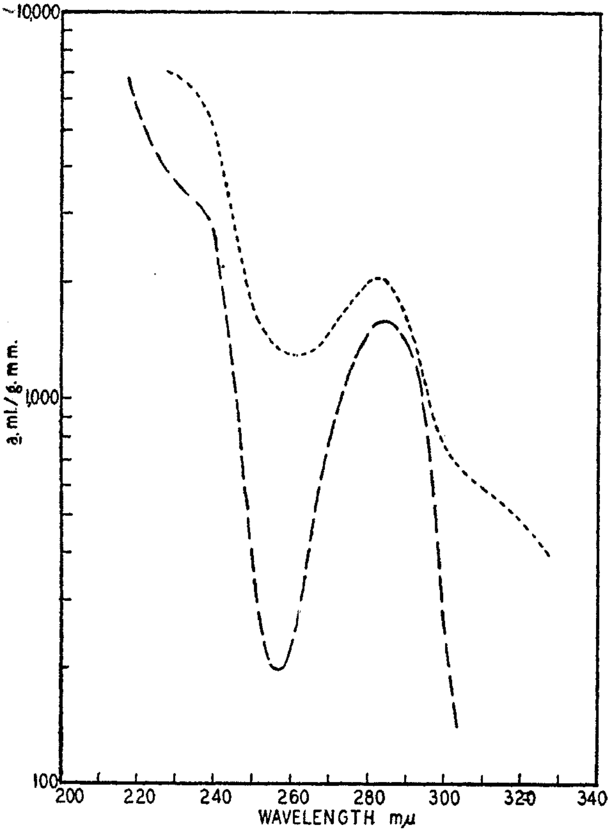

FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA IN 95% ETHANOL
---------, Native hemlock lignin; — — —, Conidendrin

Anal. Calc'd for $C_{20}H_{20}O_6$: MeO, 17.4. Found: MeO, 17.49.

Acetyl conidendrin. The acetate was prepared from 1 g. of conidendrin in 10 cc. of anhydrous pyridine and 5 cc. of acetic anhydride. The mixture was allowed to stand for 20 hours at room temperature. It was poured onto cracked ice and the acetyl conidendrin

(1.3 g.) filtered, washed, dried, and recrystallized from ethanol. It melts at 222–223°, $[\alpha]_D^{21}$ −73.53° (c = 3.249 in acetone) [Holmberg (2) reported 221–222° and −73.8°].

Anal. Calc'd for $C_{24}H_{24}O_8$: MeO, 14.1. Found: MeO, 14.35.

Benzoyl conidendrin. A solution of 1 g. of conidendrin in 10 cc. of anhydrous pyridine and 2 cc. of benzoyl chloride was allowed to stand overnight at room temperature. When the dark red mixture was poured onto cracked ice, a reddish-yellow resin separated which did not solidify. It was taken up in ether and the ether solution was washed successively with ice-cold dilute hydrochloric acid, water, ice-cold 10% NaOH, and water. When a few cc. of dioxane was added to the solution, it suddenly solidified by crystallization of the benzoyl conidendrin. Recrystallized from acetone, it melts at 145–152°, $[\alpha]_D^{19}$ −62.1° (c = 2.87 in pyridine), $[\alpha]_D^{20}$ −67.4° (c = 2.613 in acetone-pyridine 3:2).

Anal. Calc'd for $C_{34}H_{28}O_8$: MeO, 11.0. Found: MeO, 10.9.

p-Toluenesulfonyl conidendrin. When a solution of 1 g. of conidendrin in 15 cc. of pyridine was treated with 2 g. of *p*-toluenesulfonyl chloride, it dissolved very quickly with slight warming of the mixture. After standing for 16 hours, the solution was poured onto cracked ice, the toluenesulfonyl conidendrin filtered, washed, and dried in a desiccator. The yield was 1.6 g. It was recrystallized by dissolving in 5 cc. of dioxane, filtering the solution, and adding 95 cc. of ethanol. The toluenesulfonyl derivative separated as a curdy precipitate which soon changed into a fine crystalline powder. It melts at 195–196°, $[\alpha]_D^{21}$ −50.5° (c = 3.233 in acetone).

Anal. Calc'd for $C_{34}H_{32}O_{10}S_2$: MeO, 9.34; S, 9.65. Found: MeO, 9.27; S. 9.60.

Methyl conidendrin. When to a solution of 1 g. of conidendrin in 25 cc. of anhydrous dioxane, an ethereal solution of diazomethane from 10 cc. *N*-nitroso-*N*-methylurethan was added, neither nitrogen evolution nor a decoloration of the diazomethane solution was observed, and the conidendrin was recovered unchanged. It was therefore methylated with dimethyl sulfate and sodium hydroxide according to the method of Holmberg (2). The methyl conidendrin melts at 179°, $[\alpha]_D^{20}$ −103.6° (c = 3.207 in acetone) (Holmberg reported 179–180° and −100.9°).

Anal. Calc'd for $C_{22}H_{24}O_6$: MeO, 32.29. Found: MeO, 32.0.

SUMMARY

Conidendrin has been isolated from western hemlock and identified by its acetyl and methyl derivatives. Benzoyl and *p*-toluenesulfonyl conidendrin have been prepared. The ultraviolet absorption spectrum of conidendrin has been determined.

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