

l-Ethyl α -amino-*n*-caproate, $C_8H_{17}O_2N$, b. p. 86-87° at 12 mm., $[\alpha]_D = -11.65^\circ$ in a one-dcm. tube

l-Ethyl α -amino-*n*-caproate hydrochloride, $C_8H_{18}O_2NCl$, $[\alpha]_D = -7.25^\circ$.

α -Bromo-*n*-caproyl chloride $C_6H_{10}OClBr$, b. p. 102-105° at 30 mm.

α -Bromo-*n*-caproyl-glycine, $C_8H_{14}O_3NBr$, m. p. 114-115°.

α -Amino-*n*-caproyl-glycine, $C_8H_{16}O_3N_2$, m. p. 226°.

Ethyl ester of α -oxy-*n*-caproyl-glycine, $C_{10}H_{19}O_4N$, m. p. 90-91°.

Ethyl α -amino-caprylate, $C_{10}H_{21}O_2N$, b. p. 110° at 10 mm.

Ethyl α -amino-caprylate hydrochloride, $C_{10}H_{22}O_2NCl$, m. p. 76-77°.

URBANA, ILL.

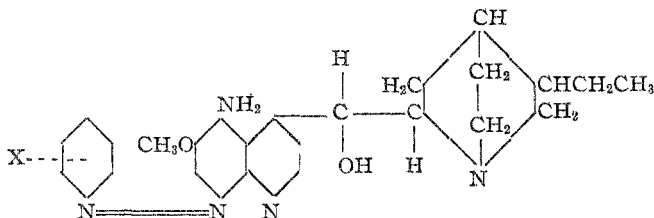
[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

SYNTHESES IN THE CINCHONA SERIES. VI. AMINOAZO AND HYDROXYAZO DYES DERIVED FROM CERTAIN 5-AMINO CINCHONA ALKALOIDS AND THEIR QUINOLINE ANALOGS.

By WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

Received June 29, 1920.

In our study of 5-amino-dihydroquinine¹ it was found to couple smoothly in dil. acetic acid solution with diazo compounds to form aminoazo dyes in which we assume the azo group to enter Position 8 in the quinoline portion of the molecule



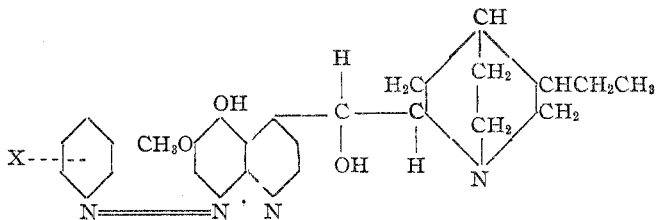
This assumption seems justified since, on the one hand, Position 8 is the only one which satisfies the usual laws of substitution for a 5-amino-6-methoxyquinoline (analogous to α -amino- β -methoxynaphthalene), and finally, since 5-aminoquinoline was also found to yield aminoazo dyes which could be reduced to 5,8-diamino-quinoline.

Of the dyes from 5-amino-dihydroquinine the phenylazo-, *p*-sulfo-phenylazo-, and the *p*-methoxy- and *p*-ethoxy-phenylazo-compounds were prepared and studied. 5-Amino-dihydroquinidine and 5-amino-ethylidihydrocupreine also readily yielded phenylazo compounds. These substances are usually red, well defined, crystalline compounds, forming orange-red solutions in neutral solvents and deep purple solutions in

¹ THIS JOURNAL, 42, 1485 (1920).

dilute mineral acids, except in the case of the *p*-methoxy- and ethoxy-dyes, the salts of which are a pronounced violet-blue.

If the solution of one of the amino dyes in mineral acid is boiled, a very rapid color change from a purplish-red to a brown-red is to be noted, due to the replacement of the amino group by hydroxyl, with elimination of ammonia which is readily detected on rendering alkaline. By this reaction it has been possible to prepare from the 5-amino-8-azo-cinchona dyes the corresponding 5-hydroxy compounds



The lability of the amino group in the 5-amino compounds is surprisingly great, since boiling on the water-bath in a mixture of equal parts of 1 : 1 hydrochloric acid and alcohol suffices in all instances to cause complete cleavage in from 5 to 15 minutes, the alcohol being added to increase the solubility of the dye salts. Although the replacement of an amino group by hydroxyl in acid solution has been previously noted and used for preparative purposes in a number of instances, as in the preparation of α -naphthol from α -naphthylamine¹ and the dihydroxybenzenes from the phenylenediamines,² as a rule high temperatures have been found essential. The ease of replacement of amino by hydroxyl in our compounds more closely resembles that occurring in salts of *sym.*-triaminobenzene and its derivatives, permitting their ready and complete conversion into phloroglucinol and its derivatives at the temperature of the water bath.³

