

XIX.—*Note on the Action of Acids on Cellulose.*

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IN a previous communication (Fenton and Gostling, Trans., 1901, 79, 361), it has been shown that all forms of cellulose, when heated to about 80° with a saturated solution of hydrochloric or hydrobromic acid in chloroform or carbon tetrachloride, yield  $\omega$ -chlorobromo-methylfurfural. It was also shown (Proc., 1901, 17, 166) that dextrose, which could be extracted with water after separation of the methylfurfural derivative, was formed at the same time. These results conclusively proved the presence of a ketose as well as an aldose nucleus in cellulose.

In every case, about 40 per cent. of a black residue which retained the fibrous structure of the original cellulose was also left after the action of the acids.

In the hope of throwing further light on the constitution of cellulose, the nature of this residue was investigated, and in order to ascertain whether it had a constant composition it was necessary to prepare the residue free from any of the original cellulose by repeated treatment with hydrochloric acid until no more of the furfural derivative was formed.

Five grams of pure cotton wool were introduced into a strong glass bottle with a well-ground stopper and covered with about 300 c.c. of carbon tetrachloride, which was then saturated with dry hydro-

chloric acid gas at  $0^{\circ}$ . The stopper was firmly fixed by means of an iron clamp and the mixture heated nearly to boiling in a water-bath for 4 hours; on cooling, the carbon tetrachloride solution was drained off, the residue washed well with ether and with hot water, and then dried in a steam oven. This treatment was repeated until the carbon tetrachloride solution contained no methylfurfural. The black residue so obtained was insoluble in all organic solvents and retained the fibrous structure of the original cotton wool.

Analysis gave C = 62.31 and 62.51; H = 4.29 and 4.07 per cent.

After being once more similarly treated, the results were C = 62.21; H = 3.68 per cent.

Pure Swedish filter paper was treated in exactly the same way, and, on analysis, the black residue, which retained the structure of the filter paper, gave C = 62.42 and 62.70; H = 3.64 and 3.74 per cent.

The ordinary cellulose solvents (cuprammonium solution, zinc chloride solution, and acetic anhydride) have no action on this black residue. To make sure that it contained none of the original cellulose, some of the residue from filter paper was heated for half an hour with acetic anhydride and a few drops of concentrated sulphuric acid. It was then collected, washed free from sulphuric acid and acetic anhydride, dried at  $100^{\circ}$ , and now contained C = 61.72; H = 3.72 per cent.

$C_{12}H_{10}O_5$  requires C = 61.54; H = 4.26 per cent.

Some of the black residue was suspended in water and chlorine passed in for some time; the flask was then closed and allowed to stand for some hours; chlorine was again passed in and the process repeated. The substance, which was still fibrous in character after repeated treatment, acquired a bright yellow colour, and by means of alcohol or ether a small quantity of a bright yellow powder could be extracted. After this extraction, the residue was again subjected to the action of chlorine and more of the yellow powder obtained, but the action, being only a surface one, was very slow.

Experiments with other solvents for chlorine, such as chloroform or carbon tetrachloride, were made, but the action seemed to take place even more slowly. The yellow powder was purified by dissolving it in dry ether and precipitating with petroleum, and several specimens were analysed. The percentage of chlorine (Cl = 25.73, 26.1, 26.48, 30.45, 34.00, and 34.35) increased as the substance was repeatedly treated with this reagent, the analyses indicating that probably a mixture of chloro-derivatives is thus produced, these substances being difficult to separate on account of their sparing solubility and uncrystallisable character.

The action of bromine was similar, but was even slower.

Nitric acid (sp. gr. 1.2) and alkaline permanganate oxidise the residue to oxalic acid.

The original black residue is quite insoluble in alkalis, water, alcohol, ether, and other organic solvents. The composition and general character of this residue is therefore closely allied to the substances known as artificial humus, obtained by Conrad and Guthzeit (*Ber.*, 1885, **18**, 439 ; 1886, **19**, 2844), and by Sestini, by the action of dilute acids on sugars. It corresponds most nearly with sacculmin, prepared by Sestini by boiling cane sugar with dilute sulphuric acid, and described as a black, amorphous mass, insoluble in caustic potash solution, &c., and reacting with chlorine to give yellow, amorphous chloro-compounds. Sestini gives to sacculmin the formula  $C_{44}H_{38}O_{15}$  (carbon, 65.5 ; hydrogen, 4.8 per cent.), which has a slightly higher percentage of carbon and hydrogen than that found in the black residue from cellulose.

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