The dyes were found to be quite fast under the usual tests, exception being made for the sulfonic acid dyes which were not fast to washing and alkali.

Summary

1. The preparation of 2,6-dinitro-*p*-cymene has been improved upon and its nitro groups have been fully established in positions indicated.

2. 2-Amino-6-nitro-*p*-cymene was made by reducing the dinitro compound with ammonium sulfide. It was characterized by its hydrochloride, hydrobromide, sulfate, nitrate, acetate and benzoate.

3. Eight new dyes were made by coupling the amine with the following phenols: phenol, resorcinol, thymol, carvacrol, 2-naphthol, 1-naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid and 1,8-dihydroxynaphthalene-3,6-disulfonic acid. Crystalline compounds were also obtained with a few amines.

4. The dyes color textiles reds, browns and yellows. The sulfonic acid dyes are particularly beautiful.

5. A new by-product, *p*-nitrotoluene, was discovered among the nitration products of cymene.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM DYSON-PERRINS LABORATORY, OXFORD UNIVERSITY]

A SYNTHESIS OF SUBSTITUTION DERIVATIVES OF INDIGO
II. ETHYL NITROTRIMETHYLGALLYL ACETATE AND RELATED COMPOUNDS

BY CALVIN J. OVERMYER

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Further application of the synthesis previously described[1] was made in the attempted formation of a hexamethoxy indigo, using gallic acid as the starting point. This hydroxy acid was methylated by a process which offers advantages over those employed by Will,[2] Graebe and Martz[3] and Perkin and Weizmann.[4]

Harding[5] secured nitrotrimethylgallic acid in small yield by the nitration of trimethylgallic acid directly, 5-nitrotrimethylpyrogallol (I) being the chief product of the reaction. That the nitro group replaced the carboxyl group directly was shown by the fact that no trimethylpyrogallol (II) with its attendant 3,5-dimethoxy-*p*-benzoquinone (III) was formed, a

[1] Overmyer, THIS JOURNAL, **48**, 454 (1926).

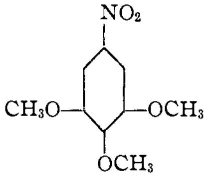
[2] Will, *Ber.*, **21**, 2022 (1888).

[3] Graebe and Martz, *Ann.*, **340**, 219 (1905).

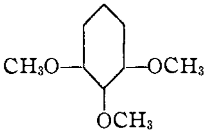
[4] Perkin and Weizmann, *Trans. Chem. Soc.*, **89**, 1655 (1906).

[5] Harding, *ibid.*, **99**, 1586 (1911).

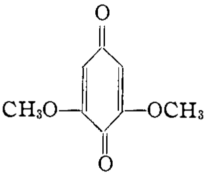
reaction which Will,[6] Schiffer,[7] Graebe and Hess[8] and others report as taking place when nitric acid reacts with trimethylpyrogallol.



I



II

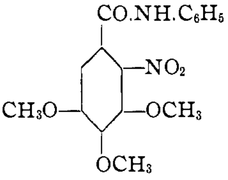


III

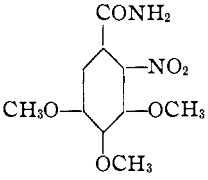
Oxalic acid is the chief product in the nitration of gallic acid and the —COCl group was directly replaced by the nitro group when the acid chloride of trimethylgallic acid was treated with nitrating agents. The desired nitrotrimethylgallic acid was finally obtained through the formation of the methyl ester of trimethylgallic acid after the method used by Hamburg[9] for the formation of the methyl ester of gallic acid, the nitration of the ester and the final hydrolysis of the nitro ester.

The acid chloride of nitrotrimethylgallic acid was prepared in the same manner as was the *o*-nitrobenzoyl chloride in the previous communication. Two derivatives of this new substance were prepared and their properties studied, nitrotrimethylgallylanilide (IV) and nitrotrimethylgallylamide (V).

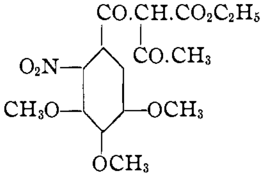
The action of the sodium compound of aceto-acetic ester upon the acid chloride of nitrotrimethylgallic acid produced ethyl nitrotrimethylgallyl aceto-acetate (VI), which in turn produced ethyl nitrotrimethylgallyl acetate (VII) when hydrolyzed in exactly the same manner as for the formation of ethyl *o*-nitrobenzoyl acetate.



