[Contribution from The Institute of Paper Chemistry]

THE INFRARED ABSORPTION SPECTRA OF TWO ISOMERS OF CONIDENDRIN AND OF THE CORRESPONDING DEMETHYLATION PRODUCTS

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The isolation of one stereoisomer of conidendrin (now termed α-conidendrin) has been described by Kawamura (1), Emde and Schartner (2), and Erdtman (3). These investigators extracted the material from various softwoods or from sulfite waste liquors of several softwoods. Brauns (4) extracted the same isomer from western hemlock (*Tsuga heterophylla*) and Pearl (5) obtained it from the sulfite waste liquor of western hemlock. Recently, Hearon, Lackey, and Moyer (6) reported the preparation of a second stereoisomer of conidendrin, which has been designated β-conidendrin. In the same papers, Hearon, *et al.* also described the preparation of the demethylation products of the two isomers of conidendrin. These hydroxylated compounds are designated as α- and β-conidendrol, respectively, to correspond with the parent substances.

The infrared spectra of β-conidendrin, α-conidendrol, and β-conidendrol have been determined.[2] The work was carried out using a Perkin-Elmer Infrared Spectrometer Model 12-B with a General Motors breaker-type amplifier and a Brown strip chart recorder. The instrument was operated under conditions similar to those described by Jones (7) who determined the spectrum of α-conidendrin (8). A sodium chloride prism was used to cover the range 3700 cm.$^{-1}$ to 725 cm.$^{-1}$.

Excellent crystalline mats of the compounds were prepared by evaporating the respective acetone solutions on salt plates. The "films" thus formed were strongly adherent to the plates, and showed little tendency to scatter the infrared radiation. Crystal mats were also deposited on salt plates from dioxane-ethanol solutions in order to clarify the regions of the spectrum where absorption resulting from retained acetone might be expected. The mats from the dioxane-ethanol solutions were not as uniform as those from acetone. When satisfactory thicknesses of the compounds were obtained on the salt plates, the "films" were dried *in vacuo* over sulfuric acid, Ascarite, and paraffin for at least 24 hours before the spectrum determination.

The identity of each substance was checked by observing the melting point (Fisher-Johns melting point block) and the optical rotation (Bausch & Lomb half-shadow saccharimeter). Table I is a summary and comparison of the observed and reported values.

The spectra of the three compounds are shown in Figure 1. That of α-conidendrin, as obtained by Jones (8), is included for comparison. The possible band assignments for each of the spectra are given in Table II.

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[2] The samples used were furnished by the Crown Zellerbach Corporation, Camas, Washington.

TABLE I

MELTING POINTS AND OPTICAL ROTATIONS

	MELTING POINT, °C.		OPTICAL ROTATION, $[\alpha]_D^{25}$	
	Obs.	Lit.	Obs.[d]	Lit.[d]
β-Conidendrin	208	210–212[a]	+30.3 (4)	+32.5 (4)[b]
α-Conidendrol	164	165–166[b, c]	−78.1 (2)	−72.5 (2)[b, e]
β-Conidendrol	247	249–251[b]	+13.0 (4)	+15 (5)[b]

[a] Holmberg, *Ber.*, **54**, 2389 (1921). [b] See ref. 6. [c] Anhydrous. [d] Parenthetical numbers are concentrations in grams of solute per 100 g. of acetone. [e] Dihydrate [the dihydrate melts at 102–103°] (6).

