

**Esters of 3,5-Dichloro-2-hydroxydiphenylmethane**

**Benzoic Ester.**—Needles from 70% alcohol, m. p. 66–67°.

*Anal.* Subs., 0.1162, 0.1785: cc. of 0.1 *N* AgNO<sub>3</sub>, 6.45, 9.75. Calcd. for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>Cl<sub>2</sub>: Cl, 19.9. Found: Cl, 19.65, 19.50.

**Benzene Sulfonic Ester.**—Elongated prisms from ethyl ether, m. p. 110–110.5°.

*Anal.* Subs., 0.2562, 0.2360: cc. of 0.1 *N* AgNO<sub>3</sub>, 12.95, 11.85. Calcd. for C<sub>20</sub>H<sub>14</sub>SO<sub>3</sub>Cl<sub>2</sub>: Cl, 18.05. Found: Cl, 17.90, 17.85.

***p*-Toluene Sulfonic Ester.**—Prismatic plates from ethyl ether, m. p. 124.5–125°.

*Anal.* Subs., 0.2239, 0.1822: cc. of 0.1 *N* AgNO<sub>3</sub>, 10.95, 8.80. Calcd. for C<sub>21</sub>H<sub>16</sub>SO<sub>3</sub>Cl<sub>2</sub>: Cl, 17.42. Found: Cl, 17.35, 17.20.

**Summary**

1. The dichloro derivatives of both ortho and para benzylphenol and their ethers were prepared by direct chlorination and by condensation of the chlorinated phenols with benzyl alcohol.

2. The aluminum chloride condensation of 2,6-dichlorophenol and benzyl alcohol gave the ether as well as the benzylated phenol.

3. No evidence was obtained of the substitution by direct chlorination of more than two chlorines in either para or ortho benzylphenol.

4. The benzoyl, benzene sulfonyl and toluene sulfonyl derivatives of each dichlorobenzylphenol were prepared.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

**TOXICAROL. II. SOME ACETYL DERIVATIVES OF TOXICAROL**

BY E. P. CLARK

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Evidence has been presented to show that toxicarol is an hydroxy-dimethoxy compound, C<sub>23</sub>H<sub>22</sub>O<sub>7</sub>.<sup>1</sup> The presence in the molecule of at least one hydroxyl group was demonstrated by the formation of a monobenzoyl derivative, but as the nature of four of the seven oxygen atoms was unknown, the existence of other hydroxyl groups was not excluded.

It has now been shown that a diacetyl derivative of toxicarol may be obtained, but because of the reactions which it and toxicarol undergo, it cannot be stated definitely that a second hydroxyl group exists in toxicarol *per se*. In fact, evidence is more in accord with the idea that the second acetyl group is introduced as a result of some reaction brought about by the reagents involved in the acetylation process.

An attempt to elucidate this point is in progress, but since the information upon the subject now available is interesting and will eventually contribute to the solution of the structure of the molecule, it is presented herewith.

<sup>1</sup> Clark, *THIS JOURNAL*, 52, 2461 (1930).

When treated with boiling acetic anhydride and sodium acetate, toxicarol yields a diacetyl derivative,  $C_{27}H_{26}O_9$ . This material upon catalytic hydrogenation gives two products, dihydrodiacetyltoxicarol,  $C_{27}H_{28}O_9$ , and monoacetyldihydrodesoxytoxicarol,  $C_{26}H_{28}O_7$ . The latter substance may be readily deacetylated, giving a good yield of dihydrodesoxytoxicarol,  $C_{23}H_{26}O_6$ , but by the methods tried it cannot be further acetylated to a diacetyl derivative.

Catalytic reduction of toxicarol under the conditions which produced the desoxy compound from the acetyl derivative resulted in the formation of only dihydrotoxicarol,  $C_{23}H_{24}O_7$ .

