XLVIII.—*Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. Part I. 5-Amino-Salicylic Acid and Related Compounds.*

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By the successive benzylation and methylation of *isopicramic acid*, Meldola and Hollely (T., 1914, **105**, 1480) obtained benzylmethyl-*isopicramic acid* (I). On treatment with ethyl sulphate this, how-

ever, gave chiefly the phenolic ether, 2:6-dinitro-4-benzylmethylaminophenetole (II), and by concentration of the alkaline filtrate they subsequently obtained a very small quantity of the desired quinone-ammonium compound, 2:6-dinitro-4-benzylmethylethylammonium-1-benzoquinone (III) (T., 1914, **105**, 2073).

Their researches on the extreme alkylation of the alkylated *iso*-
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picramic acids showed that the phenolic ether was generally formed as well as the quinone-ammonium compound.

We therefore undertook the examination of other derivatives of *p*-aminophenol in the hope of obtaining similar compounds containing an asymmetric nitrogen atom, but in more satisfactory yield. In particular, it appeared desirable to examine the derivatives of 5-aminosalicylic acid, as it might be expected that the carboxyl group would be of service in the resolution of any asymmetric nitrogen compounds that might be obtained.

At the outset of our investigation we found that although a number of substituted salicylic acids had already been described, the descriptions were imperfect, and in several cases it was necessary again to examine the preparation and properties of the compounds in question. In consequence of this, our investigation was largely diverted from the immediate search for asymmetric nitrogen compounds to a preliminary survey of the field.

An attempt to methylate 5-aminosalicylic acid directly ended in failure. It was sought to obtain 5-methylaminosalicylic acid indirectly by condensing 5-aminosalicylic acid with monochloroacetic acid, and then eliminating the carboxyl group from the side-chain in the product by the action of heat. However, the condensation did not proceed in the expected direction.

On benzylation only a dibenzyl derivative could be obtained, which on methylation gave the quinone-ammonium compound, 2-carboxy-4-dibenzylmethylammonium-1-benzoquinone (IV) or its isomeride (V):

Some further properties of 5-aminosalicylic acid were also brought to light during the research. The acid reacts readily with 2:3:6-trinitro-4-acetylaminophenol, giving an iminazole (VI) with eli-

mination of a nitro-group in the way which has been shown to be characteristic of this substance (Meldola and others, T., 1906, **89**, 1935; 1908, **93**, 1659):

Substituted 5-aminosalicylic acids were then examined. An attempt to obtain 3-nitro-5-aminosalicylic acid (VII) by the nitration of 5-acetylaminosalicylic acid led to the formation of acetyl-*isopicramic* acid (VIII) by nitration and elimination of the carboxyl group:

3:5-Dinitrosalicylic acid was then prepared and reduced to 5-nitro-3-aminosalicylic acid.

This acid is easily acetylated, and on diazotisation yields a yellow diazo-oxide, which gives a rather indefinite azo-compound with β -naphthol.

From this diazo-oxide, by means of the Sandmeyer reaction, 3-chloro-5-nitro-, 3-bromo-5-nitro-, and 5-nitro-3-cyano-salicylic acids were prepared, and on reduction the corresponding 3-chloro-5-amino- and 3-bromo-5-amino-salicylic acids were obtained. The former on acetylation gives a diacetyl compound, from which the *N*-monoacetyl derivative was obtained by hydrolysis. On benzylation the chloroaminosalicylic acid gives a mixture of the mono- and di-benzyl derivatives, from which the former was isolated.

The preparation of 5-nitro-3-cyanosalicylic acid was undertaken with a view to ascertain whether the substituted *isophthalic* acid obtainable from this by hydrolysis and reduction:

would yield a monobenzyl derivative more readily than the corresponding *isopicramic* acid:

The poisonous nature of the cyano-acid, however, led to the abandonment of this project, and an attempt to obtain the *isophthalic*

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acid by the application of the Reimer-Tiemann reaction to 5-nitrosalicylic acid:

was also unsuccessful.

Owing to war exigencies, it was not possible to prosecute the research further. The above results, however, appear to justify the expectation that 3-substituted-5-aminosalicylic acids would be mono-alkylated more readily than the parent substance. It would therefore appear probable that asymmetric nitrogen compounds of the type:

may be obtained by subsequent workers in this field.

EXPERIMENTAL.

5-Nitrosalicylic Acid.