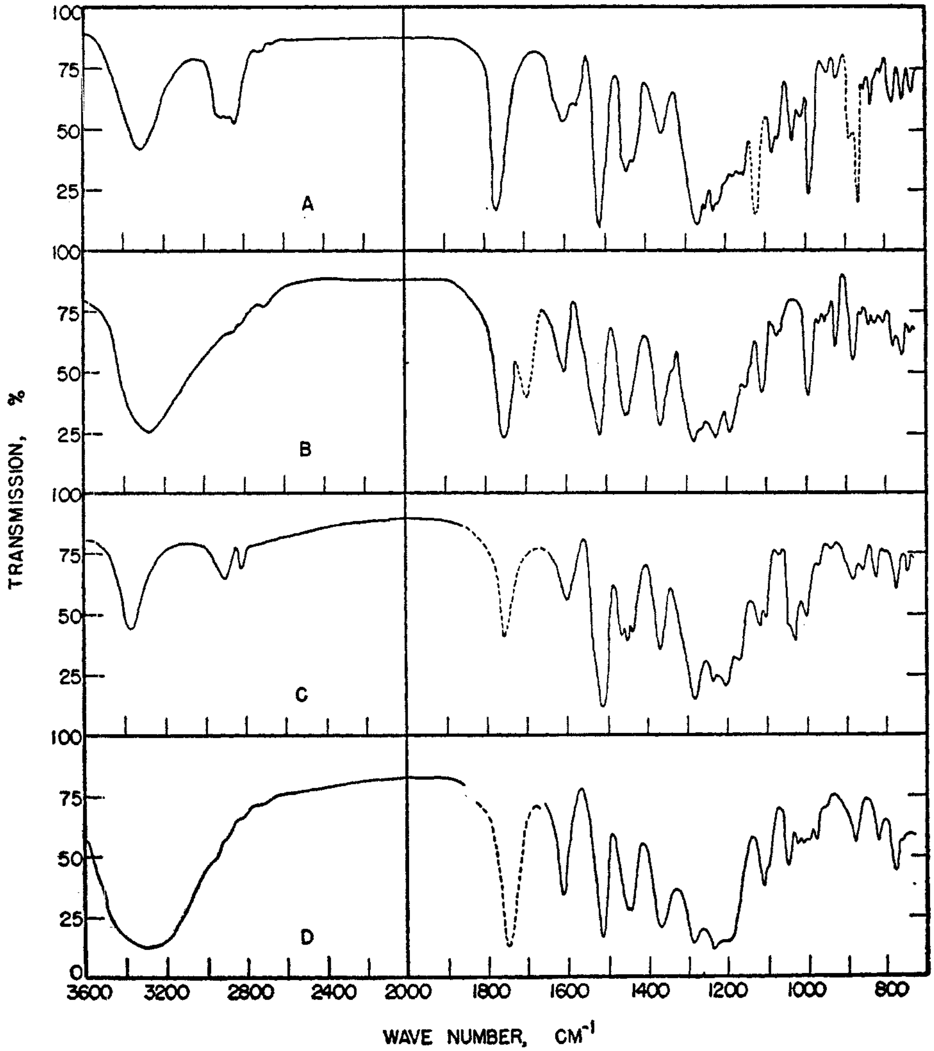

FIGURE 1. INFRARED ABSORPTION SPECTRA

A. α-Conidendrin (film from dioxane-ethanol); B. α-conidendrol (film from acetone); C. β-conidendrin (film from acetone); D. β-conidendrol (film from acetone). Dotted lines refer to absorption attributed to retained solvent and dashed lines refer to films of the respective compounds from dioxane-ethanol solution.

Inspection of Figure 1 reveals that:

1. The conidendrols exhibit a higher hydroxyl content (increased hydroxyl absorption intensity) than the conidendrins. Little difference is found in the hydroxyl absorption strengths of the conidendrols.
2. The hydroxyl groups or at least a portion of them are evidently involved in bridging of some type in each componud. However, the conidendrols show the strongest hydrogen bonding (shift to low frequency of the hydroxyl absorption band) and β-conidendrin the least.
3. The saturated C-H stretching absorption bands are nearly obscured by the strong hydroxyl absorptions in the conidendrols. The saturated C-H stretching frequencies, however, are quite clear in the spectra of the conidendrins.
4. The lactone structure involving the strained ring is clearly indicated by strong absorption occurring in the high-frequency end of the carbonyl absorption range. The intensity of this absorption remains apparently constant for the four compounds. The reasons for the shifts in frequency of the carbonyl bands between the various products are not clear, although the changes could be associated with the corresponding variations in the hydroxyl bands to indicate hydrogen bridging.

TABLE II

Tentative Absorption Band Assignments

ASSIGNMENT	ABSORPTION MAXIMUM, CM.$^{-1}$			
	α-Conidendrin[a]	β-Conidendrin	α-Conidendrol	β-Conidendrol
Hydroxyl	3310[b]	3370[c]	3270[c]	3280[c]
Saturated C-H	2920; 2870; 2820	2900; 2820	[d]	[d]
Gamma lactone	1771	1762	1754	1744
Phenyl ring	1603; 1511	1599; 1512	1606; 1515	1607; 1515

[a] See ref. 8. [b] Band position determined within ±10 cm.$^{-1}$. [c] Band position determined within ±15 cm.$^{-1}$. [d] These bands are apparently obscured by the strong hydroxyl absorption; absorption maxima could be detected but they were somewhat indefinite.

5. The aromatic nature of the materials is shown by two strong absorption bands at about 1600 cm.$^{-1}$ and 1515 cm.$^{-1}$, respectively.
6. There are several differences in the lower frequency region of the spectra of these materials. Some of these may be due to stereoisomerism or to demethylation. However, because the low frequency portion of the infrared spectrum obtained gives corroborative evidence only, little can be stated concerning it, except to support the above items.

Because an empirical method is involved, it should be pointed out that the group assignments made in this study are intended only for the compounds in question. Excellent surveys of structure-absorption band correlation in infrared spectroscopy are available; for example, see the review by Barnes, Gore, Liddel, and Williams (9), (in which is incorporated a library of reference curves and a comprehensive bibliography through 1941) and by Rasmussen (10).

SUMMARY

The infrared absorption spectra of two stereoisomers of conidendrin and of the corresponding demethylated products were determined. A tentative correlation of the structure with the absorption bands is given.

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