The alcohol precipitate of "second pressing" cider dries down to hard readily pulverized white masses. It is easily soluble in water, forming opalescent solutions very difficult to clarify. It possesses a marked acid taste.

SUMMARY.

The following points are determined.

(1) The hot water extract amounting to 40 per cent. of apple marc consists of one carbohydrate complex, a galacto-araban.

(2) The carbohydrate complexes in case of the alcohol precipitate of apple must, and in case of the alcohol precipitate of second pressing ciders, are both higher in galactan, relative to the pentosan content, than the hot water extracts of apple marc.

(3) The treatment with boiling water lessens the yield of crude fiber and cellulose, and at the same time gives a purer fiber and a purer cellulose.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 117.]

ON 5-AMINO-4-KETODIHYDROQUINAZOLINE AND 5-AMINO-2-METHYL-4-KETODIHYDROQUINAZOLINE.[1]

BY MARSTON TAYLOR BOGERT AND VICTOR JOHN CHAMBERS.

Received December 14, 1905.

THE authors have prepared 5-amino-4-ketodihydroquinazoline and 5-amino-2-methyl-4-ketodihydroquinazoline by reducing the corresponding nitro compounds with stannous chloride and hydrochloric acid. The 5-amino-4-ketodihydroquinazoline is much more easily obtained than its 2-methyl derivative, since it is soluble in hot water and can thus be readily separated from the tin, hence most of the reactions carried out were with this quinazoline. Its hydrochloride, chlorplatinate, bibrom, acetyl, benzoyl and phenyluramino derivatives, were prepared and studied, as well as its reactions with nitrous acid, chloroform and potassium hydroxide, and with benzaldehyde. The phenyluramino derivative breaks up at high temperatures into carbanilide and what appears to be the diquinazolylurea. The 5-amino-2-methyl-4-ketodihydroquinazoline was more troublesome to obtain, and only its hydrochloride and chlorplatinate were prepared.

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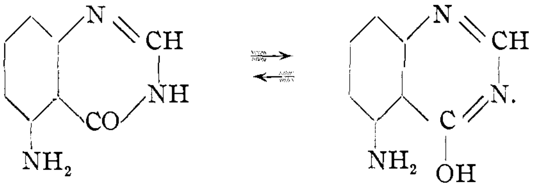
[1] Read at the General Meeting of the American Chemical Society, June 22, 1905.

In these aminoquinazolines, the amino group shows the usual aniline reactions so far as examined, while the miazine cycle exhibits its own characteristic properties. The compounds are easily soluble in solutions of the caustic alkalies, and are reprecipitated from such solutions by carbon dioxide or by mineral acids. With strong mineral acids they form salts. These salts are rather more stable than those of the corresponding unsubstituted quinazolines, but are also dissociated by boiling with much water.

EXPERIMENTAL.

5-Amino-4-ketodihydroquinazoline (*5-Amino-4-oxyquinazoline*),



—5-Nitro-4-ketodihydroquinazoline, prepared as described in a previous paper,[1] was added gradually to a hot solution of stannous chloride in concentrated hydrochloric acid, an excess (50 per cent.) of stannous chloride being used. The reduction proceeded rapidly. When all the nitro compound had been added, the solution was gently heated on the sand-bath for half an hour, and then poured into about ten volumes of water. The solution was neutralized by adding pieces of marble from time to time. It was then heated to boiling, filtered hot through a hot water funnel, and the undissolved portion repeatedly extracted with boiling water, adding these extracts to the filtrate. From this solution, on cooling, the aminoquinazoline crystallized in long, fine needles. The dimorphism noted in the case of the nitroquinazoline was not observed with this aminoquinazoline. The crystals of aminoquinazoline which separate from aqueous solution carry one molecule of water, and melt at 235–236° (corr.). They were analyzed with the following results:

Found: Water, 10.13 and 10.07; N, 23.5 and 23.6. Calculated for $C_8H_7ON_3.H_2O$: H_2O, 10.06; N, 23.4.

