Eight independent experiments of this sort were made, the orientation of the respective blocks being successively interchanged as was also the order of irradiation of the respective pairs so that positional or such chronological difference might not influence the means of all these results. These mean values of φ together with the corresponding periods of irradiation, t, are given in the table and represented graphically in the figure. In the table also is given the A.D. of each mean (the mean deviation divided by $\sqrt{8}$) which is employed as a precision measure.

TABLE I

t (in minutes)	φ (in days)	A.D.	t (in minutes)	φ (in days)	A.D.
0	5.55	.06	140	8.20	.07
35	8.09	.11	175	8.18	.07
70	9.24	.09	210	8.10	.08
105	8.36	.10	245	8.09	.08

The indication of a maximum point on the graph in the interval, 35 to 105 minutes, is statistically significant, and the decline followed by attainment of an almost level plateau is a surprising result. Here, too, the precision measures indicate that this is not due to mere chance.

ROBERT TENNANT, JR.
DEPARTMENT OF PATHOLOGY,
YALE UNIVERSITY

THE EFFECT OF SUNLIGHT ON HUMAN BLOOD CELLS

EXPERIMENTS were made to elucidate the action of sunlight on human cells under the condition of general insolation. The first experiments concerned the cells which are easiest to obtain, namely, the red blood corpuscles. The results of these experiments are described below.

It was found first that, in accord with the results obtained by Pfeiffer and Bayer, Hausman and Loewy, and Löhner, red corpuscles suspended in a salt solution exposed to direct sunlight gradually disintegrate and hemolize. This disintegration occurs, however, only if the corpuscles are illuminated by intensive sunlight (clear sky, dry air, at noon). Under such condition the first hemolysis is noticed 10 minutes after beginning of insolation. Diffuse sunlight does not produce any hemolysis. Further experiments show, however, that even diffuse light which is fifty times as weak as direct sunlight makes the corpuscles less resistant and accelerates their spontaneous hemolysis when after the illumination they are kept in the dark in a physiological salt solution. After the exposure of the suspension of corpuscles to direct sunlight their resistance against poisons and hypotony is markedly diminished. But among the rays of sunlight only visible rays decrease this resistance. If the corpuscles are exposed to direct sunlight in quartz tubes no decrease or even an increase of the resistance is observed. Special experiments showed that ultraviolet rays, if they are weak or act for a short time, increase the resistance of the corpuscles and protect them against the harmful effect of visible rays. However, strong ultra-violet rays from a mercury vapor lamp destroy the red corpuscles.

In *in vivo* experiments it was found that a total insolation of men lasting 10 minutes (December, January, in Arizona) increases the resistance of young red corpuscles and decreases the resistance of old corpuscles, the latter being more sensitive to visible light. The insolation of the same men for one hour increases the resistances of all their corpuscles very markedly, but only if the sunlight contains a sufficient amount of ultra-violet rays (clear sky). This increase of the resistance is not lasting and disappears within twenty-four hours. When the sky is partially covered by clouds and the humidity is high or when sunlight is filtered through glass plates (6 mm thick) a marked decrease of the resistance of all corpuscles is observed, and this decrease does not always disappear within twenty-four hours.

The author's experiments twenty years ago showed that the permeability of protoplasm of plant cells for water soluble substances is greater in light than in the dark. This observation was confirmed later by many scientists not only on plant but also on animal cells. We might expect, therefore, the same action of light on red corpuscles. Indeed the present experiments show that the permeability of red corpuscles for water soluble substances is increased by sunlight, and this effect is due to the visible light in this case, too. Human red corpuscles were investigated in respect of their permeability for grape sugar. It may, therefore, be assumed that the nutrition of red cells is enhanced by the action of sunlight. As the chemical and physical structure of red corpuscles is similar to that of colorless cells, the results obtained on red corpuscles can be extended to all cells of our organism, and it is likely that sunlight increases the nutrition of our organism in general.

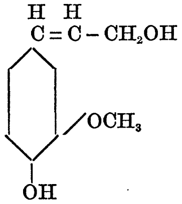
W. W. LEPESCHKIN
FROM THE LABORATORIES OF THE
DESERT-SANATORIUM AND
INSTITUTE OF RESEARCH,
TUCSON, ARIZONA

THE ISOLATION OF NORMAL PROPYL GUAIACOL AS A DEGRADATION PRODUCT OF LIGNIN

THE woody portions of plants, such as cobs, hulls, stalks, leaves, trunks of trees and shrubs, are composed principally of carbohydrates, mostly cellulose and pentosans, and a complex designated as lignin. The latter is an amorphous substance ranging in color from light brown to black, depending on the method used in its isolation.