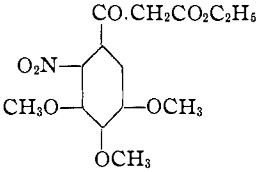
IV



V



VI



VII

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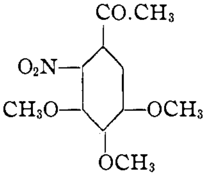
[6] Will, *Ber.*, **21**, 613 (1888).

[7] Schiffer, *Ber.*, **25**, 725 (1892).

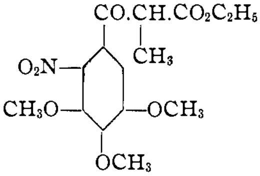
[8] Graebe and Hess, *Ann.*, **340**, 232 (1905).

[9] Hamburg, *Monatsh.*, **19**, 593 (1898).

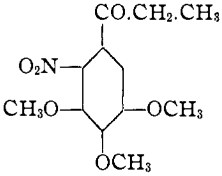
In order to confirm the constitution of the latter substance (VII), the corresponding acetophenone derivative was made by means of the well known ketonic hydrolysis process. The 3,4,5-trimethoxy-6-nitro-acetophenone (VIII) thus formed did not give a color with ferric chloride. On dissolving in sulfuric acid, on the other hand, an intense red color was produced. For the production of the next higher homolog of this ketone, it became necessary to prepare ethyl α-(nitrotrimethylgallyl) propionate (IX), and then to hydrolyze this to the corresponding ketone, 3,4,5-trimethoxy-6-nitropropiophenone (X).



VIII



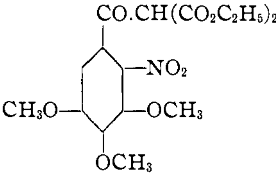
IX



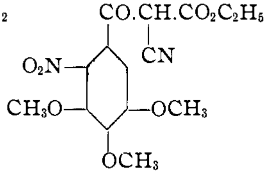
X

All efforts to hydrolyze the ethyl nitrotrimethylgallyl acetate to form the free acid, however, were unsuccessful. A long series of experiments carried out with this end in view produced one of three results: (1) black and resinous substances, (2) the ketone derivative or (3) the unchanged ester.

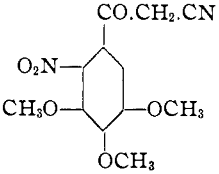
Nitrotrimethylgallyl chloride was condensed with the sodium compound of malonic ester in the hope that the resultant product, ethyl nitrotrimethylgallyl malonate (XI), could be partially hydrolyzed to form the desired acetic acid derivative, since the proposed synthesis of the hexamethoxy indigo depended upon securing this substance. The parent substance, nitrotrimethylgallic acid, the ketone VIII or the unchanged ester, was always obtained. Ethyl nitrotrimethylgallyl cyano-acetate (XII) was formed and the desired nitrile, nitrotrimethylgallyl acetonitrile (XIII), was produced when the ester was boiled with hydrochloric acid for a considerable period. All efforts to convert this nitrile into the corresponding amide or acetic acid derivative were unsuccessful, the great stability of the nitrile group being due probably to the presence of a substituent in the *ortho* position in the benzene ring.



XI

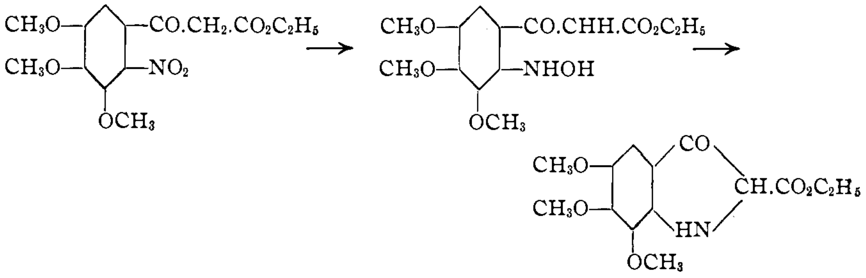


XII



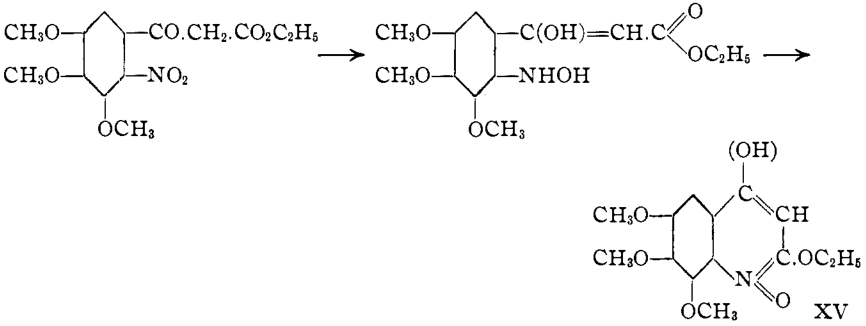
XIII

Being unable to obtain the desired nitrotrimethylgallylacetic acid, it was thought that ethyl 5,6,7-trimethoxy-indoxylate (XIV) might be obtained by the reduction of ethyl nitrotrimethylgallyl acetate according to the following scheme.