The compound is moderately soluble in water, alcohol, acetone or ethyl acetate, when boiling, but sparingly soluble in these

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[1] This Journal, 27, 654 (1905).

solvents when cold. It is almost insoluble in ether, chloroform, carbon tetrachloride or petroleum ether. In aqueous solutions of the caustic alkalies it dissolves freely, and is reprecipitated from such solutions by carbon dioxide. It also dissolves in concentrated hydrochloric acid with formation of the hydrochloride. Both the crystals, and their aqueous or hydrochloric acid solutions, gradually redden and darken in the light.

Hydrochloride.—The aminoquinazoline was dissolved in warm dry ethyl acetate and treated with a stream of dry hydrogen chloride. The hydrochloride precipitated as a white granular powder, which soon darkened in the light. In a small amount of warm water it dissolves without decomposition, and on cooling needles separate. It is dissociated, however, by warming with much water.

Chlorplatinate.—The hydrochloride was dissolved in a little warm dilute hydrochloric acid, and a solution of chlorplatinic acid added. On cooling, the chlorplatinate separated in coarse yellow needles, carrying two molecules of water.

Calculated for $(C_8H_7ON_3.HCl)_2PtCl_4.2H_2O$: Water, 4.9. Found: Water, 5.1. Calculated for $(C_8H_7ON_3.HCl)_2PtCl_4$: Pt, 26.6. Found: Pt, 26.4.

Bibrom-5-amino-4-ketodihydroquinazoline (*Bibrom-5-amino-4-oxyquinazoline*).—A few grams of the aminoquinazoline were dissolved in warm water and treated with bromine water until no further precipitation occurred. The flocculent precipitate was filtered out, washed, dissolved in dilute potassium hydroxide solution, and reprecipitated by carbon dioxide. A white amorphous powder resulted, which was soluble in glacial acetic acid or in nitrobenzene, but insoluble in all other solvents tried. It did not crystallize well from either glacial acetic acid or from nitrobenzene. In the light, it gradually darkened, while the brominated acetaminoquinazoline, referred to below, was unaffected.

Calculated for $C_8H_5ON_3Br_2$: Br, 50.1. Found: Br, 50.2.

The position of the bromine atoms in the molecule was not determined, but in view of the usual orienting effect of the amino group, it is likely that they are at positions 6 and 8.

5-*Acetamino-4-ketodihydroquinazoline* (5-*Acetamino-4-oxyquinazoline*).—The aminoquinazoline was heated for a short time with acetic anhydride and the product recrystallized from dilute alcohol containing a little acetic acid. Fine colorless needles were thus obtained, which melted at 285–286° (corr.) with darkening. The substance is soluble in warm acetone or alcohol, more readily in presence of a little acetic acid, but is very difficultly soluble in ether, chloroform, carbon tetrachloride or benzene.

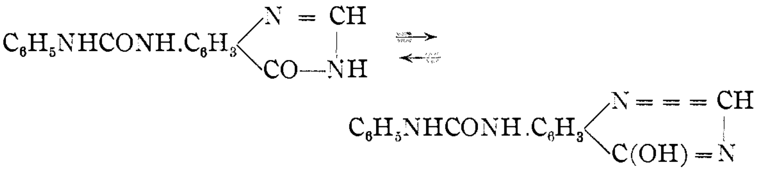
Calculated for $C_{10}H_9O_2N_3$: N, 20.7. Found: N, 20.9 and 20.9.

By the action of bromine water upon a dilute acetic acid solution of the acetaminoquinazoline a bromine derivative immediately resulted, but it has not as yet been further investigated or analyzed. It will be taken up later.

5-*Benzoylamino*-4-*ketodihydroquinazoline* (5-*Benzoylamino*-4-*oxyquinazoline*).—This substance, prepared from the aminoquinazoline and benzoyl chloride, was purified by solution in cold dilute alkali and reprecipitation with carbon dioxide. When recrystallized from alcohol, it appeared in glistening white needles or scales, which felted together when filtered. They melted at 263–264° (corr.), and showed approximately the same solubilities as the acetyl derivative.

