During the course of related investigations on the biogenesis of methyl *p*-methoxycinnamate by the mold *Lentinus lepideus*,[4] there were detected in the culture medium shikimic acid and five keto-acids, including *p*-hydroxyphenylpyruvic acid. The structural relationship of this acid to the suggested building stones of lignin, namely, coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, prompted an investigation of the possible role of this acid in the mechanism of lignification.

p-Hydroxyphenylpyruvic acid-$C^{14}OOH$ was prepared by an azlactone synthesis[5] employing *p*-hydroxybenzaldehyde and tagged acetyl glycine, which in turn was prepared by acetylation of glycine-1-C^{14} (obtained from Tracerlab, Inc., Boston, Mass.). The resulting azlactone of 4-acetoxy-α-acetamidocinnamic acid was hydrolyzed to 4-acetoxy-α-acetamido cinnamic acid, and this in turn was hydrolyzed by the standard method[5] to *p*-hydroxyphenylpyruvic acid, m.p. 218–220°.

Anal. Calcd.; C, 60.00; H, 4.44. Found: C, 59.44; H, 4.53.

76 mg. of the tagged acid was diluted with 54 mg. of "cold" compound, and the mixture was dissolved in water. An equimolar amount of KH_2PO_4 was added, and the whole was brought to 50 ml. The solution was divided into six aliquots of 8.33 ml. each, which were placed in individual test tubes.

The six uppermost leaves of a mature sugar cane plant (*Saccharum officinarum*) were cut about six inches from their tips, and the cut ends of the leaves were rolled lengthwise and immersed into the solutions of the tagged acid. Cotton plugs were inserted in the tubes and, after the acid solutions had been completely absorbed, they were replaced with equal volumes of distilled water.

Fifteen days after absorbing the tagged acid solutions, the plant was cut down, and the leaves were removed. The resulting stalk was cut, air-dried, milled to 60-mesh, and re-dried. Lignin was isolated from the powder by a standard method.[6] The lignin was then subjected to a Van Slyke–Folch oxidation,[7] and the resulting barium carbonate was collected and counted.

TABLE I

COMPARISON OF ACTIVITIES OF *p*-HYDROXYPHENYLPYRUVIC ACID AND BARIUM CARBONATE

	Activity	
	C.p.m./Mg. C	Total c.p.m.
p-Hydroxyphenylpyruvic acid	9123	750,230
$BaCO_3$	246	533,662

In Table I are recorded the activity measurements of the incorporated *p*-hydroxyphenylpyruvic acid, and of the barium carbonate obtained on combustion of the lignin together with the calculated total activities of each. From these data, it appears that most of the activity of the introduced *p*-hydroxyphenylpyruvic acid was indeed incorporated into the lignin. Hence, these results provide strong evidence that *p*-hydroxyphenylpyruvic acid is an intermediate on the pathway between shikimic acid, derived from carbohydrates, and the lignin building stones, in the biogenesis of lignin itself.

Thus, the process of lignification may now be formulated as follows: carbohydrates are enzymatically transformed *via* shikimic acid to a *p*-hydroxyphenylpropane unit. Such a primary building stone then can undergo methoxylation to give a guaiacyl unit. In softwoods, the two aromatic building stones may form lignin by repeated condensations. Obviously, in hardwood lignins a syringyl type building stone is also required.

Acknowledgments—The authors wish to express their gratitude to Dr. Wm. J. Robbins of the New York Botanical Gardens for his courtesy in arranging for the cultivation of the sugar cane plants. This study was supported by grants of the National Science Foundation, the U. S. Public Health Service and the U. S. Atomic Energy Commission.

COMMUNICATION NO. 318 FROM THE
DEPARTMENT OF ORGANIC CHEMISTRY
AND ENZYMOLOGY
FORDHAM UNIVERSITY
NEW YORK 58, N. Y.
WALTER J. SCHUBERT
SAMUEL N. ACERBO
F. F. NORD

RECEIVED NOVEMBER 1, 1956

---

[4] G. Eberhardt and F. F. Nord, *Arch. Biochem. and Biophys.*, **55**, 578 (1955); G. Eberhardt, THIS JOURNAL, **78**, 2832 (1956).

[5] J. A. Saul and V. M. Trikojus, *Biochem. J.*, **42**, 80 (1948).

[6] G. J. Ritter, R. M. Seborg and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

[7] D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940).

AN ENHANCEMENT OF CATALYTIC ACTIVITY BY GAMMA RADIATION[1]

Sir:

The possibility of altering catalytic activity by high-energy radiation has long been considered.[2] Results have been reported for gamma rays[3] and for fast neutrons[4]; in both cases the effect was small. Evidence is presented herewith for the production by gamma rays of a marked increase in catalytic activity of aluminum oxide.

Previous observations upon zinc oxide[3] showed a definite, deleterious effect of gamma rays upon the catalytic activity for ethylene hydrogenation, but the rate of decline under radiation was much lower than the rate of production of those phenomena (color centers, etc.) usually explained by electron trapping. The present work employed the H_2–D_2 exchange to permit activity measurement at −78°, where the effects of displaced electrons would be more likely to persist. Among several catalysts tried, gamma-alumina demonstrated the effect most clearly.

