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

ROTENONE. VI. DERRIC ACID

BY F. B. LAFORGE AND L. E. SMITH

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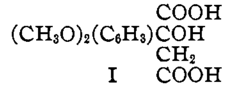
It has been established that the rotenone molecule is composed of two component parts which are joined together on the one hand by a chain of carbon atoms containing a carbonyl group and on the other by a lactone linkage.

Tubaic acid, $C_{12}H_{12}O_4$, corresponds to the first part and is obtained by boiling rotenone with alcoholic potassium hydroxide. Although a great deal has been learned about this cleavage product, its constitution has not yet been fully established, and it is at the present time the subject of further investigations.

Derric acid, which corresponds to the other half of the rotenone molecule, was isolated by us and described in a previous communication.[1] It is a dibasic acid having the formula $C_{12}H_{14}O_7$ and contains the original methoxyl groups of rotenone as well as the carboxyl group which, as the lactone group, is present in rotenone and many of its derivatives. Derric acid was prepared by peroxide oxidation of an acid having the formula $C_{23}H_{24}O_8$, which was obtained by treating dehydrorotenone with alcoholic potassium hydroxide, with or without the addition of zinc dust.[2] The yield of derric acid has been subsequently improved and it is now far more easily accessible than tubaic acid. Although its constitution is not yet fully established, we have nevertheless accumulated sufficient data to obtain a general idea of its nature. Derric acid is optically inactive. Oxidation by means of alkaline permanganate gives a dibasic acid which melts at 263° with evolution of carbon dioxide[3] and which is represented by the formula $C_{11}H_{12}O_7$. It forms a crystalline barium salt. Chromic acid oxidation of derric acid apparently gives the same compound but in much smaller yield. Energetic permanganate oxidation in neutral or acid solution destroys derric acid almost entirely, but in some experiments a very small yield of a monobasic acid was obtained which may have the formula $C_{10}H_{12}O_5$. However, the yield of this acid is at the best very small, and often none at all is obtained. In no case has it been possible to obtain a compound having the formula of a dimethoxybenzoic or dimethoxyphthalic acid.

All these facts indicate that derric acid is a dimethoxyphenylhydroxysuccinic acid of the formula



$$(CH_3O)_2(C_6H_3)\begin{array}{c}COOH\\ COH\\ CH_2\\ COOH\end{array} \qquad \text{I}$$

and that its oxidation product is a dimethoxyphenyltartronic acid. Derric acid is thus the hydroxy

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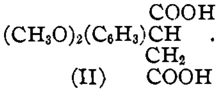
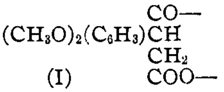
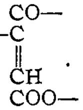
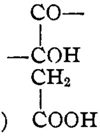
[1] LaForge and Smith, THIS JOURNAL, **52**, 1091 (1930).

[2] Butenandt, *Ann.*, **464**, 252 (1928).

[3] Derric acid itself does not evolve gas on fusion.

derivative of the acid which corresponds to the second part of the rotenone molecule and which would itself be a dimethoxy-phenylsuccinic acid of formula  (II) $(CH_3O)_2(C_6H_3)CH(COOH)\text{—}CH_2\text{—}COOH$. We are now attempting the synthesis of these acids.

Butenandt, in his most recent article,[4] gives considerable attention to dehydrorotenone and other compounds of the dehydro series. He advances the suggestion that the loss of the two hydrogen atoms involved in the formation of the dehydro compounds takes place in the half of the molecule which we represent by derric acid and not in that half corresponding to tubaic acid. This is a possibility which we have also considered. In many respects such a theory is in close agreement with the facts. For instance, if the grouping involved is represented by the partial formula I,  (I) $(CH_3O)_2(C_6H_3)CH(CO\text{—})\text{—}CH_2\text{—}COO\text{—}$, then the formation of dehydrorotenone could be represented by the change to III.  (III) $\text{—}C(CO\text{—}){=}CH\text{—}COO\text{—}$. Also, dehydrodihydroxyrotenonic acid $C_{23}H_{24}O_8$ (derris säure according to Butenandt) might contain the grouping IV  (IV) $\text{—}C(OH)(CO\text{—})\text{—}CH_2\text{—}COOH$ which in turn would be expected to yield derric acid on oxidation. Furthermore, tubaic acid does not yield dehydrotubaic acid.

