

by a natural fermentation. Although an improved product was obtained with several different organisms the only one which was consistently better than the control was *B. lactis acidi*. The data are not extensive enough to recommend the use of inoculation on a commercial scale. Further experiments are needed.

That the organisms used for inoculation dominated the fermentation was indicated by microscopic mounts made from the brine at intervals throughout the fermentation period. A chemical analysis also showed the characteristic products normally formed by these organisms.

The presence of large numbers of yeasts may cause red kraut, and undesirable flavors.

The best kraut was obtained when approximately 2.0% of salt was used. With concentration above 3.0% the kraut was tough and too salty.

The chief products formed in the fermentation of kraut are lactic acid, acetic acid, and ethyl alcohol. Mannitol in varying amounts may also be formed, depending upon the type of organisms present. These same products occur in a natural fermentation, but the relative amounts can be influenced by inoculation.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

2-PHENYLQUINOLINE-4-CARBOXYLIC ACID-6-ARSONIC ACID.¹

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In connection with the investigations being carried on in this laboratory on arsenic compounds of possible therapeutic value, 2-phenylquinoline-4-carboxylic acid-6-arsonic acid has been prepared. It is formed by the action of pyruvic acid on benzaldehyde and arsanilic acid, and is the simplest of a large number of compounds which may be made in a similar manner. This communication is merely a preliminary notice of a rather extensive research which has been carried out in this laboratory during the past 2 years upon various quinoline arsonic acids, their reduction products and other derivatives.

When aniline³ and some of the simplest aniline derivatives are treated with pyruvic acid and an aromatic aldehyde, it is generally possible to obtain both a phenyl-cinchoninic acid derivative and a phenyl-diketo-

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² This is a description of a portion of the laboratory work submitted by J. R. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

³ *Ber.*, 41, 3884 (1908).

pyrrolidine derivative. With the arsonated anilines in alcoholic suspension or solution, the reactions seem to run chiefly to the quinoline derivatives. 2-Phenylquinoline-4-carboxylic acid-6-arsonic acid is readily soluble in alkali hydroxides and carbonates and ammonium hydroxide and these solutions give precipitates with the salts of many of the heavy metals. The fact that the substance described gives off one mole of carbon dioxide on heating, and in addition forms a trisodium salt, proves without question its constitution.

Experimental.

A mixture of 21.7 g. (1 mole) of arsanilic acid, 10.6 g. of benzaldehyde (1 mole) and 200 cc. of absolute alcohol is heated to boiling under reflux on a steam-bath. After a short while most of the arsanilic acid passes into solution and 8.8 g. of pyruvic acid (1 mole) is now added. The solution is heated to boiling for $3\frac{1}{2}$ to 4 hours, and then filtered hot to remove a slight amount of insoluble material. On cooling the filtrate, a yellow precipitate results which is filtered, washed sparingly with cold alcohol, finally with ether and then dried *in vacuo*. The crude 2-phenylquinoline-4-carboxylic acid-6-arsonic acid thus obtained is pale yellow in color and melts with complete decomposition at $180-183^{\circ}$. After one crystallization from ordinary alcohol and washing with alcohol followed by ether, the substance is pure and is then a cream colored powder which starts to darken at about 180° and melts with decomposition at $186-187^{\circ}$ (corr.).

The compound forms a neutral disodium salt and a slightly alkaline tri-sodium salt. From a solution of the disodium salt, copper sulfate precipitates a green salt; silver, lead, mercurous, mercuric, cadmium nitrates light yellow salts and cobalt and ferric nitrates reddish brown salts. In order to show that the compound is a quinoline derivative, its decomposition by heating was carried out in the following way. A definite weight of the substance was suspended in ethyl benzoate and then heated to boiling for 20 minutes. Enough carbon dioxide was evolved to correspond to one mole. Owing to the fact that a gummy material is produced during the decomposition, the reaction was not as complete as might be desired, so the analytical results showed between 5 and 10% too small an amount of carbon dioxide for the amount of substance used. Phenyl-diketopyrrolidine derivatives do not decompose in this manner.

