could hardly escape the 20 cm. of copper which is at a higher temperature than ordinary, due to the hydrogen flame impinging on it. The gas is as free of oxygen as copper can make it, but if collected in an ordinary gasometer, oxygen from the air dissolved in the water of the gasometer will get into the nitrogen, so when an exceedingly pure product is required it is best to use the gas direct from the washers, and also rubber connections and stoppers are then to be avoided. With facilities for compressing a gas this nitrogen might be put into cylinders as it can be made in unlimited quantities.

UNIVERSITY OF MICHIGAN,
June, 1905.

ON THE CRYSTALLINE ALKALOID OF CALYCANTHUS GLAUCUS.

BY H. M. GORDIN.

Received August 25, 1905.

(SECOND PAPER.)[1]

THE subject of this paper is a continuation of the research upon the alkaloid calycanthine, the active principle (according to Cushny)[2] of *Calycanthus glaucus.*

In the first paper it was shown that the formula of calycanthine is $C_{11}H_{14}N_2+\frac{1}{2}H_2O$, that the alkaloid is a weak monoacid base forming a chloroplatinate of normal composition and combining with one molecule of the halogen acids, and that it gives some very characteristic color reactions.

In the present paper I wish to report upon the preparation and analysis of the salts of calycanthine with the ordinary acids, with chlorauric acid and mercuric chloride and upon the first attempts to get some idea of the constitution of the alkaloid.

It will be noticed that the analytical figures for the acid part of those salts which could not be washed with the solvent in presence of free acid, as in the case of fixed acids and nitric acid, are generally slightly too low, showing that some acid is lost upon washing away the mother-liquor.

Calycanthine Nitrate, $C_{11}H_{14}N_2.HNO_3$.—As a monoacid base calycanthine combines with one molecule of nitric acid. Like

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[1] For first paper see *Proc. Amer. Pharm. Assoc.*, 1904, p. 345, and this Journal, **27**, 144 (1905).

[2] This Journal, **27**, 155.

the other salts of calycanthine the nitrate can be recrystallized only in the presence of some free acid, but the free nitric acid must be washed away completely before drying the salt; otherwise it becomes green, even when dried in vacuum over calcium oxide, at ordinary temperature.

For this reason it is difficult to obtain a nitrate containing the exact theoretical amount of nitric acid, some of the acid being removed in washing the salt with the neutral solvent.

The best way to prepare a nitrate containing almost the full amount of acid required by theory is as follows: The calycanthine is dissolved in ten times its amount of acetone and to the solution is added a slight excess of nitric acid diluted with double its amount of water. On standing over night most of the nitrate crystallizes out. The crystals are washed with acetone and dried at ordinary temperature. Two grams of the salt are then dissolved in 30 cc. hot water, and after cooling the solution to about 60° it is carefully covered with a mixture of 2 cc. dilute nitric acid and 73 cc. acetone. The crystals which separate out after twelve hours standing are washed with a little acetone (avoiding too much unnecessary washing but nevertheless removing all the free acid adhering to the crystals) and dried in vacuum over calcium oxide.

The nitrate forms short, stout, snow-white hard prisms, is very difficultly soluble in cold water and cold alcohol but easily soluble in hot water or hot alcohol, almost insoluble in acetone. When heated it assumes a yellow color at 202° and melts at 208° to 209° to a red liquid which very soon becomes black.

In the absence of free acid the nitrate can be boiled with water without changing color, but in presence of free mineral acid the hot liquid immediately becomes green. In the cold the color is developed only slowly when only little free acid is present. The analysis gave 17.39 and 17.42 per cent. N. Calculated, 17.75 per cent.

That the nitrate loses more acid when recrystallized in absence of free nitric acid was shown by an estimation of nitrogen in a sample which had been recrystallized from hot water without the addition of nitric acid: This gave only 16.30 per cent. N.

Calycanthine Sulphates.—Calycanthine forms two sulphates: An acid sulphate containing two molecules of water of crystallization and a neutral sulphate containing two and a half molecules of water of crystallization.

The acid sulphate can be made by treating calycanthine with an excess of sulphuric acid using absolute alcohol or acetone as a solvent. The neutral sulphate is formed when dilute sulphuric acid is treated with an excess of the alkaloid using water as a solvent. Owing to the very difficult solubility of the free alkaloid in cold water, the excess of the base can be filtered off and the filtrate will contain the neutral salt in solution with only a trace of the free calycanthine.