Acetylation of dihydrotoxicarol with boiling acetic anhydride and sodium acetate gave two products, depending upon the duration of the reaction. When the components were allowed to react for ten minutes, only a monoacetyldihydrotoxicarol,  $C_{25}H_{26}O_8$ , was obtained, whereas if the reaction continued for two hours the entire product was diacetyldihydrotoxicarol, identical with the diacetyl derivative obtained by reducing diacetyltoxicarol.

Oxidation of toxicarol with potassium ferricyanide resulted in the loss of two hydrogen atoms, giving dehydrotoxicarol,  $C_{23}H_{20}O_7$ . Dihydrotoxicarol treated in the same manner gave dehydrodihydrotoxicarol,  $C_{23}H_{22}O_7$ . Dehydrotoxicarol was readily acetylated with acetic anhydride and sodium acetate, but under all the conditions tried only a monoacetyl derivative was obtained.

Reduction of dehydro or acetyldehydrotoxicarol gave, respectively, dihydrotoxicarol and monoacetyldihydrotoxicarol. The latter substance was the same as the acetyl derivative obtained by mild acetylation of dihydrotoxicarol.

In the process of reducing these dehydro derivatives not only was the double bond demonstrated by the catalytic hydrogenation reduced, but the structure which gave rise to the dehydro formation was regenerated. This is in sharp contrast to the corresponding dehydro derivatives of rotenone<sup>2</sup> and deguelin,<sup>3</sup> which do not reduce to the corresponding parent substance.

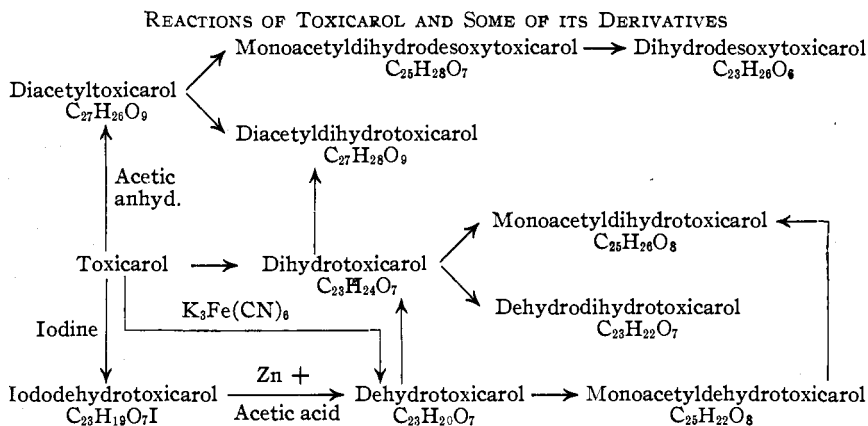
Dehydrotoxicarol may also be obtained by oxidizing toxicarol in an absolute alcoholic potassium acetate solution with iodine. Four atoms of iodine are readily consumed and a beautiful yellow iodo compound separates. This is undoubtedly iododehydrotoxicarol, but analysis of the compound was not satisfactory. This failure was probably due to the retention of an indefinite quantity of solvent which could not be removed under the condition to which the material was subjected. The melting point of the compound varied over a range of 30° depending upon the

<sup>2</sup> LaForge and Smith, *THIS JOURNAL*, 52, 1094 (1930).

<sup>3</sup> Clark, unpublished data.

solvent used for its recrystallization, but all samples readily lost their iodine when treated with zinc dust and boiling acetic acid. Upon cooling the reaction mixture, dehydrotoxicarol separated in a relatively pure condition.

The reactions which have been discussed are represented diagrammatically in the chart.



In connection with the behavior of the compounds under consideration, the following facts are pertinent. Because toxicarol gives a deep green color reaction with ferric chloride, which the benzoyl derivative does not, it is concluded that the hydroxyl group which was benzoylated is phenolic. Likewise the green color is produced by dehydrotoxicarol but not by acetyldehydrotoxicarol. It would therefore be expected that dihydrodesoxytoxicarol would also give the phenolic test, but it does not.