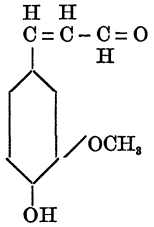
Commercially, lignin is obtained as a by-product in the preparation of paper pulp from wood. When wood is digested either with a calcium bisulphite solution or sodium hydroxide or sodium hydroxide and sodium sulfide solutions, under pressure, the lignin is dissolved, leaving the cellulose in a more or less pure state. The lignin obtained in this operation is generally discarded, and its disposal aggravates seriously the river pollution problem. When one considers that in this country alone approximately 1,500,000 tons of lignin are annually discharged from the various pulpwood mills, the wastefulness of this operation will be readily realized. Furthermore, there is produced annually on the farms of this country millions of tons of various agricultural waste materials, such as cornstalks, corn-cobs, cereal straws, flax straw and hulls, 10 to 20 per cent. of which is lignin. The fact that lignin now constitutes an enormous industrial and agricultural waste material has stimulated great research activity, on the fundamental chemistry and the economic utilization of this natural product.

Although lignin has been studied by chemists for nearly a century, the chemistry of this substance is still obscure. Considerable difference of opinion prevails among investigators as to whether this substance belongs to the aliphatic, aromatic, hydroaromatic or heterocyclic series. Among the advocates of an aromatic structure for lignin may be mentioned Klason,[1] Kürschner[2] and Freudenberg[3] and coworkers. On the other hand, Willstätter and Kalb,[4] Jonas[5] and Marcusson[6] contend that lignin is either hydroaromatic or belongs to the heterocyclic series. Klason has modified his conception of the structure of lignin from time to time, but he has generally assumed that it is structurally related to coniferyl alcohol (I)



Coniferyl alcohol (I),

or coniferyl aldehyde (II)



Coniferyl aldehyde (II).

Kürschner assumes that lignin is a polymer of the glucoside coniferin, which Tiemann and Haarmann[7] have shown yields glucose and coniferyl alcohol upon hydrolysis. The fact that lignin does not behave like a true unsaturated compound would speak against the Klason and Kürschner conception of the structure of lignin. Further, when lignin is heated with hydriodic acid as in the Zeisel determination of alkoxyl groups, methyl iodide only is given off. This has been definitely established in the case of spruce[8] and oat-hull[9] lignin. If lignin were structurally related to coniferyl alcohol or a derivative of coniferyl alcohol or were a polymer of coniferin, one ought to obtain a mixture of methyl iodide and ethyl iodide upon heating it with hydriodic acid. Tiemann and Haarmann[10] have shown that coniferyl alcohol when heated with hydriodic acid gives both methyl iodide and ethyl iodide, the latter resulting from a degradation of the pro-

---

[1] P. Klason, Svensk Kem. Tidskrift, 1897, p. 135; "Beitrag zur Kenntnis des chemischen Baues des Tannenholzlignins," *Chem. Zentralblatt,* 90, I, 92 (1919); "Über Lignin und Ligninreaktionen," *Ber. deut. chem. Ges.,* 53, 706 (1920); 'Beitrag zur Kenntnis der Konstitution des Fichtenholzlignins," *Ibid.,* 53, 1864 (1920); "Beitrag zur Konstitution des Fichtenholz-Lignins," *Ibid.,* 58, 375, 1761 (1925); *Ibid.,* 62, 2523 (1929); *Ibid.,* 63, 792, 1548, 1983 (1930).

[2] K. Kürschner, "Zur Chemie der Ligninköper," p. 141, published in F. B. Ahrens' "Sammlung Chemischer und Chemischtechnischer Vorträge," 28, Ferd. Enke, Stuttgart, 1926.

[3] K. Freudenberg, "Zur Kenntnis des Fichtenholz-Lignins," Sitzungsberichte d. Heidelberger akad. d. Wissenschaften (*Math.-Naturwissenschaft*), 1928, Abhandlung, 19; K. Freudenberg, H. Zocher and W. Dürr, "Weitere Versuche mit Lignin," *Ber. deut. chem. Ges.,* 62, 1814 (1929).

[4] R. Willstätter and L. Kalb, "Über die Reduktion von Lignin und von kohlenhydraten mit Jodwasserstoffsaure und Phosphor," *Ber. deut. chem. Ges.,* 55, 2637 (1922).

[5] K. G. Jonas, "Das Problem des Lignins," Wochenbl. f. Papierfabrikation 56, No. 24*A*, 83 (1925).

[6] J. Marcusson, "Die Struktur der Huminsäuren und Kohlen," *Z. angew. Chem.,* 34, 437 (1921); *Ibid.,* 35, 165 (1922); *Ibid.,* 36, 42 (1923); *Ber. deut. chem. Ges.,* 58, 869 (1925).

