

[CONTRIBUTION FROM THE LOUISIANA SUGAR EXPERIMENT STATION.]
THE HYDROLYTIC PRODUCTS OF SUGAR-CANE FIBER.

BY C. A. BROWNE, JR.

Received August 2, 1904.

OWING to the greater demands upon the chemist of problems dealing solely with the workings of the sugar-house, the study of the insoluble constituents of the sugar-cane has been, in the past, more or less neglected. It is only since the utilization of bagasse for paper-making has begun to attract attention that the chemical nature of sugar-cane fiber has assumed more than theoretical interest.

Cross and Bevan, in their work on cellulose (page 220), state that the fiber aggregates of the sugar-cane "are largely made up of pectocelluloses, with a greater or less proportion of lignocelluloses. But the constitution of these non-cellulose constituents are, as yet, quite unknown; and we have, therefore, none but the general basis of classification."

More specific information concerning the constituents of cane-fiber is given by Prinsen Geerligs.¹ This authority, who has made a special study of the sugar-cane in Java, states that the fiber of mature cane contains about 50 per cent. of cellulose and 30 per cent. of cane-gum, or *xylan*. The latter constituent was obtained from the fiber in an impure state by extraction with cold 5 per cent. caustic soda, and precipitation with acetic acid and alcohol. The gum possessed a specific rotation of -80° and yielded, on hydrolysis with acid, 79 per cent. of sugar. Crystals of the sugar thus obtained gave a specific rotation of $+20^\circ$; xylose was, therefore, probably present and also "probably another sugar with a higher rotatory power, perhaps arabinose or *d*-glucose proceeding from the hydrolysis of cellulose."

During the past year investigations have been conducted at the Louisiana Sugar Experiment Station upon the composition and chemical properties of cane-fiber, especially since the commercial utilization of this fiber, in a number of ways, is now giving promise of success. In these investigations the hydrolytic action of hydrochloric, sulphuric and nitric acids, and of caustic soda have each been studied, but as the full results of this work would form too compendious a contribution, the present article will be limited

¹ "Observations on Bagasse," *Sugar Cane*, 30, 91.

to a consideration of those products obtained by digesting cane-fiber with dilute caustic soda.

MICROCHEMICAL REACTION OF CANE-FIBER.

The tissues of the sugar-cane resemble very closely those of maize, sorghum, and many other monocotyledonous plants and consist of the pith (the parenchyma or fundamental tissue), the fibrovascular bundles, and the shells or rind. The reactions of thin sections of a cane stalk with various reagents are given in Table I. The sections were prepared with a microtome and then washed in cold water to remove sugars.

TABLE I.

	Pith.	Bundles.	Rind.
Chloride of zinc and iodine.....	No color	No color	No color
Phloroglucin and hydrochloric acid	Pink	Red	Red
Mäule's permanganate test.....	Pink	Red	Red
Aniline sulphate.....	Pale yellow	Yellow	Yellow
Ferric ferricyanide	Light blue	Dark blue	Dark blue
Chlorine water	Yellow	Orange	Orange.

The absence of any reaction with chloride of zinc and iodine indicates a complete combination of the cane cellulose with other substances. After boiling the sections with dilute caustic soda and washing, the blue coloration, characteristic of cellulose, was obtained without difficulty.

The reaction with phloroglucin and hydrochloric acid, formerly supposed to be indicative of lignin and later regarded as a test for pentosans, has been shown by Czapek¹ to be produced by an aldehyde body, *hadromal*, found occurring in nearly all lignified tissue.

Mäule's² permanganate test is regarded by its author as indicative of lignin groups alone. Since the details of this valuable test are not generally known, a short description may be allowable. The sections for examination are placed for five minutes in a 1 per cent. solution of potassium permanganate; they are then washed in water and decolorized with hydrochloric acid. After washing to remove acid, the sections are placed in ammonia water, when the lignified tissues will be colored a deep red.

The reactions of the cane tissues with aniline sulphate, ferric

¹ *Ztschr. physiol. Chem.*, **27**, 141 (1899).