Both sulphates are extremely easily soluble in water but very difficultly soluble in alcohol and almost completely insoluble in acetone. The presence of much free acid diminishes considerably the solubility of the sulphate in cold water. The same is true of the hydrochloride which is considerably less soluble in presence of much free hydrochloric acid than in water alone.

Both sulphates are hygroscopic and if weighed out for analysis on wet days will be found to contain a little more water than is required theoretically, unless the salts are kept in a dry atmosphere. In vacuum over sulphuric acid both sulphates very soon lose all their water of crystallization, which they reabsorb on exposure to the ordinary atmosphere. The crystalline acid sulphate does not change color on standing, but when the water of crystallization is removed from the salt it assumes a yellowish tint. On exposing the yellowish anhydrous acid sulphate to the atmosphere it quickly absorbs water and again becomes snow-white.

The neutral sulphate on standing exposed to the atmosphere assumes a yellowish tint, but if kept in vacuum does not change color on losing its water of crystallization.

Calycanthine Acid Sulphate, $C_{11}H_{14}N_2.H_2SO_4+2H_2O$.—Three grams calycanthine were dissolved with the aid of a gentle heat in 12 cc. of not very dilute sulphuric acid (25 per cent.) and after adding to the still warm liquid 50 cc. absolute alcohol it was set aside in a cool place. Crystallization began very soon and after about twenty-four hours most of the acid sulphate crystallized out. The crystals were washed with absolute alcohol (avoiding too much washing) and dried at about 25° in the air.

The acid sulphate forms beautiful snow-white, soft, silky needles showing double refraction. When quickly heated to 76° the acid sulphate melts in its own water of crystallization to a thick turbid liquid; on further heating, the turbidity disappears at about 186° but not very sharply. The lack of sharpness in the melting-point of the crystallized acid sulphate is most probably due to a gradual loss of water of crystallization. The anhydrous acid sulphate melts sharply at 184°, after having become brown at 180°. The analysis gave 11.68 and 11.90 per cent. H_2O; 10.04 and 10.02 per cent. S. Calculated, 11.68 per cent. H_2O and 10.40 per cent. S.

Calycanthine Neutral Sulphate, $(C_{11}H_{14}N_2)_2.H_2SO_4+2\frac{1}{2}H_2O$.—Digest 2.5 grams calycanthine on the water-bath for half an hour with 25 cc. of very dilute sulphuric acid (2 per cent.), cool the mixture to about 15° and filter off from undissolved base. Add to the filtrate 100 cc. acetone and set it aside. In a very short time the whole liquid is converted into a mass of crystals. Wash the crystals with acetone, avoiding too much unnecessary washing, and dry them in the air at about 25°.

The neutral sulphate crystallizes in the same form as the acid salt; the crystals of the neutral salt seem to be only a little thicker than those of the acid salt. Unlike the acid sulphate the crystallized neutral sulphate does not melt in its water of crystallization but melts at 226° to 227°. The anhydrous neutral sulphate melts at 229°. The analysis gave 9.01 and 9.46 per cent. H_2O; 6.47 and 6.31 per cent. S. Calculated, 9.16 per cent. H_2O and 6.52 per cent. S.

Calycanthine Chloraurate.—Owing to the easy reduction of calycanthine chloraurate the salt can be prepared only in presence of considerable free hydrochloric acid and must be washed with water containing hydrochloric acid. Under these conditions a definite chloraurate is formed, having the somewhat unusual formula $3(C_{11}H_{14}N_2.HCl.AuCl_3)+2C_{11}H_{14}N_2.HCl+2\frac{1}{2}H_2O$. As indicated by this formula the chloraurate is made up of the regular salt combined with calycanthine hydrochloride. This possibly accounts for the fact that, when the chloraurate is dissolved in alcohol and the solution covered with ether, calycanthine hydrochloride, not the chloraurate, soon crystallizes out. Attempts to make a normal chloraurate by using an excess of gold chloride and pouring the solution of calycanthine hydrochloride into the solution of gold chloride instead of *vice versa* showed that under all conditions only one chloraurate is formed, having the composition given above.

One gram calycanthine was dissolved in 50 cc. dilute hydrochloric acid (5 per cent.), and to the solution was added a solution of gold chloride in dilute hydrochloric acid (5 per cent.) till further addition caused no more precipitation. After standing a few hours the chloraurate was washed with dilute hydrochloric acid (5 per cent.) and dried at about 25°.

