

## The Structure of Pinopalustrin and its Relations to Other Lignans

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Long ago a new phenol was isolated in the Research Center of Hercules Inc., Wilmington, Delaware. It was obtained from benzene extracts of exhumed stumps of *Pinus palustris* Miller, "long leaf pine". After removal of the resin acids, a residue remained which was dissolved in 2-propanol, whereupon the phenol gradually crystallized with solvent of crystallization. Evaporation of the solvent afforded an amorphous product, which was called pinopalustrin and which analysed for C<sub>18</sub>H<sub>16</sub>O<sub>5</sub>(OMe)<sub>2</sub>. It showed strong UV absorption at 230 and 280 nm.

The compound was first investigated at Hercules and later in Stockholm and a preliminary account of this work was given on the occasion of the "10de Nordiska Kemistmötet", Stockholm, August 17–21, 1959, by one of us (B.C.).<sup>1</sup>

Pinopalustrin gave a dimorphous dimethyl ether, C<sub>18</sub>H<sub>14</sub>O<sub>5</sub>(OMe)<sub>4</sub>, (Me<sub>2</sub>SO<sub>4</sub>/NaOH), MS: *m/e* 402 (M<sup>+</sup>), which was soluble in hot alkali (lactone) and which on acetylation gave an acetate, C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>(OMe)<sub>4</sub>OAc, m.p. 102–103°C. Ethylation, (Et<sub>2</sub>SO<sub>4</sub>/NaOH), gave a non-crystalline diethyl ether, C<sub>18</sub>H<sub>14</sub>O<sub>5</sub>(OMe)<sub>2</sub>(OEt)<sub>2</sub>.

Permanganate oxidation of the dimethyl ether gave veratric acid (55%) and the diethyl derivative gave *O*-ethylvanillic acid (68%). The dimethyl ether reacted with phenylmagnesium bromide to give a product which furnished benzophenone with periodate. Reduction with LiAlH<sub>4</sub> in ether gave a triol, C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>(OMe)<sub>4</sub>, which consumed 1 mol of periodate.

From these results and the mass spectrum of the dimethyl ether it became evident that pinopalustrin was a lignan and structure 1 (without stereochemistry) was proposed for it.<sup>1</sup> This work was not published, pending the elucidation of the configuration.

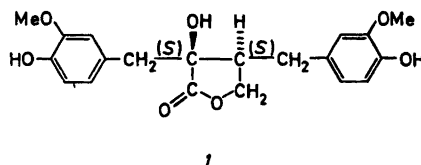
Our observations lay fallow for many years. We noticed, however, that the physical properties of pinopalustrin, of its derivatives and of the triol were closely related to those reported for the aglucone nortrachelogenin and the triol obtained from nortrachelogenin dimethyl ether.<sup>2,3</sup> Professor S. Nishibe kindly informed us that nortrachelogenin dimethyl ether was iden-

Table 1. Comparison of physical constants.

Compound	M.p./°C	[α] <sub>D</sub> /deg.
Pinopalustrin (1)	Amorphous	—
Nortrachelogenin (2)	Amorphous	– 17 (EtOH)
Wikstromol (3)	Amorphous	+ 72 (CHCl <sub>3</sub> )
Dimethyl ether of 1	96–97, 127–128	– 39 (CHCl <sub>3</sub> )
Dimethyl ether of 2	97–98.5	– 46 (EtOH)
Dimethyl ether of 3	96–97	+ 35 (CHCl <sub>3</sub> )
Triol from dimethyl ether of 1	133–134	– 25 (CHCl <sub>3</sub> )
Triol from dimethyl ether of 2	132–133	– 23 (CHCl <sub>3</sub> )
Triol from dimethyl ether of 3	130–131	+ 9 (EtOH)
Triol from gmelinol <sup>5</sup>	132	– 3 (EtOH)
Same triol from olivil <sup>2</sup>	132–133	– 22 (CHCl <sub>3</sub> )
Carinol dimethyl ether <sup>3</sup>	130–131	– 3 (EtOH)

tical with pinopalustrin dimethyl ether (mixed melting point, superimposable IR spectra).

Quite recently Tandon and Rastogi<sup>4</sup> isolated another lignan, wikstromol. The structure and configuration given are those of an enantiomer of pinopalustrin.



The pertinent data for pinopalustrin, nortrachelogenin and wikstromol are given in Table 1. It follows that the structure and absolute configuration of pinopalustrin are as in 1.

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