CCCXCVII.—*Polysaccharides. Part IX. Evidence of the Pyranose Structure of Xylan.*

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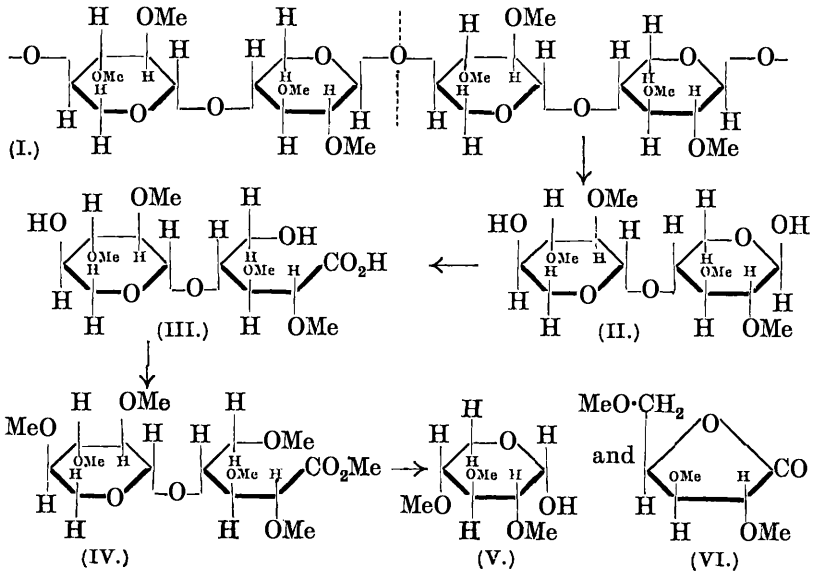
EXPERIMENTAL evidence communicated in Part IV of this series (Hampton, Haworth, and Hirst, J., 1929, 1739) has been advanced in support of the view that xylan, the occurrence of which is widespread in plant products, contains only xylose units and that positions 4 and 5 of the pentose ring are involved either in the mutual union of adjacent members or in ring formation. Our results definitely revealed hydroxyl groups at positions 2 and 3 in xylan. We have sought for evidence as to which of the remaining positions, 4 or 5, is engaged in the mutual union of the $C_5H_8O_4$ units. This evidence would enable us to decide whether the 5 or 4 position is involved in the ring formation of the individual units and whether the xylose units are of the furanose or pyranose type. From the general properties of xylan we had previously suggested that the individual members were xylopyranose units, and the new

evidence now communicated leads us finally to this conclusion. For the purpose of the present work we have prepared by a modified procedure a fully methylated specimen of xylan derived from esparto. It was shown in the former paper that methyl groups were introduced into the 2- and 3-positions, and from the present work the formulation of dimethyl xylan can be represented by a repetition of the scheme given below (I).

This specimen of dimethyl xylan has been degraded by acetolysis at 0° during the very short interval of 10 minutes. In this way the complete scission of the polysaccharide to the ultimate C_5 units was averted and we were able by subsequent analysis to recognise among the products a partly methylated *disaccharide* to which, by the sequence of operations herein described, we are able to allocate the constitution (II). Adopting now a procedure which we had applied both to starch and to glycogen (Part VIII) and earlier to maltose and cellobiose (J., 1926, 3094; 1927, 2809), we investigated both the ring structure and the position of the biose union of the substituted disaccharide. The acetolysis products from dimethyl xylan were first deacetylated and then oxidised with bromine water in order to convert the sugars generated by the hydrolysis into the corresponding monobasic acids. Among these was a *bionic acid derivative* (III) from the disaccharide of the dixylose type. The bionic acid was methylated and esterified and yielded a *methyl* ester of *hexamethyl dixylobionic acid* (IV).