² Mäule: "Das Verhalten verholzter Membranen gegen Kaliumpermanganat," *Beiträge zur wissenschaftl. Botanik.*, Band IV.

ferricyanide and chlorine water point, as does the previous test, to a higher degree of lignification in the fibrovascular bundles and rind, than in the pith, although it must be noted that the very thin character of the cell walls in the fundamental tissue tends to diminish greatly the intensity of the color reactions in this region.

SEPARATION AND COMPOSITION OF THE TISSUES OF SUGAR-CANE.

A mechanical separation of the different tissues of the cane was accomplished only with considerable difficulty, the isolation of the bundles from the pith being especially arduous. The following analyses were performed upon a mature stalk of the Louisiana purple variety of cane :

	Pith. Per cent.	Bundles. Per cent.	Rind. Per cent.
Whole cane (3 analyses)	2.39	1.81	5.51
Dry fiber	24.66	18.60	56.74

A proximate analysis of the above tissues is given below. The results were calculated to a moisture-free basis.

TABLE II.

	Pith. Per cent.	Bundles. Per cent.	Rind. Per cent.
Ash	1.68	3.58	1.64
Fat and wax	0.41	0.72	0.98
Protein	1.94	2.00	2.19
Cellulose (method of Cross and Bevan)	49.00	50.00	51.09
Pentosans (furfuroids)	32.04	28.67	26.93
Lignin (by difference)	14.93	15.03	17.17

With the exception of ash the results for the different tissues show a certain regularity, the bundles standing intermediary between the pith and rind. The analytical data confirm, in a general way, what was indicated by the microchemical tests, *viz.*, that we have in the pith a minimum and in the rind a maximum degree of lignification.

DIGESTION OF CANE-FIBER WITH CAUSTIC SODA.

Preparation of Material.—Several kilos of finely cut bagasse were washed with successive portions of cold water until all traces of sugars were removed. The mass was then allowed to soak over night in cold 2 per cent. hydrochloric acid, to dissolve as much mineral matter as possible. After pressing, the fiber was washed free from acid and dried.

Method of Digestion.—Two hundred grams of the purified fiber were digested eight hours with 3 liters of 5 per cent. caustic soda. The reaction was carried out in a large flask immersed in a boiling water-bath. After terminating the reaction, the contents of the flask were cooled and the dark brown alkaline liquid filtered through a large Büchner funnel. The residual pulp was washed several times with small quantities of cold water, and the combined filtrate and washings set aside in a tall cylinder for several days to allow suspended impurities to settle. The pulp was re-washed with hot water until free from alkali, and then with strong alcohol. After drying, an impure cellulose of light straw color was obtained, which in weight amounted to 80 grams, or 40 per cent. of the original bagasse. The soda-liquor and dried pulp were each separately examined.

EXAMINATION OF SODA-LIQUOR FROM CANE-FIBER.

