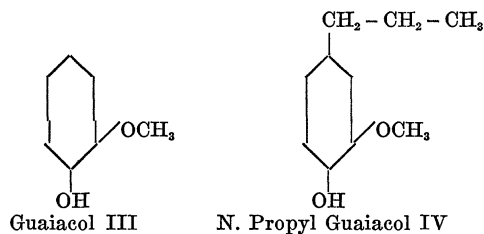


pylene side chain. The conception of Freudenberg<sup>11</sup> that lignin is made up of vanilyl and piperonyl components, the union taking place through the hydroxyl group of the vanilyl constituent, although more in harmony with the experimental facts, is still open to objection in that the assumption is made that there are no free phenolic hydroxyl groups in lignin. Klason<sup>12</sup> has recently shown that in the case of lignin sulphonic acid, free phenolic hydroxyl groups are present. Furthermore, the evidence offered by Freudenberg<sup>13</sup> in favor of the presence of a methylene oxide group in lignin is by no means convincing.

In a paper recently presented by the writer before the Cincinnati meeting of the American Chemical Society, it was reported that when lignin was distilled with zinc dust at 400° C. in an atmosphere of hydrogen, an oil was obtained which amounted to 16 per cent. of the weight of the lignin used. Approximately, 55 per cent. of the oil was phenolic in character, and in this fraction guaiacol (III) was definitely identified. In continuing this line of investigation, another fraction has now been isolated from the phenolic portion of the oil. This fraction distilled over at 203 to 215° C. The 3,5-dinitrobenzoyl derivative of this was prepared, and after repeated crystallizations from ligroin and 95 per cent. ethanol, a crystalline substance, was obtained which melted sharply at 116.8° C. (cor.). This melting point corresponded exactly to that of the 3,5-dinitrobenzoyl derivative prepared from a pure specimen of normal propyl guaiacol (IV) (1,N. Propyl-3-methoxy-4-hydroxybenzene). When the two compounds were mixed



the resulting mixture was also found to melt at 116.8° C. (cor.). The identity of these substances was further confirmed by the optical properties<sup>14</sup> of the crystals.

The isolation of guaiacol and n-propyl guaiacol as degradation products of lignin is believed to be of considerable significance from the standpoint of the constitution of lignin. It would appear, in all prob-

ability, that the two fundamental units in the structure of lignin are guaiacol and n-propyl guaiacol, the latter having the hydrogen atoms in the n-propyl side chain substituted by alcoholic hydroxyl groups. Just how the union takes place is, of course, not known, but probably through the n-propyl side chain in such a manner that leaves most of the phenolic hydroxyl groups free.

To account for the well-known reaction of lignin with bisulphites, it is not necessary to assume, as some investigators have done, the presence of an unsaturated bond in this complex, but can be explained according to Fuchs<sup>15</sup> on the basis that the phenolic nuclei may behave in their tautomeric form and, therefore, as unsaturated cyclic ketones.

This conception of the structure of lignin is in complete harmony with all the known facts as to its chemical behavior, and points the way toward a more complete understanding of its complex constitution.

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<sup>11</sup> Ref. 3-b.

<sup>12</sup> P. Klason, "Beiträge zur Konstitution des Fichtenholz Lignins," *Ber. deut. chem. Ges.*, 63, 792 (1930).

<sup>13</sup> K. Freudenberg and M. Harder, "Formaldehyd als Spaltsück des Lignins," *Ber. deut. chem. Ges.*, 60, 581 (1927).

<sup>14</sup> The optical properties of the crystals were determined by G. L. Keenan of the Food and Drug Administration of this Department.