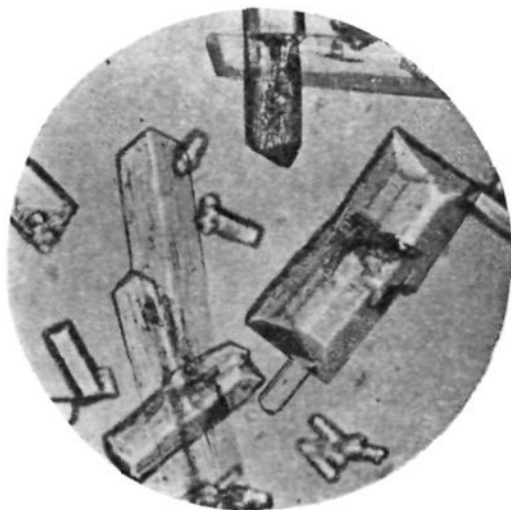


**Rotenone. XVII. Note on the Dimorphic Forms of Dihydrorotenone.**—In the first article<sup>1</sup> of this series dihydrorotenone was reported as melting at 164°. A number of different preparations were made, but in no case was a product obtained which melted at 216°, the melting point observed by several other investigators. However, the various derivatives obtained from the material melting at 164° agreed in their physical properties with those reported by others as having been made from the material melting at 216°. After an interval of several months we again had occasion to prepare dihydrorotenone, and this time it melted at 216°. On examination of several old preparations it was found that



Dihydrorotenone, m. p. 164° (×50).

they had changed to the higher melting form, and since that time we have obtained only the product melting at 216°. The crystallographic data obtained on the old form were quite different from those observed on the new form. This is a very striking case of dimorphism. **Dihydrorotenone, m. p. 164°.**—When examined under the microscope in ordinary light dihydrorotenone melting at 164° was seen to consist of well-formed rectangular and six-sided prisms. In parallel polarized light with crossed nicols, the extinction was straight and the elongation negative. In convergent polarized light with crossed nicols, fragments occasionally were found which showed a biaxial interference figure with the optic axis inclined. The refractive indices, determined in solutions of potassium mercuric iodide in glycerol and water, were as follows:  $n_{\alpha}$ , 1.550 (common on irregular fragments and lengthwise on elongated forms);  $n_{\beta}$ , indet.;  $n_{\gamma}$ , 1.682 (frequently crosswise on elongated forms); both  $\pm 0.003$ . (It is not to be assumed that the crystal forms remained intact when the optical constants were being obtained. They were determined on the finely powdered material) (Fig. 1).

**Dihydrorotenone, m. p. 216°.**—When examined in ordinary light the sample of dihydrorotenone which melts at 216° was seen to be composed

of irregular fragments of the higher melting form, and since that time we have obtained only the product melting at 216°.

The crystallographic data obtained on the old form were quite different from those observed on the new form. This is a very striking case of dimorphism.

**Dihydrorotenone, m. p. 216°.**—When examined under the microscope in ordinary light dihydrorotenone melting at 216° was seen to consist of irregular fragments of the higher melting form. In parallel polarized light with crossed nicols, the extinction was straight and the elongation negative. In convergent polarized light with crossed nicols, fragments occasionally were found which showed a biaxial interference figure with the optic axis inclined. The refractive indices, determined in solutions of potassium mercuric iodide in glycerol and water, were as follows:  $n_{\alpha}$ , 1.550 (common on irregular fragments and lengthwise on elongated forms);  $n_{\beta}$ , indet.;  $n_{\gamma}$ , 1.682 (frequently crosswise on elongated forms); both  $\pm 0.003$ . (It is not to be assumed that the crystal forms remained intact when the optical constants were being obtained. They were determined on the finely powdered material) (Fig. 1).



Dihydrorotenone, m. p. 216° (×50).

<sup>1</sup> LaForge and Smith, *THIS JOURNAL*, 51, 2574 (1929).

of wedge-shaped forms and short, stout prisms differing markedly in habit from the material melting at  $164^{\circ}$ . In parallel polarized light with crossed nicols, the material was characterized by not extinguishing sharply when the microscope stage was rotated. In convergent polarized light with crossed nicols, biaxial interference figures showing one optic axis in the center of the field or in the eccentric position were common. The material was not soluble in the ordinary organic liquids. The refractive indices were as follows:  $n_{\alpha}$ , 1.600;  $n_{\beta}$ , 1.625;  $n_{\gamma}$ , 1.680; all  $\pm 0.003$  (Fig. 2).

Dihydrorotenone exists in dimorphic forms, the one melting at  $164^{\circ}$ , the other at  $216^{\circ}$ . The high melting form is the more stable.

CONTRIBUTION FROM THE  
INSECTICIDE DIVISION  
BUREAU OF CHEMISTRY AND SOILS, AND  
THE MICROANALYTICAL LABORATORY  
FOOD AND DRUG ADMINISTRATION  
WASHINGTON, D. C.

F. B. LAForge  
G. L. KEENAN

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**Composition of Copper Xanthate.**<sup>1</sup>—Much confusion exists concerning the formula of the yellow precipitate formed on adding a cupric salt to a xanthate solution. From the time of its first analysis<sup>2</sup> until recently, the discoverer's claim that it is a cuprous salt was generally accepted. Then Johnson,<sup>3</sup> assuming that all the xanthate is precipitated—whereas half of it is oxidized to dixanthogen—believed it to be a cupric salt. This view has been accepted by recent workers,<sup>4,5,6,7,8</sup> with a few exceptions.<sup>9,10</sup>

The writer has analyzed three samples of the precipitate made by adding excess copper sulfate solution to fresh solutions of potassium xanthate. After filtering, washing with water, triturating with alcohol to remove the dixanthogen, filtering again, washing with alcohol and drying overnight, the copper in a known weight of precipitate was determined by dissolving with saturated bromine water, boiling off the excess oxidant, evaporating to a small volume, adding 1 g. of potassium iodide and titrating with thio-sulfate. From these data, assuming one atom of copper to each molecule,

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<sup>2</sup> Zeise, *Ann. Physik. Chem. (Poggendorff)*, **35**, 487-514 (1835).

<sup>3</sup> Johnson, *THIS JOURNAL*, **28**, 1210-1214 (1906).

<sup>4</sup> Harding and Doran, *ibid.*, **29**, 1476-1482 (1907).

<sup>5</sup> Calcott, English and Downing, *Eng. Mining J.-Press*, **118**, 980-981 (1924).

<sup>6</sup> Hallett and Ryder, *ibid.*, **119**, 690 (1925).

<sup>7</sup> Huff, *THIS JOURNAL*, **48**, 81-87 (1926).

<sup>8</sup> Holtz, "Dissertation," Johns Hopkins University, 1930, pp. 23-24.

<sup>9</sup> Spielmann and Jones, *J. Soc. Chem. Ind.*, **38**, 185-187T (1919).

<sup>10</sup> Duncan, Ott and Reid, *Ind. Eng. Chem.*, **23**, 382 (1931).