

LETTERS TO THE EDITORS

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Linkage between the Repeating Units in the Starch Molecule

IN an earlier paper¹ we presented evidence which indicated that the starch molecule is made up of a large number of repeating units (each consisting of an unbranched chain of some thirty glucose units) combined together in such a way that the free reducing group of one unit is linked glucosidically with a hydroxyl group of the adjacent unit. It is now apparent that in the derivatives of starch we have examined, the hydroxyl group concerned in the glucosidic union of the repeating units, is a primary alcoholic group situated at C₆ of one of the glucose residues. The occurrence of this mode of linkage was indicated previously² and was suggested simultaneously by Freudenberg and Boppel³. In this connexion it may be mentioned that we have never advocated the views on the structure of starch recently attributed to us by Kurt Meyer⁴, and that, on the other hand, if each of the units represented in the formula suggested by Meyer is considered to contain some thirty glucose residues, his formula becomes identical in type with the structure we have advocated¹.

The new results are derived from the following experiments. Methylated rice starch was disaggregated¹, giving material of low molecular weight, specially suitable for experiments on the mode of linkage in that it readily undergoes complete methylation. On hydrolysis, the fully methylated derivative gives rise to 2:3:6-trimethyl glucose, 2:3:4:6-tetramethyl glucose (end-group) and dimethyl glucose. It is evident that one of the two free hydroxyl groups of the dimethyl glucose represents the point of junction of the repeating units. Examination of the dimethyl sugar has revealed that it consists almost entirely of 2:3-dimethyl glucose, from which it follows (since C₄ is involved in the linkages of the glucose residues within the unit) that the repeating units are connected through C₆ of one of the glucose residues. The yield of dimethyl glucose (3 per cent) is consistent with the view that one such linkage exists per repeating unit. The exact position of the particular glucose residue in the chain of the repeating unit is not yet known and the problem of its determination is of special importance in connexion with enzymic degradation of starch⁵. It is to be observed also that the present evidence concerns the linkages in the disaggregated derivative, and the further question, whether all the linkages connecting repeating units in the original starch are of similar type, must await further investigation.

The following evidence served to identify the 2:3-dimethyl glucose. (a) It forms both furanose and pyranose methyl glycosides, since in cold methyl alcoholic hydrogen chloride the rotation drops from $[\alpha]_D + 59^\circ$ to -30° , and in boiling methyl alcoholic

hydrogen chloride it rises to $+75^\circ$. (b) The amide of the corresponding dimethyl gluconic acid gives a negative Weerman reaction with sodium hypochlorite. The hydroxyl at C₂ is therefore methylated. (c) The *p*-toluene sulphonyl derivative of the dimethyl methyl glucoside, when heated with sodium iodide in acetone at 100°, gave sodium *p*-toluene sulphonate (yield 87 per cent of the theoretical), and this was corroborated by an estimation of the iodine content of the syrup isolated after removal of the sodium *p*-toluene sulphonate. C₆ therefore carries a free hydroxyl group⁶ and this, in conjunction with the other evidence, fixes the constitution as 2:3-dimethyl glucose.

The quantitative aspect of these results shows that other dimethyl glucoses cannot have been present in more than minute amounts, insufficient to affect the conclusions outlined above.

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¹ Hirst and Young, *J. Chem. Soc.*, 1471 (1939).

² Bawn, Hirst and Young, Faraday Society Discussion, May 1940; *Trans. Faraday Soc.*, **36**, 881 (1940).

³ *Naturwiss.*, **28**, 264 (1940).

⁴ Meyer, K., *Helv. chim. Acta*, **23**, 880 (1940).

⁵ Hanes, *New Phyt.*, **36**, 538 (1937).

⁶ Method of Oldham and Rutherford for estimation of primary alcoholic group in sugars. *J. Amer. Chem. Soc.*, **54**, 366 (1932).

A New Method of obtaining the N Pattern of Electron Diffraction

THE *N* pattern of electron diffraction was first obtained from a thin piece of mica. It has not been obtained for many substances because of the technical difficulty of preparing single crystal films of suitable thickness for electron penetration.

I have discovered a method of preparing two-dimensional films of various substances, and a big field of investigation by electron diffraction is now opened.

The *N* patterns shown in the accompanying photographs were obtained by the new method of preparation; the films, which may properly be called synthetic, are laboratory products and are made by allowing chemical reactions to take place under physical control.

Thin films of water or hydrochloric acid were first prepared by immersing a platinum wire gauze in water or in the acid (12 *N*) and then withdrawing it. Upon bringing such films into contact with a clean piece of potassium or calcium, chemical reaction