It was of interest to determine whether the lability of the amino group in our compounds was due to the influence of the cinchona molecule as a whole, or whether analogous dyes obtained from 5-aminoquinoline would behave in the same way. As a matter of fact, phenylazo-5-aminoquinoline yielded phenylazo-5-hydroxyquinoline, but it required a definitely longer period of heating to bring about complete cleavage. On the other hand, the dyes from 5-amino-6-methoxyquinoline, which afforded a closer parallel to the 5-amino-dihydroquinine dyes, were found to be as easily converted into the hydroxy dyes as the alkaloidal derivatives themselves. It would seem, therefore, that the methoxy or ethoxy group in Position 6 contributes markedly to the lability of the amino groups in these compounds.

¹ Ger. Pat. 102,358.

² Ber., 30, 2569 (1897).

³ Monatsh., 18, 755 (1897); 19, 223, 236, 249 (1898); 21, 39 (1900).

The hydroxyazo dyes are also substances with excellent properties and crystallize very readily. In spite of the hydroxyl group they do not dissolve in dil. alkali, but after making an alcoholic solution alkaline it may be diluted freely without precipitating the dye, subsequent addition of ammonium chloride being, however, sufficient to cause precipitation.

On reduction the new cinchona and quinoline dyes yield amino compounds in which interesting relationships have been observed in the replacement of the amino group by hydroxyl. These studies are still in progress, and we shall describe them in a subsequent communication.

I.

5-Amino-8-phenylazo-dihydroquinine.—One g. of aniline dissolved in 30 cc. of normal hydrochloric acid was diazotized with 10 cc. of normal sodium nitrite, with chilling. A solution of 3.4 g. of 5-amino-dihydroquinine¹ in 20 cc. of normal acetic acid was diluted to 200 cc., treated with 20 cc. of saturated sodium acetate solution, chilled to about 10°, and slowly treated, with turbinating, with the diazo solution. The original orange-red solution rapidly changed to a deep red, and after 15 minutes the dye was precipitated as deep red flocks by the addition of an excess of ammonia, filtered off, and washed with water. On taking up the moist dye in hot alcohol it dissolved partially but almost immediately crystallized. Recrystallized from 95% alcohol, the dye gradually separated as glistening, red needles containing approximately one molecule of water of crystallization when air-dried. The yield was 2.2 g. The air-dry substance melts at 155–7° with preliminary darkening and sintering. It dissolves sparingly in the cold in methyl and ethyl alcohols, benzene, and chloroform, but readily on warming, forming red solutions. It is sparingly soluble in acetone and ether. Solutions in dilute acids are reddish-purple, and in conc. sulfuric acid an intense purple. After dissolving the dye in 10% hydrochloric acid the hydrochloride deposits on rubbing as deep brown, microscopic needles.

Subs. (air-dry), 0.4760; loss, 0.0227 *in vacuo* at 80° over H₂SO₄.

Calc. for C₂₆H₃₁O₂N₅·H₂O: H₂O, 3.89. Found: 4.77.

Subs., anhydrous, 0.1109; 15.0 cc. N (24.0°, 772 mm.).

Calc. for C₂₆H₃₁O₂N₅: N, 15.72. Found: 15.79.

5-Hydroxy-8-phenylazo-dihydroquinine.—5 g. of the preceding amino-azo dye were treated with a hot mixture of 25 cc. of alcohol and 25 cc. of 1 : 1 hydrochloric acid and the resulting deep purple solution heated on the water-bath. The mixture rapidly changed to a dark brown and set to a jelly which slowly changed to long, brown needles of the hydrochloride of the hydroxyazo dye. After 15 minutes the mass was diluted with water, chilled, and treated with an excess of ammonia, yielding a purple mass of the free base. After filtering and washing with water,

¹ *Loc. cit.*

the dye was taken up in hot alcohol, quickly separating as brownish yellow, microscopic leaflets in a yield of 4.2 g. On dissolving in hot water with the aid of dil. sulfuric acid, filtering, adding an equal volume of alcohol, and then treating hot with a slight excess of ammonia, the dye quickly crystallized as lustrous, orange-brown platelets which, when rapidly heated to 140° and then slowly, gradually sinter together and effervesce at $145-8^{\circ}$. When air-dry it contains one molecule of water of crystallization which requires heating at 100° *in vacuo* for its complete removal. The dye is readily soluble in hot benzene and chloroform, less readily in hot methyl and ethyl alcohols, and very sparingly in hot acetone, forming orange-red solutions, and is almost insoluble in ether. It dissolves in dil. sulfuric acid with an orange-red color, and in the conc. acid with a cherry-red shade, appearing purple in thin layers. In dil. hydrochloric acid it forms an insoluble, gelatinous salt.