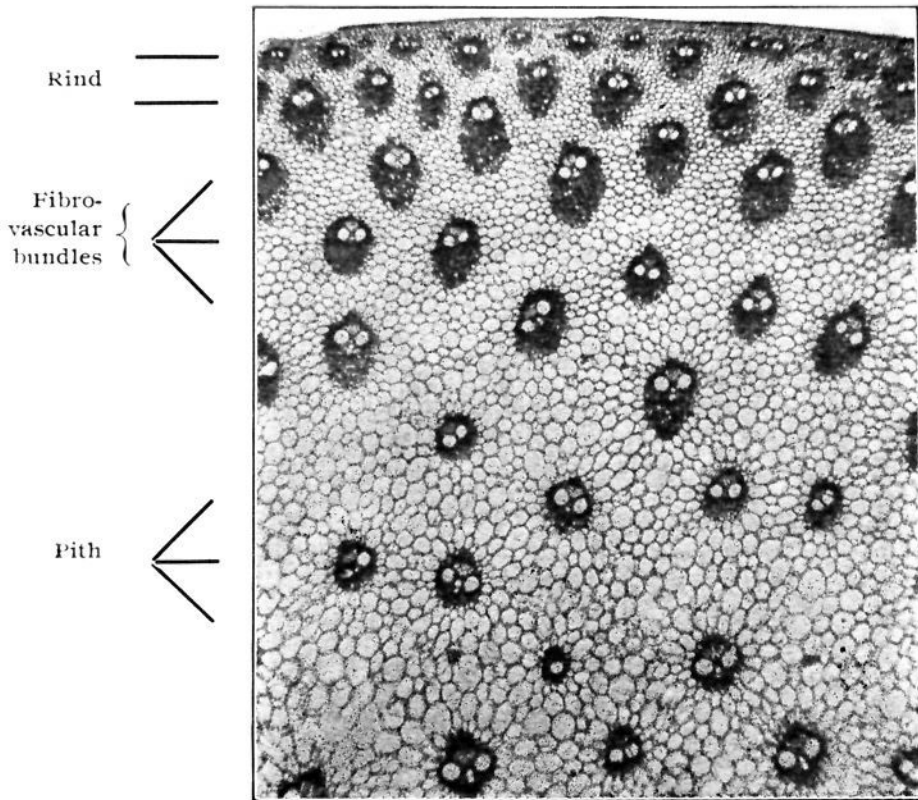
For the precipitation of the extractive matter removed by caustic soda from cane-fiber, several methods were tested, among them the use of acids, of a mixture of acids and alcohol, and the use of alcohol alone. The latter was finally adopted as the first precipitating agent, since it effected a complete separation of the hemicelluloses without precipitating any of the lignin. With methods which involve the use of acids it was found that the pentosans and lignin were precipitated together and a separation of these two groups of constituents was not secured.

I. PRECIPITATION OF CANE-GUM (PENTOSANS) FROM SODA-LIQUOR.

The original method of Tollens¹ and Wheeler for preparing wood gum was followed with a few slight modifications. The clear soda-liquor was filtered through parchmented paper from all sediment and evaporated to one-third of the original volume. Double the quantity of pure 95 per cent. alcohol was then added when a flocculent yellowish colored coagulum was thrown out. After settling, this was filtered off on parchmented paper through a Büchner funnel and the precipitate washed with alcohol until the washings were colorless. The alcoholic filtrate was preserved for subsequent examination.

The precipitate upon the filter was transferred to a large porcelain mortar and thoroughly ground up with an excess of alcoholic

¹ *Ann. Chem.* (Liebig), **254**, 504.



Transverse section of sugar-cane, highly magnified.
Showing different tissues.

hydrochloric acid to break up all alkaline compounds of the gums. The residue was again filtered off and thoroughly washed, first with 80 per cent. alcohol till free from acid, then with 95 per cent. alcohol, and finally with a little ether. The product thus obtained was dried for several weeks over concentrated sulphuric acid, after which it was ground, when it was obtained in the form of a very light powder, almost white in color. Weight of product, 50 grams, or 25 per cent. of the original fiber.

Properties and Composition of Cane-gum.—The cane-gum, as above prepared, was difficultly soluble in hot water, to which it gave a milky opalescent appearance. In dilute solution of caustic alkali it easily dissolved to a clear brown solution, from which it was reprecipitated by adding acids. One-half gram of the gum, dissolved to 200 cc. in a 0.2 per cent. solution of sodium hydroxide, gave a reading of -0.6° Ventzke in the 100 mm. tube. The specific rotation of the gum would then be

$$[\alpha]_D = \frac{-0.6 \times 0.3468 \times 200}{0.5 \times 1} = -83.2.$$

Dry distillation of the gum in a closed tube produced dense vapors of furfural. Large quantities of furfural were also obtained on distilling with hydrochloric acid. One-half gram of gum gave, by the method of Kröber and Tollens, 0.4280 gram of furfural-phloroglucide = 44.88 per cent. furfural = 76.43 per cent. pentosans. The gum contained 12 per cent. ash (mostly sodium chloride). Cellulosic gummy products, derived from cane-cellulose, were also present in small amounts, as was shown by microchemical tests with zinc chloride and iodine.

