XXXVI.—*The Action of Hydrogen Bromide on Carbohydrates.*

By HENRY J. HORSTMAN FENTON, F.R.S., and MISS MILDRED GOSTLING, B.Sc.

THE authors have shown in a previous communication (Trans., 1898, 73, 554) that certain classes of carbohydrates when acted upon at the ordinary temperature with dry hydrogen bromide in ethereal solution give an intense and beautiful purple colour.* It was further shown (Trans., 1899, 75, 423) that this purple substance, when neutralised with sodium carbonate and extracted with ether, yields golden-yellow prisms of ω -bromomethylfurfural,

This reaction is produced by lævulose, sorbose, cane sugar, and inulin, an intense colour being given within an hour or two. Dextrose, maltose, milk sugar, galactose, and the polyhydric alcohols give, if anything, only insignificant colours, and these only after long standing. The authors therefore suggested that the reaction might be employed as a means of distinguishing these classes of carbohydrates, the rapid production of the purple colour being indicative of *keto*hexoses, or of substances which produce these by hydrolysis.

By relying only on the production of the purple colour, however, a mistake might possibly arise, owing to the fact that *xylose* gives

* This purple colour would appear to be due to a highly dissociable compound of ω -bromomethylfurfural with hydrogen bromide. The aldehyde gives yellow or colourless solutions in various solvents, which are turned purple by a sufficient excess of hydrogen bromide. Dilution, or addition of water, at once discharges the colour.

a somewhat similar colour after standing for a few hours. Hence, the observations should be confirmed by isolation of the crystals of bromomethylfurfural. No trace of this substance is obtained from the xylose product.

In order to identify the substance, the ether extract, after neutralisation, is allowed to evaporate to a syrup, and crystallisation promoted either by rubbing with a glass rod, or by the more certain and highly characteristic method of 'sowing' with the most minute trace of ω -bromomethylfurfural, when crystals are almost instantly formed. These are recrystallised from ether, or a mixture of ether and light petroleum, and further identified by the melting point ($59.5-60.5^\circ$), and, if considered desirable, by estimation of the bromine.

It is now found, so reactive is the bromine atom in this compound, that the estimation may be accurately made by titration with silver nitrate according to Volhard's process, the crystals for this purpose being dissolved in dilute alcohol :

0.1970 gram required 10.5 c.c. $N/10$ AgNO_3 . Br = 42.63 per cent., calculated 42.32 per cent.

This method of applying hydrogen bromide in ethereal solution is, of course, unsuitable for investigations where a higher temperature has to be employed, or where long standing is necessary, since, under such circumstances, the ether itself is attacked. Wishing to make investigations under these conditions, the authors have tried several solvents, and, at present, find that chloroform is best suited to the purpose. In each of the following experiments, 10 grams of the substance were covered with 250 c.c. of chloroform which had been saturated at 0° with dry hydrogen bromide. The mixture was contained in an accurately stoppered bottle, firmly secured with an iron clamp, and heated in a water-bath to about the boiling temperature for 2. hours. After standing for several hours, the mixture was treated with sodium carbonate (first anhydrous solid, and afterwards a few drops of strong solution), filtered, and the solution dried over calcium chloride. Most of the chloroform was then distilled off, and the remaining solution allowed to evaporate to a thick syrup in a weighed dish.

The product was then tested for ω -bromomethylfurfural by 'sowing' with the most minute trace of the substance, as described above. It was then warmed on a water-oven, kept in a vacuum desiccator over solid paraffin, and the weight estimated. When necessary, the product was recrystallised from ether, and further identified by the tests mentioned. The following results were obtained :

	Weight of crude residue.	
Swedish filter paper	3.0	crystallised at once by 'sowing,'
Ordinary cotton.....	3.3	„ „
Mercerised cotton	2.1	„ „
Straw cellulose*.....	2.3	„ „
Lævulose.....	2.2	„ „
Inulin.....	1.3	„ „
Potato starch.....	0.37	„ „
Cane sugar.....	0.85	„ „
Dextrose.....	0.33	uncrystallisable.
Milk sugar.....	0.37	„
Glycogen	0.34	„
Galactose	0.34	„

The products from *dextrose*, *milk sugar*, and *galactose* absolutely refused to crystallise even when extracted with ether and again evaporated, or by 'sowing,' stirring, &c.