Subs. (air-dry), 0.2940: loss, 0.0122 *in vacuo* at 100° over H_2SO_4 .

Calc. for $\text{C}_{26}\text{H}_{30}\text{O}_3\text{N}_4\cdot\text{H}_2\text{O}$: H_2O , 3.88. Found: 4.15.

Subs., anhydrous, 0.1296: 14.2 cc. N (25.5° , 754 mm.).

Calc. for $\text{C}_{26}\text{H}_{30}\text{O}_3\text{N}_4$: N, 12.55. Found: 12.43.

5-Amino-8-(*p*-sulfophenylazo)-dihydroquinine.—A solution of diazotized sulfanilic acid was rapidly added to 3.4 g. of amino-dihydroquinine under the same conditions as previously given. A dark red-brown, amorphous precipitate of the dye formed at once, and was filtered off and washed with water. On treating with hot alcohol it dissolved partially, but almost immediately changed to orange, microscopic needles. The yield was 4 g. after washing with acetone. On recrystallizing from 50% alcohol it formed delicate, minute, orange needles containing about 0.5 molecule of water of crystallization. In working with large quantities of the dye it was found more convenient to dissolve it in the minimum amount of dil. alkali, add an equal volume of alcohol, warm, and reacidify with an equivalent amount of acetic acid. The air-dry substance darkens above 180° , decomposes at about 245° , and is practically insoluble in the usual neutral solvents. In dil. mineral acids it gives a deep cherry-red solution, appearing purple in thin layers, and when not too dilute sulfuric or hydrochloric acid is used the difficultly soluble salt separates as a dark-colored, crystalline powder. In conc. sulfuric acid the solution is bright red, appearing purple in thin layers. The solution in 50% acetic acid is quickly reduced by stannous chloride to diamino-dihydroquinine, which will be described in a later communication.

Subs. (air-dry), 0.5041: loss, 0.0114 *in vacuo* at 80° over H_2SO_4 .

Calc. for $\text{C}_{26}\text{H}_{31}\text{O}_3\text{N}_5\text{S}\cdot 0.5\text{H}_2\text{O}$: H_2O , 1.68. Found: 2.26.

Subs. (anhydrous), 0.1188: 13.4 cc. N (23.5° , 772 mm.).

Calc. for $\text{C}_{26}\text{H}_{31}\text{O}_3\text{N}_5\text{S}$: N, 13.32. Found: 13.18.

5-Hydroxy-8-(*p*-sulfophenylazo)-dihydroquinine.—Two g. of the amino-azo dye were treated with a hot mixture of 20 cc. of alcohol and 20

cc. of 10% hydrochloric acid and boiled on the water-bath. The solution almost immediately set to a jelly which soon began to change to the crystalline salt of the new dye. After 5-10 minutes the mixture was made alkaline with dil. sodium hydroxide, a strong odor of ammonia being at once noticeable. The deep purple solution was treated with an excess of acetic acid, yielding 1.8 g. of glistening, salmon-colored needles on diluting and rubbing. Recrystallized from 50% alcohol it separated as delicate, lustrous, scarlet needles containing approximately one molecule of water of crystallization. The dye decomposes at 275° with preliminary darkening, and is fairly readily soluble in hot 50% alcohol and methyl alcohol, sparingly in hot water and hot alcohol, and practically insoluble in the usual neutral solvents. With dil. hydrochloric and sulfuric acid it forms brown-orange salts and dissolves in conc. sulfuric acid with a deep scarlet color, appearing violet in thin layers and changing to orange on dilution with water. In alkali the color is purplish red.

Subs. (air-dry), 0.4260; loss, 0.0164 *in vacuo* at 100° over H₂SO₄.

Calc. for C₂₆H₃₀O₆N₄S.H₂O: H₂O, 3.31. Found: 3.85.

Subs. (anhydrous), 0.1358: 12.8 cc. N (24.5°, 750 mm.).

Calc. for C₂₆H₃₀O₆N₄S: N, 10.63. Found: 10.67.