The chloraurate forms beautiful orange-colored microscopic needles possessing strong dichroism (orange and yellow) and containing 2.5 molecules of water of crystallization. When kept in vacuum over dehydrating agents, the salt loses all its water of crystallization in a few days and assumes a dull cinnamon color. On exposing the anhydrous salt to the ordinary atmosphere, it quickly absorbs water and regains the orange color. The crystalline chloraurate melts at 191° to 192° to a thick turbid liquid which does not become clear even when heated to 250°. The anhydrous salt melts at 196°.

For an estimation of water of crystallization the air-dried (25°) substance was used. The analysis gave 2.22 and 2.29 per cent. H_2O. Calculated 2.24 per cent. H_2O. For the estimation of Au, Cl and N the anhydrous substance was used. The analysis gave 30.29 and 30.57 per cent. Au; 25.37 and 25.43 per cent. Cl: 7.19 per cent. N. Calculated, 30.11 per cent. Au; 25.27 per cent. Cl; 7.15 per cent. N.

In order to show that even using a large excess of gold chloride, and pouring the solution of calycanthine hydrochloride into the gold chloride solution, the same chloraurate is formed, a solution of 1 gram calycanthine hydrochloride in 50 cc. dilute hydrochloric acid (5 per cent.) was poured slowly with constant stirring into a solution of 5 grams gold chloride in 25 cc. dilute hydrochloric acid (5 per cent.). The salt made in this way had the same appearance and behaved in every respect like the chloraurate made by the other method. An estimation of gold and chlorine in this sample also showed it to be identical with the other salt, giving 30.52 per cent. Au and 24.90 per cent. Cl.

On digesting 1 gram calycanthine chloraurate with 25 cc. dilute hydrochloric acid (10 per cent.) over night at a temperature of 70 to 80°, beautiful yellow scintillating spangles of metallic gold separate out. The appearance of these spangles in the reddish liquid is very pretty. The calycanthine in this reaction must be converted into some oxidation product which it would be interesting to investigate; but, owing to the costliness of the reagent a fuller investigation of this reaction is postponed for a future date.

As was shown in the first paper[1] and mentioned above, from an alcoholic solution of calycanthine chloraurate, ether separates out calycanthine hydrochloride. It would be interesting to investigate whether the normal chloraurate or simply gold chloride is left in the ethereal solution. This problem, too, is left for a future investigation.

Calycanthine Picrate, $C_{11}H_{14}N_2.C_6H_2(NO_2)_3.OH+\frac{1}{2}H_2O$.—One gram calycanthine was dissolved in 100 cc. water containing 1 per cent. sulphuric acid, and to the solution was added an excess of a saturated solution of picric acid and enough water until upon heating the liquid to boiling, a clear solution was obtained (about 2000 cc. water were required). The solution was set aside at ordinary temperature. After forty-eight hours the picrate was washed with a little water and dried at about 25°.

The picrate forms very pretty, long and flat, silky needles having a shining yellow color. It is very difficultly soluble in cold water or cold alcohol, a little more soluble in hot water. At 160° the salt begins to lose its shining appearance, assuming a livid tint and melts at 185° to a black liquid. It loses its water of crystallization in vacuum over sulphuric acid and then melts at 186° to 187°. The analysis gave 2.22 and 1.88 per cent. H_2O; and 17.31 per cent. N. Calculated, 2.18 per cent. H_2O and 17.02 per cent. N.

Calycanthine Oxalates.—As a monoacid base calycanthine ought to form a neutral and an acid oxalate. A neutral oxalate of normal composition, $(C_{11}H_{14}N_2)_2.H_2C_2O_4$, can be easily prepared by treating oxalic acid with an excess of calycanthine in acetone solution. The neutral oxalate being difficultly soluble in cold acetone soon crystallizes out, leaving the excess of free base in the acetone solution.

An acid oxalate of normal composition, $C_{11}H_{14}N_2.H_2C_2O_4$, I was not able to prepare. On treating calycanthine with an excess of oxalic acid, a compound is formed which contains more acid than is required for the formation of the neutral oxalate but

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[1] This Journal, 27, 149 (1905).

less than is required for the formation of the acid oxalate of normal composition. The compound seems to be a combination of the acid oxalate and the free base, and to correspond to the formula $3(C_{11}H_{14}N_2.H_2C_2O_4) + C_{11}H_{14}N_2 + 2\frac{1}{2}H_2O$.