One part of salicylic acid was slowly added to one part of nitric acid (D 1.41) in four parts of water, and the mixture was heated on a water-bath for an hour with stirring. The nitrosalicylic acid separated on cooling, and was crystallised once from hot water.

When a solution in 20 per cent. sodium hydroxide solution was boiled for ten hours with chloroform, the acid was recovered unchanged.

5-Aminosalicylic Acid.

One part of nitrosalicylic acid was dissolved in eight parts of hydrochloric acid (D 1.16) and two parts of tin were dissolved in the solution by boiling. On adding a few drops of concentrated sulphuric acid to the solution after the complete reduction, a white, crystalline precipitate formed on cooling, which was evidently a double salt. This was collected and well drained, but not washed, as it was readily soluble in water. It was then treated with concentrated sodium carbonate solution until no further effervescence took place and the solution was just alkaline. The boiling solution was rapidly filtered from the precipitated tin hydroxide, the residue washed once or twice with a little hot water, and the filtrate and washings were acidified with glacial acetic acid, when the 5-aminosalicylic acid separated.

By recrystallisation from water, its melting point was considerably raised. Starting with the purest nitrosalicylic acid obtainable and crystallising the amino-acid twice from water, a specimen melting at 283° was obtained. Hübner (*Annalen*, 1879, **195**, 18), Beilstein (*ibid.*, 1864, **130**, 243), and Schmidt (*Jahresber.*, 1864, 383) state that the acid decomposes at 280° .

Attempted Methylation of 5-Aminosalicylic Acid.

(1) Two grams of aminosalicylic acid were digested with 1.65 grams of methyl sulphate and methyl alcohol under reflux. Solution was complete in about half an hour, and after about two hours the contents of the flask were evaporated nearly to dryness on the water-bath. Water was added, and the evaporation again carried nearly to dryness. The residue was dissolved in a little water, and on adding concentrated hydrochloric acid to the solution, silvery scales separated. These began to blacken at 250° , and finally melted at 270° . Further examination proved that these crystals were the hydrochloride of aminosalicylic acid, and methylation had therefore not taken place.

(2) Aminosalicylic acid was heated with methyl sulphate at 100° for an hour, but solution did not take place. The whole was then poured into water and the excess of methyl sulphate destroyed by heating with dilute hydrochloric acid, the last traces being removed with ammonia. On concentrating the solution and adding hydrochloric acid, nothing but ammonium chloride could be isolated. No precipitate was produced when an attempt was made to diazotise the solution.

(3) No definite methylated product could be isolated by treating aminosalicylic acid with methyl sulphate and sodium hydroxide.

5-Dibenzylaminosalicylic Acid.

Molecular quantities of aminosalicylic acid, benzyl chloride, and sodium acetate were digested with a little water for three days on the water-bath, and ammonia was then added until complete solution was obtained. After some hours, hydrochloric acid was added and the white precipitate was freed from unchanged aminosalicylic acid by dissolving in ammonia and reprecipitating from much warm water. The compound was difficult to crystallise, being very sparingly soluble in alcohol or acetic acid. When crystallised from alcohol it dried to a white, amorphous powder melting at $168-169^{\circ}$:

0.2578 gave 9.6 c.c. N_2 at 13.5° and 759 mm. $N=4.38$.

$C_{21}H_{19}O_3N$ requires $N=4.21$ per cent.

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The substance had distinctly acidic properties, being readily soluble in dilute ammonia. It possessed no basic properties and melted under water. Its reducing properties were revealed in an attempt to prepare a silver salt. A silver mirror was obtained when a solution of the ammonium salt was treated with silver nitrate solution.

2-Carboxy-4-dibenzylmethylammonium-1-benzoquinone (IV or V).

Dibenzylaminosalicylic acid was methylated by treatment with methyl sulphate and alkali hydroxide in the usual way. The product was a resinous substance, which was collected and digested with hydrochloric acid. The resinous mass was again collected, and from the acid extract white crystals separated after leaving it a day or two.

The substance was collected, dissolved in alkali, and reprecipitated with hydrochloric acid. The precipitate was crystallised from a small amount of alcohol, from which it separated in dense, colourless prisms melting at 103° :

0.1791 gave 6.7 c.c. N_2 at 23.5° and 754.3 mm. $N=4.16$.

$C_{22}H_{21}O_3N$ requires $N=4.04$ per cent.

Condensation Product of Trinitroacetylaminophenol and Aminosalicyclic Acid (VI).