Hydrolysis of Cane-gum with Hydrochloric Acid.—The process was carried out according to Counciler's¹ method for wood-gum. Twenty grams of cane-gum were heated with 500 cc. of 4 per cent. hydrochloric acid on a boiling water-bath for ten hours. The reaction was carried out in a flask provided with a condensing tube. At the end of the hydrolysis the hot solution was treated with an excess of lead carbonate and allowed to stand in the cold over night. The liquid was then filtered from the deposit of lead chloride and carbonate, and evaporated to about 80 cc. The syrup thus obtained was shaken up with 500 cc. of strong alcohol

¹ Counciler : "Verzuckerung von Holzgummi mittelst Salzsäure." *Chem. Ztg.*, 16, [2], 1719 (1892).

and 50 cc. of ether and the precipitate of gummy matter (reversion products) allowed to subside. The solution was then filtered and evaporated to about 50 cc. A light straw-colored syrup was thus obtained, which was set aside for crystallization in a cool place over sulphuric acid.

Separation and Identification of Xylose from Cane-gum.—Crystals began to appear in the syrup at the end of a few hours. These, when examined under a micropolarizer, were seen to be optically active. After two days the entire syrup had set to a crystalline mass; this was stirred up with strong alcohol and filtered off on a suction plate. After washing with alcohol and ether a residue of nearly white crystals were obtained, which, on drying, weighed 5.342 grams = 26.71 per cent. of the original gum. The product was recrystallized from hot alcohol, using bone-black, when it was obtained in a pure white condition.

A solution of the crystals in water reduced Fehling's solution strongly. Heating with hydrochloric acid gave off strong odors of furfural; warming with phloroglucin and hydrochloric acid produced a brilliant red coloration. These reactions indicate a pentose sugar. To determine the specific rotation, 0.8648 gram of the carefully dried sugar was dissolved in water to 25 cc. and polarized in a 200 mm. tube, using a Schmidt and Haensch triple-shadow saccharimeter. Strong multirotation was observed. The following series of observations was made:

Time after solution.	Polariscope reading.	Specific rotation,
Minutes.	* Ventzke.	$[\alpha]_D^{65}$.
10	+14.8	+74.2
20	11.0	55.1
30	8.6	43.1
40	7.1	35.6
50	6.3	31.6
60	5.5	27.6
70	5.0	25.1
80	4.7	23.6
90	4.5	22.6
Hours.		
2	4.1	20.6
3	4.0	20.0
12	3.7	18.5

The constant specific rotation of +18.5 agrees with that of *l*-xylose. The calculated value for *l*-xylose for the above concentration, according to Tollens' formula $[\alpha]_D = 18.095 +$

0.06986 *p*, is 18.33. The initial specific rotation of *l*-xylose, as calculated from the data in the above table, would be about +100, which agrees with the figure of Lippmann.¹

As additional identifications of the above sugar, an osazone was formed with phenylhydrazine, which melted at 157°-158° C. and which polarized in a 1 per cent. alcoholic solution -0.44° Ventzke. These properties agree with those of *l*-xylose-phenyl- α -azone. By oxidizing a solution of the sugar with bromine in presence of cadmium carbonate, characteristic crystals of the double xylonate and bromide of cadmium, $C_5H_9O_6CdBr + H_2O$, were obtained.²

Separation and Identification of Arabinose from Cane-gum.—The mother-liquor obtained after separating the xylose was purified with alcohol and ether, and set aside for a second crystallization, but the crop of new crystals was so small that the presence of remaining quantities of xylose was disregarded and examination was made for arabinose. For the separation of this and other sugars in mixtures, use has been made of the recently studied substituted hydrazines, such as benzyl-phenyl-hydrazine, diphenyl-hydrazine, methyl-phenyl-hydrazine, etc., reagents of growing importance in the analysis of sugars. In the present instance the first-named hydrazine was employed.

The syrup was diluted with twice its volume of strong alcohol and to this was added a solution of 10 grams benzyl-phenyl-hydrazine in 20 grams of 95 per cent. alcohol. After standing a few hours in the cold, needle-shaped crystals began to form and on stirring, the solution rapidly thickened with the formation of a dense crystalline deposit. This was filtered off and washed on a suction plate with 20 cc. of 80 per cent. alcohol. A nearly white product resulted, which was further purified by recrystallizing from boiling alcohol, using animal black. 1.6 grams of a snow-white compound were obtained, which melted sharply at 169°-170°. The melting-point of *l*-arabinose-benzyl-phenyl-hydrazone is 170°.