Calycanthine Neutral Oxalate, $(C_{11}H_{14}N_2)_2.H_2C_2O_4$.—One gram crystallized oxalic acid was dissolved in 15 cc. hot alcohol and the solution poured into a warm solution of 3.5 grams calycanthine in about 50 cc. acetone. After twenty-four hours the crystalline neutral oxalate which separated out was washed with a little acetone and dried at 25°.

The neutral calycanthine oxalate crystallizes in small, white needles which are difficultly soluble in cold water or cold alcohol, easily soluble in hot water or hot alcohol. On prolonged exposure to the atmosphere the salt assumes a yellowish tint. Upon heating, the salt commences to darken at 195° and at 231° melts with effervescence.

For an estimation of oxalic acid the neutral oxalate was dissolved in hot water and decomposed by means of calcium acetate. The precipitated calcium oxalate was then titrated in the usual way with standardized potassium permanganate, of which each cubic centimeter was equivalent to 0.003931 gram anhydrous oxalic acid. There was found 20.10 and 20.17 per cent. $H_2C_2O_4$. Calculated for $(C_{11}H_{14}N_2)_2.H_2C_2O_4$, 20.53 per cent.

These results are slightly below those required by theory, owing undoubtedly to loss of some acid in the washing of the oxalate with acetone.

Abnormal Calycanthine Acid Oxalate, $3(C_{11}H_{14}N_2.H_2C_2O_4) + C_{11}H_{14}N_2 + 2\frac{1}{2}H_2O$.

Two grams calycanthine were dissolved in 30 cc. acetone and the solution mixed with a solution of 2.5 grams of crystallized oxalic acid in 35 cc. alcohol. The mixture was warmed till the solution became clear and then set aside in a cool place. After twenty-four hours, a considerable amount of snow-white needles crystallized out. The crystals were washed with a little acetone and dried in the air.

The abnormal acid oxalate is easily soluble in water but difficultly soluble in alcohol or acetone. It begins to darken at 165° and melts with effervescence at 205° to 206°. The analysis gave 4.18 per cent. H_2O and 27.49 per cent. $H_2C_2O_4$ (for the anhydrous salt). Calculated for $3(C_{11}H_{14}N_2.H_2C_2O_4) + C_{11}H_{14}N_2 + 2\frac{1}{2}H_2O$, 4.45 per cent. H_2O and 27.93 per cent. $H_2C_2O_4$ (for the anhydrous salt).

Calycanthine Hydrochloride-Mercuric Chloride, $(C_{11}H_{14}N_2.HCl)_3.2HgCl_2 + 1\frac{1}{2}H_2O$.—With mercuric chloride, calycanthine seems to form different compounds under different conditions. The salt of the above composition was obtained as follows: 1 gram calycanthine was dissolved in 100 cc. water acidulated with hydrochloric acid, and to the solution was added an aqueous solution containing 3 per cent. mercuric chloride till no more precipitate was formed. The liquid was then heated on the water-bath till it became perfectly clear, and set aside. In about half an hour the liquid became turbid and after standing twenty-four hours a white curdy precipitate separated out. The precipitate was washed with a little water slightly acidulated with hydrochloric acid and dried in the air at about 25°.

To the naked eye the mercury salt looks very much like the white precipitate (mercuric ammonium chloride, NH_2HgCl) of the pharmacopoeias, but under the microscope the salt can be seen to consist of long, acicular crystals.

The mercury salt is very difficultly soluble in cold water or cold alcohol but quite soluble in these liquids when hot.

The salt contains 1.5 molecules of water of crystallization which is given off, in vacuum, over dehydrating agents. Crystalline, it melts at 184°; anhydrous, it melts at 186 to 187°. The analysis gave 2.43 and 2.46 per cent. H_2O; 34.00 and 33.90 per cent. Hg; 21.49 per cent. Cl (for anhydrous salt). Calculated, 2.23 per cent. H_2O; 33.34 per cent. Hg; 21.13 per cent. Cl.

The Hg is a trifle high, owing undoubtedly to some hydrochloride of the alkaloid carried down with the mercuric sulphide.

