The salt is so unstable that even carbon dioxide will decompose it, liberating the free acid.

Abietic Acid, $C_{19}H_{28}O_2$.—The ether solution from the ammonium salt of resinic acid was removed and evaporated. The residue left was a light-colored resinous substance. This soluble part represented about 30 per cent. of the total resin. It was again taken up with ether containing a little dry ammonia gas and filtered. The residue left after allowing the ether to evaporate, was hard and brittle. By repeating this process several times, the substance became almost white. The salt could not be obtained in a distinctly crystalline form. Further purification, however, failed to change the comparatively sharp melting point of 89°.

Calculated for ammonium abietate, $C_{19}H_{27}O_2(NH_4)$: C = 73.77; H = 10.16; N = 4.59
Found: C = 73.44, 73.56, 73.16; H = 9.87, 9.62, 10.22; N = 5.15, 5.93, 4.61.

The amount of nitrogen found above is practically twice as much as was found by Mach who ascribed to the ammonium salt the formula $C_{19}H_{27}O_2(NH_4).C_{19}H_{28}O_2$. This difference is doubtless due to the different methods of preparation. The acid salt, however, could not be prepared either by treating the neutral salt with water or by exposing to the air. In each case, the salt lost more than half of its ammonia. In fact, after long exposure to the air the salt lost nearly all of its ammonia. By triturating the ammonium salt with dilute hydrochloric acid and washing with water in order to remove the ammonium chloride formed together with the excess of the hydrochloric acid, an almost white granular powder was formed. After carefully washing with water, the powder was dissolved in alcohol and water added until precipitation began as indicated by the milky appearance of the solution. It was then set aside until the acid had crystallized out. After crystallizing several times, the acid melted at 129–30°. Analyses gave the following:

Calculated for $C_{19}H_{28}O_2$: C = 79.16 ; H = 9.73
Found: C = 79.02, 78.64; H = 9.64, 10.00

The potassium and barium salts were prepared but as their properties seemed to coincide with those of common abietic acid, no analyses were made.

The Mach formula for abietic acid has been assumed to be the correct one although there is still some doubt. The above analyses, however, agree almost as well with the generally accepted formula $C_{20}H_{30}O_2$.

From the above facts, one may draw the conclusion that the resin of the Norway pine contains two acids. The one is doubtless abietic acid although its melting point is lower than that recently given to abietic acid. The other, resinic acid, differs from any of the resin acids described. It resembles, to some extent, Tschirch's palabienic acid, which was prepared by a somewhat similar method.

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[FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

5-BROM-2-AMINOBENZOIC ACID, A NEW PREPARATION.

BY ALVIN S. WHEELER.

Received March 1, 1909.

The original object of this investigation was to convert trichlorethylidene-*o*-aminobenzoic acid[1] into a compound containing an asymmetric carbon atom by means of bromine or hydrobromic acid, thus

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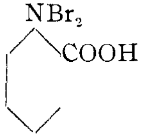
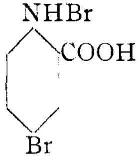
[1] Niementowski and Orzechowski, *Ber*, **28**, 2812; also Wheeler, THIS JOURNAL, 30, 139.

$CCl_3CH:NC_6H_4COOH \longrightarrow CCl_3CHBrNBrC_6H_4COOH$. A glacial acetic acid solution of the unsaturated compound absorbs bromine instantly in the cold with the immediate formation of a white precipitate. A Carius determination showed a marked deficiency of halogen and displacement of the bromine in the silver precipitate proved the entire absence of chlorine in the substance. Further proof that the chloral residue was split off was found in an examination of the acetic acid filtrate. This was made alkaline, then acid with tartaric acid and distilled in steam. A large quantity of chloroform passed over with the steam. The product was therefore a simpler derivative of anthranilic acid than the one looked for. Since the break occurs at the double bond, it might be a nitrogen bromide I or II, or the hydrobromide of a bromanthranilic acid, III.

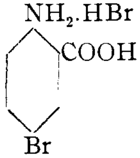
I.