5-Amino-8-(*p*-methoxyphenylazo)-dihydroquinine. — Although diazotized *p*-anisidine failed to yield a dye in dil. acetic acid as in previous cases, the following conditions were successfully employed. 1.23 g. of *p*-anisidine in 15 cc. of 2 *N* hydrochloric acid were diazotized at 0° with 2 cc. of 5 *N* sodium nitrite. 3.4 g. of amino-dihydroquinine in 10 cc. of *N* acetic acid were then added and the mixture immediately treated with sufficient saturated sodium acetate solution to bind the free hydrochloric acid. After 2 hours the mixture, from which an almost black tar had separated, was diluted with enough alcohol to form a homogeneous solution, warmed, and made alkaline with ammonia. The dye gradually separated on rubbing, and after filtering and washing with cold alcohol the yield was 2.8 g. Recrystallized twice from 95% alcohol it forms red, microscopic needles and platelets which melt slowly at 150-3°. It dissolves readily with an orange-red color in cold chloroform, on boiling in methyl or ethyl alcohol, acetone, or benzene, and but sparingly in ether. In strong mineral acid it gives a deep violet-blue color which changes to brownish-red on dilution, a phenomenon apparently due to hydrolysis of the polyacid salts originally formed. In conc. sulfuric acid the color is deep red, appearing violet in thin layers. As in the case of the other amino cinchona dyes, the deep violet-blue color in acid changes to a purplish-red on boiling, with simultaneous cleavage of ammonia.

Subs., 0.1440: 18.6 cc. N (25.0°, 765 mm.).

Calc. for C₂₇H₃₃O₃N₅: N, 14.72. Found: 14.90.

5-Amino-8-(*p*-ethoxyphenylazo)-dihydroquinine.—Under the conditions used with *p*-anisidine 1.75 g. of *p*-phenetidine hydrochloride also yielded a dark brown tar. After decanting the supernatant liquid the dye was dissolved in alcohol and treated with ammonia. On rubbing, the base crystallized and was filtered off and washed with 85% alcohol. The yield was 2.6 g. Recrystallized first from a relatively large volume of 95% alcohol, then by dissolving in warm chloroform and adding a little ligroin, it was gradually deposited as long, thin, narrow, orange platelets, often grouped in rosets. It apparently contains solvent of crystallization which is slowly lost on exposure to the air or on drying *in vacuo* at 100°. The dye decomposes at 202–3° with preliminary darkening, and dissolves readily in warm chloroform, much less easily in boiling methyl and ethyl alcohols, and quite sparingly in hot benzene. It is very difficultly soluble in acetone and ether and insoluble in water and ligroin. The solution in dil. mineral acids is blue-violet, changing on dilution to a dark wine-red, owing to hydrolysis of the polyacid salts. Conc. sulfuric acid gives a deep purple color. In boiling dilute acids it also yields an hydroxyazo dye, which was not studied. For analysis the substance was heated *in vacuo* at 80° over sulfuric acid.

Subs., 0.1224: 15.8 cc. N (22.0°, 746 mm.).

Calc. for $C_{28}H_{38}O_3N_6$: N, 14.30. Found: 14.67.

5-Amino-8-phenylazo-dihydroquinidine.—This substance was prepared exactly as was the isomeric dihydroquinine dye. The amorphous product, taken up in hot, dry acetone, crystallized on cooling and rubbing, the mother liquor yielding additional amounts on dilution with water to incipient turbidity. The total yield was 2.7 g. Recrystallized from 85% alcohol the base separates as rosets of orange-red leaflets when deposited rapidly, or as a dark red crust when allowed to crystallize slowly. The air-dry compound contains 1.5 molecules of water of crystallization and melts and intumescs at 135° with preliminary sintering. It turns dark brown on dehydrating, and then melts to a tar at about 140–5°, intumescing at about 155°. It is readily soluble in absolute alcohol, chloroform, warm benzene, and warm acetone, forming deep red solutions. The dye dissolves in 10% hydrochloric acid with a deep purplish-red color, the hydrochloride separating on rubbing as brown, hair-like needles with a greenish luster. The solution in conc. sulfuric acid is an intense violet.

Subs. (air-dry), 0.4887: loss, 0.0276 *in vacuo* at 80° over H_2SO_4 .

Calc. for $C_{28}H_{31}O_2N_5 \cdot 1.5H_2O$: H_2O , 5.72. Found: 5.65.

Subs. (anhydrous), 0.1232: 16.6 cc. N (23.5°, 771 mm.).