Some work upon the oxidation of toxicarol has been under way, but it has not progressed far enough to be reported upon at this time. It may be stated, however, that when toxicarol was treated with an acetic acid solution of chromic acid, the reaction was very slow, and after twenty-four hours all that could be isolated was approximately 50% of the unchanged starting material. Diacetyltoxicarol, on the other hand, is oxidized at once, and in some experiments as many as four products have been isolated, none of which was starting material.

It therefore seems likely that in the formation of diacetyltoxicarol a new structure is developed, and although a diacetyl derivative is indicative of two hydroxyl groups, it does not seem justifiable at present to conclude that the second hydroxyl group is present in toxicarol itself.

### Experimental

**Diacetyltoxicarol.**—A mixture of 10 g. of toxicarol, 2.5 g. of anhydrous sodium acetate and 40 cc. of acetic anhydride was boiled for thirty minutes under a reflux condenser. The resulting solution was cooled in an ice-bath, then diluted with 100 cc. of

acetic acid, and allowed to crystallize. The acetyltoxicarol which separated was removed from the mother liquor by filtration and was washed on the filter first with acetic acid, then with water, and finally with methanol. The yield of crude material, whose melting point was 227–229°, was 6 g.

The mother liquors were poured into 800 cc. of water, causing a further quantity of material to separate. Salt added to the mixture caused flocculation of the precipitate, which was separated by filtration. After the precipitate was air dried it was dissolved in ether and allowed to crystallize. One and six-tenths grams of crude diacetyltoxicarol with a melting point of 195–197° was obtained. This material was recrystallized from its chloroform solution by adding five volumes of ethanol. It then melted at 226°.

The crude diacetyltoxicarol (m. p. 226–229°) was recrystallized by dissolving 1 g. of the substance in 25 cc. of boiling acetic acid and adding 25 cc. of boiling water. Crystallization from the 50% acid began at once and was soon completed. Two such recrystallizations gave a pure product which melted at 233° and became clear at 236°. It consisted of thin irregularly shaped plates. In parallel polarized light (crossed nicols) the plates extinguished sharply and brilliant polarization colors were common. In convergent polarized light (crossed nicols) partial biaxial interference figures were shown only rarely:  $\eta_{\alpha}$ , 1.500 (very common);  $\eta_{\beta}$ , indeterminate;  $\eta_{\gamma}$ , >1.740.<sup>4</sup>

*Anal.* Calcd. for  $C_{27}H_{26}O_9$ : C, 65.58; H, 5.30;  $OCH_3$  (2), 12.6; acetyl (2), 17.4. Found: C, 65.71; H, 5.41;  $OCH_3$ , 12.7; acetyl, 17.2.

**Reduction of Diacetyltoxicarol (Diacetyldihydrotoxicarol).**—Three grams of diacetyltoxicarol dissolved in 200 cc. of hot acetic acid was reduced at atmospheric pressure and approximately 75° with hydrogen and the platinum catalyst of Voorhees and Adams.<sup>5</sup> After the catalyst was removed, the solution was heated to boiling and two volumes of boiling water was added. Crystallization began at once and was completed when the solution reached room temperature. The yield was 2 g. and the melting point of the crystals was 235°. It was recrystallized by dissolving the crude material in a small volume of boiling chloroform, adding approximately ten volumes of boiling methanol and maintaining the solution in a state of vigorous boiling until crystallization began. The material which separated consisted of colorless boat-shaped crystals which melted at 238° and became clear at 240°. In parallel polarized light (crossed nicols) the crystals exhibited deep purple, green and red colors:  $\eta_{\alpha}$ , 1.480 lengthwise (common);  $\eta_{\beta}$ , indeterminate, and  $\eta_{\gamma}$ , >1.740, although many of the crystals matched a liquid of this index or showed pale blue or orange margins in white light (crosswise).

*Anal.* Calcd. for  $C_{27}H_{28}O_9$ : C, 65.31; H, 5.69;  $OCH_3$  (2), 12.5. Found: C, 64.99; H, 5.82;  $OCH_3$ , 12.5.