XIV

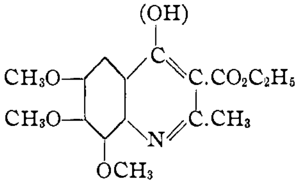
When this compound was reduced by means of zinc dust and glacial acetic acid, a product was formed which had none of the characteristic properties of an indoxylic ester, and on investigation the following reduction process was found to have taken place.



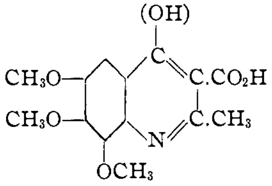
XV

The new product (XV) is 2-ethoxy-4-hydroxy-6,7,8-trimethoxyquinoline oxide, as indicated by the fact that it has all of the properties previously described for compounds of this type.

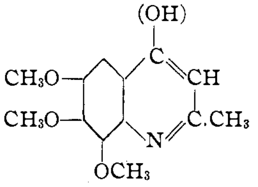
That quinoline oxide formation is not the invariable result when compounds of the ethyl *o*-nitrobenzoyl aceto-acetate type are reduced was shown by the fact that ethyl nitrotrimethylgallyl aceto-acetate upon



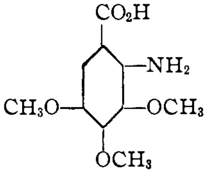
XVI



XVII



XVIII



XIX

reduction did not stop at the oxide stage, ethyl 2-methyl-4-hydroxy-6,7,8-trimethoxyquinoline-3-carboxylate (XVI) being formed. This substance was easily converted into the corresponding acid, 2-methyl-4-hydroxy-6,7,8-trimethoxyquinoline-3-carboxylic acid (XVII), and this latter acid, on being heated to its melting point, gave off carbon dioxide and formed 2-methoxy-4-hydroxy-6,7,8-trimethoxyquinoline (XVIII).

Nitrotrimethylgallic acid was reduced to form the corresponding trimethoxy-substituted anthranilic acid (XIX) and futile attempts were made to convert this substance into a derivative of phenyl-glycine-*o*-carboxylic acid in a further effort to produce the hexamethoxy indigo. A résumé of the literature[10] leads to the conclusion that molecules which contained a substituent in one *ortho* position were more inactive than those which were not substituted in this position, that this inactivity was more pronounced when both *ortho* positions were substituted, and still more evident when the *para* position was substituted as well as the former two. Since the compounds described above are substituted in one or more of the positions enumerated it is concluded that steric hindrance must be the governing factor in this marked stability and inactivity.

Experimental Part

Trimethylgallic Acid, $(CH_3O)_3[3,4,5]C_6H_2.CO_2H$.—Gallic acid is treated with dimethyl sulfate in the usual manner and the reaction product is collected and purified by warming with charcoal in a glacial acetic acid solution. After the removal of the charcoal the trimethylgallic acid separates on cooling as fine, white needles; m. p., 168°; yield, 80–85%.

Trimethylgallic Acid Methyl Ester, $(CH_3O)_3[3,4,5]C_6H_2.CO_2CH_3$.—When trimethylgallic acid and a quantity of absolute methyl alcohol saturated with hydrogen chloride are heated, the methyl ester of trimethylgallic acid is formed. It separates as large, white crystals, m. p. 82–83°, from a mixture of ligroin and ether and has a pleasant smell when freshly prepared; yield, 85–90%.