Calculated for $C_{15}H_{12}O_2N_3$: N, 15.8. Found: N, 15.8.

5-*Phenyluramino*-4-*ketodihydroquinazoline* (5-*Phenyluramino*-4-*oxyquinazoline*).



$$C_6H_5NHCONH.C_6H_3\left\langle\begin{matrix}N = CH\\ \vert\\ CO—NH\end{matrix}\right. \rightleftarrows C_6H_5NHCONH.C_6H_3\left\langle\begin{matrix}N === CH\\ \vert\\ C(OH) = N\end{matrix}\right.$$

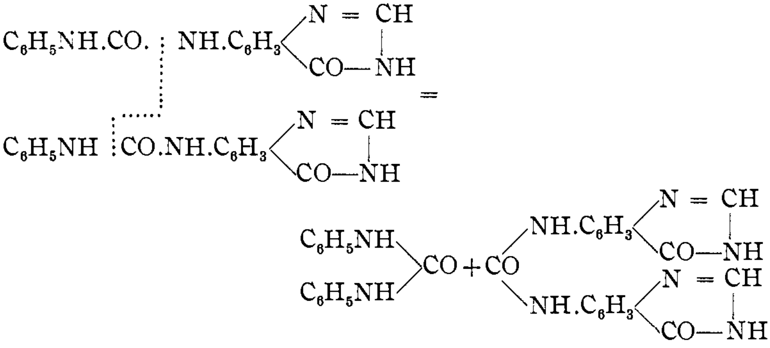
—The aminoquinazoline was heated with excess of phenyl isocyanate for an hour in an oil-bath at about 170°. The crystalline quinazoline was thereby changed to a pale brown chalky mass. This was washed with dry ether, to remove excess of isocyanate, and purified by several recrystallizations from alcohol. Fine white needles were thus obtained: easily soluble in warm alcohol; slightly soluble in warm benzene; insoluble in chloroform, ether or petroleum ether.

Calculated for $C_{15}H_{12}O_2N_4$: N, 20.0. Found: N, 19.7.

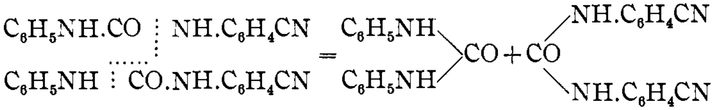
The behavior of this substance on heating was rather interesting. When the temperature was raised rapidly to 250–260° it melted with effervescence, then resolidified, and then could not be remelted at 340°, before which point was reached, however, considerable darkening occurred. The effervescence of the substance at 260° was due to the splitting off of carbanilide, which boils at this temperature (260°). The carbanilide collected in the upper part of the melting-point tube as a crystalline sublimate.

To ascertain the nature of the substance remaining after the separation of carbanilide, a larger portion of the phenyluraminoquinazoline was heated at 270–280° until all carbanilide was removed. The residue was boiled with water and then with alcohol. The material left undissolved by this treatment could not be crystallized, as it was not appreciably soluble in any of the ordinary solvents. It did dissolve in warm dilute potassium hydroxide solution, but when reprecipitated from such a solution by dilute acids or by carbon dioxide separated in a jelly-like condition. It was decomposed by boiling with concentrated caustic alkalies. Judging from previous experience with such compounds, this insoluble substance is probably the symmetrical diquinazolylurea,

the reaction by which it is formed being as follows:



Such a reaction corresponds entirely to the formation of carbanilide and di-*m*-cyancarbanilide by heating *m*-cyancarbanilide:[1]



$$\begin{matrix} C_6H_5NH.CO \vdots NH.C_6H_4CN \\ C_6H_5NH \vdots CO.NH.C_6H_4CN \end{matrix} = \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix} \rangle CO + CO \langle \begin{matrix} NH.C_6H_4CN \\ NH.C_6H_4CN \end{matrix}$$