Calc. for $C_{28}H_{31}O_2N_5$: N, 15.73. Found: 15.74.

5-Amino-8-phenylazo-ethylidihydrocupreine.—Treated as in the case of amino-dihydroquinine, 3.55 g. of amino-optochin¹ yielded 3 g. of the

¹ THIS JOURNAL, 42, 1486 (1920).

aminoazo dye. The base separates from 95% alcohol as red, glistening needles containing one molecule of water of crystallization. It starts to sinter at 145° and shrinks together and melts at 150–5°. It is sparingly soluble in cold methyl and ethyl alcohols, benzene, and chloroform, but readily on warming, forming deep reddish-orange solutions. It is difficultly soluble in acetone and very sparingly in ether. The solutions in dilute acids are deep reddish-purple in color and purple in conc. sulfuric acid.

Subs. (air-dry), 0.4098: loss, 0.0155 *in vacuo* at 100° over H₂SO₄.

Calc. for C₂₇H₃₈O₂N₅·H₂O: H₂O, 3.77. Found: 3.78.

Subs. (anhydrous), 0.1333: 17.25 cc. N (21.5°, 768 mm.).

Calc. for C₂₇H₃₈O₂N₅: N, 15.23. Found: 15.17.

5-Hydroxy-8-phenylazo-ethylidihydrocupreine.—The deep purple solution in hot aqueous-alcoholic hydrochloric acid rapidly changed to deep red. On dilution with alcohol, adding ammonia, and finally water until turbid, the crystalline base was readily obtained. Recrystallized twice from 85% alcohol the dye forms lustrous, red needles containing 3.5 molecules of water of crystallization. It starts to sinter at 85°, shrinks together and melts at 90.5°, and is soluble in alcohol, acetone, ether, and hot benzene, forming red solutions. It dissolves in 10% sulfuric acid with a deep brown-red color, and in the conc. acid with a deep purple color. The anhydrous dye softens above 100°, sinters to a tar at 110–20°, and melts completely, with decomposition, at about 200°.

Subs. (air-dry), 0.6035: loss, 0.0715 *in vacuo* at 80° over H₂SO₄.

Calc. for C₂₇H₃₂O₃N₄·3.5H₂O: H₂O, 12.03. Found: 11.84.

Subs. (anhydrous), 0.1181: 12.6 cc. N (26.5°, 761 mm.).

Calc. for C₂₇H₃₂O₃N₄: N, 12.17. Found: 12.18.

II.

5-Amino-8-phenylazoquinoline.—5-Aminoquinoline was coupled with diazotized aniline and the base isolated as in the case of the cinchona derivatives. The dye separates from 50% alcohol as arborescent masses of garnet-colored leaflets which melt at 209–11°. It is soluble in alcohol, acetone, chloroform, hot benzene, and less readily in ether. Its solution in dilute acid is deep red, appearing purple in thin layers and changing to orange on dilution. In conc. sulfuric acid the color is deep red.

Subs., 0.1224: 23.8 cc. N (22.5°, 767 mm.).

Calc. for C₁₅H₁₂N₄: N, 22.57. Found: 22.68.

On reduction with ammonium sulfide the analogous *p*-sulfophenyl-5-aminoquinoline, which was similarly prepared, yields 5,8-diaminoquinoline, melting at 161–3° and corresponding in its properties with those described by Claus and Kramer,¹ who give the uncorrected melting point of 156°.

5-Hydroxy-8-phenylazoquinoline.—The aminoazo dye was boiled

¹ Claus and Kramer, *Ber.*, 18, 1247 (1885).

with 100 parts of 10% hydrochloric acid, a portion of the amino hydrochloride separating at once. The color of the deep purplish-red solution slowly changed, with deposition of the brown hydrochloride of the hydroxyazo dye. About one hour was required for the complete disappearance of the purple color. The collected salt was suspended in 50% alcohol and the base liberated with ammonia. After several recrystallizations from alcohol the dye forms slightly purplish-red, lustrous needles, which melt at 164–5° with preliminary sintering. It is easily soluble in chloroform, fairly readily in hot alcohol, benzene and acetone, and but sparingly in ether. It gives a scarlet solution in conc. sulfuric acid, appearing purple in thin layers and changing to orange on dilution.

Subs., 0.1191: 17.6 cc. N (25.0°, 758 mm.).

Calc. for $C_{15}H_{11}ON_3$: N, 16.86. Found: 16.88.