Nitrotrimethylgallic Acid Methyl Ester, $(CH_3O)_3[3,4,5]NO_2.C_6H.CO_2CH_3$ **and Nitrotrimethylgallic Acid.**—These compounds can be satisfactorily prepared by using a modification of the method employed by Hamburg.[9]

Thirty g. of trimethylgallic acid methyl ester is dissolved in 120 g. of acetic anhydride and the solution cooled to —5°. Twenty cc. of a nitrating mixture, consisting of nitric acid (d., 1.42) which has been previously saturated with gaseous nitrous acid, is added, care being taken to keep the temperature constant. The dark red solution gradually becomes yellow, whereupon the excess of acetic anhydride is removed under reduced pressure and the remaining solution poured into water. The yellow product

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[10] Hofmann, *Ber.*, **5**, 718 (1872). Meyer and collaborators, *Ber.*, **27**, 511, 1581 (1894); **28**, 1258 (1895); **29**, 830 (1896). Sudborough, *Trans. Chem. Soc.*, **67**, 587 (1895).

which forms is rubbed into a paste with an excess of dilute, aqueous sodium carbonate and is finally collected by filtration. It separates as fine, yellow needles from dilute alcohol or as large, yellow prisms from a mixture of ligroin and ether. The nitro ester melts at 67° and is easily soluble in ether and in alcohol.

Nitrotrimethylgallic acid methyl ester, on treatment with a methyl alcoholic solution of potassium hydroxide, is converted to the corresponding acid. It separates from alcohol as fine, yellowish-white prisms and melts at 166°. It is easily soluble in alcohol and in ether, slightly soluble in hot water and almost insoluble in benzene. Its solution in methyl alcohol gives a reddish-yellow coloration with ferric chloride.

Nitrotrimethylgallyl Chloride $(CH_3O)_3[3,4,5]NO_2.C_6H.COCl$.—This compound was prepared according to the method described in the previous communication for the formation of *o*-nitrobenzoyl chloride. It crystallizes from a mixture of benzene and ligroin as fine, yellowish needles melting at 94°; yield, 92%.

Nitrotrimethylgallylanilide (IV).—In preparing this derivative of trimethylgallic acid, 2 g. of nitrotrimethylgallyl chloride is dissolved in a small quantity of dry benzene and to this solution is added 2 g. of aniline. A rather vigorous reaction takes place with the formation of a white mass. The excess of benzene and some of the aniline are removed by steam distillation. The resultant mass is collected on a filter, the remaining aniline being in solution in water as the hydrochloride. It is crystallized from alcohol in the form of white needles.

Anal. Subs., 0.1077: CO_2, 0.2277; H_2O, 0.0463. Calcd. for $C_{16}H_{16}O_6N_2$: C, 57.83; H, 4.81. Found: C, 57.66; H, 4.77.

Nitrotrimethylgallylanilide is a white, crystalline solid which melts at 158°. It is insoluble in water, difficultly soluble in ether, and is soluble in alcohol and in benzene.

Nitrotrimethylgallylamide (V).—One g. of nitrotrimethylgallyl chloride and 3 g. of ammonium carbonate are thoroughly mixed in a mortar and then carefully heated in a porcelain dish for a few minutes, with stirring. The resultant compound is washed with water until the washings contain no trace of chlorides. It crystallizes as very fine white needles from hot water.

Anal. Subs., 0.1142: N_2 (dry), 10.3 cc. (11°, 766 mm.). Calcd. for $C_{10}H_{12}O_6N_2$: N, 10.93. Found: 10.78.

Nitrotrimethylgallylamide is a white, crystalline compound which melts at 186°. It has previously been described by Harding,[11] who obtained it by adding the acid chloride in benzene solution to a large excess of concd. ammonium hydroxide. Harding gives the melting point of the amide as 182–184°. It is soluble in hot alcohol and quite insoluble in ether.

Ethyl Nitrotrimethylgallyl Aceto-acetate (VI) was prepared by the method employed in the previous communication for compounds of this type. The sodium compound of this substance may be crystallized from alcohol in the form of small, white prisms.

Anal. Subs., 0.0891: CO_2, 0.1535 + 0.005 for Na_2CO_3; H_2O, 0.0348. Subs., 0.2309: N_2 (dry), 6.7 cc. (15°, 754 mm.). Calcd. for $C_{16}H_{18}O_9NNa$: C, 49.10; H, 4.60; N, 3.58. Found: C, 48.52; H, 4.37; N, 3.81.

The sodium compound may be dissolved in the smallest quantity of cold water and acidified with cold, dil. sulfuric acid, liberating the ester as an almost colorless oil which becomes viscous on further cooling. The sodium compound may also be added to an excess of dil. hydrochloric acid contained in a separatory funnel, and cooled by the addition of powdered ice. In either case, the aqueous mixtures are thoroughly extracted with ether. The ethereal solution is washed with dilute aqueous sodium hydrogen car-

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[11] Ref. 5, p. 1586.

bonate, dried over calcium carbonate, and evaporated. A reddish-yellow oil is obtained which consists of nearly pure ethyl nitrotrimethylgallyl aceto-acetate, its solution in alcohol giving a reddish coloration when mixed with ferric chloride. It dissolves in aqueous potassium hydroxide, and on adding a concentrated solution of this reagent a crystalline potassium compound, $C_{16}H_{18}O_9NK$, separates.