By hydrolytic cleavage this product (IV), which showed accurate analytical figures for $C_{17}H_{32}O_{10}$, gave rise to crystalline 2 : 3 : 4-trimethyl xylopyranose (V) in a yield of over 80%, and there was isolated as a second component 2 : 3 : 5-trimethyl γ-xylonolactone (VI) which, although distilling as a liquid in a yield of 73%, was recognised by conversion into the crystalline phenylhydrazide of the corresponding 2 : 3 : 5-trimethyl xylonic acid. These crystalline products were compared directly with authentic specimens and their identity confirmed. It follows that, since the 4-position in the latter acid carries a free hydroxyl group, this must have been the point of linking with the 1-position of the adjoining xylopyranose unit (V). Moreover this lactone had been previously investigated by Haworth and Porter (J., 1928, 611), who degraded it to *d*-dimethoxysuccinic acid. Position 5 of the lactone represents the point of junction of the xylose ring which was opened by oxidation to the bionic acid and subsequently methylated to give the terminal CH_2·OMe group in the γ-lactone (VI).

We can therefore apply the constitution (II) to the partly methylated disaccharide which is here shown to be a *dixylopyranose*. It follows that the xylose units in the polysaccharide are of the pyranose type and that xylan can be represented by formula I (with H in place of Me).

EXPERIMENTAL.

Methylation of Xylan.—The methylation of xylan was carried out with the following quantities of reagents, which differ slightly from those previously used (Hampton, Haworth, and Hirst, J., 1929, 1739): xylan (7·5 g.), potassium hydroxide (500 g. in 650 c.c. of water), and methyl sulphate (430 c.c.). The methyl sulphate was added to the alkaline solution of xylan during 4 hours at room temperature with continuous stirring. Thereafter the temperature was raised to 100° for 1 hour, the mixture was diluted with 2 litres of boiling water, and the liquid filtered through muslin. The crude methylated xylan obtained from two such operations was again methylated by the use of potassium hydroxide (365 g. in 400 c.c. of water) and methyl sulphate (290 c.c.). The white methylated compound was washed with hot water, dissolved in chloroform, dried with magnesium sulphate, filtered through glass wool, and the dimethyl xylan precipitated by an excess of ether. The product had the same constants as those already recorded (Hampton, Haworth, and Hirst, *loc. cit.*).

Degradation of Dimethyl Xylan.—To dimethyl xylan (4 g.), dissolved in glacial acetic acid (44 c.c.) and cooled to 0°, acetic anhydride (40 c.c.) containing concentrated sulphuric acid (1·6 c.c.) was added,

this mixture having previously been cooled to 0°. After remaining for 10 mins. at 0°, the mixture was poured into ice water (300 c.c.) and cautiously neutralised with sodium carbonate (40 g.), followed by barium carbonate. After 5 hours the solution was filtered and extractions with chloroform (800 c.c.) yielded, on evaporation, a viscid yellow syrup.

Deacetylation. The above syrup was dissolved in acetone (50 c.c.) and allowed to react with *N*-sodium hydroxide (50 c.c.) at 15° for 2 hours. The excess of alkali was then neutralised with *N*-hydrochloric acid, and the acetone removed under diminished pressure at 30°.

Oxidation. The above neutral solution was oxidised with bromine (1 c.c.) in the presence of barium benzoate (7 g. in 250 c.c. of water), the halogen being added at 0°, and the oxidation allowed to proceed during 40 hours in the dark. Thereafter the mixture was aerated to remove bromine, filtered from benzoic acid, and the barium salts were precipitated with sodium sulphate (4 g.). After filtration the solution was rendered alkaline and concentrated to 50 c.c. Cautious acidification of the cold solution with dilute sulphuric acid caused the separation of more benzoic acid, which was removed. The filtrate was again rendered alkaline and concentrated for methylation.

