

washed with dilute alkali, dried, and fractionated. The residue was distilled in a small sausage flask and yielded 2.53 g. of the methylterphenyl which melted at 91–92° after recrystallization from methanol.⁷

Anal. Calcd. for C₁₅H₁₆: C, 93.34; H, 6.60. Found: C, 92.97; H, 6.58.

Terphenyl.—A sample (1.46 g.) of *p*-biphenylcyclohexene, 3.3 g. of chloranil and 18 cc. of dry xylene were refluxed and the reaction worked up as described in the preceding section; yield of terphenyl 0.63 g. The product melted at 210–211.5°. The identity of the substance was checked by preparing the nitro derivative; melting point 275°.⁷

α -Phenylnaphthalene.—Five grams of α -naphthylcyclohexene prepared as described in the literature⁸ was refluxed with 11.8 g. of chloranil in 20 cc. of xylene for five hours. The reaction mixture was cooled, diluted with an equal volume of petroleum ether (30–60°) and filtered, yielding 8.4 g. of chloranil hydroquinone. The remainder was removed by basic extraction. The resulting fractionation yielded 3.33 g. of α -phenylnaphthalene. The structure was checked by the formation of its nitro derivative which melted at 129–130°. The literature reports 132°.⁸

β -Phenylnaphthalene.⁹—Following the same procedure as given above, β -naphthylcyclohexene was dehydrogenated to give β -phenylnaphthalene in a yield of 72%. The constitution of this molecule was proved by direct oxidation to β -phenyl 1,4-naphthoquinone; melting point 108–109°.⁹

2-Methylbiphenyl.—This substance was obtained by refluxing a solution containing 12 g. of *o*-tolylcyclohexene, 36 g. of chloranil, and 115 cc. of xylene. The yield of pure product obtained by fractionation was 8.5 g. (72.6%).³

(8) Weiss and Waidich, *Monatsh.*, **46**, 456 (1925).

(9) Chattaway and Lewis, *J. Chem. Soc.*, **65**, 873 (1894).

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 5, 1940

Catalytic Action of 8-Hydroxyquinoline on the Oxidation of *p*-Phenylenediamine

BY FREDERICK BERNHEIM AND PHILIP HANDLER¹

8-Hydroxyquinoline can, under certain conditions, catalyze the oxidation of cysteine to cystine.² It has now been shown that it has a catalytic effect on the oxidation of *p*-phenylenediamine and certain related substances. Figure 1 shows this effect on *p*-phenylenediamine recrystallized from water and from alcohol. The oxygen uptake was measured at 37° in the Warburg apparatus. Successive recrystallizations of the diamine have no effect on the catalysis, showing that the 8-hydroxyquinoline is not simply removing an antioxidant. Addition of metal ions such as the cupric, ferric and vanadate does not

(1) One of us (P. H.) is indebted to the Markle Foundation for its support during this work.

(2) F. Bernheim and M. L. C. Bernheim, "Symposia on Quantitative Biology," Vol. VII, 1939, in press.

enhance the catalytic effect which is, therefore, probably not due to a metal-8-hydroxyquinoline complex. The catalysis is not affected by 0.02 *M* cyanide or pyrophosphate. It has an optimum *pH* at about 6.5 and the rate falls off rapidly in alkaline solutions. The oxidation product is deeply colored, which is characteristic of the polymer of the quinone diamine and which can be reduced by hydrosulfite. On isolation and hydrolysis with acid it gives free ammonia. From the oxygen uptake figures a small percentage of further oxidation products must be formed which have not been isolated.

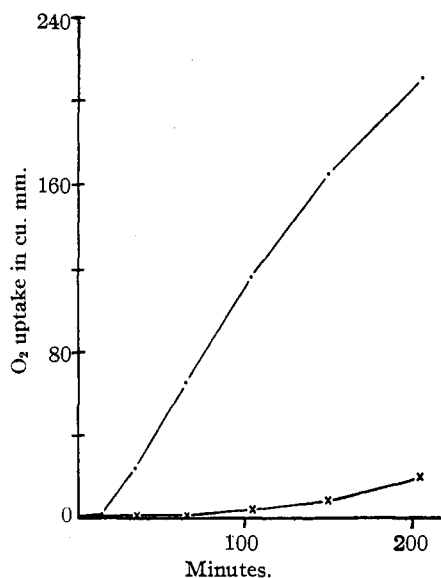


Fig. 1.—The oxygen uptake of 3.0 mg. of *p*-phenylenediamine in 2.0 cc. of water at *pH* 6.7: x—x, control; ·—·, with 0.05 mg. of 8-hydroxyquinoline. The short latent period is characteristic.

8-Hydroxyquinoline has no effect on the oxidation of *o*-phenylenediamine, catechol or hydroquinone in acid or alkaline solutions. It has a comparatively small effect on the oxidation of *p*- and *o*-aminophenols in alkaline solutions (*pH* 7.8). 2-Hydroxyquinoline and certain other quinoline derivatives are without catalytic action.

