LX. THE HEMICELLULOSES. II. THE HEMICELLULOSE CONTENT OF STARCHES.

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IN the first paper [Clayson and Schryver, 1923] a "hemicellulose" very similar to starch but differing from this in many particulars has been described. Some evidence has been given to show this is not an intermediate product of degradation of ordinary starch by taka-diastrase, but a distinct chemical entity. If this were the case, it might be expected that it would be yielded in different amounts by the digestion of ordinary starches and that there might exist some correlation between the amount obtained and the properties of the various starches investigated. This has been found to be the case, and yields varying between practically 0 and 4 % have been found in the six commercial varieties of starch which have been studied.

Preparation of the hemicellulose from starches.

The six starches investigated were those from sago, maize, wheat, rice, tapioca and potato. The authors are indebted to Messrs Hibbert and Co. of Chorley, the Corn Products Co., Manchester, and Young and Strang of Glasgow for their kindness in providing materials for the research.

The method of preparation of the hemicellulose was practically identical with that employed for obtaining it from gliadin-free wheat flour as described in the first paper. The material was gelatinised and treated three times with taka-diastrase, the filtrations after each digestion being carried out by means of the Sharples centrifuge in exactly the manner therein described. The residue after digestion and treatment with 0.1 % caustic soda was dissolved in 2-4 % caustic soda solution, from which the hemicellulose was precipitated by acetic acid.

With potato starch, which gives a nearly clear gel on gelatinisation, only an insignificant residue was obtained after two digestions with taka-diastrase, whereas sago and maize starches, which yielded on gelatinisation thick pastes,

gave relatively large yields. In each case the digestion was carried out with 1 kilo. of starch and the following yields were obtained:

Origin of starch	Crude hemicellulose %	Nitrogen content %	Nett yield of hemicellulose
Sago	4.1	1.3	3.8
Maize	3.9	1.35	3.6
Tapioca	2.0	1.7	1.7
Wheat	1.65	2.1	1.35
Rice	1.2	2.3	1.0
Potato	Practically none	—	—

The hemicellulose still contained nitrogen (column 3), and if this be in the form of protein, the nett yields of hemicellulose from the various starches may be calculated as given in the last column.

Purification of the crude hemicellulose.

Washing the crude hemicellulose with 0.1 % caustic soda solution was not found to be completely effective in removing the protein. Separation of the hemicellulose from a filtered solution in hot water was somewhat difficult, owing to the ease with which deposition took place, even when a hot-water funnel was used. A method similar to that employed by Baker and Pope [1900] was used. The hemicellulose was dissolved in 2 % NaOH solution and copper sulphate was added till no further precipitation took place. The light blue precipitate was centrifuged off, and washed repeatedly on the centrifuge with 0.2 % NaOH solution. It was then treated with dilute acetic acid and the product thus obtained was washed until the blue copper coloration was removed. It was then treated with graded strengths of alcohol, and then ether and finally air-dried. The white flocculent mass thus obtained still held large amounts of the liquids used in the preparation, but could be readily dried to constant weight by heating to 110°, when it was obtained in the form of a granular powder, free from nitrogen and ash. The specific rotations of the samples in $N/2$ NaOH obtained from the different varieties of starch were practically identical, viz.:

Sago	+ 151.6°
Maize	+ 150.6
Wheat starch	+ 150.0
Tapioca	+ 151.0
Rice	+ 150.9
Wheat flour	+ 150.6

The product gave the following results on combustion:

I. C. 41.3 %; H 6.8 %. II. C 41.6 %; H 6.7 %.

This corresponds with a formula $C_{18}H_{34}O_{17}$ or $(3C_6H_{10}O_5 + 2H_2O)$ (this latter is intended only as an empirical representation of the formula) which requires C = 41.3 % and H = 6.5 %.

Hydrolysis of the hemicellulose.

The hemicellulose is readily hydrolysed by dilute acids. About 20 g. of material were purified by the copper salt method, and the purified product,

without drying, was put immediately into a flask containing about 300 cc. of 1 % sulphuric acid and heated with a reflux condenser for about 6 hours. During the first hour, the greater part of the product disappeared, but the solution remained turbid even after quite prolonged heating. In this and every other hydrolysis carried out, there was always obtained a small amount of a white flocculent substance, which obstinately resisted hydrolysis. The nature of this material, which is only formed in small quantity has not yet been ascertained. After its removal by centrifuging, the clear liquid was treated with the exact requisite amount of barium hydroxide, the barium sulphate was filtered off, and the filtrate concentrated to a syrup under diminished pressure. The syrup on treatment with absolute alcohol gave an almost white solid. From a solution of this an osazone was obtained in large yield, which under the microscope appeared to consist entirely of glucosazone, uncontaminated by the osazone of any other sugar. After recrystallisation it gave a M.P. of 204° . A diphenylhydrazone was also prepared, which agreed in properties with the diphenylhydrazone of dextrose. All attempts to discover other sugars (Seliwanoff's reaction for fructose, Tollens' pentose reaction, etc.) yielded negative results. The solution did not, however, contain pure glucose, for quantitative estimations by Bertrand's method and rotation determinations carried out on the same solution gave instead of a specific rotation of about $+52^{\circ}$, one of about 30° . The glucose was, therefore, contaminated with a substance of lower or opposite rotation.

In other samples of the solution an effort was made to estimate the glucose, by determining the total solids and their reducing power by Bertrand's method. The results of two experiments were as follows:

	I	II
Total solids present	0.1130	0.1445
Glucose therein by Bertrand's method	0.1200	0.1469

The reducing power is therefore a little larger than it should have been if the total solids had consisted entirely of glucose.

Finally, an effort was made to obtain the glucose pure by a method employed by Monier-Williams [1921]. The syrup obtained by the hydrolysis of hemicellulose was taken up in pure methyl alcohol. A small amount of amorphous matter remained undissolved. The filtrate from this was evaporated to a syrup which was again taken up with methyl alcohol, the solution was boiled with animal charcoal, filtered, and evaporated to a syrup. This on standing in a desiccator commenced to crystallise. A small portion of it was dried at 100° and the rotation of the solid residue was determined. This was found to be about $+40^{\circ}$. The crystals which separated out had an $[\alpha]_D^{20}$ of $+52.4^{\circ}$. There is no doubt, therefore, that the main product of hydrolysis is glucose. This is, however, contaminated with a small amount of other substances including one insoluble in water. Probably they are of a dextrin-like character, such as are generally obtained on the hydrolysis of starch by dilute acids. On hydrolysing the hemicellulose with 1 % oxalic acid at 120° an insoluble product was also obtained.

SUMMARY.

A method is described for isolating from the starches a hemicellulose identical with that previously described as having been obtained from wheat flour. The substance has an $[\alpha]_D$ in $N/2$ sodium hydroxide solution of $+150^\circ$. It has a composition corresponding with $C_{18}H_{34}O_{17}(3C_6H_{10}O_5 + 2H_2O)$. It yields on hydrolysis with dilute acids glucose as the only reducing sugar mixed with small amounts of other products, probably of a dextrin-like character. The various starches give yields of this substance varying from practically 0 in the case of potato starch up to nearly 4 % in the case of sago.

REFERENCES.

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