The mercury salt cannot be recrystallized without undergoing a change in melting-point, amount of water of crystallization, mercury and chlorine.

Calycanthine Tartrates.—Attempts to make either a neutral or an acid tartrate of calycanthine were not successful. Both salts could, of course, be prepared by mixing molecular quantities of base and acid in presence of water, in which both tartrates are extremely easily soluble, and evaporating the water completely. In this way the neutral tartrate can be obtained in solid condition.

The acid tartrate could only be obtained in the form of a semisolid, very sticky mass. Attempts to obtain the tartrates in crystalline form were made as follows: On mixing a solution of 4 grams tartaric acid in 20 cc. hot alcohol with a solution of 2 grams calycanthine in 10 cc. alcohol containing a little acetic acid (to make the calycanthine more soluble) and warming the liquid, a clear solution was obtained from which, on cooling, a pasty mass of the acid tartrate separated out, adhering strongly to the bottom and the sides of the vessel.

An attempt to prepare a neutral tartrate of a definite composition was made as follows: 1 gram tartaric acid was dissolved in 10 cc. alcohol and the solution poured into a warm solution of 3.5 grams calycanthine in 40 cc. acetone. On gently warming the mixture, a clear solution was obtained from which no solid substance separated out, even after standing in a cool place for forty-eight hours. The liquid was then mixed with 50 cc. ether and the white curdy precipitate formed upon the addition of the ether collected on a filter, washed with ether and dried in the air. The compound thus obtained was extremely easily soluble in water and had no definite melting-point, beginning to melt at 162° but not becoming liquid even at 200°. As the lack of sharpness in the melting-point indicated indefiniteness of composition, an attempt was made to recrystallize the compound. It was dissolved in 40 cc. hot alcohol and the liquid set aside. On cooling, the whole liquid solidified to such a stiff jelly that the vessel containing it could be inverted without anything flowing out. The jelly was then brought into solution by adding 40 cc. more alcohol and warming the mixture. On cooling, the whole again solidified to a jelly. No further attempts were made to prepare a tartrate in an analyzable form.

Calycanthine Nitrosamine, $C_{11}H_{13}N_2.NO$.—Of the two nitrogen atoms in calycanthine, one is secondary. This is shown by the fact that the alkaloid combines with nitrous acid to form a nitrosamine. On mixing a solution of calycanthine hydrochloride with a solution of an alkaline nitrite, no reaction can be noticed as long as there is no free acid in the solution, but the addition of hydrochloric acid to the liquid immediately precipitates the insoluble nitroso compound.

Three grams calycanthine were dissolved in 100 cc. dilute hydrochloric acid (5 per cent.) and to the solution was added a solution of 4 grams sodium nitrite in 50 cc. water and the liquid with the yellow precipitate set aside for about an hour and a half. The yellow precipitate was washed with water and dried on porous plates.

The nitrosamine thus obtained forms a greenish yellow flocculent powder completely insoluble in water and very little soluble in ether, benzene, alcohol or chloroform. It is easily soluble in warm phenol and slowly but completely soluble in cold pyridine. In hot pyridine it is extremely easily soluble. From its hot solution in pyridine the nitrosamine does not separate out on cooling, but addition of much water to the pyridine solution precipitates most of the nitrosamine in an amorphous condition.

The nitrosamine can be obtained in a crystalline form. For this purpose the amorphous nitrosamine is dissolved in five times its weight of warm pyridine, and to the solution an amount of alcohol is added equal to twice the amount of pyridine used. Water is now slowly added to the liquid till a permanent turbidity appears, the liquid warmed till it again becomes clear and then set aside in a cool place. After forty-eight hours a good crop of soft, short feathery needles of a dull yellow color crystallizes out. These were collected, washed with cold alcohol and dried in the air at about 25°.

The crystalline nitrosamine becomes brown at 172° and melts at 175° to 176° with effervescence. It gives Liebermann's nitroso reaction with great brilliancy.

The analysis gave C, 60.53 and 59.64; H, 6.38 and 5.82; N, 20.54. Calculated, C, 60.02; H, 6.46; N, 20.72.

While these figures are quite satisfactory, better ones yet could possibly be obtained by a second recrystallization of the nitrosamine. Lack of material prevented repeated recrystallization.