Anal. Subs., 0.1337: CO_2, 0.2571; H_2O, 0.0633. Subs., 0.1300: N_2 (dry), 4.0 cc. (12°, 753 mm.). Calcd. for $C_{16}H_{19}O_9N$: C, 52.03; H, 5.15; N, 3.79. Found: C, 52.43; H, 5.25; N, 3.60.

Ethyl Nitrotrimethylgallyl Acetate (VII).—The crude sodium compound of ethyl nitrotrimethylgallyl aceto-acetate, in quantities of 26 g., is mixed with a solution of 13 g. of ammonium chloride in 200 cc. of water, and 20 cc. of dil. ammonium hydroxide is then added. The mass is evaporated almost to dryness on a water-bath, taken up with water, and thoroughly extracted with ether. The ester is dissolved out of the ethereal solution by means of dil. potassium hydroxide and is precipitated as the yellow potassium derivative by the addition of a more concentrated solution of this reagent. This substance is collected at the pump and washed with ether. On cooling it separates as fine, yellow needles from hot alcohol, in which it is rather sparingly soluble.

Anal. Subs., 0.1184: K_2SO_4, 0.0287. Calcd. for $C_{14}H_{16}O_8NK$: K, 10.71. Found: 10.84.

The potassium compound of ethyl nitrotrimethylgallyl acetate is then dissolved in water, forming a strongly alkaline solution from which the free ester is precipitated upon being acidified with carbon dioxide. It crystallizes from alcohol as fine, white prisms, m. p. 85°, is readily soluble in ether, soluble in alcohol, and almost insoluble in water. It gives a red coloration when its solution in alcohol is mixed with ferric chloride.

Anal. Subs., 0.0822: CO_2, 0.1556; H_2O, 0.0391. Subs., 0.0681: N_2 (dry), 2.5 cc. (14°, 760 mm.). Calcd. for $C_{14}H_{17}O_8N$: C, 51.38; H, 5.20; N, 4.28. Found: C, 51.26; H, 5.28; N, 4.29.

3,4,5-Trimethoxy-6-nitro-acetophenone (VIII).—In order to establish further the constitution of the ethyl nitrotrimethylgallyl acetate its ketone was prepared. The ester is boiled with an excess of dil. sulfuric acid for a short time, the solution becoming dark in color. After cooling, the product is poured into water and extracted with ether. The dark ethereal solution is decolorized with charcoal and then washed with dilute aqueous sodium carbonate, dried over calcium chloride and evaporated. The crude ketone separates as yellowish needles which may be purified by recrystallization from ether in the form of long, white needles which melt at 118°.

Anal. Subs., 0.0896: CO_2, 0.1707; H_2O, 0.0418. Subs., 0.0980: N_2 (dry), 4.7 cc. (20°, 768 mm.). Calcd. for $C_{11}H_{13}O_6N$: C, 51.77; H, 5.09; N, 5.49. Found: C, 51.95; H, 5.18; N, 5.54.

3,4,5-Trimethoxy-6-nitro-acetophenone is soluble in methyl alcohol, ether and ethyl alcohol, and is insoluble in water. No color is produced when its solution in alcohol is mixed with ferric chloride; on dissolving in concd. sulfuric acid an intense red coloration is produced. This phenone is also formed when ethyl nitrotrimethylgallyl aceto-acetate is boiled with dil. sulfuric acid and the resultant product treated as above.

3,4,5-Trimethoxy-6-nitropropiophenone (X).—In the preparation of this phenone it is necessary to prepare ethyl α-(nitrotrimethylgallyl) propionate (IX). Two g. of the crystalline potassium compound of ethyl nitrotrimethylgallyl acetate is dissolved in 10 cc. of alcohol, and 1.5 g. of methyl iodide added. The reddish solution is boiled under a reflux condenser until it does not react with turmeric paper (about three hours). The excess of methyl iodide is evaporated and the solution poured into water, whereupon a dark red oil separates. This oil is extracted with ether, the ethereal solution washed with water, dried over anhydrous sodium sulfate, and evaporated; a heavy, red oil remains. It is soluble in alcohol, benzene and ether, and is insoluble in water and dil. sodium carbonate. Its solution in alcohol gives a deep red color when treated with ferric chloride. The oil consists of ethyl α-(nitrotrimethylgallyl) propionate. In order to produce the corresponding ketone from this ester, it was boiled a short time with dil. sulfuric acid, poured into water, and the resultant oil extracted with ether. The ethereal solution is decolorized with charcoal, washed with dilute, aqueous sodium carbonate, dried over calcium chloride and evaporated, a heavy brown oil separating which does not solidify on cooling. Its solution in alcohol gives a deep red color when treated with ferric chloride. For analysis it was dried in a vacuum over sulfuric acid.