The alumina catalyst was prepared from Fischer Adsorption Alumina (originally inactive) by moistening with water and evacuating at 400° for several hours. Its identity as gamma alumina was established by X-ray diffraction. The analysis for HD was by mass spectrometer. Irradiation was done *in vacuo* between activity measurements using a Co^{60} source. It is estimated that the samples absorbed about 2×10^{17} e.v./g., min.

Catalysts prepared at 400° showed an approximate seven-fold increase in catalytic activity when irradiated at −78° for as little as thirty minutes.

---

[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] P. Guenther, *Ergebnisse tech. Roentgenkunde*, **4**, 100 (1934).

[3] E. H. Taylor and J. A. Wethington, THIS JOURNAL, **76**, 971 (1954).

[4] P. B. Weisz and E. W. Swegler, *J. Chem. Phys.*, **23**, 1567 (1955).

The enhancement disappeared on standing for two to four days at room temperature, but could be restored by further irradiation. Feebly catalytic samples, prepared by annealing the standard preparation at 200° without further pumping, showed a several thousandfold increase in activity when irradiated, but the increase disappeared in a few hours, even at −78°. Irradiation during activity measurement on the assumption that short-lived states might play a role as in photosensitization gave results not greatly different from those irradiated *in vacuo* between measurements, indicating that short-lived states need not be invoked.

The reality of the radiation effect is attested by some 49 separate irradiations which produced in 38 cases appreciable increase in activity. Some instances of lack of change appear to indicate saturation of the effect, while some decreases are thought to have resulted from poisoning. No activity was induced by gamma rays in samples that had not been activated in the manner described above.

The high rate of change of activity with irradiation and the ready annealing of the change suggest that the effects observed may be attributable to electrons or positive holes trapped in special sites in the alumina lattice. Experiments intended to show more about the phenomena are in progress.

CHEMISTRY DIVISION ELLISON H. TAYLOR
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE HAROLD W. KOHN

RECEIVED NOVEMBER 9, 1956

THE STABILITY RELATIONSHIP OF 1-METHYLCYCLOPENTENE AND METHYLENECYCLOPENTANE

Sir:

Evidence bearing on the problem of stability differences that exist between isomers possessing exocyclic and endocyclic double bonds in 5- and 6-membered ring systems has been summarized by Brown, Brewster and Shechter.[1] The conclusions reached by these authors are expressed in the generalization that "reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring and to avoid the formation or retention of the exo double bond in the 6-ring systems." Although the position adopted with respect to 6-membered ring compounds is well-supported,[2] evidence available concerning the 5-ring cases is less convincing.

In connection with a general study of heats of catalytic hydrogenation in solution, currently in progress in this Laboratory, we have had an opportunity to examine the heat changes accompanying hydrogenations of 1-methylcyclohexene, methylenecyclohexane, 1-methylcyclopentene, and methylenecyclopentane. The results obtained for these substances are listed in Table I. In each isomer pair the methylenecycloalkane shows a higher heat of hydrogenation than does the 1-methylcycloalkene, the differences being 2.1 kcal./mole for the 6-membered, and 3.8 kcal./mole for the 5-membered ring compounds. Since these values reflect differences in heat content rather than in free energy, we were prompted to investigate the equilibrium behavior of the methylene derivatives in the presence of acid. Our results for methylenecyclohexane are in complete accord with those of Wallach and his associates,[2] and it was further established that in acetic acid containing *p*-toluenesulfonic acid methylenecyclopentane is converted essentially quantitatively into 1-methylcyclopentene. The amounts of methylenecyclopentane present in the equilibrated product are too small to be detectable by infrared analysis, although trace contamination by acetate ester is indicated. The conclusion that 1-methylcyclopentene is *more* stable than methylenecyclopentane is therefore inescapable.

TABLE I

HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION (25° C.)

Compound	$-\Delta H$, kcal./mole
1-Methylcyclohexene	25.70 ± 0.10
Methylenecyclohexane	27.82 ± 0.07
1-Methylcyclopentene	23.01 ± 0.04
Methylenecyclopentane	26.82 ± 0.08

A complete report of this work will be published shortly.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE RICHARD B. TURNER
HOUSTON 1, TEXAS ROBERT H. GARNER

RECEIVED DECEMBER 6, 1956

---

(1) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(2) Of special relevance is the demonstration of O. Wallach, E. Evans, J. B. Churchill, M. Rentschler and H. Mallison, *Ann.*, **360**, 26 (1908), that various alkylidenecyclohexanes are converted into the corresponding 1-alkylcyclohexenes by the action of acid.

BOOK REVIEWS

Statistical Mechanics. Principles and Selected Applications. By TERRELL L. HILL, Naval Medical Research Institute, Bethesda, Maryland. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 56, N. Y. 1956. xiii + 432 pp. 16 × 23.5 cm. Price, $9.00.

This book gives an excellent discussion of some of the recent advances which have been made in the applications of statistical mechanics. According to the author, "the primary aim of this volume is to provide a rather detailed account of a selected group of these developments, namely, fluctuation theory, imperfect gas and condensation theory, distribution functions, nearest neighbor (Ising) statistics, and free volume and hole theories of liquids and solids."

The book opens with introductory chapters on classical statistical mechanics, quantum statistical mechanics, and the relation of statistical mechanics to thermodynamics. The