**Monoacetyldihydrodesoxytoxicarol.**—The acetic acid mother liquors from the foregoing experiment were concentrated to a sirup under reduced pressure, and the residue was dissolved from the flask with a small quantity of boiling methanol. The solution was set aside and allowed to crystallize. The product which separated had a melting point of 155°, and the yield was usually one-third of the starting material. It was recrystallized by adding five volumes of boiling methanol to its solution in boiling chloroform and maintaining the solution in a state of vigorous boiling until the chloroform was removed. Upon cooling, the solution deposited pure colorless needles and rectangular rods whose melting point was 156°.

In parallel polarized light (crossed nicols) the material had inclined extinction and

<sup>4</sup> The optical data recorded in this communication were determined by George L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture. Appreciation is gratefully expressed for this cooperation.

<sup>5</sup> Voorhees and Adams, *THIS JOURNAL*, **44**, 1397 (1922).

negative elongation. In convergent polarized light (crossed nicols) the substance exhibited partial biaxial interference figures, often showing one optic axis up:  $\eta_{\alpha}$ , 1.547;  $\eta_{\beta}$ , 1.633;  $\eta_{\gamma}$ , >1.740; all  $\approx 0.003$ .

*Anal.* Calcd. for  $C_{25}H_{28}O_7$ : C, 68.17; H, 6.41;  $OCH_3$  (2), 14.1. Found: C, 68.09; H, 6.47;  $OCH_3$ , 14.3.

When a relatively large quantity of fresh catalyst was used (1 g. of platinum dioxide for 10 g. of diacetyltoxicarol), no diacetyldihydrotoxicarol was obtained. Under these conditions, in the first crop of crystals 2.4 g. of monoacetyldihydrodesoxytoxicarol was obtained from 5 g. of diacetyltoxicarol.

**Dihydrodesoxytoxicarol.**—The acetyl derivative of dihydrodesoxytoxicarol was dissolved in a boiling 2.5% methyl alcoholic solution of sodium methylate. The liquid was then immediately made acid with acetic acid and set aside to crystallize. In a short time the deacetylated product separated as colorless rods. Upon recrystallization from 50% ethanol the product was pure and melted at 188°. In this state it consisted of fine colorless needles having parallel extinction and negative elongation (parallel polarized light),  $\eta_{\alpha}$ , 1.567 (lengthwise);  $\eta_{\beta}$ , 1.625 (crosswise); and  $\eta_{\gamma}$ , 1.680 (crosswise); all  $\approx 0.003$ . It gave no color test with ferric chloride.

*Anal.* Calcd. for  $C_{23}H_{26}O_6$ : C, 69.32; H, 6.58;  $OCH_3$  (2) 15.6. Found: C, 69.29; H, 6.66;  $OCH_3$ , 15.6.

**Dihydrotoxicarol.**—Five grams of toxicarol was reduced with hydrogen as outlined under the reduction of diacetyltoxicarol. Approximately 90% of the solvent was removed by vacuum distillation, and the residue was washed from the flask with five volumes of methanol. Crystallization began at once, yielding 3.4 g. of dihydrotoxicarol melting at 205°.

The crude material was recrystallized from a boiling chloroform solution by the addition of five volumes of methanol. It separated as thin hexagonal plates and occasional rods which melted at 206° and became clear at 209°. Macroscopically the preparation had a slight greenish tinge, but microscopically the crystals were colorless. In parallel polarized light (crossed nicols) most of the plates exhibited first order white, and when the stage was rotated many of the plates did not extinguish sharply. In convergent polarized light (crossed nicols) such plates showed partial biaxial interference figures frequently with one axis up:  $\eta_{\alpha}$ , 1.575;  $\eta_{\beta}$ , 1.627;  $\eta_{\gamma}$ , 1.658 (all  $\approx 0.003$ ).