For the separation of sugars from their hydrazones the practice of decomposing the latter with concentrated hydrochloric acid has, at present, given place almost entirely to the method of digesting an alcoholic solution of the hydrazone with formaldehyde

¹ Lippmann's "Die Chemie der Zuckerarten," 3 Auflage, p. 128.

² "Bertrand's Reaction," *Bull. Soc. Chim.*, 3, [5], 557.

or benzaldehyde. The writer has employed both of the above aldehydes with equal success, but has found formaldehyde preferable in most cases, since the process is more easily controlled.

1.2 grams of the hydrazone, obtained from the cane-gum, were dissolved in a small flask in 15 cc. of boiling alcohol and the solution treated with 3 cc. of formaldehyde (40 per cent. solution). The flask was closed with a condensing tube and the contents kept in gentle ebullition for an hour. After cooling, a yellowish colored oil (formal-hydrazone) separated and no crystallization of undecomposed hydrazone occurring, the process of decomposition was judged complete. After filtering from the oily deposit, the clear filtrate was shaken out several times with ether and the aqueous solution filtered and evaporated to 5 cc.; the syrup was set aside in a cool place over sulphuric acid and in a few hours solidified to a crystalline mass. The crystals were ground up with 90 per cent. alcohol and washed by decantation, first with strong alcohol and then with ether. 0.35 gram of a pure white sugar was obtained.

To determine the specific rotation 0.3392 gram of the carefully dried sugar was dissolved to 10 cc. and polarized in a 100 mm. tube. Strong multirotation was noted. The following series of readings was obtained:

Time after solution. Minutes.	Polariscope reading. ° Ventzke.	Specific rotation, $[\alpha]_D^{20}$.
10	16.0	+163.5
15	15.0	157.3
20	14.0	143.1
40	11.5	117.5
Hours.		
2	10.4	106.3
4	10.2	104.2
20	10.2	104.2

The constant specific rotation of +104.2 agrees with that of *l*-arabinose. The values given by Landolt¹ range from +103.9 to +105.4. The initial specific rotation of arabinose, as calculated from the data above, would be about +190, which agrees with the figure of Lippmann.²

The results of the experiments show that both xylose and arabinose are formed by the hydrolysis of cane-gum. The mother substances of these sugars, xylan and araban, make up, as was

¹ Landolt's "Das optische Drehungsvermögen," 2 Auflage, p. 512.

² Lippmann's "Die Chemie der Zuckerarten," 3 Auflage, p. 62.

shown, nearly 80 per cent. of the cane-gum, in the probable ratio of 4 to 6 parts xylan to 1 of araban.

A method has been devised by Salkowski¹ for the separation of xylan from other carbohydrates, based upon its precipitation from alkaline solution with Fehling's reagent. The gelatinous xylan copper compound is strained off, washed with a little water, and then rubbed up with dilute hydrochloric acid. Alcohol is then added and the gum washed and dried in the usual way. In case much araban is present the process of purification is repeated.

The method of Salkowski was applied to a quantity of the gum obtained from sugar-cane fiber. The yield of xylan after two precipitations with Fehling's solution was only 36 per cent. of the original gum, showing that the process of purification is attended with great loss. The final product was nearly white and gave, on analysis, the following results:

Specific rotation $[\alpha]_D = -88.8$.

Ash = 5.16 per cent.

Xylan ($C_5H_8O_4$) = 80.15. (Furfural = 51.72 per cent.)

Undetermined, 14.69.