Methylation. The above aqueous solution was mixed with acetone (100 c.c.) and treated with 30% sodium hydroxide solution (81 c.c.) and methyl sulphate (33 c.c.) at 35—40° for ½ hour and finally at 55—60°, the reagents being added in $\frac{1}{10}$ portions every 10 minutes in the usual way. The organic acids were liberated by adding dilute sulphuric acid (using Congo-red as indicator) in the presence of ice, and the solution was now extracted with chloroform. The aqueous residues were rendered alkaline, evaporated under diminished pressure, and extracted with boiling 95% alcohol. This extract was evaporated in a vacuum, and the solid material remaining was dissolved in water, added to the syrup obtained from the above chloroform extraction, and submitted to another methylation with the same quantities of reagents as before. This yielded a viscid brown syrup (2·5 g.). Several such preparations of material were carried out and finally the combined syrups were dissolved in methyl iodide and methylated twice by the Purdie method. From 10 g. of dimethyl xylan, the mixed esters resulting from this treatment weighed 5·6 g. A first distillation yielded the following: Fraction 1 (bath temperature 90—135°/0·06 mm.) 2 g., $n_D^{15°}$ 1·4452; fraction 2 (bath temperature 135—170°/0·06 mm.) 0·3 g., $n_D^{15°}$ 1·4561; fraction 3 (170—210°/0·06 mm.) 2·4 g., $n_D^{15°}$ 1·4618; fraction 4 (210—250°/0·06 mm.) 0·4 g., $n_D^{15°}$ 1·4680; residue 0·5 g. Fraction 3 was redistilled and showed b. p. about 170°/0·06 mm., $n_D^{15°}$ 1·4610; $[\alpha]_D^{17°}$ + 10·4°

(*c*, 1·06 in water) (Found: C, 51·2; H, 8·1; OMe, 54·5; CO_2Me, 15·2. $C_{17}H_{32}O_{10}$ requires C, 51·5; H, 8·1; OMe, 54·8; CO_2Me, 14·9%). Redistillation of fractions 2 and 4 yielded a further quantity (0·2 g.) of the same material as fraction 3, so that the combined yields of this ester (IV) amounted to 21% of the theoretical.

Hydrolysis of the Bionic Ester.—The above ester (2·0 g.) was hydrolysed at 100° with 2% hydrochloric acid (60 c.c.) and underwent the following polarimetric changes. $[\alpha]_D^{17°}$ + 10° (initial); + 25° (10 mins.); + 30° (20 mins.); + 31·8° (45 mins., constant).

Isolation of 2 : 3 : 4-Trimethyl Xylose.—The acid solution was neutralised with excess of barium carbonate and aerated during 2—3 hours at 50° in contact with animal charcoal. The filtrate, on evaporation under diminished pressure, yielded a mixture of barium salts and a sugar. These residues were dried by distilling from them a mixture of benzene and alcohol, and were extracted repeatedly with dry ether. This extract yielded a syrup which crystallised on nucleation with 2 : 3 : 4-trimethyl xylopyranose. The crude product weighed 0·82 g. (84% of the theoretical yield). On recrystallisation this showed m. p. 90—92°, $[\alpha]_D^{17°}$ + 20·4° (after ½ hour). It was identified as α-2 : 3 : 4-trimethyl xylopyranose by mixed m. p. determination (compare Hampton, Haworth, and Hirst, *loc. cit.*) and by the following analysis (Found: C, 50·2; H, 8·7; OMe, 48·1. Calc.: C, 50·0; H, 8·3; OMe, 48·4%). Among the products derivatives of furfural were detected.

Isolation of 2 : 3 : 5-Trimethyl γ-Xylonolactone.—The residue of barium salts remaining from the previous extraction was dissolved in water (10 c.c.) and acidified with *N*-hydrochloric acid (10 c.c.), and the aqueous solution was evaporated under diminished pressure. The residue, dried at 100°, was repeatedly extracted with dry ether and gave a pale yellow syrup, which was distilled: b. p. 80—90°/0·05 mm., $n_D^{16°}$ 1·4450, $[\alpha]_D^{17°}$ + 95·2° (after ½ hour); + 90·5° (2½ days); + 75·5° (14 days); 70·0° (20 days) (*c*, 1·05 in water). Yield, 0·7 g. (73% of the theoretical). The phenylhydrazide of the corresponding acid was prepared from this lactone (compare Haworth and Porter, J., 1928, 611) and showed m. p. 88° alone or mixed with an authentic specimen (Found: C, 56·3; H, 7·2; N, 9·6; OMe, 31·1. Calc.: C, 56·4; H, 7·4; N, 9·4; OMe, 31·2%).

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