# Rotenone

## XXVIII. Preparation of Dihydrorotenone[1]

H. L. Haller and P. S. Schaffer
Insecticide Division, Bureau of Chemistry and Soils, Washington, D. C.

When rotenone is applied to foliage as an insecticide, it is gradually oxidized to inert compounds, especially on exposure to direct sunlight. This loss in toxicity is a considerable disadvantage for large-scale operations.

Of the large number of rotenone derivatives which have been tested against insects, all have been found to be relatively nontoxic with the exception of dihydrorotenone which equals or surpasses rotenone itself as an insecticide. This derivative appears also to be considerably more stable to oxidation when exposed on foliage than is rotenone (*3*). Therefore a method whereby dihydrorotenone may be obtained conveniently in good yield is of considerable practical importance.

Dihydrorotenone is formed on hydrogenation of rotenone with palladium barium sulfate or platinum oxide catalyst in acetone or ethyl acetate solution (*4*). With either catalyst in neutral solution in addition to dihydrorotenone, variable quantities of the relatively nontoxic rotenonic acid are formed (*5*). The use of platinum or palladium catalysts is too expensive when large quantities of dihydrorotenone are to be produced; moreover, with these catalysts a considerable proportion of rotenone is reduced to the relatively nontoxic rotenonic acid.

Among the catalysts that suggest themselves is nickel. This is inexpensive and extensively used commercially for the saturation of double bonds. However, a molecule possessing such a complicated structure as rotenone may give products other than the desired dihydrorotenone with different nickel catalysts, as these catalysts vary in their mode of action. For example, hydrogenation of rotenone in butyl acetate at 95° to 105° C. and 25 to 60 pounds per square inch pressure (1.8 to 4.2 kg. per sq. cm.)[2] with an active nickel catalyst prepared from oxidized nickel wool, turnings, or wire (*1*) gave no dihydrorotenone or rotenonic acid, but it produced dihydrorotenol (*6*) in quantitative yields. This product, like rotenonic acid, is considerably less toxic to insects than is rotenone.

With a nickel catalyst prepared from a nickel-aluminum alloy (*2*) (Raney catalyst), however, hydrogenation of rotenone in neutral solution resulted in excellent yields of dihydrorotenone. The reaction can be carried out at room temperature and at atmospheric pressure, and the catalyst can be used repeatedly. For example, when 10-gram lots of rotenone with 2.5 grams of catalyst were reduced successively in ethyl acetate solution, the catalyst was still active after the tenth reduction. This method should be a practical one for large-scale preparation of dihydrorotenone.

It was also found that dihydrorotenone could be obtained readily by the hydrogenation of derris or cubé extracts containing rotenone. In these cases the extract, which was prepared in the usual manner, was concentrated to a small volume, dissolved in a suitable solvent, and then hydrogenated.

### Experimental Procedure

All the hydrogenations of rotenone were carried out at 35° to 40° C. under atmospheric pressure, and at a concentration of 5 to 10 per cent. The solvents used were benzene, ethyl acetate, butyl acetate, and acetone. The solution of rotenone was placed in the reaction bottle of a Burgess-Parr catalytic reduction apparatus, and the catalyst was added. The quantity of catalyst can be varied over a wide range without altering the final products. The apparatus was evacuated and then filled with hydrogen, and the mixture was shaken until one mole of hydrogen had been absorbed. The solution was then decanted from the solvent, filtered, and concentrated to a small volume. A suitable quantity of 95 per cent ethyl alcohol was then added. The crystals which deposited were in most cases pure dihydrorotenone. The yield of dihydrorotenone was: In benzene, 90 to 93 per cent; in ethyl acetate, 85 to 90; in butyl acetate, 85 to 90; in acetone, 60 to 70. In the case of acetone, 30 to 40 per cent of rotenonic and dihydrorotenonic acids were formed.

For the preparation of dihydrorotenone from plant extracts containing rotenone, the following procedure was used: When ether was used for extracting the root, the extract was concentrated to a thick sirup. This sirup was then dissolved in a suitable solvent and hydrogenated until the absorption of hydrogen had practically ceased. When acetone was used as the extracting solvent, the extract was concentrated to a suitable volume and the solution was hydrogenated until there was no longer an appreciable absorption of hydrogen. Hydrogenation in ethyl acetate of an ether extract of cubé root, which assayed 8.6 per cent rotenone, gave 7 per cent dihydrorotenone; an acetone extract of another aliquot of the same root yielded 8.2 per cent dihydrorotenone. The hydrogenation of an acetone extract of derris root containing 1.4 per cent rotenone yielded one per cent dihydrorotenone.

### Literature Cited

(1) Bolton, E. R., British Patent 162,370 (April 26, 1921); Technical Research Works, Ltd., and Lush, E. J., British Patent 203,218 (Sept. 6, 1923).
(2) Covert and Adkins, *J. Am. Chem. Soc.*, 54, 4116 (1932).
(3) Jones, Gersdorff, Gooden, Campbell, and Sullivan, *J. Econ. Entomol.*, **26**, 451 (1933).
(4) Kariyone, Kimura, and Kondo, *J. Pharm. Soc. Japan*, **43**, 10 (1923).
(5) LaForge and Smith, *J. Am. Chem. Soc.*, **51**, 2578 (1929).
(6) LaForge and Smith, *Ibid.*, **51**, 2580 (1929).

Received June 7, 1933.

---

[1] Parts I to XXVII of this series appeared in *J. Am. Chem. Soc.*, Vols. 51 (1929) to 55 (1933).

[2] The authors are indebted to Derris, Inc., for having these experiments made.

---

French Chemical Notes. The Société St. Gobain, a leading French producer of glass and chemicals, in its recent report on 1932 results stated that demand for sulfuric acid was appreciably less than in previous years because of decreased deliveries of domestic superphosphate to French farmers. The acid and superphosphate plant in Marennes was closed and the trade transferred to a plant in Tonnay.

Sales of nitrogenous fertilizers during 1932 were comparatively good, and a new plant was opened in Rouen in addition to the sodium nitrate factory in Chauny, which commenced production in March as a joint operation of the St. Gobain and the Société de la Grande Paroisse.