*Anal.* Calcd. for  $C_{23}H_{24}O_7$ : C, 66.97; H, 5.87;  $OCH_3$  (2), 15.1. Found: C, 67.08; H, 5.89;  $OCH_3$ , 15.1.

**Monoacetyldihydrotoxicarol.**—A mixture of 0.25 g. of dry sodium acetate, 1 g. of dihydrotoxicarol and 4 cc. of acetic anhydride was boiled for ten minutes. The excess of acetic anhydride was decomposed by the cautious addition of methanol, after which eight volumes more of methanol were added. One gram of monoacetyldihydrotoxicarol with a melting point of 202° separated. It was twice recrystallized from its saturated boiling butanol solution by adding two volumes of methanol. Thus obtained it consisted of colorless prisms which began to sinter at 200° and melted at 207°. In parallel polarized light (crossed nicols) it exhibited negative elongation and straight extinction. In convergent polarized light (crossed nicols) only partial biaxial interference figures were shown:  $\eta_{\alpha}$ , 1.583 (not common);  $\eta_{\beta}$ , indeterminate;  $\eta_{\gamma}$ , 1.655 (common crosswise). An intermediate index  $\eta$ , 1.615, frequently occurs lengthwise on the rods (all  $\approx 0.003$ ).

*Anal.* Calcd. for  $C_{25}H_{26}O_8$ : C, 66.06; H, 5.77;  $OCH_3$  (2), 13.7. Found: C, 66.03; H, 5.79;  $OCH_3$ , 13.7.

**Diacetyldihydrotoxicarol.**—The diacetyldihydrotoxicarol was obtained by the method just given for the monoacetyl derivative except that the reaction mixture was refluxed for two hours. The solution was then cooled, diluted with an equal volume of

acetic acid and allowed to crystallize. The diacetyl compound which separated melted at 235–236°. It was recrystallized by the procedure given for the same product obtained by reducing diacetyltoxicarol.

The material had the same melting point as the former product and when mixed with it there was no depression of the melting point. It also had the optical properties characteristic of the diacetyl derivative obtained by reducing diacetyltoxicarol.

*Anal.* Found: C, 65.32; H, 5.67; OCH<sub>3</sub>, 12.5.

**Oxidation of Toxicarol with Potassium Ferricyanide: Dehydrotoxicarol.**—Five grams of toxicarol dissolved in 500 cc. of boiling ethanol was treated with 75 cc. of a hot aqueous solution of 9 g. of potassium ferricyanide and 2.8 g. of potassium hydroxide. The mixture was allowed to stand until the following day and then quickly diluted with 1500 cc. of water. Dehydrotoxicarol separated as brownish-yellow crystals, and the residual organic material, dispersed in the milky mother liquor, was carefully decanted. The crystals were then washed with water by decantation, transferred to a filter and finally washed with methanol. One and one-tenth grams of dehydrotoxicarol with a melting point of 223° was obtained.

The material was recrystallized by adding five volumes of hot methanol to its solution in chloroform. This procedure gave a product which melted at 230–231°. For analysis the compound was again recrystallized from hot cyclohexanol. In this operation a yield of 85% was obtained. The material separated as yellow rods and needles whose melting point was 234°. The crystals exhibited parallel extinction and negative elongation:  $\eta_{\alpha}$ , 1.460 (lengthwise);  $\eta_{\beta}$ , 1.685 (crosswise); and  $\eta_{\gamma}$ , >1.740 (both = 0.003).

*Anal.* Calcd. for C<sub>23</sub>H<sub>20</sub>O<sub>7</sub>: C, 67.63; H, 4.94; OCH<sub>3</sub> (2), 15.2. Found: C, 67.47; H, 4.97; OCH<sub>3</sub>, 15.3.