The above gum was hydrolyzed with dilute hydrochloric acid, and an examination of the sugars formed failed to detect the presence of arabinose. We may conclude, therefore, that all araban was eliminated in the process of purification. According to Salkowski, xylan, as above prepared, exists as a hydrate $(C_5H_8O_4)_2 + H_2O$; recalculating the xylan in the above table to this formula would give 85.6 per cent. There still remains, however, nearly 10 per cent. of undetermined matter, consisting probably of a hexane carbohydrate, $(C_6H_{10}O_5)_n$, formed by the action of the alkali upon the cane-cellulose (cellulose gum). Oxidation of the gum with nitric acid gave large amounts of oxalic acid, but no mucic acid could be detected; galactan groups were, therefore, absent. It should be noted, however, that in the fiber from immature cane, galactan has been found in small amounts (0.72 per cent.).

II. PRECIPITATION OF LIGNIN FROM SODA-LIQUOR.

The alkaline filtrate from the cane-gum was evaporated until all alcohol was expelled and then acidified in a large flask with

¹ Salkowski: *Ztschr. phys. Chem.*, 34, 162; 35, 240.

dilute sulphuric acid. A dark brown precipitate was thrown down which, on heating, collected together as a sticky, gummy mass. After cooling, the clear liquid above the deposit was filtered off and preserved for subsequent examination. The gummy deposit, which had hardened to a solid cake, was readily detached from the walls of the flask. Any adherent particles were dissolved in dilute caustic soda, reprecipitated in a small beaker with sulphuric acid and combined with the main portion. The product thus obtained, when warmed in the moist condition, softened into a gummy plastic mass, but when cold hardened into a brittle resinous body, which was easily reduced to a powder. After washing with cold water to remove all traces of acid, the product was dried, first over sulphuric acid and then at 90° . Weight of material, 21.56 grams, or 10.78 per cent. of the cane-fiber.

Properties of Lignin Precipitate.—The product obtained, as above described, formed a brown-colored powder, insoluble in water and alcohol, but easily soluble in alkaline solutions, from which it is reprecipitated by acids, but *not* by alcohol. Heating with hydrochloric acid gave not the slightest trace of furfural, showing the complete absence of pentosans. Dry distillation in a closed tube produced large quantities of tarry products and oily acid compounds of a phenol nature.

Chlorination Product of the Lignin Precipitate.—By subjecting jute and other fibers to the action of free chlorine Cross¹ and Bevan have isolated a well defined chlorination product, lignone chloride, to which they have given the formula $C_{10}H_{15}Cl_4O_9$. A product very similar to the above was prepared from the lignin residue obtained from cane-fiber.

Five grams of the lignin precipitate were dissolved in dilute sodium hydroxide and the solution saturated with chlorine gas. The solution gradually changed in color from a dark brown to a deep yellow and was finally rendered turbid through the precipitation of yellowish colored flakes. The contents of the beaker were then heated to boiling and hot alcohol added with constant stirring until complete solution was effected. The acid solution was then filtered into a large beaker of water, when a flocculent lemon-colored precipitate was thrown out. After standing several hours the clear liquid was decanted and the precipitate filtered

¹ Cross and Bevan's "Cellulose," page 135.

upon a hardened paper through a Büchner funnel. The precipitate was washed thoroughly with cold water to remove all acid, when it was removed from the filter and dried.

The chlorination product, as above prepared, formed a yellowish powder, insoluble in water, but easily soluble in hot alcohol, acetone and glacial acetic acid; chloroform and carbon disulphide exerted no solvent action. Repeated attempts were made to crystallize the body, but without success. A solution of the compound in alcohol is not readily reprecipitated by pouring into water unless a certain amount of free acid is present.

A determination of chlorine in the compound gave 27.98 per cent. Cross and Bevan obtained for the lignone chloride from jute 26.83 per cent. The two compounds from their similarity in composition and reaction are undoubtedly one and the same.

III. ACETIC ACID FROM SODA-LIQUOR.

The acid filtrate from the lignin precipitate was made up to a liter, and 50 cc. of the solution (10 grams fiber) were subjected to distillation in a current of steam. 87.1 cc. of N/10 barium hydroxide were required to neutralize the distillate. The neutralized solution was evaporated and the barium salt obtained in crystalline form. The product was dried and analysis showed it to consist entirely of barium acetate. Per cent. of barium found = 53.64. Theoretical for barium acetate, 53.79 per cent.

The amount of acetic acid found in the soda-liquor would equal 5.23 per cent. of the original fiber.