The trinitroacetylaminophenol (1.7 grams) was boiled with aminosalicyclic acid in aqueous solution for three-quarters of an hour. A brown solid separated, which crystallised from alcohol, in which it is sparingly soluble, in ochreous nodules, decomposing between 220° and 300° :

0.1124 gave 14.8 c.c. N_2 at 20.5° and 763 mm. $N=15.02$.

$C_{15}H_{10}O_8N_4$ requires $N=14.98$ per cent.

4-Hydroxy-3-carboxybenzeneazo- β -naphthol,

Aminosalicyclic acid (2.5 grams) was diazotised in the usual way, and the solution, from which the diazo-compound had partly separated, was added to a well-cooled alkaline solution of β -naphthol (2.4 grams). The solution was acidified with hydrochloric acid, when a red, colloidal mass separated. For purification, this was dissolved in dilute sodium hydroxide and precipitated hot with acid, followed by digestion with boiling alcohol, in which it was practically insoluble:

0.1976 gave 15.1 c.c. N_2 at 17.5° and 763.4 mm. $N=8.89$.

$C_{17}H_{12}O_4N_2$ requires $N=9.09$ per cent.

The azo-compound when freshly precipitated possessed a bright red colour, but dried to a dark red, amorphous powder. It dissolved in sulphuric acid, giving a magenta-red coloration, and melted and decomposed at 245°.

Action of Nitric Acid on Aminosalicyclic Acid.

No definite nitration product was obtained by treating aminosalicyclic acid in sulphuric acid solution with fuming nitric acid.

Acetylaminosalicyclic acid was therefore prepared by boiling aminosalicyclic acid with acetic anhydride for a few minutes. After dilution with water, the solution was evaporated to dryness on the water-bath, and the product crystallised from alcohol. The acetylaminosalicyclic acid obtained in this way melted at 197° (Hübner, *Annalen*, 1879, **195**, 19, and Grandmougin, *Ber.*, 1906, **39**, 3930, give 218°). An attempt to esterify it with methyl-alcoholic sulphuric acid only resulted in its hydrolysis.

The acetylaminosalicyclic acid was added to an excess of fuming nitric acid cooled in ice. The substance gradually dissolved with evolution of gas, and in a few minutes the production of a substance forming a somewhat insoluble ammonium salt was shown by a test on a drop of the solution. The whole product was then poured into water, and immediately neutralised at as low a temperature as possible by the gradual addition of ammonia. The ammonium salt, which separated in the cold in flat, orange needles, was decomposed with hydrochloric acid, and the product purified by solution in very dilute potassium hydroxide solution and reprecipitation with hydrochloric acid. The substance, which separated slowly in long, flat, ochreous needles, melted at 177°, and appeared to be identical with that obtained by nitrating acetylaminosalicyclic acid in acetic acid solution with fuming nitric acid. (Found, N=17·63. $C_8H_7O_6N_3$ requires N=17·44 per cent.) The identity of the substance with acetyl*isopicramic* acid was shown by hydrolysing it with concentrated sulphuric acid and a little water. The product had all the properties of *isopicramic* acid, and a mixture of the two showed no depression of the melting point.

3:5-Dinitrosalicyclic Acid.

A mixture of 50 c.c. of fuming nitric acid with 20 c.c. of concentrated sulphuric acid was cooled in ice, and 10 grams of salicylic acid were gradually added with constant stirring. After an hour the mixture was poured on ice. After several hours, the product was collected, and, after crystallising once from water,

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was usually pure enough for use. The dinitrosalicylic acid so obtained melted at 173—174°.

When larger quantities of the acid were required, it was found better to nitrate 10 grams at a time than to nitrate in batches of 20 or more grams. Pure dinitrosalicylic acid shows the phenomenon of supersaturation in its solutions to a marked degree, and care must be taken to avoid loss through this in crystallising.

5-Nitro-3-aminosalicylic Acid.

Hübner, Babcock, and Schaumann (*Ber.*, 1879, **12**, 1345) state that this acid can be obtained by the partial reduction of 3:5-dinitrosalicylic acid with ammonium sulphide. They give no details, however, and their description of the properties of the nitroaminosalicylic acid is inaccurate.

It was found necessary to avoid as much as possible both excess and deficiency of ammonium sulphide, as the formation of diamino-salicylic acid or the presence of unchanged dinitrosalicylic acid caused trouble in the purification.