**Monoacetyldehydrotoxicarol.**—The acetylation of dehydrotoxicarol was performed in the usual way with sodium acetate and acetic anhydride. The reaction mixture was refluxed for thirty minutes, then diluted with two volumes of acetic acid and allowed to crystallize. The yield was 1.6 g. from 2 g. of starting material. The crude product was recrystallized from a boiling chloroform solution upon the addition of five volumes of methanol. It separated as long light cream-colored rods and needles which melted at 231–232°. The extinction was inclined and the elongation was negative:  $\eta_{\alpha}$ , 1.563;  $\eta_{\beta}$ , indeterminate;  $\eta_{\gamma}$ , >1.740.

*Anal.* Calcd. for C<sub>25</sub>H<sub>22</sub>O<sub>8</sub>: C, 66.65; H, 4.93; OCH<sub>3</sub> (2), 13.8. Found: C, 66.47; H, 5.05; OCH<sub>3</sub>, 13.8.

**Reduction of Dehydrotoxicarol.**—Dehydrotoxicarol was reduced by the procedure given for the preparation of dihydrotoxicarol. One and six-tenths grams of dihydrotoxicarol was obtained from 2.6 g. of dehydrotoxicarol. After recrystallization the product melted at 209°. It caused no melting-point depression when mixed with dihydrotoxicarol and possessed the same optical properties that are characteristic of dihydrotoxicarol.

**Reduction of Monoacetyldehydrotoxicarol.**—Four and thirty-five hundredths grams of monoacetyldehydrotoxicarol was reduced in the usual manner and the resulting solution concentrated to a sirup under reduced pressure. The residue was dissolved from the flask with 25 cc. of hot methanol and allowed to crystallize. The yield was 3.5 g. of monoacetyldihydrotoxicarol which melted at 206°. When it was recrystallized as outlined before it melted at 207° and caused no depression of the melting point when mixed with the preparation previously described. The optical properties were also identical with those characteristic of monoacetyldihydrotoxicarol.

**Oxidation of Toxicarol with Iodine in an Alcoholic Solution of Potassium Acetate.**—

Five grams of toxicarol and 7.5 g. of potassium acetate were dissolved in 250 cc. of boiling absolute ethanol and treated portion-wise with 100 cc. of an absolute ethanolic solution of 6 g. of iodine. The reaction mixture was allowed to stand for a day, after which the crystalline iodo compound was removed by filtration. The yield was usually 1.6 g. The product melted with decomposition at various temperatures from 198 to 204°. The crude material when recrystallized from various solvents melted with decomposition over a wide temperature range. The solvents used and the melting points of the crystals obtained from them are as follows: acetic acid, 206°; benzene and ether, 222°; pyridine and butanol, 225°; chloroform and ether, 214°; chloroform and butanol, 215°. However, various preparations obtained from the same solvents frequently showed considerable difference in the melting point. In all cases the material separated as fine yellow needles and rods.

The filtrate from the original crystals was treated with 1500 cc. of water. The precipitate formed was separated, dried, dissolved in 15 cc. of boiling acetic acid and allowed to crystallize for a day. Usually there separated 2.5 g. of iodo compound which melted at 204–205°.

*Anal.*<sup>6</sup> Calcd. for  $C_{23}H_{19}O_7I$ : C, 51.69; H, 3.58; I, 23.76;  $OCH_3$  (2), 11.62. Found: C, 49.00; H, 3.53; I, 22.88;  $OCH_3$ , 11.5.

**Dehydrotoxicarol from the Iodo Compound.**—A mixture of 4 g. of iododehydrotoxicarol, 8 g. of zinc dust and 60 cc. of acetic acid was boiled for forty-five minutes. The clear yellow solution which resulted was decanted from the zinc and allowed to crystallize. After the crystals were removed from the mother liquors, washed with acetic acid, then water and finally methanol, 3.4 g. of crude dehydrotoxicarol was obtained. After it was recrystallized as outlined before, it melted at 235–236°. When mixed with dehydrotoxicarol prepared by the ferricyanide oxidation of toxicarol, there was no depression of the melting point. It also possessed the optical properties of dehydrotoxicarol.