5-Amino-6-methoxyquinoline.—The 5-nitro-6-methoxyquinoline¹ used for this preparation was easily obtained in excellent yield by nitrating 6-methoxyquinoline with fuming nitric acid at 0°.

28 g. of the nitro compound were suspended in 200 cc. of 1 : 1 hydrochloric acid, treated with 125 g. of stannous chloride, and heated on the water-bath for one hour. A clear, deep red solution was soon obtained, and the free base was finally precipitated with excess alkali as a yellow oil which crystallized on cooling. Extraction of the mother liquor with ether yielded an additional quantity, the total amounting to 90% of that theoretically possible. Recrystallized first from benzene and then from ligroin, it forms yellow, arborescent platelets and needles which melt at 154–6° (corr.) with slight preliminary sintering. It has a faint odor, resembling that of anise, and dissolves readily in alcohol, acetone, chloroform, and hot benzene, but less easily in ether. Its solution in dilute acid is reddish-orange.

Subs., 0.1393: 19.2 cc. N (22.5°, 765 mm.).

Calc. for $C_{10}H_{10}ON_2$: N, 16.08. Found: 16.02.

5-Amino-6-methoxy-8-phenylazoquinoline.—Obtained in the usual way, the crude dye was precipitated by ammonia as red, amorphous flocks which soon crystallized on dissolving in a small volume of acetone. It separates slowly and incompletely from 85% alcohol as thin, deep red rods which exhibit a green reflex when dry, and melt at 163–4°. It dissolves, especially on warming, in the usual solvents, forming deep orange-red solutions. In dilute acids the color is purplish-red, and in conc. sulfuric acid a deep purple.

Subs., 0.1062: 18.6 cc. N (25.0°, 758 mm.).

Calc. for $C_{16}H_{14}ON_4$: N, 20.12. Found: 20.02.

5-Hydroxy-6-methoxy-8-phenylazoquinoline.—On treating the amino-azo dye with 30 parts of a mixture of equal amounts of alcohol and 1 : 1

¹ Decker and Engler, *Ber.*, **42**, 1739 (1909).

hydrochloric acid a deep purple mass of the salt separated and gradually dissolved when heated on the water-bath, the color of the solution changing to red, with subsequent deposition of the brown salt of the hydroxy dye. This was converted into the base as usual, and this recrystallized from alcohol, forming broad, scarlet, often curved needles which melt at $181-3^{\circ}$. It is readily soluble in chloroform and in the other usual solvents on warming. It is but sparingly soluble in cold dilute mineral acids, and on boiling forms deep red-orange solutions. The color in conc. sulfuric acid is wine-red, appearing purple in thin layers.

Subs., 0.1133: 15.0 cc. N (24.5° , 759 mm.).

Calc. for $C_{16}H_{13}O_2N_3$: N, 15.04. Found: 15.16.

Summary.

It is shown that 5-amino-dihydroquinine couples readily with diazotized aromatic amines to form crystalline azo dyes in which the amino group is remarkably labile, boiling for a few minutes with dil. mineral acid being sufficient to replace the amino group by the hydroxyl group, with elimination of ammonia. The resulting hydroxyazo dyes are also easily crystallizable substances. Similar results were obtained using 5-amino-dihydroquinidine and 5-amino-ethylidihydrocupreine (amino-optochin) as couplers. Since it was of interest to determine whether the observed phenomena were a function of the quinoline portion of the cinchona structure, parallel experiments were run with 5-aminoquinoline and 5-amino-6-methoxyquinoline. Both of these bases coupled as did the amino alkaloids, and the amino group of the resulting dyes was also readily eliminated and replaced by hydroxyl, the lability being greater in the case of the methoxy derivatives.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE OKLAHOMA AGRICULTURAL EXPERIMENT STATION.]

THE CARBOHYDRATES OF THE PECAN.

By W. G. FRIEDEMANN.

Received July 7, 1920.

The pecan (*Carya olivaeformis*) is the most widely distributed and economic important nut-bearing tree in Oklahoma. Two references were found in the literature on the chemical composition of the pecan kernel. Deiler and Fraps¹ determined the characteristics of the pecan oil obtained from the kernel. A study of the proteins of pecans has been made by Dowell and Menaul.² This investigation was undertaken to determine the carbohydrates of the edible portion of the pecan.

¹ A. C. Deiler and G. S. Fraps, *Am. Chem. J.*, **43**, 90 (1910).

² C. T. Dowell and P. L. Menaul. Unpublished report. Oklahoma Agr. Expt. Sta. Also E. H. Nollan, *J. Biol. Chem.*, **21**, 614(1915).