II.



III.



Difficulty was experienced in obtaining products of the same melting point, different solvents giving slightly varying results. While none of the reactions of nitrogen halides as indicated by Chattaway and Orton[1] could be obtained, it was thought this might be due to the insolubility of the compound. But the idea of a nitrogen bromide was abandoned when it was observed that cold water immediately and completely removed one molecule of hydrobromic acid, showing the substance to be the salt of a bromaminobenzoic acid. It is still hoped to isolate in some way the nitrogen bromide which must certainly be the first product of the reaction. The case is an especially interesting one because it is quite unique in that the substance employed contains the grouping $N = X$ and so seems to offer an unusually good chance to form a nitrogen halide.

It was next observed that direct bromination of anthranilic acid in glacial acetic acid solution gave a similarly large yield of the bromaminobenzoic acid hydrobromide. The reaction therefore offers a new method of preparing this acid far superior in point of time and convenience to the method of Alt[2] which has been recently used by Bogert and Hand.[3] This old method consists in brominating *o*-acettoluide, oxidizing the brom-*o*-acettoluide with permanganate and saponifying the bromacetanthranilic acid. The method requires as many days as this new method requires hours. A comparison of the bromination of the chloral-anthra-

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[1] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1046.

[2] Alt, *Ber.*, **22**, 1645 (1889).

[3] Bogert and Hand, THIS JOURNAL, **27**, 1476 (1905).

nilic acid and of anthranilic acid shows that the chloral residue has some influence on the course of the reaction.

Bromination of Chloralanthranilic Acid. 5-Brom-2-aminobenzoic Acid Hydrobromide, $C_6H_3(COOH)Br(NH_2.HBr)$.—A saturated solution of chloralanthranilic acid (m. 152°) was made by dissolving 13.3 grams in 100 cc. glacial acetic acid by warming and then cooling nearly to the room temperature. Bromine, 8 grams, was added drop by drop with stirring. Crystals began to form before half of the bromine was added. Finally a very thick pulp was obtained, the temperature having risen to about 45°. The proportions of the materials were 1 molecule of acid and 2 atoms of bromine. The precipitate was filtered off and washed several times with benzene. The compound so obtained is snow-white and nearly pure. It gives a melting point of 238–40°, decomposing and becoming an indigo-blue liquid immediately above this temperature. The yield was equal to the weight of the chloralanthranilic acid used or 91 per cent. of the theoretical. Analysis: Calculated for $C_7H_7O_2NBr_2$, Br 53.86; found, Br 53.49, 54.16, 53.45.

The hydrobromide is broken down at once by cold water into the free amine and hydrobromic acid, which accounts for difficulties arising in recrystallizing from solvents not especially dried. It is insoluble in ether, benzene, ligroin, carbon tetrachloride and chloroform, slightly soluble when these solvents are hot. It is insoluble in cold glacial acetic acid but soluble in about 150 parts when boiling, separating out in needles. It is rather soluble in cold absolute alcohol, soluble in 6 parts when boiling, crystallizing out in needles grouped in rosettes.

5-Brom-2-aminobenzoic Acid, $C_6H_3COOHBrNH_2$.—Although the acid is set free from its hydrobromide by cold water, hot water was used in order to effect a recrystallization of the acid simultaneously. The acid was found to agree in all its properties with the acid as described by Alt and later by Bogert and Hand except in one particular. Alt gives the melting point as 211–211.5° (uncorr.) while Bogert and Hand give 219–20° (corr.). Our acid melts at 215–6° (uncorr.) or 218–9° (corr.), in practical agreement with Bogert and Hand. We have observed further that a partial decomposition takes place. As Alt has stated, an aqueous solution of the acid turns violet in the sunlight and a solution of its ammonium salt gives colored precipitates with certain other salts. Its acetyl derivative consists of splendid prisms, melting at 218–20°. Alt gives 214–5°. Analysis: calculated for $C_9H_8O_3NBr$, Br 31.01; found, Br 31.62. The position of the bromine atom was positively located by conversion of the acid into *m*-brombenzoic acid by the diazo reaction.