Twenty grams of dinitrosalicylic acid, 60 c.c. of water, 40 c.c. of concentrated ammonia, and 79 c.c. of yellow ammonium sulphide were heated on the water-bath to the boiling point for about twenty minutes with frequent shaking. After cooling somewhat, concentrated hydrochloric acid was added in sufficient excess to redissolve everything except sulphur. The solution was boiled and filtered. The cooled filtrate was nearly neutralised by adding concentrated ammonia, and the brown crystals which separated were collected in the cold and purified by solution in dilute hydrochloric acid (one part of acid to two of water) and reprecipitation with ammonia. The nitroaminosalicylic acid so obtained was pure enough for most purposes.

For analysis, the product was treated once more with acid, precipitated with ammonia, and then crystallised twice from hot water. These crystals were suspended in a very little water and treated with hydrochloric acid. The white, crystalline hydrochloride was crystallised twice from hydrochloric acid and then decomposed with dilute ammonia. After a further crystallisation from hot water, the nitroaminosalicylic acid obtained in this way was analysed.

5-Nitro-3-aminosalicylic acid crystallises from hot water in scarlet needles, which melt and decompose at 234° (constant) if the temperature of the bath is raised rapidly. The crystals slowly change to an ochreous powder at 100°, losing one molecule of water of crystallisation. (Found, $H_2O=8.34$. Calc., $H_2O=8.34$ per

cent.) The acid is very readily soluble in alcohol, but only very sparingly so in cold water. It dissolves readily in water above 85°. The solution of the acid in ammonia possesses a deep red colour, the solution in hydrochloric acid showing a yellowish-brown coloration. (Found, C=42·19; H=2·90; N=13·99. Calc., C=42·41; H=3·05; N=14·15 per cent.)

Diazotisation of 5-Nitro-3-aminosalicylic Acid.

A small quantity of nitroaminosalicylic acid was dissolved in an excess of dilute hydrochloric acid, and the solution was treated with sodium nitrite. The yellow product when crystallised from alcohol separated in bright yellow needles, which became brown on drying at 100°. It exploded violently if suddenly heated, but decomposed gradually at 145—150°. The substance dissolved in alkali to a deep red solution:

0·0936 gave 15·8 c.c. N₂ at 16° and 767·7 mm. N=19·88.

C₇H₅O₅N₃ requires N=20·10 per cent.

Two grams of the dry diazo-oxide were gradually added to an alkaline solution of 1·4 grams of β-naphthol, cooled in ice. After some time, the solution was acidified, but the resinous, brown mass which separated could not be crystallised, and on account of its indefinite and unsatisfactory character it was not further investigated.

5-Nitro-3-acetylaminosalicylic Acid.

A mixture of nitroaminosalicylic acid and acetic anhydride soon became pasty on stirring, through the separation of a voluminous, yellow solid, and in about half an hour the whole was poured into water. The ochreous, crystalline product when crystallised from dilute alcohol separated in pale ochreous needles melting at 249°; it was very readily soluble in alcohol and fairly so in water:

0·1129 gave 0·1855 CO₂ and 0·0328 H₂O. C=44·81; H=3·22.

0·1211 „ 12·35 c.c. N₂ at 24° and 764·9 mm. N=11·51.

C₉H₈O₆N₂ requires C=44·98; H=3·36; N=11·67 per cent.

3-Chloro-5-nitrosalicylic Acid.

Nitroaminosalicylic acid was diazotised as described above, and the diazo-oxide was collected and drained. It was then added to an excess of a solution of freshly prepared cuprous chloride in hydrochloric acid, with vigorous stirring. Evolution of gas occurred, and the solution became pasty through the separation of a white solid. The liquid was warmed on the water-bath for about

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an hour until all the nitrogen had been evolved. The chloro-nitrosalicylic acid was collected and crystallised two or three times from a small quantity of hot water.

3-Chloro-5-nitrosalicylic acid crystallises from water in long, white, silky needles melting at 202—203°. It is very readily soluble in alcohol:

0.1199 gave 0.0786 AgCl. Cl=16.22.

0.2111 „ 12.25 c.c. N₂ at 19.5° and 761 mm. N=6.66.

C₇H₄O₅NCl requires Cl=16.30; N=6.44 per cent.

3-Chloro-5-aminosalicylic Acid.

The chloronitrosalicylic acid was added to a hot mixture of hydrochloric acid and tin. Reduction at once took place, with some evolution of heat, and after boiling to complete the reduction, the solution was decanted from the undissolved tin. On cooling, a considerable deposit of glistening, white scales was observed, consisting probably of the tin double salt. The crystals were drained, but not washed. They were then boiled with a slight excess of a hot concentrated solution of sodium carbonate, and on acidifying the filtrate, the chloroaminosalicylic acid separated as a white, microcrystalline powder. It could be crystallised from water, in which it was not very readily soluble. The acid melted and decomposed at 259—260°, and was practically insoluble in alcohol:

0.1105 gave 0.1808 CO₂ and 0.0457 H₂O. C=44.63; H=4.59.