**Dehydrodihydrotoxicarol.**—One gram of dihydrotoxicarol was treated with an alkaline potassium ferricyanide solution as outlined for the preparation of dehydrotoxicarol. There was obtained 0.11 g. of dehydrodihydrotoxicarol which melted at 254°. It was recrystallized from boiling acetic acid, from which it separated as long yellow rods whose melting point was 260°. The substance apparently is monoclinic. In parallel polarized light (crossed nicols) the extinction is usually inclined, although occasionally rods are found having straight extinction (crystals elongated parallel to the *b* axis). In convergent polarized light (crossed nicols) partial biaxial interference figures are common, frequently showing one optic axis up:  $\eta_{\alpha}$ , 1.500;  $\eta_{\beta}$ , 1.680;  $\eta_{\gamma}$ , >1.740 (both = 0.003).

*Anal.* Calcd. for  $C_{23}H_{22}O_7$ : C, 67.30; H, 5.41;  $OCH_3$  (2), 15.1. Found: C, 67.05; H, 5.45;  $OCH_3$ , 14.9.

### Summary

1. Acetylation of toxicarol yields a diacetyl derivative which upon catalytic reduction is changed to diacetyldihydrotoxicarol and monoacetyldihydrodesoxytoxicarol.

2. Catalytic reduction of toxicarol, under the conditions used to reduce diacetyltoxicarol, yields only dihydrotoxicarol. This substance may be acetylated in such a way as to introduce either one or two acetyl groups.

<sup>6</sup> The sample upon which carbon and hydrogen were determined was recrystallized from acetic acid. That upon which halogen and methoxyl were determined was obtained from chloroform and ether, melting point 210°.

3. Oxidation of toxicarol with ferricyanide yields dehydrotoxicarol involving the loss of two hydrogen atoms from the mother substance.

4. Dehydrotoxicarol is also formed by the oxidation of toxicarol with iodine in an alcoholic potassium acetate solution. In this reaction an intermediate iododehydrotoxicarol is formed which can be dehalogenated with zinc dust and acetic acid.

5. Reduction of dehydrotoxicarol or its acetyl derivative not only results in the reduction of the double bond, demonstrated by the dihydro formation, but it also regenerates the structure responsible for the dehydro formation.

6. It seems possible that the second acetyl group introduced into toxicarol is the result of some reaction brought about by the reagents involved in the acetylation process.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

## ROTENONE. XII. SOME NEW DERIVATIVES OF ROTENOL

BY H. L. HALLER AND F. B. LAForge

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When rotenone ( $C_{23}H_{22}O_6$ ) is refluxed with zinc and alkali in alcohol solution, two products are obtained, derritol, which is soluble in alkali, and rotenol, which is alkali insoluble. Rotenol is a white compound which possesses two hydrogen atoms more than rotenone, and Butenandt<sup>1</sup> assumes that it is formed by the reduction of the carbonyl group to a secondary alcohol group because, unlike rotenone, it does not yield an oxime and because it liberates one mole of methane with the Grignard reagent. The presence of an hydroxyl group in rotenol has not been satisfactorily demonstrated, however, as all attempts to obtain acyl derivatives have failed, and we have lately found several new facts which contradict the assumption that it is an alcohol.

In the course of our work on the structure of rotenone it has been found that rotenol readily yields isotubaic acid on alkali fusion<sup>2</sup> and that dihydro-rotenolic acid is readily cleaved with alkaline hydrogen peroxide, forming netoric acid<sup>3</sup> ( $C_{12}H_{14}O_5$ ), which contains the original methoxyl groups.

Both these reactions are best explained by the assumption of cleavage at a carbonyl group, as is generally assumed for other derivatives of rotenone. An attempt was made, therefore, to determine whether or not rotenol possesses a ketone group or whether this group has been reduced as suggested by Butenandt.

<sup>1</sup> Butenandt, *Ann.*, **464**, 253 (1928).

<sup>2</sup> Haller and LaForge, *THIS JOURNAL*, **52**, 4505 (1930).

<sup>3</sup> Smith and LaForge, *ibid.*, **52**, 4595 (1930).