We have, however, abandoned this theory for the following reasons. First, dehydrorotenone and its analogs dihydrodehydrorotenone and dehydroisorotenone are formed by dehydration of hydroxyl derivatives.[1] As far as this goes, it is also possible that these hydroxy derivatives could contain the grouping IV but with the lactone group still intact, and that the elements of water could be extracted to form dehydrorotenone and then two molecules of water added again to form the acid of formula $C_{23}H_{24}O_8$, with the opening of the lactone ring. In that case the hydroxyl derivatives (rotenolone, etc.) would be expected to give the same acid as the corresponding dehydro derivatives. Nothing of the kind happens, but rotenolone or acetylrotenolone on treatment with zinc and alcoholic potassium hydroxide yield rotenol and derritol exactly as does rotenone itself. Moreover, if the acid $C_{23}H_{24}O_8$ did actually contain the grouping IV, then it should be easily dehydrated by alcoholic sulfuric acid; but instead of such a reaction taking place, simple esterification results and a quantitative yield of the ethyl ester of the original acid is obtained.

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[4] Butenandt, *Ann.*, **477**, 245 (1930).

Second, although formula III contains an acid methylene group which might react with oxidizing reagents to form diketones of the rotenonone type, we have shown that such derivatives are in all cases derivatives of the dehydro series[1] which would not contain the necessary methylene group according to the above scheme.

Third, it is difficult to understand how the loss of two hydrogen atoms in the part of the molecule represented by derric acid could so alter the properties of the whole molecule with respect to the formation of derritol.

Although we realize that the scheme which we have already proposed[5] to explain the dehydro derivatives is open to objections, we have nevertheless preferred it to the theory which we have discussed above.

Derric Acid.—Two grams of dehydrodihydroxyrotenonic acid of formula $C_{23}H_{24}O_8$ is dissolved in 25 cc. of 5% potassium hydroxide. The solution is warmed to 60°, and 6 cc. of 30% hydrogen peroxide added in small portions, after which it is boiled to remove any excess hydrogen peroxide. The reaction is complete when a test portion of the solution, diluted with water, gives no precipitate on acidifying with hydrochloric acid. Usually there is formed a small amount of a black precipitate which is removed mechanically. A slight excess of hydrochloric acid is added, and the solution is extracted with ether. The ether solution is dried with sodium sulfate and the solvent removed. The resulting crystalline material is washed with chloroform and recrystallized by dissolving in ethyl acetate and adding warm *n*-butyl ether. The compound melts at 171°. The yield varies somewhat but averages 0.45 g. of recrystallized acid.

Subs., 0.1806 g. in 10 cc. of water showed no rotation in a 1-dm. tube, $[\alpha]_D$ 0.

Oxidation of Derric Acid.—Eight-tenths of a gram of derric acid is dissolved in 100 cc. of water, and the solution is made slightly alkaline with potassium hydroxide. The solution is heated on the steam-bath, and 1.8 g. of potassium permanganate dissolved in 100 cc. of water is added in small portions. After the manganese dioxide has settled out the solution is filtered and the filtrate evaporated to a small volume. When the solution is acidified with hydrochloric acid, a white crystalline precipitate is formed which is filtered off and recrystallized from water. The substance crystallizes in two forms, one of which contains water of crystallization. When dried at 110° it melts at 261–263°. The yield is 0.5 g.

Anal. Subs., 0.0646, 0.0645: CO_2, 0.1220, 0.1221; H_2O, 0.0270, 0.0263. Calcd. for $C_{11}H_{12}O_7$: C, 51.56; H, 4.68. Found: C, 51.50, 51.66; H, 4.65, 4.53. Subs., 0.0207: cc. of $N/10$ KOH, 1.55. Calcd. mol. wt.: 256. Found: 266.