Bromination of Chloral-di-anthranilic Acid.—This acid is described by Niementowski[1] and by Wheeler and Dickson.[2] 2.0 Grams of chloral-di-anthranilic acid (1 mol.) were dissolved in 30 cc. glacial acetic acid and treated with 1.6 grams (2 mols.) bromine. The abundant white precipitate was worked up as in the previous case. The yield was 2.7 grams or 91.5 per cent. of the theoretical. The melting point was 238–9° with decomposition to an indigo-blue liquid. Cold water removed one molecule of hydrobromic acid. The residue was recrystallized from water, forming needles melting at 215–6° with partial decomposition. The reaction is therefore identical with the bromination of the chloral-mono-anthranilic acid.

Rapid Preparation of 5-Brom-2-aminobenzoic Acid. First Method, with the Use of Chloral.—Since it is immaterial whether the chloral-mono-anthranilic acid or the chloral-di-anthranilic acid is used in the bromination, the products of the action of chloral upon anthranilic acid need not be separated. Twenty-five grams of anthranilic acid are rubbed up in a mortar to a powder, 27.5 grams of chloral are added and the

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[1] Niementowski, *Ber.*, **35**, 3898 (1902).

[2] Wheeler and Dickson, THIS JOURNAL, **30**, 140 (1908).

mixture is rapidly triturated a few minutes. The mass partially liquefies with the development of heat and then becomes quite hard. It is at once dissolved in 350 cc. glacial acetic acid by warming and then cooled to 16°. Bromine, 29.4 grams, is added slowly enough to keep the temperature from rising above 16°, the beaker being surrounded by cold water. The precipitate is filtered off and washed with benzene. It melts at 239–40° and weighs 51 grams or 94 per cent. of the theoretical. Its conversion into the free acid and its purification were effected as follows: 5 grams of the hydrobromide were boiled up in 250 cc. water three times, filtering hot with suction into a flask standing in boiling water. The filtrates were cooled by surrounding with ice water and then filtered. Extract I, m. 215–6°, weight 1.35 gram; extract II, m. 215–6°, weight 0.95 gram; extract III, m. 208–10°, weight 0.35 gram. Insoluble residue none. By adding 3 volumes of water to the glacial acetic acid filtrate, a precipitate was obtained, melting at 185–200° and weighing 0.3 gram. Analysis of this product showed it to be a tribromaminobenzoic acid. The bromine (29.4 grams) is accounted for as follows: 2 grams lost in the original preparation, 13.7 grams lost as HBr, 10.4 grams appear in the 5-brom-2-aminobenzoic acid, 1.9 grams appear in the tribromaminobenzoic acid. The balance, 1.4 grams, disappear in the mother liquors. Recrystallization of extract I from toluene effected no rise in melting point. In some preparations the first extracts were not quite so pure and one recrystallization from toluene was necessary. At no time was bone-black necessary as in the old method. Analysis: calculated for $C_7H_6O_2NBr$, Br 37.04; found, Br 37.39.

Second Method. Direct Bromination of Anthranilic Acid. (With W. M. Oates).—Twenty-five grams anthranilic acid were dissolved in 250 cc. glacial acetic acid and cooled to 15–6°. Bromine, 29.4 grams, was added slowly enough to keep the temperature from rising. Further procedure was the same as described above. The product melted at 236–8° and weighed 51.5 grams which is 95.3 per cent. of the theoretical. Conversion and purification were carried out as already described. Five grams of the hydrobromide gave the following results: extract I, m. 212–4°, weight 1.4 grams; extract II, m. 212–4°, weight 0.8 gram; extract III, m. 203–5°, weight 0.3 gram; extract IV, m. 226–32°, weight 0.1 gram. Undissolved residue, m. 228–30°, weight 0.4 gram. The first extract was recrystallized from toluene and analyzed. Analysis: calculated for $C_7H_6O_2NBr$, Br 37.04; found, Br 37.44, 37.65. The undissolved residue, m. 228–30°, was also analyzed. Analysis: calculated for $C_7H_5O_2NBr_2$, Br 54.24; found, Br 52.18. It was therefore a dibrom derivative of anthranilic acid. The bromine, 29.4 grams, is accounted for as follows: 1.7 grams lost in the original preparation; 13.8 grams lost as HBr; 9.5 grams appear in the 5-brom-2-aminobenzoic acid; 2.8 grams appear in the dibrom anthranilic acid and the balance, 1.6 grams, are lost in the mother liquors. The acetic acid filtrate in this method of preparation did not yield any precipitate on the addition of water. A comparison of results in the two methods is as follows:

I.	II.
Mainly 5-brom-2-aminobenzoic acid.	Similar amount.
Small amount tribrom acid.	No tribrom acid.
No dibrom acid.	Small amount dibrom acid.

m-Brombenzoic Acid.—This acid was prepared in order to locate positively the bromine atom in the bromaminobenzoic acid described in this paper. It proved to be a convenient method of preparation because the product is so quickly purified, which can not be said of the product of the action of bromine on benzoic acid. 5.0 grams 5-brom-2-aminobenzoic acid were dissolved in 50 cc. absolute alcohol. After the addition of 5 grams H_2SO_4, conc., the solution was brought to boiling and 2.5 grams $NaNO_2$ dissolved in a very little water were added. The solution was filtered from the sodium sulphate and added to a large volume of water. The pinkish colored precipitate was filtered off and dried. It showed a melting point of 145–7° and weighed 3.82 grams or 82 per cent. of the theoretical. On recrystallizing from boiling water a very small amount of a dark red substance was gotten rid of and the *m*-brombenzoic acid was obtained in pure condition, m. 154°. Analysis: calculated for $C_7H_5O_2Br$, Br 39.80; found, Br 39.97.

CHAPEL HILL, N. C., February 25, 1909.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, DEPARTMENT OF ANIMAL HUSBANDRY, UNIVERSITY OF ILLINOIS.]

THE CHEMISTRY OF ANIMAL FECES.

FIRST PAPER.—A COMPARISON OF THE ANALYSIS OF FRESH AND AIR-DRIED FECES.

BY A. D. EMMET AND H. S. GRINDLEY.

Received March 2, 1909.

It has been the usual custom in agricultural chemical work to prepare feces, and feeding stuffs high in water content, for analysis by first air-drying them and then grinding the resulting residue or product until it will pass through a sieve having 1 mm. openings. It is highly desirable, however, to ascertain, if at all possible, the chemical composition of the fresh, undried sample. This procedure was found to be possible in the case of meats which contained as high as 76 per cent. of water.[1] In metabolism experiments with men, the fresh undried feces have been examined for fatty matter by Long[2] with his paper coil method. In this laboratory[3] it has been found that fresh human feces can be kept safely with thymol together with a reduced temperature for several days, then, after compositing and thoroughly mixing, the resulting fresh sample can be analyzed with a high degree of accuracy. In nutrition experiments with swine, cattle, sheep, and horses, the feces are of a very different physical composition than in the case of the carnivora, being abundant in carbohydrate materials which ferment easily, and they are also composed of coarser undigested particles, and are, therefore, apparently much more difficult to sample. However, in view of the fact that in our experiments, thus far, the feeds have been either ground or chopped to a medium fineness before feeding, it seemed plausible to undertake a comparative chemical study of the composition of the fresh and air-dried feces. The added value of the results, in determining the coefficients of digestibility of the various constituents and the nature of the metabolic changes, upon the fresh substance seemed well worth studying.

Considerable work has already been done along this line by several

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[1] Grindley and Emmett, THIS JOURNAL, 27, 658 (1905).

[2] THIS JOURNAL, 28, 704 (1906).

[3] Howe, Rutherford, and Hawk, *Proc. Am. Soc. Biol. Chem.* (Feb.), 1909.