The *glycogen* product deposited a very small amount of crystalline matter on standing, but the quantity was too minute for examination; moreover, it refused altogether to crystallise in contact with the aldehyde. It may fairly be stated, therefore, that these last four substances give absolutely negative results as regards the formation of ω -bromomethylfurfural; if any is formed, its quantity is altogether too small to be detected.

The specimen of *starch* examined was freshly prepared from potato, and purified by digestion for 24 hours each with $N/10$ KOH, $N/4$ HCl, and strong alcohol; it was then washed with water and allowed to dry in the air. It will be seen that this substance gave a positive result, but that the yield was extremely small, and might yet be due to impurity. Considering the importance of the behaviour of starch, for the purpose of drawing general conclusions from these observations, it was thought advisable to make further experiments with specimens which could be relied upon, and also to investigate the behaviour of dextrin. This the authors have been enabled to do, through the kindness of Mr. C. O'Sullivan, who has placed some remarkably beautiful specimens at their disposal.

His description of the specimens is as follows:

1. Rice starch, specially purified by the permanganate method.
2. Wheat starch „ „ „

* Other forms of cellulose, likewise kindly supplied by Mr. C. F. Cross, were also examined, for example, pine-wood cellulose, and the substances separated from solution in thiocarbonate (powder and film). All of these gave good yields of ω -bromomethylfurfural.

3. Oat starch, contains traces of oil, washed with dilute KOH and dilute HCl.

4. Pea starch, first crop, washed with alkali, acid (HCl), and strong alcohol.

5. Natural dextrin, $D = 3.87$, $[\alpha]_D = 194.7$; $K = 0.95$, (c 2.628).

6. α -Dextrin, C equation purified without fermentation, 30 precipitations with alcohol (Trans., 1879, 35, 772).

The examination of these specimens was conducted on a smaller scale, but under the same conditions as before, *one gram* of the substance being treated with 12.5 c.c. of the saturated chloroform solution and heated in sealed tubes for 2 hours as above. The results were as follows:

	Weight of crude residue.	
1. Rice starch	0.046	crystallised at once by 'sowing.'
2. Wheat starch	0.044	„ „
3. Oat starch	0.049	„ „
4. Pea starch	0.064	„ „
5. Natural dextrin	0.088	„ „
6. α -Dextrin	0.055	„ „

The results may therefore be summarised as follows. All forms of cellulose give large yields of ω -bromomethylfurfural, some varieties giving as much as 33 per cent. Lævulose, inulin, and cane sugar give yields varying from 22 to 8.5 per cent.; various starches give small yields (average about 4.5 per cent.); and dextrans 5 to 8 per cent., whereas dextrose, milk sugar, and galactose give, apparently, none at all.

The yields represent the solid crystalline residue; this when purified by recrystallisation gives, probably, about three-quarters of its weight of pure crystals. (In the case of dextrose, &c., the yields represent the weight of syrup.)

These numbers, however, by no means represent the maximum yields obtainable, owing to the comparatively slight solubility of hydrogen bromide in chloroform. The process was conducted in the above manner only for the sake of uniform comparison. The ether method previously described gives much larger yields; for example, 12 grams of inulin treated with only 60 c.c. of the saturated ether gave 2.5 grams of substance. For the purpose of obtaining larger yields, other methods are being investigated.

The facts recorded above, taken in conjunction with those given in our previous communications, appear to point definitely to the following general conclusions. First, that the various forms of *cellulose*

The nature of this grouping is, according to the generally accepted constitution of *lævulose*, the six carbon chain with a ketonic group:

* The change is empirically represented as