The arsenic was determined by Ewins' method⁴ the nitrogen by the Kjeldahl method and the carbon by the Parr total carbon method.⁵

Subs., 0.5001, 0.5005 : CO₂, 563.5 cc., (28.5° , 746 mm.), 565.3 cc. (30.0° , 746 mm.)

Subs., 0.1999, 0.2023 : 14.46 cc., 14.49 cc. 0.0736 N I.

⁴ Ewins, *J. Chem. Soc.*, 109, 1356 (1916).

⁵ Parr, *THIS JOURNAL*, 26, 296 (1904).

Subs., 0.5001, 0.5034. 18.32 cc., 18.36 cc. 0.0699 *N* HCl.

Calc. $C_{16}H_{19}O_6NAs$: C, 51.47; As, 20.10; N, 3.75. Found C, 51.54, 51.20. As 19.97, 19.77; N, 3.58, 3.57.

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NOTE.

Bromo-quinaldines.—6-Bromo-quinaldine has been prepared by Barton and MacCollum¹ by the condensation of *p*-bromo-aniline and acetaldehyde, but, this method not proving satisfactory or our purposes, the following method was used.

Ten g. of *p*-bromo-aniline was mixed with 13 g. of conc. hydrochloric acid. The mixture was cooled and 6 g. of paraldehyde was added. Condensation was brought about by heating the mixture on a boiling-water bath during 3 hours. Five hundred g. of water was added, and the aldehyde resin coagulated by heating on the water-bath. The clear liquid was then poured off, made alkaline and distilled with steam.

The crude mixture thus obtained was heated with an equal bulk of acetic anhydride at 100° for 15 minutes, the excess of acetic anhydride removed by boiling with alcohol and subsequently evaporating the ester, and the solid extracted with chloroform in the cold and crystallized from light petroleum ether.

6-Bromo-quinaldine Methiodide.—A mixture of 10 g. of 6-bromo-quinaldine and 6.4 g. of methyl iodide was heated for 24 hours in a sealed tube at 79–80°. A yellow crystalline solid was obtained which, when crystallized from alcohol, gave 12 g. of greenish-yellow needles melting at 237° (decomp.).

Analysis. Subs., 0.3110: AgI, 0.1995. Calc. for $C_{11}H_{11}BrNI$: I, 34.9. Found: 34.7.

6-Bromo-quinaldine Ethiodide.—A mixture of 16.1 g. of 6-bromo-quinaldine and 11.7 g. of ethyl iodide was heated in a boiling-water bath for 36 hours. The product was purified as above. M. p. 218°.

Analysis. Subs., 0.3000: AgI, 0.1860. Calc. for $C_{12}H_{12}BrNI$: I, 33.6. Found: 33.5.

m-Bromo-aniline was condensed with paraldehyde in the same way and the crude oily product diazotized and distilled with steam to get rid of the unchanged primary amine. A yellow solid was obtained (11 g.) which was heated with 3.5 cc. of nitric acid, sp. gr. 1.42, in 20 cc. of water. Yellow crystals of bromo-quinaldine nitrate were obtained and the base precipitated from an aqueous solution with ammonia. It was recrystallized from petroleum ether (60–80°), when white leaflets melting at 77° were obtained.

Analyses. Subs., 0.1735: CO_2 , 0.3470; H_2O , 0.636. Calc. for $C_{10}H_9BrN$: C, 54.3; H, 3.7. Found: C, 53.97; H, 3.99.

Subs., 0.2393: AgBr, 0.2015. Calc. for $C_{10}H_9BrN$: Br, 35.98. Found: 35.83.

When condensations are made with paraldehyde and *m*-bromo-aniline, it is evident that two bromo-quinaldines may be obtained, the bromine atom in the *meta* position with respect to the amino group in the primary base occupying the 5-, or 7-, position in the bromo-quinaldine. Only one of these two possible isomers has been isolated. The position of the bromine atom has been left undetermined for the present.

The ethiodide was prepared in the same way as the ethiodide of 6-bromo-quinaldine, m. p. 217°. The nitrate melts at 102°. The salts of the other two common mineral acids are very soluble in water. The double salts with zinc chloride, mercuric chloride and stannic chloride have been prepared by boiling together solutions in hydrochloric acid

¹ Barton and MacCollum, *THIS JOURNAL*, 26, 704 (1904).