Examination of Soda Cellulose from Cane-fiber.—The dry cellulose obtained by digesting cane-fiber with caustic soda amounted to only 42 per cent. of the original fiber. This low yield of cellulose, compared with a determination of cellulose by the chlorination method, is to be explained by the solvent effect of the soda, particularly upon the cellulose of the pith. The following figures show the relative resistance of the different tissues of the cane to various chemical treatments.

	Pith. Per cent.	Bundles. Per cent.	Rind. Per cent.
Cellulose by chlorination (Cross and Bevan)....	49.00	50.00	51.09
“ “ Weende method (treatment with 1.25 per cent. H ₂ SO ₄ and 1.25 per cent. NaOH)	42.86	48.64	54.76

The results show a large amount of cellulose dissolved from the

pith by the Weende method—a circumstance due largely to the very spongy and cellular character of the pith, which renders it more easily attacked than the rest of the fiber. The pith cellulose, after the removal of other cellular groups, appears, moreover, to exist in an extremely hydrated, almost colloidal, form, which is an additional explanation of its greater susceptibility to chemical treatment. These facts have an important bearing upon the utilization of cane-fiber for paper-making, since a chemical treatment necessary for the proper re-solution of the shells would result in a large loss of pith. To prevent this loss a process¹ has been patented consisting in a preliminary separation of the pith from sugar-cane, corn-stalks, etc., before digesting the shells. The pith is not fibrous and has no felting properties, yet paper made from it possesses the quality and strength of parchment; this is to be explained by the intense cementation which the hydrated cellulose undergoes during the process of dehydration.

Reactions of Soda Cellulose.—The cellulose prepared from cane-fiber by the soda process was by no means pure. Microchemical tests by Mäule's method showed lignin to be present and pentosans were also indicated by heating the fiber with hydrochloric acid and testing the filtered solution with phloroglucinol. A distillation with hydrochloric acid gave 5.07 per cent. furfural, a considerable portion of which, however, must have resulted from the action of the acid upon oxycellulose.²

Hydrolysis of Soda Cellulose.—Twenty grams of the finely divided cellulose were treated in the cold with 50 cc. of 90 per cent. sulphuric acid for twenty-four hours. The dark-colored mixture was then poured into 500 cc. of water and heated for five hours on a steam-bath in a flask provided with a condensing tube. The contents of the flask were then neutralized with an excess of calcium carbonate, filtered, and the solution evaporated to about 80 cc.; the liquid was then shaken up with an excess of alcohol and ether to precipitate gummy matters; after standing a short time the clear solution was filtered off and evaporated to 50 cc. A bright straw-colored syrup was obtained, which was set aside in a cool place over sulphuric acid to crystallize.

¹ U. S. Patent 731,290, by Dr. Viggo Drewsen.

² Cross and Bevan's "Cellulose," page 82.

Separation and Polarization of d-Glucose from Cane Cellulose.—After standing a few days the syrup began to crystallize and at the end of a week had set to a thick mass of crystals. These were stirred up with alcohol and filtered off on a suction plate. A nearly white product was obtained which, after recrystallization from alcohol, using bone-black, was obtained perfectly pure. After washing with ether, the sugar was dried over sulphuric acid and then at 60° C.; the temperature was finally gradually raised to 90°. In this manner the hydrates of the sugar were broken up without the troublesome melting. 0.2658 gram of the sugar was dissolved to 10 cc. and polarized in a 100 mm. tube. Strong multirotation was observed. The following series of readings was obtained:

Time after solution. Minutes.	Polariscope reading. ° Ventzke.	Specific rotation. $[\alpha]_D^{20}$.
10	+7.5	+97.9
20	6.9	90.0
30	6.1	79.6
60	4.2	54.8
Hours.		
2	4.1	53.5
20	4.05	52.8

The constant specific rotation of *d*-glucose for a 3 per cent. solution, according to the formula of Tollens, $[\alpha]_D^{20} = +52.50 + 0.018796p + 0.00051683p^2$, is +52.6.