In further support of the above deduction, the aminoquinazo-

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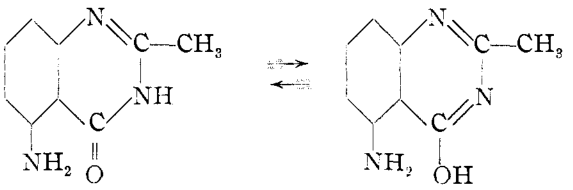
[1] Bogert and Beans: This Journal, **26**, 466 (1904).

line was dissolved in pyridine and carefully treated with a 20 per cent. solution of phosgene in toluene. After the first vigorous reaction was over, the mixture was heated for a few minutes, then poured into water, dilute acetic acid added to acid reaction, and the undissolved material filtered out. This insoluble portion showed exactly the same behavior as the product obtained by heating the phenyluraminoquinazoline above 260°. On account of the great insolubility of the substance, it has not been possible to get it in a condition that we could regard as sufficiently pure for analysis.

Other Reactions of 5-Amino-4-ketodihydroquinazoline.—Besides the above, the aminoquinazoline gave other typical aniline reactions. With chloroform and potassium hydroxide solution, an isonitrile odor was developed. With benzaldehyde, an insoluble condensation product was obtained, presumably the benzylidene derivative. With nitrous acid, a diazonium body was produced, and also a nitroso derivative. The presence of the former was demonstrated by coupling the diazotized quinazoline with β-naphthol, when a reddish-brown dyestuff resulted, while the nitroso group was detected by the Liebermann reaction. These reactions indicate the presence of both the primary amino group (in the benzene cycle) and the secondary imino group (in the miazine cycle).

5-Amino-2-methyl-4-ketodihydroquinazoline (5-Amino-2-methyl-4-oxyquinazoline).



—5-Nitro-2-methyl-4-ketodihydroquinazoline was reduced with stannous chloride and hydrochloric acid in the manner already described for the 5-amino-4-ketodihydroquinazoline, but the separation of the reduction product was much more troublesome, on account of its insolubility in hot water. At the conclusion of the reduction, the mass was made alkaline with sodium carbonate, boiled for a short time, allowed to cool, and filtered. The material thus filtered out was dried in the air, extracted repeatedly with boiling alcohol or boiling ethyl acetate, the extracts combined, concentrated, and the concentrated solution allowed to cool. Pale, reddish-brown needles of the aminoquinazoline separated, in poor yield.

Calculated for $C_9H_9ON_3$: N, 24.0. Found: N, 24.0.

This aminoquinazoline melts with decomposition at 295–310°. It slowly darkens in the light. It is moderately soluble in alcohol, acetone or ethyl acetate, when boiling, less so when cold, and is practically insoluble in cold water, benzene or ether. In dilute caustic alkalies, it dissolves readily, and is reprecipitated from such solutions by carbon dioxide or by dilute acids. It is also soluble in strong hydrochloric acid.

Hydrochloride.—Dry hydrogen chloride, passed into an ethyl acetate solution of the aminoquinazoline, caused the separation of the hydrochloride as a nearly white crystalline precipitate. This salt is dissociated when boiled with plenty of water.

Chlorplatinate.—The hydrochloride was dissolved in a small amount of dilute hydrochloric acid, and treated with a solution of chlorplatinic acid. The chlorplatinate separated at once as a crystalline precipitate.

Calculated for $(C_9H_9ON_3.HCl)_2PtCl_4$: Pt, 25.66. Found: Pt, 25.56.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY.
December, 1905.

[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

NITRIFICATION AND AMMONIFICATION OF SOME FERTILIZERS.

BY G. S. FRAPS.

Received October 31, 1905.

IN 1901, Withers and Fraps found[1] that in a certain soil, the amount of nitrates produced from organic materials was in the order of their availability as measured by vegetation tests and solubility in potassium permanganate. A later study by the same authors[2] showed that this relation does not hold for all soils, but the rank of the fertilizer, if measured by nitrates formed under similar conditions, varied with different soils. Placing

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[1] This Journal, 23, 318 (1901).

[2] Report for the N. C. Experiment Station for 1902–'03, p. 31.