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°. 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 $C_{16}H_{18}O_2N_3$: 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-ethyldihydrocupreine (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 Fraps[1] 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 Unpublished report.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).

Experimental.

A proximate analysis of the pecan kernels gave results as tabulated below:

	%
Moisture	3.75
Ash	1.70
Crude protein	12.27
Crude fiber	1.71[a]
Nitrogen-free extract	10.81
Ether extract	69.76

[a] Protein-free. The crude fiber uncorrected was 1.90%. Protein in crude fiber was 10.19%.

The carbohydrates were determined in pecan flour obtained from the pecan kernels by completely removing the pecan oil by extraction with ether.

Sugars, pentoses, pentosans (araban), methylpentosans[1] and crude fiber were determined according to the A. O. A. C. methods.

No precipitate formed when the 5% sodium hydroxide extract of pecan flour was diluted with an equal volume of alcohol; therefore xylan[2] was absent.

Araban was considered present as other pentosans were not identified; a gum separated when the combined filtrates from the crude fiber determination were slightly acidified and evaporated to a volume of several cc. at room temperature.

Mannans[3] were not identified as no precipitate formed when the 3% sodium hydroxide extract of the sugar-free flour was heated on the water-bath with Fehling's solution.

Amyloid was identified by the blue coloration with iodine when added to the hot-water extract obtained according to Winterstein's[4] method. The amyloid was calculated from the mucic acid obtained by the A. O. A. C. method for galactan.

Starch was absent, as no blue color was noticed when an iodine solution was added to the flour. Also no more reducing sugars were found than were accountable from the pentosans when the sugar-free flour was subjected to the diastase method[5] for the determination of starch.

Tannins (a constituent of the nitrogen-free extract) were shown to be present by the bitter taste and the characteristic tests of the water extract of pecan flour. The difference between the combustible water-soluble solids and total sugars was considered as tannins. Only the thin, hard brown outer coating of the kernel was colored blue by neutral ferric chlo-

[1] C. A. Browne, "Handbook of Sugar Analysis," 1912, p. 456.

[2] *Ibid.*, p. 553.

[3] *Ibid.*, p. 594.

[4] Winterstein, *Ber.*, **25**, 1273 (1892).

[5] E. Abderhalden, "Biochemisches Handlexikon," Vol. II, 1911, p. 126.

ride solution when a cross-section was examined under the microscope, indicating tannins.

The hemicellulose, calculated by difference, was considered a dextran, as no other sugar than dextrose was formed when it was subjected to the action of dilute alkalies and acids. This dextran was also proven to be present by subtracting the carbohydrates identified from the total carbohydrates found in the combined filtrates from the crude fiber determination.

The percentage composition is as follows:

	Total carbohydrates.	Pecan kernel.[a]
Sucrose	9.03	1.18
Invert sugars	21.90	2.88
Pentoses	.....	....
Araban	14.82	1.95
Xylan	.....	....
Methylpentosans	1.68	0.22
Cellulose (crude fiber)	14.29	1.76
Mannans	.....	....
Amyloid	4.54	0.59
Starch	.....	....
Tannins	2.57[c]	0.33[c]
Hemicellulose (dextran), etc.[b]	31.17	4.09
	100.00	13.00

[a] Moisture-free basis.

[b] By difference in the nitrogen-free extract plus crude fiber.

[c] Same result by Proctor's modification of Lowenthal's method.

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THE CONDENSATION OF FORMALDEHYDE WITH ORTHO-NITROPHENOL.[1]

BY JACOB B. FISHMAN.

Received July 9, 1920.

During the last 2 years the attention of pharmacologists has been directed to benzyl alcohol as a local anesthetic. The pharmacological action of this alcohol was first investigated by Macht[2] in 1918. He found it to be a powerful local anesthetic of very low toxicity as compared with cocaine and its substitutes. While it has been found to be active on mucous membranes as well as in subcutaneous injection, nevertheless the compound possesses several objectionable properties which prevent its wide application. Not only does it undergo slow oxidation

[1] Constructed from a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, June 1920 (T. B. Johnson).

[2] Macht, *J. Pharmacol.*, **13**, 263 (1918); **14**, 323 (1919).