0.1519 „ 9.6 c.c. N₂ at 19° and 761.7 mm. N=7.29.

0.1743 „ 0.1309 AgCl. Cl=18.58.

C₇H₆O₃NCl requires C=44.62; H=3.20; N=7.47; Cl=18.91 per cent.

Diacetyl Compound.—The chloroaminosalicylic acid was warmed with acetic anhydride for a short time on the water-bath. The substance did not dissolve, and on pouring the mixture into water a white solid was obtained, which crystallised from dilute alcohol in small, stout, white needles melting at 218°. The substance is insoluble in water, but very readily soluble in alcohol:

0.1738 gave 8.3 c.c. N₂ at 25° and 753.3 mm. N=5.27.

C₁₁H₁₀O₅NCl requires N=5.16 per cent.

The same substance was obtained by acetylating the chloroaminosalicylic acid with acetic anhydride and a few drops of sulphuric acid.

3-Chloro-5-acetylaminosalicylic Acid.

The above diacetyl compound was partly hydrolysed by boiling for a few minutes with sodium carbonate solution, in which it is readily soluble. On acidifying the solution, a white substance separated, which crystallised from much water in white needles melting and decomposing at 258° . The substance is sparingly soluble in water, very readily so in alcohol, and turns pink on long exposure to the air:

01051 gave 0.1818 CO_2 and 0.0421 H_2O . $\text{C}=47.13$; $\text{H}=4.45$.

0.1527 „ 8.05 c.c. N_2 at 23° and 755.6 mm. $\text{N}=5.91$.

$\text{C}_9\text{H}_8\text{O}_4\text{NCl}$ requires $\text{C}=47.05$; $\text{H}=3.51$; $\text{N}=6.10$ per cent.

Diazotisation of Chloroaminosalicylic Acid. Formation of the Diazo-oxide.

Chloroaminosalicylic acid was dissolved in dilute hydrochloric acid, and to the solution, cooled in ice, sodium nitrite was added in excess. A yellow substance separated which was almost insoluble in water or alcohol, but crystallised from acetic acid in ochreous scales detonating at 193° :

0.1158 gave 14.4 c.c. N_2 at 195° and 760.5 mm. $\text{N}=14.27$.

$\text{C}_7\text{H}_3\text{O}_3\text{N}_2\text{Cl}$ requires $\text{N}=14.11$ per cent.

5-Chloro-4-hydroxy-3-carboxybenzeneazo- β -naphthol.

Two grams of chloroaminosalicylic acid were diazotised as described above, and the solution was poured into cold alkaline β -naphthol solution. After some time, the deep red solution was acidified with hydrochloric acid, and the bright red colloidal precipitate was purified by precipitation with acid from hot dilute alkaline solution, followed by digestion with boiling alcohol.

The substance is extremely sparingly soluble in alcohol or hot acetic acid, imparting an orange colour to these solvents. The trace dissolved by acetic acid separates in a non-crystalline form on dilution with water.

The azo-compound dried to a dark brick-red, amorphous solid melting and decomposing at 287° . It dissolves in sulphuric acid to a magenta-red solution. A trace of mineral matter was still present, for which the analysis was corrected:

0.2280 gave 15.9 c.c. N_2 at 19.5° and 764.9 mm. $\text{N}=8.05$.

$\text{C}_{17}\text{H}_{11}\text{O}_4\text{N}_2\text{Cl}$ requires $\text{N}=8.18$ per cent.

Benzylation of Chloroaminosalicylic Acid.

Five grams of chloroaminosalicylic acid were heated on the water-bath with benzyl chloride (3.4 grams), a little water, and sodium acetate (4 grams) for two days. Ammonia was then added until the solution was alkaline, and a small quantity of a non-acidic residue was removed. The filtrate was rendered just acid, and a brown resin separated, which slowly became granular. This was dissolved in dilute ammonia, and on precipitating in the cold with dilute hydrochloric acid, it separated in almost white, flocculent masses. Analysis (Found, $N=4.56$) showed it to consist of a mixture of the mono- and di-benzyl derivatives. The substance was very readily soluble in alcohol, and slowly separated from this solvent in brown nodules. By recrystallising twice from this solvent, a small quantity of the *monobenzyl* derivative was obtained:

0.1684 gave 7.7 c.c. N_2 at 23.5° and 756.0 mm. $N=5.11$.