Anal. Subs., 0.1852: N_2 (dry), 8.0 cc. (11°, 766 mm.). Calcd. for $C_{12}H_{15}O_6N$: N, 5.20. Found: 5.16.

Ethyl Nitrotrimethylgallyl Malonate (XI) was prepared by the method usually employed for the formation of the corresponding aceto-acetate derivative.

Anal. Subs., 0.0901: CO_2, 0.1693; H_2O, 0.0424. Calcd. for $C_{17}H_{21}O_{10}N$: C, 51.12; H, 5.26. Found: C, 51.24; H, 5.22.

Ethyl nitrotrimethylgallyl malonate is a white, crystalline compound which melts at 96°. It is soluble in ether, benzene and alcohol, and is insoluble in ligroin and in water. Its solution in methyl alcohol gives a wine-red color when treated with ferric chloride. It dissolves in concd. sulfuric acid with a deep red color.

Ethyl Nitrotrimethylgallyl Cyano-acetate (XII).—One and seven-tenths g. of sodium is dissolved in 30 cc. of absolute alcohol and to this solution 4.5 g. of cyano-acetic ester is added. Ten g. of finely powdered nitrotrimethylgallyl chloride is then added, in small quantities at a time and with frequent shaking. There is no apparent rise in the temperature of the reacting mass, so the experiment may be performed at the ordinary temperature. After remaining overnight, the alcohol was removed from the finely divided mass under reduced pressure, the sodium compound being too finely divided to filter. Water was then added to the remainder and, after the yellow compound had gone into solution, it was carefully acidified with hydrochloric acid. A white crystalline mass separated which was collected and recrystallized from alcohol as fine, white needles. For analysis the compound was dried in a vacuum over sulfuric acid.

Anal. Subs., 0.1204: CO_2, 0.2263; H_2O, 0.0485. Calcd. for $C_{15}H_{16}O_8N_2$: C, 51.1; H, 4.5. Found: C, 51.25; H, 4.47.

Ethyl nitrotrimethylgallyl cyano-acetate is a white, crystalline compound, m. p. 110°, is soluble in ether, benzene and alcohol, but insoluble in water and ligroin. Its solution in methyl alcohol gives a deep red color with ferric chloride. No color is produced when it dissolves in concd. sulfuric acid.

Nitrotrimethylgallyl Acetonitrile (XIII).—Two g. of ethyl nitrotrimethylgallyl cyano-acetate is boiled with 100 cc. of 20% hydrochloric acid for at least seven hours, a reflux condenser being used. The light yellow oil which forms as the solid melts gradually solidifies as the reaction nears completion. When the solution has cooled, the crystalline mass which forms is removed and then purified by dissolving in alcohol and warming with animal charcoal. After the alcoholic solution has been filtered fine, silky, white needles separate on cooling. For analysis this compound is dried in an oven at 100°.

Anal. Subs., 0.1040: CO_2, 0.1974; H_2O, 0.0408. Subs., 0.1243: N_2 (dry), 10.2 cc. (12°, 760 mm.). Calcd. for $C_{12}H_{12}O_6N_2$: C, 51.4; H, 4.3; N, 10.0. Found: C, 51.76; H, 4.35; N, 9.81.

Nitrotrimethylgallyl acetonitrile is a white, crystalline compound, m. p. 180°, is soluble in alcohol and benzene, and almost insoluble in ether. It is insoluble in ligroin and dilute, aqueous sodium carbonate. When dissolved in concd. sulfuric acid an intense red color is produced. Its solution in methyl alcohol does not give a red color with ferric chloride.

2-Ethoxy-4-hydroxy-6,7,8-trimethoxyquinoline Oxide (XV).—When ethyl nitrotrimethylgallyl acetate is reduced by the action of zinc dust and glacial acetic acid, heat is generated. As soon as the reacting mass ceases to generate heat on the addition of more zinc dust, the reaction is completed by warming on a water-bath for a few minutes. The solution is then quickly filtered and the filtrate poured into an excess of water. No solid separates, so the dil. acetic acid solution is partially neutralized with solid potassium carbonate and thoroughly extracted with ether. The ethereal solution is washed with water, then with dilute, aqueous sodium carbonate, and dried over calcium chloride and solid potassium carbonate. On evaporation of the ether, a dark red oil is obtained which quickly solidifies. The compound crystallizes as yellowish-white prisms from a mixture of benzene and ligroin.