[7] F. Tiemann and W. Haarmann, "Über das coniferin und seine Unwandlung in das aromatische Princip. der Vanille," *Ber. deut. Chem. Ges.,* 7, 608 (1874); F. Tiemann, "Zur Kenntnis des Glieder der Protocatechureihe," *Ber. deut. Chem. Ges.,* 11, 659 (1878).

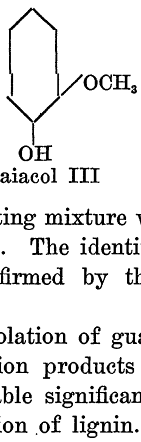
[8] E. Hägglund and B. Sundroos, "Zur Kenntniss Alkoxylgruppen des Holzes und des Lignins von Fichte," *Biochem. Zeitsch.,* 146, 221 (1924).

[9] M. Phillips, "The Chemistry of Lignin. IV. Lignin from Oat Hulls," *J. Am. Chem. Soc.,* 52, 793 (1930).

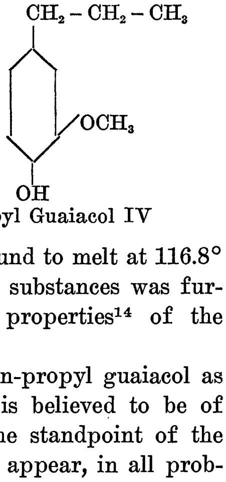
[10] Ref. 7.

pylene side chain. The conception of Freudenberg[11] 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[12] has recently shown that in the case of lignin sulphonic acid, free phenolic hydroxyl groups are present. Furthermore, the evidence offered by Freudenberg[13] 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[14] of the crystals.



Guaiacol III



N. Propyl Guaiacol IV

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 probability, 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[15] 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.

Max Phillips

Contribution from the Color and Farm
Waste Division, Bureau of Chemistry
and Soils, U. S. Department of Agriculture,
Washington, D. C.

BOOKS RECEIVED

Curtman, Louis J. *Qualitative Chemical Analysis.* Pp. x + 539. 41 figures. Macmillan. $4.00.

East, Edward M., Editor. *Biology in Human Affairs.* Pp. xi + 399. Whittlesey House, McGraw-Hill. $3.50.

Emmons, William H. *Geology of Petroleum.* Pp. xi + 736. 433 figures. McGraw-Hill. $6.00.

Hill, A. V. *Adventures in Biophysics.* Pp. ix + 162. Illustrated. University of Pennsylvania Press. $3.00.

Holmes, Harry N. *Introductory College Chemistry.* Revised edition. Pp. viii + 550. 153 figures. Macmillan. $3.25.

Mott-Smith, Morton. *This Mechanical World.* Pp. xvi + 233. 45 figures. Illustrated by Emil Kosa, Jr. Appleton. $2.00.

Newsholme, Sir Arthur. *International Studies on the Relation Between the Private and Official Practice of Medicine with Special Reference to the Prevention of Disease;* Conducted for the Milbank Memorial Fund. Volume I: The Netherlands, Scandinavia, Germany, Austria, Switzerland. Pp. 245. Williams and Wilkins.

Newton, Sir Isaac. *Opticks:* A Treatise of the Reflections, Refractions, Inflections and Colours of Light. Reprinted from the fourth edition. Pp. xxviii + 414. Illustrated. Whittlesey House, McGraw-Hill. $2.50.

Sanders, J. Edward. *Safety and Health in Organized Camps.* Pp. viii + 133. National Bureau of Casualty and Surety Underwriters.

Spinney, Louis B. *A Text-book of Physics.* Fourth edition. Pp. xiii + 679. 422 figures. Macmillan. $3.75.

Tisserant, R. P. Charles. *Essai sur la grammaire Banda.* Pp. 185. Institut d'Ethnologie, Paris. 45 francs.

Tôhoku Imperial University. *Science Reports.* First series: Mathematics, Physics and Chemistry. Volume XX, No. 1: Pp. 196. Illustrated. Maruzen Company, Tokyo.

---

[11] Ref. 3-b.

[12] P. Klason, "Beiträge zur Konstitution des Fichtenholz Lignins," *Ber. deut. chem. Ges.*, 63, 792 (1930).

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

[14] The optical properties of the crystals were determined by G. L. Keenan of the Food and Drug Administration of this Department.

[15] W. Fuchs, "Uber Lignin und den Sulfit-Kochprozess," *Ber. Deut. chem. Ges.*, 54, 484 (1921).