Barium Salt.—One gram of the acid was dissolved in 20 cc. of hot water, and a hot solution of barium hydroxide was added until the solution was slightly alkaline. The barium salt crystallized out at once and was dried at 110°.

Anal. Subs., 0.1505: $BaSO_4$, 0.0890. Calcd. for $C_{11}H_{12}O_7$: Ba, 35.05. Found: 34.8.

The original acid was obtained when the barium salt was dissolved in water and the barium removed with sulfuric acid; melting point, 263°.

Anal. Subs., 0.0636: CO_2, 0.1210; H_2O, 0.0263. Calcd. for $C_{11}H_{12}O_7$: C, 51.66; H, 4.68. Found: C, 51.87; H, 4.59.

When 0.8 g. of derric acid in 100 cc. of water with the addition of 1 g. of magnesium sulfate was oxidized by adding 1.8 g. of potassium permanganate in 100 cc. of water in the same manner as described above, another acid was sometimes obtained with a

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[5] LaForge, THIS JOURNAL, **52**, 1102 (1930).

maximum yield of 0.07 g. It melted at 183° and was probably a monobasic hydroxy acid. This acid has not been available in sufficient quantity for satisfactory study.

Anal. Subs., 0.0520, 0.0520: CO_2, 0.1095, 0.1098; H_2O, 0.0272, 0.0266. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66. Found: C, 57.41, 57.57; H, 5.81, 5.68. *Titration.* Subs., 0.0159: 0.7 cc. of $N/10$ KOH. Calcd. mol. wt.: 212. Found: 227.

Dehydrodihydroxyrotenonic Acid Ethyl Ester.—One gram of the acid was boiled for three hours in 10 cc. of 10% alcoholic sulfuric acid. The ester crystallized on cooling and was recrystallized from 95% alcohol. It crystallized in needles melting at 98°. The yield was nearly quantitative.

Anal. Subs., 0.0704: CO_2, 0.1692; H_2O, 0.0383. Calcd. for $C_{25}H_{28}O_8$: C, 65.78; H, 6.14. Found: C, 65.55; H, 6.04.

Summary

Derric acid of formula $C_{12}H_{14}O_7$ which is obtained by peroxide oxidation of dehydrodihydroxyrotenonic acid of formula $C_{23}H_{24}O_8$ is oxidized by permanganate to a new dibasic acid of formula $C_{11}H_{12}O_7$ having the properties of a dimethoxytartronic acid. It seems likely that the rotenone molecule contains the grouping corresponding to a dimethoxyphenylsuccinic acid. Such an assumption might explain the formation and properties of dehydrorotenone. A possible explanation of the formation of dehydrodihydroxyrotenonic acid by the addition of the elements of water to the double bond is open to theoretical objections.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

SPIRANS WITH FOUR AROMATIC RADICALS ON THE SPIRO CARBON ATOM[1]

BY R. G. CLARKSON AND M. GOMBERG

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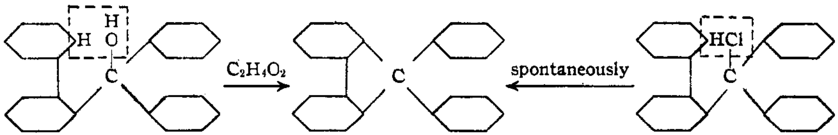
Ullmann and Wurstemberger,[2] by heating the crude 2-phenyltriphenylcarbinol (A) with sulfuric acid, and Khotinsky and Patzewitch[3] by heating the same with acetic acid obtained 9,9-diphenylfluorene (C). We have now succeeded in preparing the carbinol pure and in crystalline state, but our attempts to convert it into carbinol chloride (B) resulted invariably



(A) (C) (B)

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[1] Part of a dissertation submitted by R. G. Clarkson to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Science, 1929.

[2] Ullmann and Wurstemberger, *Ber.*, **38**, 4105 (1905).

[3] Khotinsky and Patzewitch, *ibid.*, **42**, 3106 (1909).