From the mother-liquor of the crystalline nitrosamine, a little more was obtained by adding more water. This second lot had a darker color than the crystals of the first and also had a lower melting-point, but on recrystallizing a second time from a mixture of pyridine, alcohol and water, the second lot assumed the same color and had the same melting-point as the first.

When the nitrosamine, which is difficultly soluble in methyl alcohol, is covered with a mixture of one part of strong hydrochloric acid and two parts methyl alcohol, it immediately goes into solution with a reddish color. The color changes, slowly on standing and quickly upon warming the liquid, to a magnificent green. If the liquid be diluted with water before it becomes green, the nitrosamine is reprecipitated. If the liquid be warmed on the water-bath for about fifteen minutes, it still retains its green color but can then be diluted with water without the separation of the nitrosamine; the addition of sodium carbonate to the liquid immediately precipitates a dark amorphous substance.

If the solution of the nitrosamine in the mixture of methyl alcohol and hydrochloric acid be kept for a longer time on the water-bath, the green color disappears and a brown tint takes its place. If potassium hydroxide be then added to the liquid, after diluting it largely with water, a brown crystalline precipitate separates out, which will be investigated later.

Estimation of Methyl Imide in Calycanthine.—Calycanthine contains one methyl group linked to nitrogen. This was shown by Herzig and Meyer's method.[1]

0.1989 gram substance gave 0.2348 gram AgI.

Calculated for $(C_{10}H_{11}N)=N.CH_3$, 8.63 per cent. CH_3. Found, 7.56 per cent. CH_3.

The results obtained by this method generally vary according to the authors from +3 to −15 per cent. of total alkyl. Hence the results obtained are sufficiently accurate to prove the presence of an N-methyl group in calycanthine.

As a secondary base, calycanthine ought to give alkyl and acyl derivatives. So far I have not been able to obtain an acetyl derivative by means of acetic anhydride or acetyl chloride or a benzoyl derivative by means of benzoyl chloride. The alkaloid is certainly acted upon by these reagents, as no unchanged calycanthine could be recovered after treating it with acetic anhydride or benzoyl chloride. What compounds are produced by these reagents I shall try to establish later.

Methyl iodide converts calycanthine into a mixture of several compounds, of which one is a quaternary base not precipitable by sodium carbonate. The exact nature of these compounds will form the subject of my next paper.

On digesting calycanthine with sulphuric acid, the alkaloid seems to be converted into a sulphonic acid of which a barium

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[1] *Ber.*, **27**, 319.

salt was obtained. The analysis of the sulphonic acid and its salts will be reported upon later.

A new lot of *Calycanthus glaucus* seeds has been ordered and the work is to be continued.

NORTHWESTERN UNIVERSITY SCHOOL OF PHARMACY.

DERIVATIVES OF TRIMETHYLPARACONIC AND OF CAMPHORONIC ACIDS.[1]

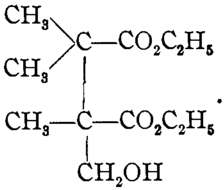
BY WILLIAM A. NOYES AND HOWARD W. DOUGHTY.

Received September 25, 1905.

IN THE last paper on this subject published by one of us,[2] a brief account has been given of attempts to secure a synthesis of a derivative of camphor by the aid of trimethylparaconic acid. Such a synthesis has not been obtained, but, although results in this direction are negative, since we can no longer continue the work together it seems desirable to give a brief account of what has been done.

It had been shown by Noyes and Patterson[3] that when the diethyl ester of trimethylitamalic acid is treated with phosphorus tribromide, ethyl bromide is split off and trimethylparaconic ester is formed. As the ester used by them was not pure and was not at all thoroughly examined, it seemed advisable to repeat the experiment, using the dimethyl ester instead of the diethyl ester, principally because of the fact that the percentages of carbon and hydrogen in the diethyl ester of trimethylitamalic acid and in the ethyl ester of trimethylparaconic acid are so nearly the same that analysis would not serve to distinguish between them.

Dimethyl Ester of Trimethylitamalic Acid,



—Three times the calculated quantity of methyl iodide was put into a small flask, which was so arranged as to be easily connected

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[1] This investigation was carried out by means of a grant from the Carnegie Institution, partly in the laboratories of the Johns Hopkins University and partly in those of the Bureau of Standards, Washington, D. C. We desire to express our thanks to each of these institutions for the assistance rendered.

[2] *Am. Chem. J.*, **33**, 356.

[3] *Ibid.*, **28**, 232.