Anal. Subs., 0.0949: CO_2, 0.1976; H_2O, 0.0490. Subs., 0.1521: N_2 (dry), 6.4 cc. (15°, 730 mm.). Calcd. for $C_{14}H_{17}O_6N$: C, 56.9; H, 5.8; N, 4.7. Found: C, 56.78; H, 5.73; N, 4.73.

2-Ethoxy-4-hydroxy-6,7,8-trimethoxyquinoline oxide is a yellowish-white, crystalline compound, m. p. 61°, is soluble in alcohol, benzene, chloroform, ether and acetone, slightly soluble in hot water and dil. sodium hydroxide solution, but insoluble in ligroin and dil. sodium carbonate solution. It dissolves in concd. sulfuric acid with a green color which changes to a deep blue on warming. On pouring into water the color disappears and no precipitate forms. Its solution in methyl alcohol does not give a color with ferric chloride, the same being true of its aqueous solution. An alkaline solution of this compound quickly decolorizes a potassium permanganate solution, forming an emerald-green solution. It does not reduce Fehling's solution.

Ethyl 2-Methyl-4-hydroxy-6,7,8-trimethoxyquinoline-3-carboxylate (XVI).—When ethyl nitrotrimethylgallyl aceto-acetate is treated with stannous chloride after the manner described in the previous communication[12] a white compound forms which, on crystallizing from alcohol, melts without decomposition at 182°. The former process being cumbersome for the yield obtainable, it was found advisable to employ zinc dust and glacial acetic acid as the reducing agents.

Seven g. of ethyl nitrotrimethylgallyl aceto-acetate is dissolved in glacial acetic acid contained in a flask, and to the red solution are added small quantities of zinc dust, with shaking. The temperature rises after each addition until the reduction is complete. When no change in temperature occurs on the further addition of zinc dust, the reaction mass is warmed on a water-bath for three minutes, after which it is rapidly filtered, the zinc residue being washed with a small amount of glacial acetic acid. The acetic acid solution is poured into water, and it is then necessary to reduce the acidity of the aqueous solution with potassium carbonate before a precipitate separates. This compound is collected, washed with water, and crystallized as fine, white needles from alcohol; yield, 5 g.

Anal. Subs., 0.0814: CO_2, 0.1780; H_2O, 0.0433. Subs., 0.0526: N_2 (dry), 2.1 cc. (14°, 742 mm.). Calcd. for $C_{16}H_{19}O_6N$: C, 59.8; H, 5.9; N, 4.4. Found: C, 59.63; H, 5.91; N, 4.58.

Ethyl 2-methyl-4-hydroxy-6,7,8-trimethoxyquinoline-3-carboxylate is a white, crystalline compound which melts without decomposition at 183°. It is easily soluble in alcohol, acetone, chloroform, sodium hydroxide, acetic anhydride and ammonium hydroxide, slightly soluble in benzene, and insoluble in sodium carbonate and ligroin.

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[12] Ref. 1, p. 459.

It gives a red coloration when its solution in sodium hydroxide is mixed with ferric chloride. It does not decolorize an acetone solution of potassium permanganate and its solution in sodium hydroxide does not decolorize potassium permanganate to form an emerald-green solution. The products obtained in the two reductions were identical.

2-Methyl-4-hydroxy-6,7,8-trimethoxyquinoline-3-carboxylic Acid (XVII).—The acid is prepared from the ethyl ester by hydrolysis with aqueous potassium hydroxide. It crystallizes as clusters of fine, white needles from alcohol.

Anal. Subs., 0.0880: CO_2, 0.1893; H_2O, 0.0424. Calcd. for $C_{14}H_{15}O_6N$: C, 57.3; H, 5.1. Found: C, 57.0; H, 5.35.

2-Methyl-4-hydroxy-6,7,8-trimethoxyquinoline-3-carboxylic acid is a white, crystalline compound which decomposes at 202° with loss of carbon dioxide to give 2-methyl-4-hydroxy-6,7,8-trimethoxyquinoline. It is easily soluble in sodium carbonate, sodium hydroxide, ammonium hydroxide, chloroform and acetone, rather difficultly soluble in alcohol, and insoluble in benzene, ligroin and ether. It does not decolorize an acetone solution of potassium permanganate, and its solution in sodium hydroxide does not decolorize potassium permanganate to form an emerald-green solution. It gives a red coloration when its solution in methyl alcohol is mixed with ferric chloride.

