

## Studies on the Chemistry of Aspenwood. IX. *p*-Hydroxybenzoic Acid in Aspen Klason Lignin

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Received March 18, 1960

In a previous study on the Klason lignin determination of trembling aspen (*Populus tremuloides*), *p*-hydroxybenzoic acid was found to be a major component of the Klason lignin filtrate.<sup>1</sup> Furthermore, the Klason lignin precipitate resisted alkaline nitrobenzene oxidation and did not yield monomolecular products under these conditions. Other studies in our laboratories<sup>2</sup> indicated that *p*-hydroxybenzoic acid was probably present in aspenwood lignin in a combined form, and therefore an attempt was made to release it by more drastic means than alkaline nitrobenzene oxidation.

### Experimental

A number of identical Klason lignin determinations were made on the same extracted wood and in the same manner as reported earlier.<sup>1</sup> The average yield of Klason lignin was 16.8% and the methoxyl value was 20.5%. Five grams of this lignin was added slowly to a fused mixture of 13 g. solid potassium hydroxide and 2 g. of water at 170°. The temperature rose to 190°. After addition was complete, the

fused mixture was stirred for five min. between 175 and 190° and allowed to cool. The cooled mixture was dissolved in water, acidified with dilute sulfuric acid, and extracted continuously with ether. The ether extract was dried, and the ether removed to yield 0.21 g. (4.2%) of ether-soluble material. Qualitative paper chromatography in the butanol-2% aqueous ammonia and 10:3:3 butanol-pyridine-water developers<sup>1</sup> indicated *p*-hydroxybenzoic, syringic, and vanillic acids as the chief components of the ether-soluble material and several unidentified phenolic acids as minor components. Quantitative studies by previously described paper chromatographic and spectrophotometric procedures<sup>3</sup> indicated that the ether-soluble material contained 51.0% *p*-hydroxybenzoic acid, 13.1% syringic acid, and 8.7% vanillic acid. Thus, the Klason lignin precipitate of trembling aspenwood comprises over 2% *p*-hydroxybenzoic acid in the combined form.

### Results

This finding of the *p*-hydroxybenzoic acid moiety in the Klason lignin precipitate of trembling aspenwood with a methoxyl content of 20.5% indicates that this Klason lignin precipitate must be different from the Klason lignin precipitates of similar methoxyl content from other hardwoods such as birch and maple which do not give *p*-hydroxybenzoic acid under similar alkali fusion conditions. In addition, these data suggest the possibility that hardwood Klason lignin precipitates vary somewhat in composition from species to species.

- (1) I. A. Pearl and D. L. Beyer, *Tappi*, **40**, 45 (1957).
- (2) D. A. Stanek, *Tappi*, **41**, 601 (1958).
- (3) I. A. Pearl, D. L. Beyer, B. Johnson, and S. Wilkinson, *Tappi*, **40**, 374 (1957).