$C_{14}H_{12}O_3NCl$ requires $N=5.11$ per cent.

On attempting to effect the benzylation without the addition of sodium acetate, unchanged chloroaminosalicylic acid formed the main bulk of the product.

3-Bromo-5-nitrosalicylic Acid.

The preparation of this acid by the bromination of 5-nitrosalicylic acid has been described by Lellmann and Grothmann (*Ber.*, 1884, **17**, 2724). We prepared it by applying the Sandmeyer reaction to nitroaminosalicylic acid.

5-Nitro-3-aminosalicylic acid was diazotised as already described, and the freshly prepared diazo-oxide, after being quickly freed from as much water as possible, was added to a solution of cuprous bromide in hydrobromic acid. A considerable evolution of gas occurred on warming on the water-bath, but the bulky solid which separated at first passed into solution as the temperature rose. The solid which separated on cooling was crystallised frequently from water. It was very readily soluble in alcohol or hot water, but sparingly so in cold water. From dilute aqueous solution it crystallised in long, transparent needles, and from more concentrated solutions in dense, white rosettes.

The substance was found to be identical with that obtained by Lellmann and Grothmann, but the above method appears to give a larger yield and a purer product than by the bromination process. The bromonitrosalicylic acid process melted at $226-227^\circ$. Lellmann and Grothmann give 222° .

3-Bromo-5-aminosalicylic Acid.

Lellmann and Grothmann (*ibid.*) obtained the hydrochloride of this acid, but stated that the free amino-acid could not be isolated.

3-Bromo-5-nitrosalicylic acid was easily reduced by a hot solution of stannous chloride containing metallic tin. After a short time, the nitro-acid completely dissolved, and concentrated sulphuric acid was added to the solution, when the sulphate of the amino-acid slowly separated in flat, silvery needles. These were washed with a little dilute sulphuric acid and then decomposed in the usual way by boiling with concentrated sodium carbonate solution. The solution was rendered slightly alkaline with ammonia and filtered to remove hydroxides of tin. On neutralising the filtrate with acetic acid, the amino-acid separated as a white, crystalline substance, which was purified by solution in ammonia and neutralising the hot solution with hydrochloric acid. The amino-acid separated on cooling in white, microscopic crystals which began to darken at 240° , and melted and decomposed at 255° :

0.2202 gave 11.9 c.c. N_2 at 16° and 754.5 mm. $N = 6.25$.

0.1050 „ 0.0849 AgBr. $Br = 34.41$.

$C_7H_6O_3NBr$ requires $N = 6.04$; $Br = 34.45$ per cent.

5-Nitro-3-cyanosalicylic Acid.

The diazo-oxide of nitroaminosalicylic acid, obtained as already described, was added to a solution of cuprous cyanide. The solution was kept stirred during the addition of the diazo-oxide, which was accompanied by a vigorous evolution of gas. The reaction was completed on the water-bath, and the dark substance which separated on cooling was crystallised from a small quantity of water, with the addition of a little animal charcoal. From the deep red solution, pale yellow crystals separated at first, but these speedily acquired a red tint if the solution was not rapidly cooled.

The substance was readily soluble in sodium carbonate solution, being precipitated by acid. It was fairly readily soluble in water, but very sparingly so in alcohol. It lost one molecule of water of crystallisation on drying at 100° , and the anhydrous cyano-acid melted at 205° .

The acid was readily oxidised by the air. An attempt was made on a small scale to hydrolyse it, but it proved to be remarkably

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stable, although some change was produced by heating with 80 per cent. sulphuric acid:

0·6921 lost 0·0556 H_2O . $\text{H}_2\text{O}=8\cdot03$.

$\text{C}_8\text{H}_4\text{O}_5\text{N}_2, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=7\cdot96$ per cent.

0·1158 gave 0·1955 CO_2 and 0·0218 H_2O . $\text{C}=46\cdot05$; $\text{H}=2\cdot09$

0·1050 „ 12·4 c.c. N_2 at 25° and 767·8 mm. $\text{N}=13\cdot31$.

$\text{C}_8\text{H}_4\text{O}_5\text{N}_2$ requires $\text{C}=46\cdot14$; $\text{H}=1\cdot98$; $\text{N}=13\cdot47$ per cent.

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