2-Methyl-4-hydroxy-6,7,8-trimethoxyquinoline, XVIII.—The acid described above, contained in a test-tube, is immersed in a paraffin-bath which has been previously heated to 202°, until the evolution of carbon dioxide has ceased. The dark melt is then dissolved in a 1% solution of potassium hydroxide, decolorized with charcoal and filtered. The filtrate is reduced to small volume by evaporation and is acidified with carbon dioxide, the quinoline compound separating from the aqueous solution as fine, white needles. For analysis it is crystallized from dil. alcohol as white prisms.

Anal. Subs., 0.0850: CO_2, 0.1949; H_2O, 0.0465. Calcd. for $C_{13}H_{15}O_4N$: C, 62.65; H, 6.02. Found: C, 62.53; H, 6.06.

2-Methyl-4-hydroxy-6,7,8-trimethoxyquinoline is a white, crystalline compound which melts without decomposition at 182°. It is soluble in alcohol, acetone, chloroform, sodium hydroxide and dil. sulfuric acid, insoluble in water, benzene, ligroin, ether and sodium carbonate. Its solution in methyl alcohol gives a yellowish-red coloration when mixed with ferric chloride. A dil. sulfuric acid solution does not decolorize potassium permanganate solution, the same being true of an acetone solution of the permanganate. No immediate decolorizing, with subsequent formation of an emerald-green color, takes place when its solution in sodium hydroxide is mixed with aqueous potassium permanganate.

Aminotrimethylgallic Acid, XIX.—Two g. of nitrotrimethylgallic acid is dissolved in 20 g. of concd. ammonium hydroxide and to this solution is added 18 g. of ferrous sulfate in a hot, saturated solution. The whole is shaken until the rather vigorous reaction is complete, after which the ferric hydroxide is removed by filtration. When the filtrate is made slightly acid with acetic acid, the amino acid is precipitated. The product is soluble in hot water and any coloring matter which may be present is removed with animal charcoal. It is recrystallized from hot water as light gray needles.

Anal. Subs., 0.0883: CO_2, 0.1704; H_2O, 0.0450. Calcd. for $C_{10}H_{13}O_5N$: C, 52.86; H, 5.73. Found: C, 52.62; H, 5.66.

Aminotrimethylgallic acid is a light gray, crystalline compound which melts at 137°. It is soluble in alcohol, ether, benzene, sodium carbonate and sodium hydroxide. It imparts a blue fluorescence when in solution in alcohol and in water.

The writer expresses appreciation to Professor W. H. Perkin for his inspiration and guidance while this work was in progress.

Summary

All attempts at the formation of a hexamethoxy indigo by means of the synthesis employed in these communications were unsuccessful; many interesting derivatives of gallic acid, however, were obtained.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

SOME NEW REACTIONS OF THE MIXED AQUO-AMMONOCARBONIC ACIDS

BY L. A. PINCK AND J. S. BLAIR

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In a recent paper[1] defining the term "mixed aquo-ammonocarbonic acid," it was shown that there is a large discrepancy between the number of known compounds of this type and the number which may be formulated. Furthermore, there are several reactions, rather simple in nature, which would be expected to characterize these compounds as mixed aquo-ammonocarbonic acids, but which have not as yet received experimental verification. In this paper are presented the results of some work bearing upon this problem, which has been carried out at various times in this Laboratory.

Many investigators have demonstrated the conditions under which ammonia may act to synthesize one compound of this type from another by ammonation or partial ammonalysis; for example, the ammonalysis of urea to guanidine. A few such reactions are also described in the present paper. The reverse type of reaction, namely, the hydration or partial hydrolysis of one compound to another, is considerably more difficult to control. The action of water ordinarily leads to disruption of substances containing two or more carbon atoms per molecule to form aquocarbonic acid or other simple carbonic acids, such as urea or guanidine which, while thermodynamically unstable in water solution, are only slowly hydrolyzed. However, when anhydrous alcohol is substituted for water, the solvolysis is less extensive and the esters of the more complex acids may be isolated. This may be illustrated by the experiments described below.

Action of Alcohol on Guanylurea

Guanylurea, a mixed aquo-ammonocarbonic acid containing two carbon atoms, was found to react with anhydrous ethyl alcohol to form a carbethoxy-guanidine identical with that obtained by Nencki[2] by the action of ethyl chlorocarbonate on guanidine. The reaction may be expressed by

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[1] Blair, THIS JOURNAL, **48**, 87 (1926).

[2] Nencki, *Ber.*, **7**, 1594 (1874).