To determine whether or not mannose or other sugars beside glucose were present among the hydrolytic products of the cane cellulose, the filtrate from the glucose was treated in the cold with a solution of phenyl hydrazine acetate. No insoluble hydrazones were formed, such as is characteristic of mannose. An examination of the hydrolytic products of the original cane-fiber also failed to indicate other sugars than glucose and the pentoses.

Purification of the Soda Cellulose by Chlorination.—By treatment with chlorine, according to the process of Cross and Bevan, the soda cellulose underwent a loss of 7.7 per cent. in weight and was obtained perfectly white. Microchemical tests failed to indicate the presence of either lignin or pentosans. A distillation with hydrochloric acid gave 4.52 per cent. furfural, which was probably derived entirely from oxycellulose.

CONCLUSION.

Owing to unavoidable mechanical and chemical losses, the results of the foregoing work have more of a qualitative than a quantitative value; an approximation may be made, however, as to the relative yield of the different hydrolytic products. The following results are calculated to 100 parts of pure cane-fiber (protein, ash, fat, etc., excluded):

	Per cent.
Cellulose (including oxycellulose)	55
Xylan	20
Araban	4
Lignin	15
Acetic acid	6

It will be seen that the term pecto-cellulose, which has been applied to sugar-cane fiber, has no chemical value. The term pectose, introduced long ago by Fremy, has been made to cover a large group of unknown cellular substances; now that the composition of the latter is in many cases cleared up, the pecto-celluloses, as a group classification, require a much greater restriction.

The fiber of the sugar-cane resembles very closely in composition the pithy stalks of maize,¹ both being allied to the cereal straws. A distinguishing characteristic of this group is a cellular complex low in cellulose and high in pentosans. This will be made more evident if we compare the sugar-cane with other types.

	Sugar-cane. Per cent.	Oak wood. Per cent.	Hemlock wood. Per cent.
Cellulose	50	55	65
Pentosans (furfuroids)	28	20	7
	—	—	—
Lignin, etc., by difference...	78	75	72
	22	25	28

The sum of cellulose and pentosans in each case foots up approximately the same, the ratio between the two being complementary. Such a ratio will also be noted in Table II, between the cellulose and pentosans of the different tissues of the cane. These observations are in complete harmony with the theory, that the pentosans may be derived physiologically through modifications of cellulose. Closely related to this formation of pentosans

¹ See work of Tollens and Browne: "Ueber die Bestandtheile des Mais-Marks," *Ber. d. chem. Ges.*, 35, 1457.

is the formation of the acetic acid group. Cross¹ and Bevan call attention to this fact and point out that the formation of pentosans and acetic acid "increases, *pari passu*, with age, which is in accordance with the view of a common origin." The mechanism of this transformation is not yet fully explained; it seems, however, to be primarily a process of dehydration.

The various substances into which woody fiber may be resolved by hydrolysis have led many to believe that we are dealing with more or less of a mechanical mixture—a substratum of cellulose overlaid with "incrusting substances." This view, however, is no longer tenable. The cellulose, pentosans, lignin and acetic acid obtained from cane-fiber are all hydration products, which, in the parent substances, are intimately combined. While, therefore, a study of the groups split off by hydrolysis is our chiefest aid in investigating the problems of constitution, the mistake must not be committed of regarding the products obtained by chemical treatment as absolutely identical with fiber constituents.

A study of the progressive changes, which the fiber of sugar-cane undergoes during its period of growth, is at present being conducted, and it is hoped that the results of the work will throw additional light upon the theoretical and practical questions involved.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 83.]

OBSERVATIONS ON THE METALLIC ACIDS.²

BY ROY D. HALL.

Received July 26, 1904.

THE results presented here constitute a very brief chapter in a much larger investigation which has been in progress for some time and which will be published in full in due course. The observations, while preliminary in character, possess distinct value in various lines which the larger research has taken and along which it has been and will continue to be carried in the future.

The starting-out material for the columbic and tantalic oxides was columbite from Haddam, Conn., and from South Dakota.

The Haddam mineral was very iridescent, lamellar and brittle.

¹ Cross and Bevan's "Cellulose," page 192.

² From the author's thesis for the Ph.D. degree.