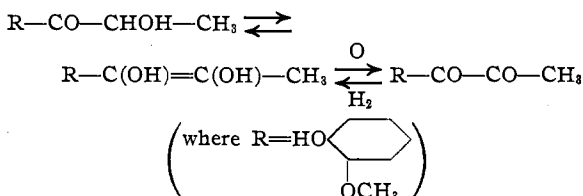
DEPARTMENT OF PHYSIOLOGY AND PHARMACOLOGY
DUKE MEDICAL SCHOOL
DURHAM, NORTH CAROLINA RECEIVED JANUARY 26, 1940

The Mechanism of Plant Respiration

BY HAROLD HIBBERT

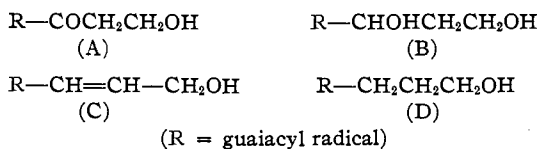
The discovery (see following note) in the ethanolsis products from spruce wood of methyl guaiacyl diketone alongside the previously re-

ported α -hydroxypropiovanillone¹ raises a question of considerable biochemical significance. The latter product, in its ene-diol form, is evidently the "donator" in a new oxidation-reduction system, the newly discovered diketone being the "acceptor."



Such a system with its presumptive accompanying dioxypropylene guaiacolase is thus closely related to the ene-diol catechol, -ascorbic acid and -dioxymaleic acid systems shown recently by Szent-Györgyi and co-workers² to form an integral part of the cycle of changes involved in plant (and presumably animal) respiration. The wide occurrence of this new oxidation-reduction system in various forms of higher plant life^{1,3} and the fact that both methyl guaiacyl diketone and α -hydroxypropiovanillone apparently are derived from methyl glyoxal provide additional support for the author's theory of plant synthesis⁴ in which this intermediate of carbohydrate metabolism appears to play such an extraordinarily important role.

In the suggested new system of plant respiration the roles of oxalacetic, malic, fumaric, and succinic acids are taken by (A), (B), (C) and (D), respectively

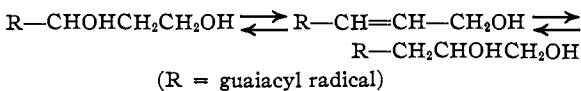


Of these, coniferyl alcohol (C) is known to be a very widely distributed plant product.

It may also be pointed out that in this new conception the important biological system⁵ known to function in intermediary metabolism

(1) Cramer, Hunter and Hibbert, *THIS JOURNAL*, **61**, 509 (1939).
 (2) For review see *Ber.*, **72**, 53 (1939).
 (3) (a) Hunter, Cramer and Hibbert, *THIS JOURNAL*, **61**, 516 (1939); (b) Brickman, Pyle and Hibbert, *ibid.*, **61**, 523 (1939).
 (4) Hibbert, *ibid.*, **61**, 725 (1939).
 (5) Martius and Knoop, *Z. physiol. Chem.*, **242**, 1 (1936); Martius, *ibid.*, **247**, 104 (1937); **257**, 29 (1938); Krebs and Johnson, *Enzymologia*, **4**, 148 (1937); Johnson, *Biochem. J.*, **33**, 1046 (1939).

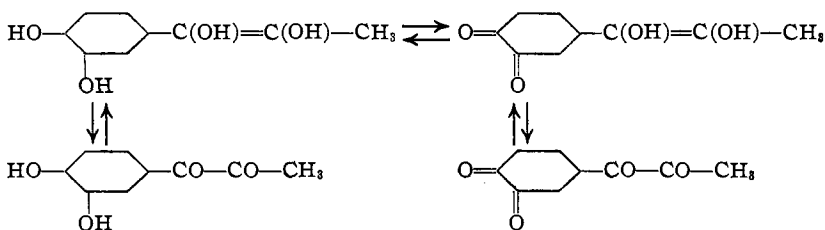
citric acid \rightleftharpoons *cis*-aconitic acid \rightleftharpoons isocitric acid has its counterpart in that of



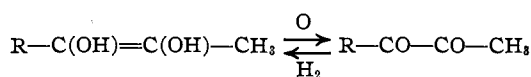
these last three products having a close biochemical relationship to the above ene-diol form.

Obviously the same considerations apply to the case of the corresponding syringyl compounds obtained in the ethanolysis of hard woods.³

Since in the early stages of plant growth the phenolic substances present are unmethoxylated, presumably the above new oxidation-reduction mechanism is represented there by a *di*-ene-diol system



in which not only the catechol \rightleftharpoons orthoquinone portion can function, but also the side chain grouping, as indicated by the changes



Such a combination is quite unique in cell oxidation systems and presumably is intimately related to the very much slower rate of reduction-oxidation changes involved in plant, as contrasted with animal, cell respiration.

It seems very probable that the above oxidation-reduction phenomena are intimately associated with (a) the very marked change in color taking place when chlorine and other oxidizing agents are brought into contact with unbleached pulps, and (b) the discoloration of newsprint and other papers in the presence of light and air.

Experiments with this new system on plant and animal tissues are to be undertaken and a full discussion of the subject is to appear in a forthcoming publication wherein the role of the ene-diol oxidation-reduction system as the almost certain forerunner of lignin synthesis is to be discussed comprehensively.